Jenő Sólyom

Fundamentals of the Physics of Solids

Volume 3 — Normal, Broken-Symmetry, and Correlated Systems



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Fundamentals of the Physics of Solids

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Volume III

Normal, Broken-Symmetry, and Correlated Systems

With 193 Figures and 10 Tables



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To Márta, Gyöngyvér, Tünde, and Iringó

Preface

The reader is holding the third volume of a three-volume textbook on solidstate physics. This book is the outgrowth of the courses I have taught for many years at Eötvös University, Budapest, for undergraduate and graduate students under the titles *Solid-State Physics* and *Modern Solid-State Physics*.

The main motivation for the publication of my lecture notes as a book was that none of the truly numerous textbooks covered all those areas that I felt should be included in a multi-semester course. Especially, if the course strives to present solid-state physics in a unified structure and aims at discussing not only classic chapters of the subject matter but also (in more or less detail) problems that are of great interest for today's researcher as well. Besides, the book presents a much larger material than what can be covered in a two- or three-semester course. In the first part of the first volume the analysis of crystal symmetries and structure goes into details that certainly cannot be included in a usual course on solid-state physics. The same applies, among others, to the discussion of the methods used in the determination of band structure, the properties of Fermi liquids and non-Fermi liquids, and the theory of unconventional superconductors in the present and third volumes. These parts can be assigned as supplementary reading for interested students or can be discussed in advanced courses.

The line of development and the order of the chapters are based on the prerequisites for understanding each part. Therefore, a gradual shift can be observed in the style of the book. While the intermediate steps of calculations are presented in considerable detail and explanations are also more lengthy in the first and second volumes, they are much sparser and more concise in the third one, thus that volume relies more on the individual work of the students. On account of the prerequisites, certain topics have to be revisited. This is why magnetic properties are treated in three and superconductivity in two parts. The magnetism of individual atoms is presented in an introductory chapter of the first volume. The structure and dynamics of magnetically ordered systems built up of localized moments are best discussed after lattice vibrations, along the same lines. Magnetism is then revisited in the third volume, where the

role of electron–electron interactions is discussed in more detail. Similarly, the phenomenological description of superconductivity is presented in this volume after the analysis of the transport properties of normal metals, in contrast to them, while the microscopic theory is outlined later, in the third volume, when the effects of interactions are discussed.

Separating the material into three similar-sized volumes is a necessity in view of the size of the material – but it also reflects the internal logical structure of the subject matter. At those universities where the basic course in solid-state physics runs for three semesters, working through one volume per semester is a natural schedule. In this case the discussion of the electron gas – which is traditionally part of the introduction – is left for the second semester. This choice is particularly suited to curricula in which the course on solid-state physics is held parallel with quantum mechanics or statistical physics. If the lecturer feels more comfortable with the traditional approach, the discussion of the Drude model presented in this volume can be moved to the beginning of the whole course. Nevertheless, the discussion of the Sommerfeld model should be postponed until students have familiarized themselves with the fundamentals of statistical physics. For the same reason, the lecturer may prefer to change the order of other chapters as well. This is, to a large extent, up to the personal preferences of the lecturer.

In presenting the field of solid-state physics, special emphasis has been laid on discussing the physical phenomena that can be observed in solids. Nevertheless, I have tried to give – or at least outline – the theoretical interpretation for each phenomenon, too. As is common practice for textbooks, I have omitted precise references that would give the publication data of the discussed results. I have made exceptions only for figures taken directly from published articles. At the end of each chapter I have listed textbooks and review articles only that present further details and references pertaining to the subject matter of the chapter in question. The first chapter of the first volume contains a longer list of textbooks and series on solid-state physics.

Bulky as it might be, this three-volume treatise presents only the fundamentals of solid-state physics. Today, when articles about condensed matter physics fill tens of thousands of pages every year in *Physical Review* alone, it would be obviously overambitious to aim at more. Therefore, building on the foundations presented in this series, students will have to acquire a substantial amount of extra knowledge before they can understand the subtleties of the topics in the forefront of today's research. Nevertheless, at the end of the third volume students will also appreciate the number of open questions and the necessity of further research.

A certain knowledge of quantum mechanics is a prerequisite for studying solid-state physics. Various techniques of quantum mechanics – above all field-theoretical methods and methods employed in solving many-body problems – play an important role in present-day solid-state physics. Some essential details are listed in one of the appendices of the third volume; however, I have omitted more complicated calculations that would have required the application of the modern apparatus of many-body problems. This is especially true for the third volume, where central research topics of presentday solid-state physics are discussed, in which the theoretical interpretation of experimental results is often impossible without some extremely complex mathematical formulation.

The selection of topics obviously bears the stamp of the author's own research interest, too. This explains why the discussion of certain important fields – such as the mechanical properties of solids, surface phenomena, or amorphous systems, to name but a few – have been omitted.

I have used the International System of Units (SI) and have given the equations of electromagnetism in rationalized form. Since nonrationalized equations as well as gaussian CGS (and other) units are still widely used in the solid-state physics literature, the corresponding formulas and units are indicated at the appropriate places. In addition to the fundamental physical constants used in solid-state physics, the commonest conversion factors are also listed in Appendix A of the first volume. I deviated from the recommended notation in the case of the Boltzmann constant using $k_{\rm B}$ instead of k – reserving the latter for the wave number, which plays a central role in solid-state physics.

To give an impression of the usual values of the quantities occurring in solid-state physics, typical calculated values or measured data are often tabulated. To provide the most precise data available, I have relied on the Landolt–Börnstein series, the CRC Handbook of Chemistry and Physics, and other renowned sources. Since these data are for information only, I have not indicated either their error or in many cases the measurement temperature, and I have not mentioned when different measurement methods lead to slightly disparate results. As a rule of thumb, the error is usually smaller than or on the order of the last digit.

I would like to thank all my colleagues who read certain chapters and improved the text through their suggestions and criticism. Particular thanks go to professors György Mihály and Attila Virosztek for reading the whole manuscript. I am grateful to F. I. B. (Tito) Williams for reading the present volume and for his comments. In spite of all efforts, some mistakes have certainly remained in the book. Obviously, the author alone bears the responsibility for them.

Special thanks are due to Károly Härtlein for his careful work in drawing the majority of the figures and to Karlo Penc for drawing a few figures. The figures presenting experimental results are reproduced with the permission of the authors or the publishers.

Finally, I am indebted to my family, my wife and children, for their patience during all those years when I spent evenings and weekends in writing this book.

Budapest, Hungary November 2010 Jenő Sólyom

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Electron-Electron Interaction and Correlations

Throughout Volume 2 the electronic properties of solids were studied in the independent electron approximation. The spectrum of Bloch electrons was calculated in the presence of a periodic one-particle potential $V(\mathbf{r})$,¹ which could incorporate the contribution of electron–electron interaction at a mean-field level, and the states of the many-body system were obtained by filling the electronic bands successively with independent particles. The interactions with impurities and lattice vibrations could be given a simple interpretation in this picture and we were able to understand some (e.g., transport and optical) properties of insulators, metals, and semiconductors.

One notable exception to this independent electron treatment was made in Volume 1, when covalent bonding was studied. In order to get a physical picture of the nature of this type of bond, we computed the possible states of two interacting electrons. This led to the concept of exchange interaction, which proved to be extremely important in understanding the magnetic properties of solids. However, when magnetically ordered systems were considered in Chapter 14, instead of treating the electron–electron interaction in its full complexity, localized spins were assumed and the effects of their interaction were discussed.

This simplistic, one-particle approach was adopted out of necessity, since a serious treatment of electron–electron interaction can only be done by using techniques of the many-body problem. In this volume, we go beyond the independent electron approximation and will study how electron–electron interaction influences the properties of solids. These calculations will also help us to understand under what circumstances the single-particle picture is applicable to real solids.

In this chapter we first give the Hamiltonian of the electron–electron interaction in various forms. Then we discuss a few simple approximation schemes that allow us to calculate the ground-state energy and excitation energies of

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¹ In Volume 2 the notation $U(\mathbf{r})$ was used for the potential. In this volume $V(\mathbf{r})$ stands for the one-particle potential and the notation $U(\mathbf{r})$ is reserved for the two-particle interaction. The subscript e-e will be dropped from U_{e-e} .

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the electron system. It will also be pointed out that the Pauli exclusion principle and the electron–electron interaction give rise to spatial and temporal correlations between electrons that cannot be understood in the one-particle approximation. During these studies second quantization (summarized briefly in Appendix H) will often be used. Only knowledge of the elements of the many-body problem will be supposed, as presented in Appendix K. The interested reader can find further details in textbooks on the subject.

28.1 Models of the Interacting Electron System

To study the effects of electron–electron interaction, the straightforward approach would be to solve the Schrödinger equation as a many-variable differential equation for the total Hamiltonian of the many-particle system that includes the Coulomb interaction between electrons. It turns out that the formalism of second quantization is better adapted to this problem. In this approach the complete set of Bloch or Wannier states (or plane waves if the periodic potential of the lattice can be neglected) is taken as a basis set and one writes the many-particle states of the system as well as the Hamiltonian in terms of the creation and annihilation operators of these one-particle states. Depending on the representation used we arrive at different formulations.

28.1.1 The Hamiltonian

Since we wish to understand how electron–electron interaction influences the properties of solids, we will, in what follows, assume that the ions sit rigidly in their equilibrium positions on a regular lattice; their vibrations will be neglected. The Coulomb interaction between ions gives only an additive constant to the total energy that will be omitted. Thus, if the relativistic effect of spin–orbit coupling is neglected, the Hamiltonian to be considered contains in addition to the kinetic energy of $N_{\rm e}$ electrons the interaction with the ions and the direct Coulomb repulsion between electrons:

$$\mathcal{H} = \sum_{i=1}^{N_{\rm e}} \left(-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}_i^2 \right) + \sum_{i=1}^{N_{\rm e}} V_{\rm ion}(\boldsymbol{r}_i) + \frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{\rm e}} U(\boldsymbol{r}_i - \boldsymbol{r}_j) \,, \qquad (28.1.1)$$

where $V_{ion}(\mathbf{r}_i)$ is the potential created by the ions and

$$U(\mathbf{r}_{i} - \mathbf{r}_{j}) = \frac{1}{4\pi\epsilon_{0}} \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} = \frac{\tilde{e}^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}$$
(28.1.2)

describes the electronic Coulomb repulsion. Our task is to solve the Schrödinger equation

$$\mathcal{H}\Psi(\boldsymbol{r}_{1}, s_{1}, \boldsymbol{r}_{2}, s_{2}, \dots, \boldsymbol{r}_{N_{\rm e}}, s_{N_{\rm e}}) = E\Psi(\boldsymbol{r}_{1}, s_{1}, \boldsymbol{r}_{2}, s_{2}, \dots, \boldsymbol{r}_{N_{\rm e}}, s_{N_{\rm e}}). \quad (28.1.3)$$

For later convenience the spin variable s_i has been written out explicitly in the wavefunction, although the total Hamiltonian is spin independent in the absence of spin–orbit coupling.

So far the ionic potential has not been specified. If bare nuclei with charge Ze are considered, then

$$V_{\rm ion}(\boldsymbol{r}_i) = -\frac{1}{4\pi\epsilon_0} \sum_{\boldsymbol{R}_m} \frac{Ze^2}{|\boldsymbol{r}_i - \boldsymbol{R}_m|} = -\sum_{\boldsymbol{R}_m} \frac{Z\tilde{e}^2}{|\boldsymbol{r}_i - \boldsymbol{R}_m|}, \qquad (28.1.4)$$

and $N_{\rm e}$ is the total number of electrons. However, significant simplification can be achieved by treating the localized core electrons differently from the delocalized valence electrons lying in bands close to the Fermi energy and participating in the chemical bonding. The effect of electrons on deep levels can be incorporated into the potential of the ions by identifying Ze with the ionic charge. Using this effective ionic potential in (28.1.1), $N_{\rm e}$ is just the number of electrons in the valence bands.² In some cases an average potential coming from the electron–electron interaction in the valence bands is also included in the one-particle potential. In this case, naturally, only the deviation from this average should be considered in the two-particle interaction, and the one-particle term has to be evaluated self-consistently.

In a perturbative approach, the one-particle potential is usually incorporated into the unperturbed Hamiltonian

$$\mathcal{H}_0 = \sum_{i=1}^{N_e} \left(-\frac{\hbar^2}{2m_e} \boldsymbol{\nabla}_i^2 \right) + \sum_{i=1}^{N_e} V_{\text{ion}}(\boldsymbol{r}_i) , \qquad (28.1.5)$$

and the electron–electron interaction is treated as a perturbation,

$$\mathcal{H}_{1} = \mathcal{H}_{e-e} = \frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{e}} U(\boldsymbol{r}_{i} - \boldsymbol{r}_{j}).$$
(28.1.6)

Both the one-particle potential due to ions and the two-particle term of the Hamiltonian describing the interaction between electrons can be given in terms of the number-density operator of electrons,

$$n(\mathbf{r}) = \sum_{i=1}^{N_{\rm e}} \delta(\mathbf{r} - \mathbf{r}_i) \,. \tag{28.1.7}$$

For the one-particle potential we have

$$\sum_{i=1}^{N_{e}} V_{\text{ion}}(\boldsymbol{r}_{i}) = \int V_{\text{ion}}(\boldsymbol{r}) n(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$
(28.1.8)

² Contrary to the convention used in semiconductors, in our subsequent treatment of solids bands occupied by electrons that participate in the formation of metallic or covalent bonds will be called valence bands.

When both the potential and the number-density operator are written in Fourier representation, we have

$$\sum_{i=1}^{N_{\rm e}} V_{\rm ion}(\boldsymbol{r}_i) = \frac{1}{V} \sum_{\boldsymbol{q}} V_{\rm ion}(\boldsymbol{q}) n(-\boldsymbol{q}) , \qquad (28.1.9)$$

where the summation goes over the Brillouin zone, and

$$n(\boldsymbol{q}) = \int_{V} n(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \,\mathrm{d}\boldsymbol{r} = \sum_{i=1}^{N_{\mathrm{e}}} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i}} \,. \tag{28.1.10}$$

We have to take into account that there is no self-interaction in the twoparticle term. That is why the term i = j is missing in the third term on the right-hand side of (28.1.1). We therefore obtain

$$\frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{\rm e}} U(\boldsymbol{r}_i - \boldsymbol{r}_j) = \frac{1}{2} \left[\iint \mathrm{d}\boldsymbol{r} \,\mathrm{d}\boldsymbol{r}' U(\boldsymbol{r} - \boldsymbol{r}') n(\boldsymbol{r}) n(\boldsymbol{r}') - N_{\rm e} U(0) \right]. \quad (28.1.11)$$

In case of spin-independent interactions, the interaction between particles at sites r and r' is weighted by the number density at these sites. The second term containing the potential at r = r' serves to eliminate the self-interaction. This term is infinitely large for Coulomb interaction, but in fact it only cancels a divergent contribution in the first term. In Fourier representation we have

$$\frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{\rm e}} U(\boldsymbol{r}_i - \boldsymbol{r}_j) = \frac{1}{2V} \sum_{\boldsymbol{q}} U(\boldsymbol{q}) \left[n(-\boldsymbol{q})n(\boldsymbol{q}) - N_{\rm e} \right].$$
(28.1.12)

If the bare Coulomb potential is used, then according to (C.1.63) the Fourier transform appearing here is

$$U(\mathbf{q}) = \frac{e^2}{\epsilon_0 q^2} = \frac{4\pi \tilde{e}^2}{q^2} \,. \tag{28.1.13}$$

28.1.2 Second-Quantized Form of the Hamiltonian

When a complete (orthonormal) set of single-particle states $\{\phi_k(\mathbf{r})\}\$ is taken where k denotes all quantum numbers except spin, a complete set of states for the many-body system can be obtained by forming totally antisymmetric combinations, Slater determinants, from the single-particle states. An arbitrary state of the many-particle system can then be written as a linear combination of Slater determinants. The Slater determinants themselves can be constructed unequivocally once we know which one-particle states are present; in other words, which states are occupied. That is why the wavefunction can be given in the occupation-number representation. The operators acting on the many-particle states can then be given in second-quantized form by specifying how the occupation of single-particle states is changed. For this reason a creation operator $c_{k\sigma}^{\dagger}$ acting in Fock space is introduced, which adds an electron in the one-particle state (orbital) $\phi_k(\mathbf{r})$ with spin σ to the system. Its adjoint, the annihilation operator $c_{k\sigma}$, removes a particle from this state. The number operator $c_{k\sigma}^{\dagger}c_{k\sigma}$ counts the number of particles in the particular single-particle state $\phi_k(\mathbf{r})$ with spin σ . The total Hamiltonian containing the kinetic energy of electrons, the one-particle potential, and the electron– electron interaction can be written in terms of these operators according to (H.2.25) in the form

$$\mathcal{H} = \sum_{kl\sigma} H_{kl} c^{\dagger}_{k\sigma} c_{l\sigma} + \frac{1}{2} \sum_{\substack{klmn\\\sigma\sigma'}} U_{klmn} c^{\dagger}_{k\sigma} c^{\dagger}_{l\sigma'} c_{m\sigma'} c_{n\sigma} , \qquad (28.1.14)$$

where

$$H_{kl} = \int \phi_k^*(\boldsymbol{r}) \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 + V_{\rm ion}(\boldsymbol{r}) \right] \phi_l(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \tag{28.1.15}$$

and

$$U_{klmn} = \iint \mathrm{d}\boldsymbol{r} \,\mathrm{d}\boldsymbol{r}' \,\phi_k^*(\boldsymbol{r}) \phi_l^*(\boldsymbol{r}') U(\boldsymbol{r} - \boldsymbol{r}') \phi_m(\boldsymbol{r}') \phi_n(\boldsymbol{r}) \,. \tag{28.1.16}$$

This shows that the electron–electron interaction can be considered as a collision process in which two electrons are scattered from their initial states into some final states. This was supposed already earlier when the interaction between electrons was depicted in Fig. 6.5.

A different, perhaps more transparent, form is obtained when the field operators defined in (H.2.15) by the expressions

$$\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) = \sum_{k} \phi^{*}_{k}(\boldsymbol{r}) \eta^{\dagger}_{\sigma} c^{\dagger}_{k\sigma} , \qquad \hat{\psi}_{\sigma}(\boldsymbol{r}) = \sum_{k} \phi_{k}(\boldsymbol{r}) \eta_{\sigma} c_{k\sigma}$$
(28.1.17)

are used. Here η_{σ} is the wavefunction of the spin state with quantum number σ . These states are conveniently given by the spinors

$$\eta_{\uparrow} = \begin{pmatrix} 1\\ 0 \end{pmatrix}, \qquad \eta_{\downarrow} = \begin{pmatrix} 0\\ 1 \end{pmatrix}, \qquad (28.1.18)$$

and η^{\dagger}_{σ} is their adjoint. They satisfy the orthogonality relationship

$$\eta_{\sigma_i}^{\dagger}(s_l)\eta_{\sigma_j}(s_l) = \delta_{\sigma_i,\sigma_j}. \qquad (28.1.19)$$

The creation operator $c_{k\sigma}^{\dagger}$ adds a particle of quantum numbers k and σ to the system, whereas the field operator $\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})$ adds a particle to the system at site \mathbf{r} with spin σ , and $\hat{\psi}_{\sigma}(\mathbf{r})$ removes an electron at site \mathbf{r} . The Hamiltonian then takes the form 28 Electron–Electron Interaction and Correlations

$$\mathcal{H} = \sum_{\sigma} \int d\mathbf{r} \, \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \left[-\frac{\hbar^2}{2m_{\rm e}} \nabla^2 + V_{\rm ion}(\mathbf{r}) \right] \hat{\psi}_{\sigma}(\mathbf{r}) + \frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r} \, d\mathbf{r}' \, \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') U(\mathbf{r} - \mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) \,.$$
(28.1.20)

When the addition of an electron to the system at point r is represented by an oriented line starting at r and the removal of an electron by an oriented line ending at r, the interaction between electrons can be represented by the diagram shown in Fig. 28.1.



Fig. 28.1. Diagrammatic representation of the electron–electron interaction. Solid lines denote the electrons annihilated and created at positions r and r'. The wavy line indicates the interaction potential between r and r'

Owing to the anticommutation relation of the field operators [see (H.2.17)],

$$\left[\hat{\psi}_{\sigma}(\boldsymbol{r}), \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}')\right]_{+} = \delta_{\sigma\sigma'}\delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad (28.1.21)$$

the interaction Hamiltonian can be written as

$$\mathcal{H}_{e-e} = \frac{1}{2} \left[\sum_{\sigma\sigma'} \iint d\mathbf{r} \, d\mathbf{r'} \, \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) U(\mathbf{r} - \mathbf{r'}) \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r'}) \hat{\psi}_{\sigma'}(\mathbf{r'}) - N_{e} U(0) \right].$$
(28.1.22)

This is nothing other than the second-quantized form of (28.1.11), since the density of electrons can readily be expressed by the field operators as

$$n(\mathbf{r}) = \sum_{\sigma} \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \,. \tag{28.1.23}$$

In what follows, different choices will be made for the single-particle basis functions leading to somewhat different forms of the Hamiltonian.

28.1.3 The Homogeneous Electron Gas

For the sake of simplicity we will often suppose that the potential $V_{\text{ion}}(\mathbf{r})$ created by positive ions can be replaced by a spatially uniform constant V_0 , as if the charge of the ions had been smeared out uniformly.³ The details of the interaction with ions are thus neglected in this model, and we concentrate

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³ This model is often referred to as the jellium model.

on phenomena caused by the interaction between electrons. The uniformly smeared positive ions are kept only to satisfy charge neutrality. The interaction of electrons with the positive background gives a negative constant contribution to energy. A constant but positive contribution arises from the Coulomb repulsion between ions themselves. V_0 is the sum of these terms. Its value is fixed by the charge neutrality requirement.

When this uniform background is added to the kinetic energy, the eigenfunctions of the one-particle Hamiltonian

$$\mathcal{H}_{0}^{(1)}(\boldsymbol{r}) = -\frac{\hbar^{2}}{2m_{\rm e}}\boldsymbol{\nabla}^{2} + V_{0}$$
(28.1.24)

are plane waves indexed by the wave vector \boldsymbol{k} and spin quantum number σ ,

$$\phi_{\boldsymbol{k}\sigma}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \eta_{\sigma} , \qquad (28.1.25)$$

just as in the empty-lattice approximation. Their energy is $\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}}^{(0)} + V_0$, where $\varepsilon_{\mathbf{k}}^{(0)} = \hbar^2 k^2 / (2m_{\rm e})$ is the energy of free particles.

The operators $c_{k\sigma}^{\dagger}$ and $c_{k\sigma}$ create and annihilate, respectively, these states. The noninteracting Hamiltonian, the first term of (28.1.14), has only diagonal elements:

$$\mathcal{H}_0 = \sum_{k\sigma} \varepsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} \,, \qquad (28.1.26)$$

and the total unperturbed energy of the system, described by a single Slater determinant, is equal to the sum of the energies of the occupied one-particle states.

The Hamiltonian of the electron-electron interaction takes the simple form

$$\mathcal{H}_{e-e} = \frac{1}{2V} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q}\\\sigma\sigma'}} U(\mathbf{q}) c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma} c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma'} c_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma}$$
(28.1.27)

in the plane-wave basis. Since the homogeneous electron gas is invariant under arbitrary translations, the total momentum is conserved. When two particles with wave vectors \mathbf{k} and \mathbf{k}' interact, they are scattered into states with wave vectors $\mathbf{k} + \mathbf{q}$ and $\mathbf{k}' - \mathbf{q}$.

We make two further remarks about the Hamiltonian. First, the value of V_0 has not yet been fixed. We know that it represents some average of the electron-ion and ion-ion Coulomb interactions. It follows from the charge neutrality of the system that – apart from a sign difference – it has to be identical to the $\mathbf{q} = 0$ component of the electron–electron interaction. For this reason, when studying the homogeneous electron gas, we neglect V_0 , provided the $\mathbf{q} = 0$ Fourier component is eliminated from the electron–electron interaction. The bare interaction between electrons is the Coulomb repulsion, whose Fourier transform $U(\mathbf{q})$ is given in (28.1.13). Therefore, we will use

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$$U(\boldsymbol{q}) = \frac{4\pi\tilde{e}^2}{q^2} \left(1 - \delta_{\boldsymbol{q},0}\right)$$
(28.1.28)

for the electron–electron interaction in the homogeneous electron gas.

Second, one has to pay attention to the fact that the Coulomb interaction is long ranged and cannot be treated as a weak perturbation. Certain processes have to be summed up to infinite order or self-consistent procedures have to be applied.

28.1.4 Interaction Between Bloch Electrons

Although the homogeneous electron gas gives a qualitatively correct picture of the effects of electron–electron interaction, this approximation is rather drastic and the results may be quantitatively correct only for the simplest alkali metals. For other metals, where the Fermi surface is not spherical, the effect of the ion potential $V_{\rm ion}(\mathbf{r})$ has to be treated more accurately. One possibility is to choose Bloch functions – the solutions of the single-particle problem in the presence of the periodic lattice potential – as the complete set of single-particle basis states. Denoting the creation and annihilation operators of a Bloch electron in state $\psi_{nk\sigma}(\mathbf{r})$ with energy $\varepsilon_{nk\sigma}$ by $c_{nk\sigma}^{\dagger}$ and $c_{nk\sigma}$, respectively, these operators diagonalize the noninteracting Hamiltonian \mathcal{H}_0 :

$$\mathcal{H}_0 = \sum_{n \boldsymbol{k} \sigma} \varepsilon_{n \boldsymbol{k} \sigma} c^{\dagger}_{n \boldsymbol{k} \sigma} c_{n \boldsymbol{k} \sigma} \,. \tag{28.1.29}$$

The Hamiltonian of the electron–electron interaction then takes the form

$$\mathcal{H}_{e-e} = \frac{1}{2} \sum_{\substack{\{n_i\}, \{k_i\}\\\sigma,\sigma'}} U_{\sigma\sigma'}(n_1, k_1, n_2, k_2, n'_1, k'_1, n'_2, k'_2) \\ \times c^{\dagger}_{n'_1 k'_1 \sigma} c^{\dagger}_{n'_2 k'_2 \sigma'} c_{n_2 k_2 \sigma'} c_{n_1 k_1 \sigma}, \qquad (28.1.30)$$

where the strength of the interaction is given by

$$U_{\sigma\sigma'}(n_1, \mathbf{k}_1, n_2, \mathbf{k}_2, n_1', \mathbf{k}_1', n_2', \mathbf{k}_2') = \iint d\mathbf{r} \, d\mathbf{r}' \, \psi_{n_1' \mathbf{k}_1' \sigma}^*(\mathbf{r}) \psi_{n_2' \mathbf{k}_2' \sigma'}^*(\mathbf{r}') \\ \times U(\mathbf{r} - \mathbf{r}') \psi_{n_2 \mathbf{k}_2 \sigma'}(\mathbf{r}') \psi_{n_1 \mathbf{k}_1 \sigma}(\mathbf{r}) \,.$$
(28.1.31)

The scattering between electrons is not restricted to electrons in the same band; there might be interband processes as well. Thus, in general, the coupling strength should be indexed by four band indices and three wave vectors – if conservation of quasimomentum is taken into account – and it may depend on the spin variables, too. If electrons on completely filled deep levels are incorporated into the ion cores, it is sufficient to consider explicitly only the delocalized electrons of the valence bands. With this assumption we may arrive at a model in which only a single band is retained. In what follows we will often make this simplification and the band index n_i will be neglected. We remark that such a simplified model cannot be valid for transition metals. Their physical properties are determined not solely by the electrons in the 4s (5s) bands. The 3d (4d) bands may play an equally important role.

Since the electron-electron interaction depends on the difference of the spatial coordinates of electrons, the conservation of quasimomentum as given in (6.2.42) has to be satisfied. This can be checked simply by using the Bloch theorem valid for the single-particle wavefunctions $\psi_{nk\sigma}(\mathbf{r})$. To see this the interaction is written in Fourier representation and the integral over the volume of the sample is replaced by a sum over the primitive cells and the integral is performed within the cells. When the spatial coordinate \mathbf{r} is written as $\mathbf{r} = \mathbf{R}_m + \tilde{\mathbf{r}}$, where $\tilde{\mathbf{r}}$ is inside the primitive cell, and the known translational property of Bloch functions is exploited,

$$U_{\sigma\sigma'}(\mathbf{k}_{1},\mathbf{k}_{2},\mathbf{k}_{1}',\mathbf{k}_{2}')$$
(28.1.32)
$$=\sum_{\mathbf{R}_{m}} \int_{v} d\widetilde{\mathbf{r}} \sum_{\mathbf{R}_{n}} \int_{v} d\widetilde{\mathbf{r}}' e^{-i\mathbf{k}_{1}'\cdot\mathbf{R}_{m}} \psi_{\mathbf{k}_{1}'\sigma}^{*}(\widetilde{\mathbf{r}}) e^{-i\mathbf{k}_{2}'\cdot\mathbf{R}_{n}} \psi_{\mathbf{k}_{2}'\sigma'}^{*}(\widetilde{\mathbf{r}}')$$
$$\times \frac{1}{V} \sum_{\mathbf{q}} U(\mathbf{q}) e^{i\mathbf{q}\cdot(\widetilde{\mathbf{r}}+\mathbf{R}_{m}-\widetilde{\mathbf{r}}'-\mathbf{R}_{n})} e^{i\mathbf{k}_{2}\cdot\mathbf{R}_{n}} \psi_{\mathbf{k}_{2}\sigma'}(\widetilde{\mathbf{r}}') e^{i\mathbf{k}_{1}\cdot\mathbf{R}_{m}} \psi_{\mathbf{k}_{1}\sigma}(\widetilde{\mathbf{r}})$$
$$= \frac{1}{V} \sum_{\mathbf{q}} \sum_{\mathbf{G}\mathbf{G}'} U(\mathbf{q}) I_{\sigma\sigma'}(\mathbf{k}_{1},\mathbf{k}_{2},\mathbf{q},\mathbf{G},\mathbf{G}') \delta_{\mathbf{k}_{1}',\mathbf{k}_{1}+\mathbf{q}+\mathbf{G}} \delta_{\mathbf{k}_{2}',\mathbf{k}_{2}-\mathbf{q}+\mathbf{G}'},$$

where G and G' are reciprocal-lattice vectors and

$$I_{\sigma\sigma'}(\boldsymbol{k}_{1},\boldsymbol{k}_{2},\boldsymbol{q},\boldsymbol{G},\boldsymbol{G}') = N^{2} \iint_{v} \mathrm{d}\widetilde{\boldsymbol{r}} \,\mathrm{d}\widetilde{\boldsymbol{r}}' \,\psi_{\boldsymbol{k}_{1}+\boldsymbol{q}+\boldsymbol{G}\sigma}^{*}(\widetilde{\boldsymbol{r}})\psi_{\boldsymbol{k}_{2}-\boldsymbol{q}+\boldsymbol{G}'\sigma'}^{*}(\widetilde{\boldsymbol{r}}') \times \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\widetilde{\boldsymbol{r}}-\widetilde{\boldsymbol{r}}')}\psi_{\boldsymbol{k}_{2}\sigma'}(\widetilde{\boldsymbol{r}}')\psi_{\boldsymbol{k}_{1}\sigma}(\widetilde{\boldsymbol{r}}).$$
(28.1.33)

Electrons with wave vectors k_1 and k_2 are scattered into states with wave vectors $k_1 + q$ and $k_2 - q$, respectively. If necessary, these wave vectors are reduced into the first Brillouin zone by G or G'. In the summations over G and G' in (28.1.32) only that single term contributes through which this reduction is achieved. As before, processes for which no reduction is needed, i.e., G = G' = 0, are called normal processes, while the others are called umklapp processes. Their appearance is an important new feature compared to the homogeneous electron gas, where momentum conservation is rigorously valid.

If umklapp processes can be neglected, the Hamiltonian of interacting Bloch electrons,

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}\\\sigma\sigma'}} U(\boldsymbol{q}) I_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}', \boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma},$$
(28.1.34)

has a form similar to that of the homogeneous electron gas [compare this expression with (28.1.26) and (28.1.27)], except that here the calculated band energies of Bloch electrons have to be used in the kinetic energy and the interaction potential is multiplied by the factor $I_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}', \boldsymbol{q})$. Incorporating this factor into the potential U we will use

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}\\\sigma\sigma'}} U(\boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma}$$
(28.1.35)

as the Hamiltonian of a general interacting electron system.

28.1.5 The Hubbard Model

As has been discussed in Chapter 17, an alternative choice for the complete set of single-particle states is provided by the Wannier functions $\phi_n(\mathbf{r} - \mathbf{R}_i)$. The creation and annihilation operators of the Wannier states, $c_{ni\sigma}^{\dagger}$ and $c_{ni\sigma}$, add or remove the *n*th localized state at lattice point \mathbf{R}_i . However, since the Wannier states are not eigenstates of the one-particle Schrödinger equation for electrons moving in a periodic potential, the unperturbed second-quantized Hamiltonian \mathcal{H}_0 is not diagonal, when these states are used as a basis. As has been shown in (17.5.19),

$$\mathcal{H}_0 = \sum_{n,\sigma} \sum_{ij} t_{n,ij} c^{\dagger}_{nj\sigma} c_{ni\sigma} , \qquad (28.1.36)$$

where

$$t_{n,ij} = \int \phi_n^*(\boldsymbol{r} - \boldsymbol{R}_j) \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 + V_{\rm ion}(\boldsymbol{r}) \right] \phi_n(\boldsymbol{r} - \boldsymbol{R}_i) \,\mathrm{d}\boldsymbol{r} \,.$$
(28.1.37)

Usually the Wannier functions are localized to the neighborhood of the lattice sites and their overlap is small beyond nearest neighbors. Therefore, in most cases it is sufficient to restrict the summation over the lattice sites in \mathcal{H}_0 to nearest-neighbor lattice points.

The interaction between electrons appears in the form

$$\mathcal{H}_{e-e} = \frac{1}{2} \sum_{mnm'n'} \sum_{\sigma\sigma'} \sum_{iji'j'} U^{mnn'm'}_{ijj'i'} c^{\dagger}_{mi\sigma} c^{\dagger}_{nj\sigma'} c_{n'j'\sigma'} c_{m'i'\sigma}, \qquad (28.1.38)$$

where

$$U_{ijj'i'}^{mnn'm'} = \iint \phi_m^*(\boldsymbol{r} - \boldsymbol{R}_i)\phi_n^*(\boldsymbol{r}' - \boldsymbol{R}_j)U(\boldsymbol{r} - \boldsymbol{r}') \times \phi_{n'}(\boldsymbol{r}' - \boldsymbol{R}_{j'})\phi_{m'}(\boldsymbol{r} - \boldsymbol{R}_{i'})\,\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'\,.$$
(28.1.39)

In this representation, too, the interaction can be interpreted as a collision in which two electrons in different Wannier states are scattered into two other Wannier states. In the most general case the four sites \mathbf{R}_i , \mathbf{R}_j , $\mathbf{R}_{i'}$, and $\mathbf{R}_{j'}$ may be different. Two electrons from different sites may be scattered to a third and fourth site. In the physically most relevant processes, however, far away sites are not involved. This is not trivial since the terms with i = i' and j = j' correspond to Coulomb repulsion between electrons at sites i and j, and this interaction is long ranged. However, as will be seen later in the next chapter, the interaction dynamically rearranges the occupied electron states and screens the long-range Coulomb repulsion. Thus the interaction between Wannier states can be taken to be short ranged.

The interaction is rather complicated even if it is supposed to act dominantly between electrons on the same site. Separating the terms corresponding to Wannier states with identical and different spin indices, and the terms involving spin flip,

$$\mathcal{H}_{e-e} = \frac{1}{2} \sum_{i\sigma} \bigg\{ \sum_{mm'} U_{mm'} n_{mi\sigma} n_{m'i,-\sigma}$$

$$+ \sum_{m \neq m'} \bigg[(U_{mm'} - J_{mm'}) n_{mi\sigma} n_{m'i\sigma} - J_{mm'} c^{\dagger}_{mi\sigma} c_{mi,-\sigma} c^{\dagger}_{m'i,-\sigma} c_{m'i\sigma} \bigg] \bigg\},$$
(28.1.40)

where $n_{mi\sigma} = c^{\dagger}_{mi\sigma}c_{mi\sigma}$ is the number operator. The term containing $U_{mm'} = U_{iiii}^{mm'm'm}$ corresponds to the intra-atomic Coulomb interaction and the term with $J_{mm'} = U_{iiii}^{mm'mm'}$ is due to exchange. Assuming that their strength is independent of the band index m we arrive at

$$\mathcal{H}_{e-e} = \frac{1}{2} U_{H} \sum_{i\sigma} \sum_{mm'} n_{mi\sigma} n_{m'i,-\sigma} + \frac{1}{2} (U_{H} - J) \sum_{i\sigma} \sum_{m\neq m'} n_{mi\sigma} n_{m'i\sigma} - \frac{1}{2} J \sum_{i\sigma} \sum_{mm'} c^{\dagger}_{mi\sigma} c_{mi,-\sigma} c^{\dagger}_{m'i,-\sigma} c_{m'i\sigma} .$$

$$(28.1.41)$$

For the sake of simplicity we will take one nondegenerate Wannier state per atom. Then the only surviving term is the intra-atomic Coulomb repulsion between electrons of opposite spins. The exchange term is missing. The Hamiltonian then reduces to

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U_{\rm H}}{2} \sum_{i\sigma} n_{i,\sigma} n_{i,-\sigma}$$
$$= \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U_{\rm H} \sum_{i} n_{i\uparrow} n_{i\downarrow} .$$
(28.1.42)

It follows from the anticommutation rules for fermion operators that

$$n_{i\sigma}^2 = n_{i\sigma} \,,$$
 (28.1.43)

and therefore the Hamiltonian can be written in the equivalent form:

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$$\mathcal{H} = \sum_{ij\sigma} \left(t_{ij} - \frac{1}{2} U_{\mathrm{H}} \delta_{ij} \right) c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{1}{2} U_{\mathrm{H}} \sum_{i\sigma\sigma'} n_{i,\sigma} n_{i,\sigma'} \,. \tag{28.1.44}$$

This model in which the Coulomb repulsion is taken into account only between electrons on the same site is the *Hubbard model.*⁴ Despite its simple form, the model cannot be solved exactly, except in one dimension, when electrons hop along a chain only. Although the approximate solutions obtained in higher dimensions are in qualitative agreement with some magnetic properties of transition metals and give a qualitatively correct description of the metal-insulator transition due to interaction, it is not clear at all whether a more reliable solution of the model, to which many efforts have been devoted, would reproduce the experimentally observed features or whether a more general model with many more parameters would be necessary to understand these phenomena.

One possibility for going beyond the Hubbard model is to include the Coulomb interaction between electrons on nearest-neighbor sites. This is the *extended Hubbard model* or t-U-V model with Hamiltonian

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U_{\rm H} \sum_{i} n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle \sigma \sigma'} n_{i\sigma} n_{j\sigma'} , \qquad (28.1.45)$$

where $\langle ij \rangle$ denotes that *i* and *j* are nearest neighbors. When a site is singly occupied with a spin-up or spin-down electron, it has a magnetic moment. Exchange between neighboring singly occupied sites leads to a usual Heisenberg-like coupling with a *J* on the order of $t^2/U_{\rm H}$. When this term is included in the Hubbard model with an independent coupling *J*, the so-called t-U-J model defined by

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U_{\rm H} \sum_{i} n_{i\uparrow} n_{i\downarrow} + J \sum_{\langle ij \rangle} \boldsymbol{S}_{i} \cdot \boldsymbol{S}_{j}$$
(28.1.46)

is obtained. A special case of that is the t-J model. When U is much larger than the bandwidth, which is the other characteristic energy scale of the model, doubly occupied sites are practically forbidden. The on-site Coulomb repulsion can then be omitted from the Hamiltonian,

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + J \sum_{\langle ij \rangle} \boldsymbol{S}_{i} \cdot \boldsymbol{S}_{j}, \qquad (28.1.47)$$

keeping in mind that only empty and singly occupied sites are allowed.⁵ The physics of these models will be discussed in later chapters. Since the original

⁴ J. HUBBARD, 1963. The model is named after Hubbard although the same model was proposed by M. C. GUTZWILLER and J. KANAMORI at the same time to describe the magnetic properties of transition metals.

⁵ Note that also three-site terms of the form $c_{i,\sigma}^{\dagger}c_{j,-\sigma}^{\dagger}c_{j,\sigma}c_{k,-\sigma}$ and $c_{i,\sigma}^{\dagger}c_{j,-\sigma}^{\dagger}c_{j,-\sigma}c_{k,\sigma}$ appear in the effective Hamiltonian as the doubly occupied sites are eliminated.

Hubbard model is the simplest interacting electron model defined on a lattice and one of the most studied models of solid-state physics, we will often refer to it in what follows.

The Hubbard model has been defined in the Wannier representation. It could be given in terms of the creation and annihilation operators of Bloch states using (17.5.6) and (17.5.20) that relate the creation and annihilation operators in Bloch and Wannier representations, respectively. It becomes

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{U_{\mathrm{H}}}{N} \sum_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}} c_{\boldsymbol{k}+\boldsymbol{q}\uparrow}^{\dagger} c_{\boldsymbol{k}'-\boldsymbol{q}\downarrow}^{\dagger} c_{\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}\uparrow}, \qquad (28.1.48)$$

where N is the number of lattice sites. In an alternative form, starting from (28.1.44),

$$\mathcal{H} = \sum_{k\sigma} \varepsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} + \frac{U_{\rm H}}{2N} \sum_{\substack{kk'q\\\sigma\sigma'}} c^{\dagger}_{k+q\sigma} c^{\dagger}_{k'-q\sigma'} c_{k'\sigma'} c_{k\sigma} \,. \tag{28.1.49}$$

The term containing $U_{\rm H}$ drops out of the kinetic energy if the operators are arranged in the order as they appear here in the interaction.

Introducing a coupling U via

$$U_{\rm H} = U \frac{N}{V} \tag{28.1.50}$$

the Hubbard model can be written in the Bloch representation as

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{U}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}\\\sigma\sigma'}} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma} \,. \tag{28.1.51}$$

Comparison of (28.1.51) with (28.1.34) shows that the choice of a local interaction in the Hubbard model corresponds to a momentum-independent $U(\mathbf{q})I_{\sigma\sigma'}(\mathbf{k},\mathbf{k}',\mathbf{q}) = U$, in sharp contrast to the strong \mathbf{q} dependence in the homogeneous electron gas. This is because the screening of the long-range Coulomb interaction, to be discussed in the next chapter, has already been taken into account in the Hubbard model, when only on-site interaction is included.

We have derived two forms for the interaction. One, (28.1.34), is given in terms of Bloch states and the other, (28.1.38), in terms of Wannier states. They can be used in principle equivalently to get a full description of the effects of interaction. In practical calculations, however, approximations have to be made. The more appropriate representation – Bloch or Wannier – of the electron states and the most adequate approximation scheme for studying the physical properties of a given system depend on the band structure. It turns out that the interaction is treated more easily in terms of delocalized Bloch states when the behavior of simple metals with a single broad valence band
is studied. On the other hand, when the properties of transition metals are treated, where the band states formed from 3d (4d) electronic levels are important, the description in terms of Wannier states may be more convenient. Accordingly, in what follows, we will frequently treat the homogeneous electron gas, since it gives a qualitatively correct physical picture of the effects of interaction. However, when we want to get a simple description of the magnetic properties of transition metals, the Hubbard model will be considered.

28.2 Normal Fermi Systems

We know that the one-particle states with wave vector within the Fermi sphere are completely filled in the ground state of noninteracting fermions and the states outside the Fermi sphere are empty. One might think that the Fermi edge, the discontinuity in the momentum distribution function, which is a characteristic feature of the ground state of a free fermion system, will be smeared out by processes in which electrons inside the Fermi sphere are scattered outside, leaving holes behind. In reality quite often though not always, this is not the case: A discontinuity remains in the momentum distribution function. To illustrate this, we calculate the momentum distribution, the average number of electrons with wave vector \mathbf{k} and spin σ in the ground state $|\Psi\rangle$ of the interacting system,

$$\langle n_{\boldsymbol{k}\sigma} \rangle = \langle \Psi | c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} | \Psi \rangle,$$
 (28.2.1)

in perturbation theory for the Hubbard model.

According to (G.1.10) the perturbed wavefunction can be written to first order in the electron–electron interaction in the form

$$|\Psi\rangle = |\Psi_{\rm FS}\rangle + \frac{U}{V} \sum_{\boldsymbol{k}_1 \boldsymbol{k}_2 \boldsymbol{q}} \frac{1}{\varepsilon_{\boldsymbol{k}_1} + \varepsilon_{\boldsymbol{k}_2} - \varepsilon_{\boldsymbol{k}_1 + \boldsymbol{q}} - \varepsilon_{\boldsymbol{k}_2 - \boldsymbol{q}}} c^{\dagger}_{\boldsymbol{k}_1 + \boldsymbol{q}\uparrow} c^{\dagger}_{\boldsymbol{k}_2 - \boldsymbol{q}\downarrow} c_{\boldsymbol{k}_2 \downarrow} c_{\boldsymbol{k}_1 \uparrow} |\Psi_{\rm FS}\rangle,$$
(28.2.2)

where $|\Psi_{\rm FS}\rangle$ denotes the wavefunction of the unperturbed Fermi sea. The perturbed wavefunction clearly shows that configurations with two holes in the Fermi sphere and two occupied states outside the Fermi sphere appear with nonzero probability in the ground state of the interacting system.

We consider first the case $|\mathbf{k}| > k_{\rm F}$. A nonvanishing perturbative correction to the momentum distribution is obtained only if – depending on the spin – either $\mathbf{k}_1 + \mathbf{q}$ or $\mathbf{k}_2 - \mathbf{q}$ is equal to \mathbf{k} . The conditions that \mathbf{k}_1 and \mathbf{k}_2 are inside the Fermi sphere, while $\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}$ is outside, can be expressed by the Fermi distribution function. Thus we find

$$\left\langle n_{\boldsymbol{k}\sigma} \right\rangle_{|\boldsymbol{k}| > k_{\mathrm{F}}} = \left(\frac{U}{V}\right)^{2} \sum_{\boldsymbol{k}_{1}\boldsymbol{k}_{2}} \frac{\left[1 - f_{0}(\varepsilon_{\boldsymbol{k}_{1}+\boldsymbol{k}_{2}-\boldsymbol{k}})\right] f_{0}(\varepsilon_{\boldsymbol{k}_{1}}) f_{0}(\varepsilon_{\boldsymbol{k}_{2}})}{(\varepsilon_{\boldsymbol{k}_{1}} + \varepsilon_{\boldsymbol{k}_{2}} - \varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}_{1}+\boldsymbol{k}_{2}-\boldsymbol{k}})^{2}} .$$
(28.2.3)

For wave numbers inside the Fermi sphere it is more convenient to calculate $\langle \Psi | c_{k\sigma}^{\dagger} c_{k\sigma} | \Psi \rangle$ by writing it as $1 - \langle \Psi | c_{k\sigma} c_{k\sigma}^{\dagger} | \Psi \rangle$. In lowest order, the mean occupation of state k is reduced from unity owing to processes in which two electrons are kicked out of the Fermi sea into states k_1 and k_2 , and holes with wave vectors k and $k_1 + k_2 - k$ are left behind. The contribution of these processes gives

$$\langle n_{\boldsymbol{k}\sigma} \rangle_{|\boldsymbol{k}| < k_{\mathrm{F}}} = 1 - \left(\frac{U}{V}\right)^{2} \sum_{\boldsymbol{k}_{1}\boldsymbol{k}_{2}} \frac{f_{0}(\varepsilon_{\boldsymbol{k}_{1}+\boldsymbol{k}_{2}-\boldsymbol{k}}) \left[1 - f_{0}(\varepsilon_{\boldsymbol{k}_{1}})\right] \left[1 - f_{0}(\varepsilon_{\boldsymbol{k}_{2}})\right]}{(\varepsilon_{\boldsymbol{k}} + \varepsilon_{\boldsymbol{k}_{1}+\boldsymbol{k}_{2}-\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}_{1}} - \varepsilon_{\boldsymbol{k}_{2}})^{2}}.$$
(28.2.4)

These rather cumbersome expressions can be evaluated analytically in an isotropic model if the sums over \mathbf{k}_i are replaced by integrals. Figure 28.2 shows the region of integration allowed by the Fermi distribution functions for \mathbf{k}_2 – at fixed values of \mathbf{k}_1 – when \mathbf{k} is right on the Fermi surface, infinitesimally above or below it.



Fig. 28.2. Allowed values of k_2 (shaded region) in the integral determining the momentum distribution: (a) for wave vector k right outside the Fermi surface, when k_1 has to be within the Fermi sphere; (b) for wave vector k right inside the Fermi surface, when k_1 has to be outside the Fermi sphere

Performing first the integral over k_2 in cylindrical coordinates using $k_1 - k$ as the axis, and then the integral over k_1 , again in cylindrical coordinates, using now the direction of k as the axis, we get

$$\langle n_{\boldsymbol{k}\sigma} \rangle_{k=k_{\rm F}+\delta} = \frac{1}{8} \left[U \rho(\varepsilon_{\rm F}) \right]^2 \left(\ln 2 - \frac{1}{3} \right)$$
 (28.2.5)

for wave vectors infinite simally outside the Fermi sphere. For ${\boldsymbol k}$ inside the Fermi sphere we have

$$\langle n_{\boldsymbol{k}\sigma} \rangle_{k=k_{\mathrm{F}}-\delta} = 1 - \frac{1}{8} \left[U\rho(\varepsilon_{\mathrm{F}}) \right]^2 \left(\ln 2 + \frac{1}{3} \right).$$
 (28.2.6)

The momentum distribution is not continuous as we cross the Fermi surface. A finite jump is found which is somewhat smaller than unity and depends on the strength of the interaction: 16 28 Electron–Electron Interaction and Correlations

$$\langle n_{\boldsymbol{k}\sigma} \rangle_{k=k_{\rm F}-\delta} - \langle n_{\boldsymbol{k}\sigma} \rangle_{k=k_{\rm F}+\delta} = 1 - \frac{1}{4} \left[U\rho(\varepsilon_{\rm F}) \right]^2 \ln 2.$$
 (28.2.7)

For a general k away from the Fermi surface, the integrals can be evaluated numerically. The momentum distribution is shown in Fig. 28.3.



Fig. 28.3. Momentum distribution for an interacting, but normal Fermi system

In higher orders of perturbation theory more and more holes are created inside the Fermi sphere, while more and more electrons occupy states outside. Nevertheless, it can be shown using methods of the many-body theory that a sharp discontinuity, a sharp finite jump – known as the *Fermi edge* – survives in the momentum distribution function of both the uniform electron gas and the Hubbard model even if all perturbative corrections are summed up to infinite order. The results of Compton scattering experiments on alkali metals, i.e., the inelastic scattering of photons, can be interpreted by assuming a value 0.5 for the discontinuity in the momentum distribution. This is reasonably close to the values between 0.6 and 0.8 valid for the homogeneous electron gas at densities characteristic of metals.

Although the particles are interacting, a Fermi surface may be defined in k-space as the locus of points where the momentum distribution is discontinuous. In isotropic systems this discontinuity appears exactly at the Fermi momentum $k_{\rm F}$ of the unperturbed system, which means that in isotropic systems the interaction does not distort the spherical Fermi surface. In more realistic models, where the periodic potential of the ions gives rise to a nonspherical Fermi surface, the electron–electron interaction may modify its shape. However, according to the *Luttinger theorem* the k-space volume of the Fermi surface defined by the discontinuity is unaffected by the interaction.

The existence of a sharp Fermi edge and the Luttinger theorem stating the conservation of the volume enclosed by the Fermi surface can be proven quite generally, provided that perturbation theory is applicable and the perturbation series converges. Fermi systems for which this assumption is valid are called *normal Fermi systems*. Their perturbed ground state can be obtained from the noninteracting ground state by turning on the interaction adiabatically. This is the case for ordinary metals.

There are systems, however, in which the interaction cannot be treated in perturbation theory. This is the case, for example, in one-dimensional systems. To demonstrate the breakdown of the perturbation series we calculate the first nonvanishing correction to the momentum distribution for $k > k_{\rm F}$ applying (28.2.3) to a one-dimensional model. A nonvanishing correction is obtained if k_1 and k_2 are in the range $(-k_{\rm F}, k_{\rm F})$ and $k_1 + k_2 - k$ is outside this range. These requirements can be satisfied if k_1 is in the neighborhood of $+k_{\rm F}$ and k_2 in the neighborhood of $-k_{\rm F}$ or vice versa. For the sake of simplicity the dispersion curve is approximated by a linear dependence in the neighborhood of the Fermi points $k_{\rm F}$ and $-k_{\rm F}$ in a range of width $2k_{\rm c}$, that is we choose the energy vs. momentum relation in the form

$$\varepsilon_{k} = \begin{cases} \hbar v_{\rm F}(k - k_{\rm F}) & \text{for } k_{\rm F} - k_{\rm c} < k < k_{\rm F} + k_{\rm c} ,\\ -\hbar v_{\rm F}(k + k_{\rm F}) & \text{for } -k_{\rm F} - k_{\rm c} < k < -k_{\rm F} + k_{\rm c} , \end{cases}$$
(28.2.8)

where $v_{\rm F}$ is the Fermi velocity. Performing the integrals we get

$$\langle n_{\boldsymbol{k}\sigma} \rangle_{k>k_{\rm F}} = 2U^2 \int_{k_{\rm F}-k_c}^{k_{\rm F}} \frac{\mathrm{d}k_1}{2\pi} \int_{-k_{\rm F}}^{-k_{\rm F}+k_c} \frac{\mathrm{d}k_2}{2\pi} \frac{\theta(-k_{\rm F}-(k_1+k_2-k))}{[2\hbar v_{\rm F}(k_1-k)]^2}$$

$$= 2\left(\frac{U}{4\pi\hbar v_{\rm F}}\right)^2 \int_{k_{\rm F}-k_c}^{k_{\rm F}} \mathrm{d}k_1 \frac{1}{k-k_1}$$

$$= 2\left(\frac{U}{4\pi\hbar v_{\rm F}}\right)^2 \ln\left(\frac{k_c}{k-k_{\rm F}}\right).$$

$$(28.2.9)$$

As k tends to $k_{\rm F}$ this second-order correction diverges logarithmically, indicating that the perturbative approach is not applicable to one-dimensional systems. As we will see later, the physical properties of one-dimensional fermion systems differ substantially from that of normal systems due to the absence of a sharp Fermi surface. Later we will also encounter three-dimensional fermion systems with no Fermi edge. These systems, too, exhibit novel properties. In the next few chapters, however, we will first consider the properties of normal systems, where the perturbative approach is applicable.

28.3 Simple Approximate Treatments of the Interaction

The correct treatment of electron–electron interaction is a difficult task and most of this volume is devoted to this problem. In this introductory chapter the simplest approximation methods are presented.

We have seen in Chapter 14 that the magnetic properties of solids can be understood qualitatively rather well if the effects of the environment on a given spin – the influence of other, neighboring spins – are taken into account approximately as a mean, self-consistently determined effective field. A similar approach could be used for electrons by assuming that the electrons feel an effective one-particle potential created by the others. However, this effective field has to be calculated with much more care due to the fermionic nature of electrons. After presenting the methods, they will be applied to the homogeneous electron gas and the Hubbard model. The latter problem will be elaborated in more detail in the next chapter and in Chapter 33.

28.3.1 Hartree Approximation

As early as 1929 D. R. HARTREE proposed a simple approach by which a self-consistent effective potential can be defined. He assumed that the electron system can be fully characterized by the number density $n_{\rm e}(\mathbf{r})$, and the electrons do not feel each other individually, only through the Coulomb potential created by the charge density $\rho(\mathbf{r}) = -en_{\rm e}(\mathbf{r})$. The Coulomb potential at point \mathbf{r} is

$$\varphi_{\rm e-e}(\boldsymbol{r}) = \frac{1}{4\pi\epsilon_0} \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} = -\frac{e}{4\pi\epsilon_0} \int d\boldsymbol{r}' \frac{n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}, \qquad (28.3.1)$$

and thus the effective one-particle Hartree potential is

$$V_{\rm H}(\boldsymbol{r}) = -e\varphi_{\rm e-e}(\boldsymbol{r}) = \tilde{e}^2 \int \mathrm{d}\boldsymbol{r}' \frac{n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \,. \tag{28.3.2}$$

For a general two-particle interaction $U(\boldsymbol{r} - \boldsymbol{r}')$ the Hartree potential is

$$V_{\rm H}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' U(\boldsymbol{r} - \boldsymbol{r}') n_{\rm e}(\boldsymbol{r}') \,. \tag{28.3.3}$$

The total effective potential $V_{\text{eff}}(\mathbf{r})$ acting on the electrons includes the external potential $V_{\text{ion}}(\mathbf{r})$ due to ions, thus

$$V_{\rm eff}(\mathbf{r}) = V_{\rm ion}(\mathbf{r}) + V_{\rm H}(\mathbf{r}).$$
 (28.3.4)

The number density $n_{\rm e}(\mathbf{r})$ appearing in (28.3.1) or (28.3.3) has to be calculated self-consistently from the ground-state wavefunction Ψ of the manyelectron system as the expectation value of the number-density operator $n(\mathbf{r})$ defined in (28.1.7):

$$n_{\rm e}(\boldsymbol{r}) = \left\langle n(\boldsymbol{r}) \right\rangle = \left\langle \Psi \middle| \sum_{i=1}^{N_{\rm e}} \delta(\boldsymbol{r} - \boldsymbol{r}_i) \middle| \Psi \right\rangle.$$
(28.3.5)

In this approach the total Hamiltonian is the sum of one-particle contributions, which themselves are the sum of the kinetic energy and the one-particle potential:

$$\mathcal{H} = \sum_{i=1}^{N_{\rm e}} \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}_i^2 + V_{\rm eff}(\boldsymbol{r}_i) \right].$$
(28.3.6)

The wavefunction of the many-body system can then be constructed from solutions of the one-particle Schrödinger equation

$$-\frac{\hbar^2}{2m_{\rm e}}\nabla^2\phi_{\lambda}(\boldsymbol{r}) + V_{\rm eff}(\boldsymbol{r})\phi_{\lambda}(\boldsymbol{r}) = \varepsilon_{\lambda}\phi_{\lambda}(\boldsymbol{r}). \qquad (28.3.7)$$

The quantum number λ of the single-particle states is not specified yet, although we know that in a system that is invariant under discrete translations of the lattice, the wave vector \mathbf{k} , the band index n, and the spin quantum number σ could be used. The solution of this single-particle problem does not pose a problem of principle. The complete orthonormal set of single-particle eigenfunctions and the corresponding energies can be computed.

Let us suppose that the first, second, ..., $N_{\rm e}$ th electron occupies the state $\phi_{\lambda_1,\sigma_1}(\boldsymbol{r}_1,s_1), \phi_{\lambda_2,\sigma_2}(\boldsymbol{r}_2,s_2), \ldots, \phi_{\lambda_{N_{\rm e}},\sigma_{N_{\rm e}}}(\boldsymbol{r}_{N{\rm e}},s_{N_{\rm e}})$, respectively. The wave-function $\phi_{\lambda_i,\sigma_i}(\boldsymbol{r}_i,s_i)$ denotes the product of the spatial and spin functions,

$$\phi_{\lambda_i}(\boldsymbol{r}_i)\eta_{\sigma_i}(s_i). \tag{28.3.8}$$

Of course, owing to the Pauli exclusion principle, all these states have to have different quantum numbers.

In the Hartree approximation, the many-body wavefunction $\Psi_{\rm H}$ is written as a product of the wavefunctions of the occupied single-particle states,

$$\Psi_{\rm H} = \phi_{\lambda_1,\sigma_1}(\boldsymbol{r}_1, s_1) \phi_{\lambda_2,\sigma_2}(\boldsymbol{r}_2, s_2) \cdots \phi_{\lambda_{N_{\rm e}},\sigma_{N_{\rm e}}}(\boldsymbol{r}_{N_{\rm e}}, s_{N_{\rm e}}) \,. \tag{28.3.9}$$

Substituting this wavefunction into (28.3.5), the self-consistency requirement for the density leads to

$$n_{\rm e}(\mathbf{r}) = \sum_{i=1}^{N_{\rm e}} \int d\xi_1 \int d\xi_2 \dots \int d\xi_{N_{\rm e}} \, \phi^*_{\lambda_1,\sigma_1}(\xi_1) \phi^*_{\lambda_2,\sigma_2}(\xi_2) \cdots \phi^*_{\lambda_{N_{\rm e}},\sigma_{N_{\rm e}}}(\xi_{N_{\rm e}}) \\ \times \delta(\mathbf{r} - \mathbf{r}_i) \phi_{\lambda_1,\sigma_1}(\xi_1) \phi_{\lambda_2,\sigma_2}(\xi_2) \dots \phi_{\lambda_{N_{\rm e}},\sigma_{N_{\rm e}}}(\xi_{N_{\rm e}}), \qquad (28.3.10)$$

where ξ_i is a short-hand notation for r_i and s_i , and integration over ξ_i implies integration over the spatial variable and summation over the spin variable. Using the orthonormality relation (28.1.19) of the spin functions, one obtains readily that for a spin-independent quantity like the electron density the product of the spin functions in (28.3.10) gives unity. Integration over the spatial variables can be performed using the orthonormality of the single-particle wavefunctions. We then get

$$n_{e}(\boldsymbol{r}) = \sum_{i=1}^{N_{e}} \int d\boldsymbol{r}_{1} \int d\boldsymbol{r}_{2} \cdots \int d\boldsymbol{r}_{N_{e}} \, \phi_{\lambda_{1}}^{*}(\boldsymbol{r}_{1}) \phi_{\lambda_{2}}^{*}(\boldsymbol{r}_{2}) \cdots \phi_{\lambda_{N_{e}}}^{*}(\boldsymbol{r}_{N_{e}}) \\ \times \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) \phi_{\lambda_{1}}(\boldsymbol{r}_{1}) \phi_{\lambda_{2}}(\boldsymbol{r}_{2}) \cdots \phi_{\lambda_{N_{e}}}(\boldsymbol{r}_{N_{e}}) \\ = \sum_{i=1}^{N_{e}} |\phi_{\lambda_{i}}(\boldsymbol{r})|^{2} \,.$$
(28.3.11)

The total electron density is obtained by summing the contributions of the $N_{\rm e}$ occupied one-particle states. If we were to use it in the Hartree potential, self-interaction would be included, while it should be excluded on physical grounds. The procedure has to be refined. An electron in state λ_i feels only the potentials generated by the $N_{\rm e} - 1$ other electrons, that is, the effective potential acting on that electron is

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \tilde{e}^2 \sum_{\substack{j=1\\j\neq i}}^{N_{\text{e}}} \int d\mathbf{r}' \frac{|\phi_{\lambda_j}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \qquad (28.3.12)$$

and the single-particle wavefunctions have to be calculated from the equations

$$-\frac{\hbar^{2}}{2m_{e}}\nabla^{2}\phi_{\lambda_{i}}(\boldsymbol{r}) + V_{ion}(\boldsymbol{r})\phi_{\lambda_{i}}(\boldsymbol{r}) + \tilde{e}^{2}\sum_{\substack{j=1\\j\neq i}}^{N_{e}}\int d\boldsymbol{r}' \frac{|\phi_{\lambda_{j}}(\boldsymbol{r}')|^{2}}{|\boldsymbol{r}-\boldsymbol{r}'|}\phi_{\lambda_{i}}(\boldsymbol{r}) = \varepsilon_{\lambda_{i}}\phi_{\lambda_{i}}(\boldsymbol{r})$$
(28.3.13)

known as the *Hartree equations*. For a general two-particle interaction they have the form

$$-\frac{\hbar^{2}}{2m_{e}}\nabla^{2}\phi_{\lambda_{i}}(\boldsymbol{r}) + V_{ion}(\boldsymbol{r})\phi_{\lambda_{i}}(\boldsymbol{r}) + \sum_{\substack{j=1\\j\neq i}}^{N_{e}}\int d\boldsymbol{r}' U(\boldsymbol{r}-\boldsymbol{r}')|\phi_{\lambda_{j}}(\boldsymbol{r}')|^{2}\phi_{\lambda_{i}}(\boldsymbol{r}) = \varepsilon_{\lambda_{i}}\phi_{\lambda_{i}}(\boldsymbol{r}).$$

$$(28.3.14)$$

Note that the Hartree equations are not usual Schrödinger equations. The third term of the left-hand side depends on the quantum numbers of the state to be calculated, and the system of equations has to be solved self-consistently. In many-body systems, where $N_{\rm e}$ is large, the full number density given in (28.3.11) may be used in the Hartree potential, since inclusion of the i = j term would give only a negligible shift of the energies.

28.3.2 Hartree Approximation as a Mean-Field Theory

In the Hartree approximation electrons move in an effective, self-consistent potential (28.3.12) created by the others. It should not surprise us that this approximation is in fact a mean-field theory (MFT) of the electron gas in the sense MFT was introduced in Chapter 14 in the study of magnetic properties of solids. Since that treatment shows better what is neglected in the approximation, we will rederive the Hartree equations following standard mean-field theory.

The idea behind this approximation is that fluctuations are weak for some quantities and so the mean-square deviations from the expectation values of the corresponding operators can be neglected. When this method is applied to fermions, we may assume that certain pairs of fermion operators could be replaced by their expectation values in the Hamiltonian, but these expectation values have to be determined self-consistently. In order to get the total energy of the system correctly, a term containing only expectation values has to be added to the energy. Of course, one has to be careful in choosing the operators that are to be replaced by their expectation values. The choice depends on the system or more precisely on the nature of the state under study.

According to (28.1.11) the electron–electron interaction can be written in terms of the electron densities at sites \mathbf{r} and $\mathbf{r'}$, more precisely the strength of the interaction $U(\mathbf{r} - \mathbf{r'})$ has to be multiplied by the densities and integrated over the volume of the sample. Leaving out the constant term that eliminates self-interaction, we have

$$\frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{e}} U(\boldsymbol{r}_{i} - \boldsymbol{r}_{j}) = \frac{1}{2} \iint \mathrm{d}\boldsymbol{r} \,\mathrm{d}\boldsymbol{r}' U(\boldsymbol{r} - \boldsymbol{r}') n(\boldsymbol{r}) n(\boldsymbol{r}') \,.$$
(28.3.15)

In normal Fermi systems, where there are no anomalous, symmetry-breaking averages, the natural choice is to approximate the number-density operator by its expectation value, supposing that density fluctuations can be neglected. The standard procedure of neglecting $[n(\mathbf{r}) - \langle n(\mathbf{r}) \rangle][n(\mathbf{r}') - \langle n(\mathbf{r}') \rangle]$ leads to

$$\frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{\mathbf{c}}} U(\mathbf{r}_{i} - \mathbf{r}_{j}) \approx \iint \mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' U(\mathbf{r} - \mathbf{r}') n(\mathbf{r}) \langle n(\mathbf{r}') \rangle - \frac{1}{2} \iint \mathrm{d}\mathbf{r} \,\mathrm{d}\mathbf{r}' U(\mathbf{r} - \mathbf{r}') \langle n(\mathbf{r}) \rangle \langle n(\mathbf{r}') \rangle.$$
(28.3.16)

The first term on the right-hand side can be written in an equivalent form by substituting (28.1.7) for $n(\mathbf{r})$ and we have

$$\sum_{i=1}^{N_{\rm e}} \int \mathrm{d}\boldsymbol{r}' U(\boldsymbol{r}_i - \boldsymbol{r}') \langle n(\boldsymbol{r}') \rangle. \qquad (28.3.17)$$

Making use of this expression in (28.1.1) gives

$$\mathcal{H} \approx \sum_{i=1}^{N_{\rm e}} \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}_i^2 + V_{\rm ion}(\boldsymbol{r}_i) + \int \mathrm{d}\boldsymbol{r}' U(\boldsymbol{r}_i - \boldsymbol{r}') \langle n(\boldsymbol{r}') \rangle \right] - \frac{1}{2} \iint \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' U(\boldsymbol{r} - \boldsymbol{r}') \langle n(\boldsymbol{r}) \rangle \langle n(\boldsymbol{r}') \rangle$$
(28.3.18)

for the mean-field Hamiltonian. The first term is indeed the sum of one-particle terms with the effective potential given in (28.3.3) and (28.3.4). The physical

meaning of the constant correction term will be discussed later. The Hartree equations are the eigenvalue equations of this one-particle problem:

$$\mathcal{H}_{\rm H}^{(1)}(\boldsymbol{r})\phi_{\lambda}(\boldsymbol{r}) = \varepsilon_{\lambda}\phi_{\lambda}(\boldsymbol{r}), \qquad (28.3.19)$$

where

$$\mathcal{H}_{\rm H}^{(1)}(\boldsymbol{r}) = -\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 + V_{\rm ion}(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}' \, U(\boldsymbol{r} - \boldsymbol{r}') \langle n(\boldsymbol{r}') \rangle \,, \qquad (28.3.20)$$

and the density $\langle n(\mathbf{r}) \rangle = n_{\rm e}(\mathbf{r})$ has to be calculated self-consistently using (28.3.11) or, more precisely, an expression where self-interaction is omitted.

When the same mean-field approximation is applied to the Hamiltonian (28.1.20) written in terms of the field operators, we have

$$\begin{aligned} \mathcal{H}_{\mathrm{H}} &= \sum_{\sigma} \int \mathrm{d}\boldsymbol{r} \, \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) \left[-\frac{\hbar^{2}}{2m_{\mathrm{e}}} \boldsymbol{\nabla}^{2} + V_{\mathrm{ion}}(\boldsymbol{r}) \right] \hat{\psi}_{\sigma}(\boldsymbol{r}) \\ &+ \sum_{\sigma\sigma'} \iint \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' \, \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) U(\boldsymbol{r} - \boldsymbol{r}') \big\langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}') \hat{\psi}_{\sigma'}(\boldsymbol{r}') \big\rangle \hat{\psi}_{\sigma}(\boldsymbol{r}) \\ &- \frac{1}{2} \sum_{\sigma\sigma'} \iint \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' \, U(\boldsymbol{r} - \boldsymbol{r}') \big\langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}') \hat{\psi}_{\sigma'}(\boldsymbol{r}') \big\rangle \big\langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) \big\rangle \,. \end{aligned}$$
(28.3.21)

This can be written in the form

$$\mathcal{H}_{\mathrm{H}} = \sum_{\sigma} \int \mathrm{d}\boldsymbol{r} \, \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) \mathcal{H}_{\mathrm{H}}^{(1)}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) - \frac{1}{2} \sum_{\sigma\sigma'} \int \!\!\!\int \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' \, U(\boldsymbol{r} - \boldsymbol{r}') \big\langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}') \hat{\psi}_{\sigma'}(\boldsymbol{r}') \big\rangle \big\langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) \big\rangle$$
(28.3.22)

with the one-particle Hamiltonian

$$\mathcal{H}_{\rm H}^{(1)}(\boldsymbol{r}) = -\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 + V_{\rm ion}(\boldsymbol{r}) + \sum_{\sigma'} \int \mathrm{d}\boldsymbol{r}' \, U(\boldsymbol{r} - \boldsymbol{r}') \left\langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}') \hat{\psi}_{\sigma'}(\boldsymbol{r}') \right\rangle.$$
(28.3.23)

The Hamiltonian takes an even simpler form when it is written in terms of the creation and annihilation operators of the one-particle states $\phi_{\lambda\sigma}(\mathbf{r})$. The creation operator $c^{\dagger}_{\lambda\sigma}$ adds a particle with spatial wavefunction $\phi_{\lambda}(\mathbf{r})$ and spin σ to the system. Its adjoint, the annihilation operator $c_{\lambda\sigma}$, removes a particle with quantum numbers λ and σ . Since $\phi_{\lambda}(\mathbf{r})$ is an eigenfunction of the one-particle problem, the full Hamiltonian becomes diagonal in the Hartree approximation:

$$\mathcal{H}_{\rm H} = \sum_{\lambda\sigma} \varepsilon_{\lambda} c_{\lambda\sigma}^{\dagger} c_{\lambda\sigma} - \frac{1}{2} \iint \mathrm{d}\boldsymbol{r} \,\mathrm{d}\boldsymbol{r}' U(\boldsymbol{r} - \boldsymbol{r}') \langle n(\boldsymbol{r}) \rangle \langle n(\boldsymbol{r}') \rangle \,. \tag{28.3.24}$$

It is important to note that while the summation in the first term of (28.3.24) goes over all allowed quantum numbers, while the summation in the density [see (28.3.11)], that is in the effective field generated by the other electrons, goes over the occupied states only.

In the presence of a realistic periodic potential $V_{\rm ion}(\mathbf{r})$, this coupled set of nonlinear equations can be solved only numerically for the $N_{\rm e}$ occupied states. The homogeneous electron gas is an exception. Due to charge neutrality, the mean potential created by the uniform electron density cancels exactly the potential of the uniform positive background,

$$V_0 - e\phi_{\rm e-e}(\mathbf{r}) = 0. \qquad (28.3.25)$$

Then the Hartree equations are identical to the Schrödinger equation of free electrons and the plane waves $\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$ are their solutions. In consequence, the energies of the single-particle states are

$$\varepsilon_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}}^{(0)} = \frac{\hbar^2 \boldsymbol{k}^2}{2m_{\rm e}} \,. \tag{28.3.26}$$

Thus, the interaction – if treated in the Hartree approximation – gives no contribution to the energy of the homogeneous electron gas. For a general two-particle interaction U and a uniform background potential V_0 , all energy levels are shifted by the same amount:

$$\varepsilon_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}}^{(0)} + V_0 + \int \mathrm{d}\boldsymbol{r}' U(\boldsymbol{r} - \boldsymbol{r}') n_{\mathrm{e}}(\boldsymbol{r}')$$

$$= \varepsilon_{\boldsymbol{k}}^{(0)} + V_0 + U(\boldsymbol{q} = 0) n_{\mathrm{e}},$$

(28.3.27)

where $n_{\rm e}$ is the uniform density of particles and it is multiplied by the q = 0Fourier component of the interparticle interaction.

28.3.3 Hartree Equations Derived from the Variational Principle

We note before going on that the Hartree equations can be derived from the variational principle of quantum mechanics. Instead of choosing the potential approximately – as was done in (28.3.1) – a variational ansatz is made for the wavefunction and we require that the total energy of the electron system

$$E = \langle \mathcal{H} \rangle = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$
(28.3.28)

be minimum, where

$$\mathcal{H} = \sum_{i=1}^{N_{\rm e}} \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}_i^2 + V_{\rm ion}(\boldsymbol{r}_i) + \frac{1}{2} \sum_{\substack{j=1\\j\neq i}}^{N_{\rm e}} \frac{\tilde{e}^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right].$$
(28.3.29)

As the simplest choice, we write the many-body wavefunction as the product of unknown single-particle wavefunctions in the form given in (28.3.9). One readily obtains

$$\langle \Psi | \mathcal{H} | \Psi \rangle = \sum_{i=1}^{N_{\rm e}} \int \mathrm{d}\boldsymbol{r} \, \phi_{\lambda_i}^*(\boldsymbol{r}) \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 + V_{\rm ion}(\boldsymbol{r}) \right] \phi_{\lambda_i}(\boldsymbol{r}) + \frac{\tilde{e}^2}{2} \sum_{\substack{i,j=1\\i \neq j}}^{N_{\rm e}} \iint \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' \frac{\left| \phi_{\lambda_j}(\boldsymbol{r}') \right|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \left| \phi_{\lambda_i}(\boldsymbol{r}) \right|^2.$$

$$(28.3.30)$$

To get the energy minimum, one has to minimize this quantity with the constraint that the single-particle wavefunctions are orthogonal,

$$\int \mathrm{d}\boldsymbol{r} \,\phi_{\lambda_i}^*(\boldsymbol{r})\phi_{\lambda_j}(\boldsymbol{r}) = \delta_{\lambda_i,\lambda_j} \,. \tag{28.3.31}$$

This constraint can be enforced by introducing a set of Lagrange multipliers. The optimum wavefunctions are the solutions of the variational problem

$$\frac{\delta}{\delta \psi_{\lambda_i}^*} \left[\langle \mathcal{H} \rangle - \varepsilon_i \int \mathrm{d}\boldsymbol{r} \, |\phi_{\lambda_i}^*(\boldsymbol{r})|^2 \right] = 0 \,. \tag{28.3.32}$$

This yields precisely the Hartree equations given in (28.3.13) and the Lagrange multipliers are equal to the single-particle energies.

28.3.4 Hartree–Fock Approximation

The effect of the other electrons is taken into account in the Hartree approximation rather crudely. A better approximation can be achieved if a better form is assumed for the variational wavefunction. The most obvious problem with the Hartree approximation is that – although each single-particle state is occupied by at most one electron in agreement with the Pauli exclusion principle – the indistinguishability of electrons has not been taken into account.

If states $\phi_{\lambda_1,\sigma_1}$, $\phi_{\lambda_2,\sigma_2}$, ..., $\phi_{\lambda_{N_e},\sigma_{N_e}}$ are occupied, one cannot tell which electron occupies which state. All possible distributions among the states have to be allowed for, and the many-body wavefunction is a linear combination of all allowed configurations. Since electrons are fermions, the total wavefunction has to be completely antisymmetric, i.e., it has to change sign whenever the spatial and spin variables of any two electrons are exchanged:

$$\Psi(\ldots, \boldsymbol{r}_i, s_i, \ldots, \boldsymbol{r}_j, s_j, \ldots) = -\Psi(\ldots, \boldsymbol{r}_j, s_j, \ldots, \boldsymbol{r}_i, s_i, \ldots).$$
(28.3.33)

The wavefunction satisfying this requirement can be written in a compact form as a Slater determinant:

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$$\Psi_{\rm HF} = \frac{1}{\sqrt{N_{\rm e}!}} \begin{vmatrix} \phi_{\lambda_1,\sigma_1}(\boldsymbol{r}_1,s_1) & \phi_{\lambda_1,\sigma_1}(\boldsymbol{r}_2,s_2) & \dots & \phi_{\lambda_1,\sigma_1}(\boldsymbol{r}_{N_{\rm e}},s_{N_{\rm e}}) \\ \phi_{\lambda_2,\sigma_2}(\boldsymbol{r}_1,s_1) & \phi_{\lambda_2,\sigma_2}(\boldsymbol{r}_2,s_2) & \dots & \phi_{\lambda_2,\sigma_2}(\boldsymbol{r}_{N_{\rm e}},s_{N_{\rm e}}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{\lambda_{N_{\rm e}},\sigma_{N_{\rm e}}}(\boldsymbol{r}_1,s_1) & \phi_{\lambda_{N_{\rm e}},\sigma_{N_{\rm e}}}(\boldsymbol{r}_2,s_2) & \dots & \phi_{\lambda_{N_{\rm e}},\sigma_{N_{\rm e}}}(\boldsymbol{r}_{N_{\rm e}},s_{N_{\rm e}}) \end{vmatrix} .$$
(28.3.34)

This is a natural generalization of the two-particle Slater determinant introduced in Chapter 4.

Evaluating the expectation value of the energy with this wavefunction, we get

$$E_{\rm HF} = \langle \mathcal{H} \rangle = \sum_{i=1}^{N_{\rm e}} \int d\mathbf{r} \, \phi_{\lambda_i}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m_{\rm e}} \nabla^2 + V_{\rm ion}(\mathbf{r}) \right] \phi_{\lambda_i}(\mathbf{r}) + \frac{\tilde{e}^2}{2} \sum_{i,j=1}^{N_{\rm e}} \int d\mathbf{r} \int d\mathbf{r} \int d\mathbf{r}' \frac{|\phi_{\lambda_j}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} |\phi_{\lambda_i}(\mathbf{r})|^2$$
(28.3.35)
$$- \frac{\tilde{e}^2}{2} \sum_{i,j=1}^{N_{\rm e}} \int d\mathbf{r} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \delta_{\sigma_i,\sigma_j} \phi_{\lambda_i}^*(\mathbf{r}) \phi_{\lambda_j}^*(\mathbf{r}') \phi_{\lambda_j}(\mathbf{r}') \, .$$

Unlike in the Hartree approximation, there is no need here to impose the restriction $j \neq i$, since contributions coming from the j = i terms cancel each other in the last two terms. To get the optimum wavefunctions that at the same time satisfy the orthogonality condition, the constraints are again enforced by the method of Lagrange multipliers. Independent variation with respect to ϕ_{λ_i} and $\phi_{\lambda_i}^*$ leads to

$$-\frac{\hbar^2}{2m_{\rm e}} \nabla^2 \phi_{\lambda_i}(\boldsymbol{r}) + V_{\rm ion}(\boldsymbol{r}) \phi_{\lambda_i}(\boldsymbol{r}) + \tilde{e}^2 \sum_{j=1}^{N_{\rm e}} \int \mathrm{d}\boldsymbol{r}' \frac{|\phi_{\lambda_j}(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \phi_{\lambda_i}(\boldsymbol{r}) - \tilde{e}^2 \sum_{j=1}^{N_{\rm e}} \int \mathrm{d}\boldsymbol{r}' \frac{\phi_{\lambda_j}^*(\boldsymbol{r}') \phi_{\lambda_i}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \phi_{\lambda_j}(\boldsymbol{r}) \delta_{\sigma_i,\sigma_j} = \tilde{\epsilon}_{\lambda_i} \phi_{\lambda_i}(\boldsymbol{r}) \,.$$

(28.3.36)

These equations are referred to as the *Hartree–Fock equations*. For a general two-particle interaction we find

$$-\frac{\hbar^2}{2m_{\rm e}} \nabla^2 \phi_{\lambda_i}(\boldsymbol{r}) + V_{\rm ion}(\boldsymbol{r})\phi_{\lambda_i}(\boldsymbol{r}) + \sum_{j=1}^{N_{\rm e}} \int \mathrm{d}\boldsymbol{r}' U(\boldsymbol{r}-\boldsymbol{r}') |\phi_{\lambda_j}(\boldsymbol{r}')|^2 \phi_{\lambda_i}(\boldsymbol{r}) -\sum_{j=1}^{N_{\rm e}} \int \mathrm{d}\boldsymbol{r}' U(\boldsymbol{r}-\boldsymbol{r}') \phi_{\lambda_j}^*(\boldsymbol{r}') \phi_{\lambda_i}(\boldsymbol{r}') \phi_{\lambda_j}(\boldsymbol{r}) \delta_{\sigma_i,\sigma_j} = \tilde{\varepsilon}_{\lambda_i} \phi_{\lambda_i}(\boldsymbol{r}) .$$

$$(28.3.37)$$

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As in the Hartree approximation, the values of the Lagrange multipliers at the minimum give the energy eigenvalues. They are denoted by $\tilde{\varepsilon}_{\lambda_i}$ to distinguish them from the energies obtained in the Hartree approximation. The new term compared to the Hartree approximation is due to the indistinguishability of the particles, i.e., the quantum mechanical exchange. For this reason, this term is called exchange term or *Fock term* after V. FOCK, who derived it first in 1930.⁶ The factor $\delta_{\sigma_i,\sigma_j}$ appears because only particles with identical spins can be exchanged. Of course, similar to the Hartree equations, these equations have to be solved self-consistently.

The local Hartree potential introduced in (28.3.3) can be written in terms of the single-particle wavefunctions in the form

$$V_{\rm H}(\boldsymbol{r}) = \sum_{j=1}^{N_{\rm e}} \int d\boldsymbol{r}' \, U(\boldsymbol{r} - \boldsymbol{r}') |\phi_{\lambda_j}(\boldsymbol{r}')|^2 \,. \tag{28.3.38}$$

In contrast to the Hartree term, the exchange term can be written only in terms of a nonlocal exchange potential $V_{\rm x}(\boldsymbol{r}, \boldsymbol{r}')$ defined by

$$-\sum_{j=1}^{N_{\rm e}} \int \mathrm{d}\mathbf{r}' U(\mathbf{r}-\mathbf{r}')\phi_{\lambda_j}^*(\mathbf{r}')\phi_{\lambda_j}(\mathbf{r})\delta_{\sigma_i,\sigma_j}\phi_{\lambda_i}(\mathbf{r}') = \int V_{\rm x}(\mathbf{r},\mathbf{r}')\phi_{\lambda_i}(\mathbf{r}')\,\mathrm{d}\mathbf{r}'\,.$$
(28.3.39)

The Hartree–Fock equations are then equivalent to the nonlocal Schrödinger equations

$$\int \mathcal{H}_{\rm HF}^{(1)}(\boldsymbol{r}, \boldsymbol{r}') \phi_{\lambda_i}(\boldsymbol{r}') \, \mathrm{d}\boldsymbol{r}' = \widetilde{\varepsilon}_{\lambda_i} \phi_{\lambda_i}(\boldsymbol{r}) \,, \qquad (28.3.40)$$

where

$$\mathcal{H}_{\rm HF}^{(1)}(\boldsymbol{r}, \boldsymbol{r}') = \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 + V_{\rm ion}(\boldsymbol{r}) + V_{\rm H}(\boldsymbol{r}) \right] \delta(\boldsymbol{r} - \boldsymbol{r}') + V_{\rm x}(\boldsymbol{r}, \boldsymbol{r}') \,. \tag{28.3.41}$$

28.3.5 Hartree–Fock Approximation as a Mean-Field Theory

The Hartree approximation could be interpreted as a mean-field theory. One of the density operators in the interaction was replaced by its expectation value. This is, however, not the only possible choice for a mean-field-like interaction. When the interaction part of (28.1.20) is written in terms of the field operators, we have

$$\mathcal{H}_{e-e} = \frac{1}{2} \tilde{e}^2 \sum_{\sigma\sigma'} \iint d\mathbf{r} \, d\mathbf{r}' \, \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) \,, \qquad (28.3.42)$$

where we used the bare Coulomb interaction. This expression contains four operators, and one could choose other combinations than the local densities

⁶ The Hartree term is also called direct term.

that could be approximated by their mean value. We may suppose that the nonlocal quantity, the expectation value of $\hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}')\hat{\psi}_{\sigma}(\mathbf{r})$ describing a process in which the particles are added and removed at different positions, is also finite. Then, in addition to the term corresponding to the Hartree approximation a new term appears in the Hamiltonian,

$$\mathcal{H}_{\mathbf{x}} \approx -\tilde{e}^2 \sum_{\sigma\sigma'} \iint \mathrm{d}\boldsymbol{r} \,\mathrm{d}\boldsymbol{r}' \,\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \frac{\left\langle \hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}')\hat{\psi}_{\sigma}(\boldsymbol{r}) \right\rangle}{|\boldsymbol{r}-\boldsymbol{r}'|} \hat{\psi}_{\sigma'}(\boldsymbol{r}') \,. \tag{28.3.43}$$

The factor 1/2 in the original Hamiltonian has disappeared since there are two ways to arrive at such terms. The negative sign arises because the order of two field operators had to be interchanged. Mean-field theory is, however, more subtle than simply replacing some quantities by their average. The total energy is obtained correctly when a term containing the product of averages is added. In the present case a term

$$\frac{1}{2} \sum_{\sigma\sigma'} \iint \mathrm{d}\boldsymbol{r} \,\mathrm{d}\boldsymbol{r}' \,U(\boldsymbol{r}-\boldsymbol{r}') \big\langle \hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}') \hat{\psi}_{\sigma}(\boldsymbol{r}) \big\rangle \big\langle \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\psi}_{\sigma'}(\boldsymbol{r}') \big\rangle \tag{28.3.44}$$

has to be added to the total energy.

In a homogeneous, isotropic, unpolarized system, the expectation value $\langle \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}')\hat{\psi}_{\sigma}(\mathbf{r})\rangle$ depends on $|\mathbf{r} - \mathbf{r}'|$; it is nonvanishing only if $\sigma = \sigma'$ and its value is spin independent. We will see in Chapter 33 that this is not true any more in broken-symmetry phases such as in a polarized electron gas or in charge-density- or spin-density-wave states. The superconducting state to be discussed in Chapter 34 is even more delicate. It can be described by a mean-field-like generalized Hartree–Fock theory in which an anomalous average takes nonvanishing value.

By adding the new terms with $\sigma = \sigma'$ to the Hamiltonian of the Hartree approximation, the total Hamiltonian can be written in a form analogous to (28.3.22) with a nonlocal spin-dependent term in the one-particle part:

$$\mathcal{H}_{\rm HF} = \sum_{\sigma} \iint d\mathbf{r} \, d\mathbf{r}' \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \mathcal{H}_{\rm HF\sigma}^{(1)}(\mathbf{r}, \mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}')$$

$$-\frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r} \, d\mathbf{r}' \, U(\mathbf{r} - \mathbf{r}') \langle \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \rangle \langle \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \rangle$$

$$+\frac{1}{2} \sum_{\sigma} \iint d\mathbf{r} \, d\mathbf{r}' \, U(\mathbf{r} - \mathbf{r}') \langle \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) \rangle \langle \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}') \rangle ,$$
(28.3.45)

where

$$\mathcal{H}_{\mathrm{HF}\sigma}^{(1)}(\boldsymbol{r},\boldsymbol{r}') = \mathcal{H}_{\mathrm{H}}^{(1)}\delta(\boldsymbol{r}-\boldsymbol{r}') - \tilde{e}^2 \frac{\left\langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}')\hat{\psi}_{\sigma}(\boldsymbol{r})\right\rangle}{|\boldsymbol{r}-\boldsymbol{r}'|}, \qquad (28.3.46)$$

or for a general electron-electron interaction,

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$$\mathcal{H}_{\mathrm{HF}\sigma}^{(1)}(\boldsymbol{r},\boldsymbol{r}') = \left[-\frac{\hbar^2}{2m_{\mathrm{e}}} \boldsymbol{\nabla}^2 + V_{\mathrm{ion}}(\boldsymbol{r}) + \sum_{\sigma'} \int \mathrm{d}\boldsymbol{r}'' \, U(\boldsymbol{r} - \boldsymbol{r}'') \langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}'') \hat{\psi}_{\sigma'}(\boldsymbol{r}'') \rangle \right] \delta(\boldsymbol{r} - \boldsymbol{r}') - U(\boldsymbol{r} - \boldsymbol{r}') \langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}') \hat{\psi}_{\sigma}(\boldsymbol{r}) \rangle.$$
(28.3.47)

To prove the equivalence to the Hartree–Fock approximation we take the solutions of the nonlocal Schrödinger equation

$$\int \mathcal{H}_{\mathrm{HF}\sigma}^{(1)}(\boldsymbol{r},\boldsymbol{r}')\phi_{\lambda_i\sigma}(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}' = \widetilde{\varepsilon}_{\lambda_i\sigma}\phi_{\lambda_i\sigma}(\boldsymbol{r}) \qquad (28.3.48)$$

as basis functions. The field operators can be expanded in terms of the creation and annihilation operators, $c_{\lambda\sigma}^{\dagger}$ and $c_{\lambda\sigma}$, of these states in analogy to (28.1.17) as

$$\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) = \sum_{\lambda_i} \phi^*_{\lambda_i,\sigma}(\boldsymbol{r}) c^{\dagger}_{\lambda_i\sigma}, \qquad \hat{\psi}_{\sigma}(\boldsymbol{r}) = \sum_{\lambda_i} \phi_{\lambda_i,\sigma}(\boldsymbol{r}) c_{\lambda_i\sigma}.$$
(28.3.49)

Since the only nonvanishing average is that of the number operator $c_{\lambda\sigma}^{\dagger}c_{\lambda\sigma}$ when no symmetry is broken, $\mathcal{H}_{\mathrm{HF}\sigma}^{(1)}(\boldsymbol{r},\boldsymbol{r}')$ is identical to $\mathcal{H}_{\mathrm{HF}}^{(1)}(\boldsymbol{r}-\boldsymbol{r}')$ of (28.3.41) and this eigenvalue problem is indeed identical to the Hartree–Fock equations.

Alternatively one could start with the Hamiltonian (28.1.35) written in terms of the creation and annihilation operators of the single-particle states of the noninteracting system:

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}\\\sigma\sigma'}} U(\boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma} \,. \tag{28.3.50}$$

In normal metals, where the ground state does not break any symmetry of the Hamiltonian – i.e., it is neither superconducting nor does it show a static charge or spin density – the only nonvanishing average of the product of two fermion operators is the number of electrons with wave vector \mathbf{k} and spin σ :

$$\langle c_{\boldsymbol{k}\sigma}^{\dagger}c_{\boldsymbol{k}\sigma}\rangle = f_0(\varepsilon_{\boldsymbol{k}}).$$
 (28.3.51)

It would seem natural to single out the q = 0 term in the interaction and to write the four-fermion product after a rearrangement of the operators in the form

$$c_{\boldsymbol{k}\sigma}^{\dagger}c_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}'\sigma'}^{\dagger}c_{\boldsymbol{k}'\sigma'} = \left(c_{\boldsymbol{k}\sigma}^{\dagger}c_{\boldsymbol{k}\sigma} - \langle c_{\boldsymbol{k}\sigma}^{\dagger}c_{\boldsymbol{k}\sigma} \rangle + \langle c_{\boldsymbol{k}\sigma}^{\dagger}c_{\boldsymbol{k}\sigma} \rangle \right) \\ \times \left(c_{\boldsymbol{k}'\sigma'}^{\dagger}c_{\boldsymbol{k}'\sigma'} - \langle c_{\boldsymbol{k}'\sigma'}^{\dagger}c_{\boldsymbol{k}'\sigma'} \rangle + \langle c_{\boldsymbol{k}'\sigma'}^{\dagger}c_{\boldsymbol{k}'\sigma'} \rangle \right).$$
(28.3.52)

If fluctuations, i.e., terms of second order in the deviation from the mean value, are neglected, we have

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$$c^{\dagger}_{\boldsymbol{k}\sigma}c^{\dagger}_{\boldsymbol{k}'\sigma'}c_{\boldsymbol{k}'\sigma'}c_{\boldsymbol{k}\sigma} \approx c^{\dagger}_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}\sigma}\langle c^{\dagger}_{\boldsymbol{k}'\sigma'}c_{\boldsymbol{k}'\sigma'}\rangle + \langle c^{\dagger}_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}\sigma}\rangle c^{\dagger}_{\boldsymbol{k}'\sigma'}c_{\boldsymbol{k}'\sigma'} - \langle c^{\dagger}_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}\sigma}\rangle \langle c^{\dagger}_{\boldsymbol{k}'\sigma'}c_{\boldsymbol{k}'\sigma'}\rangle.$$

$$(28.3.53)$$

Substituting this into the Hamiltonian gives

$$\mathcal{H}_{\mathrm{H}} = \sum_{\boldsymbol{k}\sigma} \left[\varepsilon_{\boldsymbol{k}} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q} = 0) \langle c_{\boldsymbol{k}'\sigma'}^{\dagger} c_{\boldsymbol{k}'\sigma'} \rangle \right] c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} - \frac{1}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\sigma\sigma'}} U(\boldsymbol{q} = 0) \langle c_{\boldsymbol{k}'\sigma'}^{\dagger} c_{\boldsymbol{k}'\sigma'} \rangle \langle c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \rangle .$$

$$(28.3.54)$$

This is exactly the result of the Hartree approximation. We can go beyond that if we choose the operator products that are approximated by their expectation values differently. After a change of the order of two operators (this leads to a factor -1 when $q \neq 0$) the following identical transformation can be made:

$$c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}'\sigma'}c_{\mathbf{k}\sigma} = -c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'\sigma'}c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}\sigma} \qquad (28.3.55)$$
$$= -\left(c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'\sigma'} - \langle c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'\sigma'} \rangle + \langle c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'\sigma'} \rangle \right)$$
$$\times \left(c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}\sigma} - \langle c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}\sigma} \rangle + \langle c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}\sigma} \rangle \right).$$

Again neglecting fluctuations,

$$c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}'\sigma'}c_{\mathbf{k}\sigma} \approx -c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'\sigma'}\langle c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}\sigma}\rangle - \langle c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'\sigma'}\rangle c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}\sigma} \\ + \langle c_{\mathbf{k}+q\sigma}^{\dagger}c_{\mathbf{k}'\sigma'}\rangle \langle c_{\mathbf{k}'-q\sigma'}^{\dagger}c_{\mathbf{k}\sigma}\rangle.$$
(28.3.56)

The expectation values give finite contribution only when $\mathbf{k} = \mathbf{k}' - \mathbf{q}$ and $\sigma = \sigma'$. If $U(\mathbf{q})$ is an even function of \mathbf{q} , the Hamiltonian in this approximation takes the form

$$\mathcal{H}_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \left[\varepsilon_{\boldsymbol{k}} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q} = 0) \langle c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'\sigma'} \rangle \right] - \frac{1}{V} \sum_{\boldsymbol{k}'} U(\boldsymbol{k}' - \boldsymbol{k}) \langle c^{\dagger}_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}'\sigma} \rangle \right] c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} - \frac{1}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\sigma\sigma'}} U(\boldsymbol{q} = 0) \langle c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'\sigma'} \rangle \langle c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \rangle + \frac{1}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\sigma\sigma'}} U(\boldsymbol{k}' - \boldsymbol{k}) \langle c^{\dagger}_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}'\sigma} \rangle \langle c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \rangle .$$

$$(28.3.57)$$

The operator part of $\mathcal{H}_{\rm HF}$ is diagonal in the quantum numbers and the coefficient of the particle-number operator is

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$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q}=0) \left\langle c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'\sigma'} \right\rangle - \frac{1}{V} \sum_{\boldsymbol{k}'} U(\boldsymbol{k}'-\boldsymbol{k}) \left\langle c^{\dagger}_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}'\sigma} \right\rangle,$$
(28.3.58)

where in the ground state

$$\left\langle c_{\boldsymbol{k}'\sigma}^{\dagger}c_{\boldsymbol{k}'\sigma}\right\rangle = \begin{cases} 1 & \text{for} & |\boldsymbol{k}'| < k_{\rm F}, \\ 0 & \text{for} & |\boldsymbol{k}'| > k_{\rm F}. \end{cases}$$
(28.3.59)

Thus

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + \frac{N_{\rm e}}{V}U(\boldsymbol{q}=0) - \frac{1}{V}\sum_{|\boldsymbol{k}'| < k_{\rm F}} U(\boldsymbol{k}'-\boldsymbol{k}).$$
(28.3.60)

Note that (28.3.58) allows for a simple generalization of the Hartree–Fock approximation to finite temperatures. The ground-state average of the occupation number should be replaced by the Fermi distribution function. This approach is self-consistent if the energy in the Fermi distribution function contains already the finite-temperature corrections, that is

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q}=0) f_0(\widetilde{\varepsilon}_{\boldsymbol{k}'\sigma'}) - \frac{1}{V} \sum_{\boldsymbol{k}'} U(\boldsymbol{k}'-\boldsymbol{k}) f_0(\widetilde{\varepsilon}_{\boldsymbol{k}'\sigma}) \,. \quad (28.3.61)$$

It is due to this self-consistency requirement that the single-particle energy may become spin dependent.

28.3.6 Quasiparticles in the Hartree–Fock Approximation

When the Hartree–Fock Hamiltonian is written in terms of the creation and annihilation operators of the optimal single-particle states, it takes the particularly simple form

$$\mathcal{H}_{\rm HF} = \sum_{\lambda\sigma} \tilde{\varepsilon}_{\lambda_i\sigma} c^{\dagger}_{\lambda\sigma} c_{\lambda\sigma}$$

$$-\frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r} \, d\mathbf{r}' \, U(\mathbf{r} - \mathbf{r}') \big\langle \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \big\rangle \big\langle \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \big\rangle$$

$$+\frac{1}{2} \sum_{\sigma} \iint d\mathbf{r} \, d\mathbf{r}' \, U(\mathbf{r} - \mathbf{r}') \big\langle \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) \big\rangle \big\langle \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}') \big\rangle.$$
(28.3.62)

The first part is the Hamiltonian of a free fermion gas with one-particle energy $\tilde{\epsilon}_{\lambda_i\sigma}$. To understand the physical meaning of these eigenvalues we calculate the energy needed to remove a particle of index l with quantum numbers λ_l and σ_l from the solid. The Hamiltonian \mathcal{H}' of this $(N_{\rm e} - 1)$ -particle system is easily obtained from the Hamiltonian \mathcal{H} of the $N_{\rm e}$ -particle system:

$$\mathcal{H}' = \mathcal{H} - \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}_l^2 + V(\boldsymbol{r}_l) + \sum_{\substack{j=1\\j\neq l}}^{N_{\rm e}} \frac{\tilde{e}^2}{|\boldsymbol{r}_l - \boldsymbol{r}_j|} \right].$$
(28.3.63)

The self-consistent solutions of the Hartree–Fock equations with this Hamiltonian differ from the wavefunctions of the $N_{\rm e}$ -particle system. For a large enough system, however, the relaxation of the wavefunction is on the order of $1/N_{\rm e}$. If the system was originally described by a Slater-determinant wavefunction (28.3.34), a good approximation for the wavefunction of the $N_{\rm e} - 1$ -particle system is obtained by deleting simply the appropriate row and column of the Slater determinant, leaving the single-particle wavefunctions unchanged.⁷ That is we choose

$$\Psi_{l} = \frac{1}{\sqrt{(N_{\rm e}-1)!}} \begin{vmatrix} \phi_{\lambda_{1}}(\boldsymbol{r}_{1}) & \dots & \phi_{\lambda_{1}}(\boldsymbol{r}_{l-1}) & \phi_{\lambda_{1}}(\boldsymbol{r}_{l+1}) & \dots & \phi_{\lambda_{1}}(\boldsymbol{r}_{N_{\rm e}}) \\ \phi_{\lambda_{2}}(\boldsymbol{r}_{1}) & \dots & \phi_{\lambda_{2}}(\boldsymbol{r}_{l-1}) & \phi_{\lambda_{2}}(\boldsymbol{r}_{l+1}) & \dots & \phi_{\lambda_{2}}(\boldsymbol{r}_{N_{\rm e}}) \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \phi_{\lambda_{l-1}}(\boldsymbol{r}_{1}) & \dots & \phi_{\lambda_{l-1}}(\boldsymbol{r}_{l-1}) & \phi_{\lambda_{l-1}}(\boldsymbol{r}_{l+1}) & \dots & \phi_{\lambda_{l-1}}(\boldsymbol{r}_{N_{\rm e}}) \\ \phi_{\lambda_{l+1}}(\boldsymbol{r}_{1}) & \dots & \phi_{\lambda_{l+1}}(\boldsymbol{r}_{l-1}) & \phi_{\lambda_{l+1}}(\boldsymbol{r}_{l+1}) & \dots & \phi_{\lambda_{l+1}}(\boldsymbol{r}_{N_{\rm e}}) \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \phi_{\lambda_{N_{\rm e}}}(\boldsymbol{r}_{1}) & \dots & \phi_{\lambda_{N_{\rm e}}}(\boldsymbol{r}_{l-1}) & \phi_{\lambda_{N_{\rm e}}}(\boldsymbol{r}_{l+1}) & \dots & \phi_{\lambda_{N_{\rm e}}}(\boldsymbol{r}_{N_{\rm e}}) \end{vmatrix},$$

$$(28.3.64)$$

where the spin variables and quantum numbers are not written out explicitly for the sake of brevity. The energy difference between the two states,

$$\Delta E = \langle \Psi_l | \mathcal{H}' | \Psi_l \rangle - \langle \Psi_{\rm HF} | \mathcal{H} | \Psi_{\rm HF} \rangle, \qquad (28.3.65)$$

gives the energy needed to remove the particle with quantum number λ_l .

When (28.3.35) is used for the energy of the system with $N_{\rm e}$ particles, this energy difference is equal to the contribution of all terms that contain the one-particle wavefunction with quantum number λ_l , that is

$$-\Delta E = \int \mathrm{d}\boldsymbol{r} \,\phi_{\lambda_{l}}^{*}(\boldsymbol{r}) \left[-\frac{\hbar^{2}}{2m_{\mathrm{e}}} \boldsymbol{\nabla}^{2} + V_{\mathrm{ion}}(\boldsymbol{r}) \right] \phi_{\lambda_{l}}(\boldsymbol{r}) + \tilde{e}^{2} \sum_{j=1}^{N_{\mathrm{e}}} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}' \frac{|\phi_{\lambda_{j}}(\boldsymbol{r}')|^{2}}{|\boldsymbol{r} - \boldsymbol{r}'|} |\phi_{\lambda_{l}}(\boldsymbol{r})|^{2}$$
(28.3.66)
$$- \tilde{e}^{2} \sum_{j=1}^{N_{\mathrm{e}}} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}' \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} \delta_{\sigma_{l},\sigma_{j}} \phi_{\lambda_{l}}^{*}(\boldsymbol{r}) \phi_{\lambda_{j}}(\boldsymbol{r}') \phi_{\lambda_{j}}(\boldsymbol{r}') \,.$$

It follows from the Hartree–Fock equations that the right-hand side is exactly equal to the eigenvalue $\tilde{\epsilon}_{\lambda_l}$, and so

$$\Delta E = -\widetilde{\varepsilon}_{\lambda_l} \,. \tag{28.3.67}$$

This shows that the eigenvalues of the Hartree–Fock equations have a simple physical meaning: they give the energy needed to remove a particle with the

⁷ This approximation may give incorrect result in quantum chemistry calculations for atoms or molecules, where the number of electrons is not large.

given quantum number. In other words, the Hartree–Fock energy of an occupied orbital is the negative of the ionization energy for the corresponding state. Similarly, one can calculate the energy needed to add a particle to the system. The solutions of the Hartree–Fock equations provide a complete basis set, not only for the wavefunctions and energies of occupied orbitals but also for the wavefunctions and energies of unoccupied, virtual states. These eigenvalues are equal to the energies needed to add a particle to an unoccupied orbital. This result is known as *Koopmans' theorem.*⁸ It implies that if an electron is excited from the state with quantum number λ_l into the state with quantum number λ_k , the excitation energy is

$$\Delta E = \tilde{\varepsilon}_{\lambda_k} - \tilde{\varepsilon}_{\lambda_l} \,. \tag{28.3.68}$$

The energy $\tilde{\varepsilon}_{\lambda_l}$ needed to add a particle to the interacting system is modified, renormalized, compared to the energy ε_{λ_l} of a free particle. The effect of interaction with the other particles is incorporated into this modified singleparticle energy. The elementary excitations of the interacting system are not bare electrons but quasiparticles having energy $\tilde{\varepsilon}_{\lambda\sigma}$. When this energy is written in the form

$$\widetilde{\varepsilon}_{\lambda\sigma} = \varepsilon_{\lambda\sigma} + \Sigma_{\lambda\sigma} \,, \tag{28.3.69}$$

the correction $\Sigma_{\lambda\sigma}$ is called the self-energy.

The interesting physical properties of the system can be explained in terms of quasiparticles. One has to take into account, however, that the concept of quasiparticles can be used only when a small number of them are excited. Only in this limit can one write the excitation energy of a state as the sum of the energies of independent quasiparticles. When a large number of quasiparticles are present in the system, the interaction between them becomes important. This interaction and how it influences the properties of normal Fermi systems will be discussed in more detail in Chapter 32, in the framework of Landau's theory of Fermi liquids. Here we only show that the ground-state energy of the interacting system is not equal to the sum of the energies of $N_{\rm e}$ quasiparticles.

28.3.7 Total Energy in the Hartree–Fock Approximation

The total ground-state energy can be calculated as the expectation value of the Hamiltonian. Staring from the expression given in (28.3.57) we get

$$E_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \left[\varepsilon_{\boldsymbol{k}} + \frac{1}{2V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q}=0) \langle c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'\sigma'} \rangle - \frac{1}{2V} \sum_{\boldsymbol{k}'} U(\boldsymbol{k}'-\boldsymbol{k}) \langle c^{\dagger}_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}'\sigma} \rangle \right] \langle c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \rangle.$$

$$(28.3.70)$$

⁸ T. KOOPMANS, 1934. TJALLING CHARLES KOOPMANS (1910–1985) was awarded the 1975 Nobel Memorial Prize in economic sciences.

If the quasiparticle energy $\tilde{\varepsilon}_{k\sigma}$ given in (28.3.58) is used instead of the bare energy, we find

$$E_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \left[\tilde{\varepsilon}_{\boldsymbol{k}\sigma} - \frac{1}{2V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q}=0) \langle c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'\sigma'} \rangle + \frac{1}{2V} \sum_{\boldsymbol{k}'} U(\boldsymbol{k}'-\boldsymbol{k}) \langle c^{\dagger}_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}'\sigma} \rangle \right] \langle c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \rangle.$$

$$(28.3.71)$$

Since the self-energy is

$$\Sigma_{\boldsymbol{k}\sigma} = \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q}=0) \left\langle c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'\sigma'} \right\rangle - \frac{1}{V} \sum_{\boldsymbol{k}'} U(\boldsymbol{k}'-\boldsymbol{k}) \left\langle c^{\dagger}_{\boldsymbol{k}'\sigma} c_{\boldsymbol{k}'\sigma} \right\rangle \quad (28.3.72)$$

in the Hartree–Fock approximation, the total energy can be written either as

$$E_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \left(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} - \frac{1}{2} \Sigma_{\boldsymbol{k}\sigma} \right) \left\langle c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \right\rangle$$
(28.3.73)

or as

$$E_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \left(\varepsilon_{\boldsymbol{k}} + \frac{1}{2} \Sigma_{\boldsymbol{k}\sigma} \right) \left\langle c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \right\rangle.$$
(28.3.74)

When the energies of occupied quasiparticle states are summed, the correction coming from two-particle interactions appears in the energy of both quasiparticles, and thus twice in the sum. This double counting is corrected in (28.3.73) by subtracting half of the self-energy. Alternatively, when the bare energies are summed, only half of the self-energy has to be added for each occupied state.

28.3.8 Hartree–Fock Theory of the Uniform Electron Gas

The Hartree–Fock equations can in general be solved only numerically. The homogeneous electron gas, where $V_{\text{ion}}(\mathbf{r})$ is uniform in space and the Hartree term is compensated exactly by the potential of the positive background, is an exception. It is readily seen that plane waves are self-consistent solutions of the Hartree–Fock equations, but the quasiparticle energies differ from the free electron energies due to the Fock term.

Assuming that the one-particle states that fill the Fermi sphere in the ground state are plane waves, the same plane waves are indeed eigenfunctions of the Hartree–Fock equations

$$-\frac{\hbar^2}{2m_{\rm e}}\boldsymbol{\nabla}^2\phi_{\boldsymbol{k}}(\boldsymbol{r}) - \sum_{|\boldsymbol{k}'| < k_{\rm F}} \frac{1}{V} \int \mathrm{d}\boldsymbol{r}' \frac{\tilde{e}^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}'} \mathrm{e}^{\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}}\phi_{\boldsymbol{k}}(\boldsymbol{r}') = \widetilde{\epsilon}_{\boldsymbol{k}}\phi_{\boldsymbol{k}}(\boldsymbol{r})$$
(28.3.75)

with eigenvalues

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$$\widetilde{\varepsilon}_{\boldsymbol{k}} = \frac{\hbar^2 \boldsymbol{k}^2}{2m_{\rm e}} - \frac{1}{V} \sum_{|\boldsymbol{k}'| < k_{\rm F}} \int \mathrm{d}\boldsymbol{r}' \frac{\widetilde{e}^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{e}^{-\mathrm{i}(\boldsymbol{k} - \boldsymbol{k}') \cdot (\boldsymbol{r} - \boldsymbol{r}')} \,.$$
(28.3.76)

Since exchange is possible only between electrons of the same spin, each wave vector \mathbf{k}' has to be taken once. Recognizing that the second term on the right-hand side is a sum of the $\mathbf{k} - \mathbf{k}'$ Fourier components of the Coulomb potential we indeed recover the result derived in (28.3.60). Note that the uniform positive background precisely cancels the $\mathbf{q} = 0$ component of the potential. Substitution of (C.1.63) into (28.3.76) gives

$$\widetilde{\epsilon}_{k} = \frac{\hbar^{2} k^{2}}{2m_{e}} - \frac{1}{V} \sum_{|\mathbf{k}'| < k_{F}} \frac{4\pi \widetilde{e}^{2}}{|\mathbf{k} - \mathbf{k}'|^{2}}.$$
(28.3.77)

Comparison of the second term of (28.3.75) with (28.3.39) shows that the exchange potential is

$$V_{\mathbf{x}}(\boldsymbol{r},\boldsymbol{r}') = -\frac{1}{V} \sum_{|\boldsymbol{k}'| < k_{\mathrm{F}}} \frac{\tilde{e}^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{e}^{\mathrm{i}\boldsymbol{k}' \cdot (\boldsymbol{r} - \boldsymbol{r}')} .$$
(28.3.78)

The summation can be performed with the aid of (C.2.29) yielding

$$V_{\mathbf{x}}(\boldsymbol{r}-\boldsymbol{r}') = -\frac{\tilde{e}^{2}k_{\mathrm{F}}^{4}}{2\pi^{2}} \frac{\sin k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'| - k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'| \cos k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'|}{(k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'|)^{4}} = -\frac{\tilde{e}^{2}k_{\mathrm{F}}^{4}}{2\pi^{2}} \frac{j_{1}(k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'|)}{(k_{\mathrm{F}}|\boldsymbol{r}-\boldsymbol{r}'|)^{2}},$$
(28.3.79)

where $j_1(x) = (\sin x - x \cos x)/x^2$ is the first-order spherical Bessel function of the first kind. At short distances a $1/|\mathbf{r} - \mathbf{r}'|$ dependence resembling the Coulomb potential is obtained, while the exchange potential decays to zero much faster at large distances oscillating with wavelength $1/k_{\rm F}$.

Another picture for the exchange potential is obtained if the Fock term is written in the form

$$-\frac{e}{4\pi\epsilon_0}\int d\mathbf{r}' \frac{\rho_{\rm HF}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \phi_{\lambda_i}(\mathbf{r}), \qquad (28.3.80)$$

where

$$\rho_{\rm HF}(\boldsymbol{r},\boldsymbol{r}') = e \sum_{j} \frac{\phi_{\lambda_j}^*(\boldsymbol{r}')\phi_{\lambda_i}(\boldsymbol{r}')\phi_{\lambda_i}^*(\boldsymbol{r})\phi_{\lambda_j}(\boldsymbol{r})}{\phi_{\lambda_i}^*(\boldsymbol{r})\phi_{\lambda_i}(\boldsymbol{r})} \delta_{\sigma_i,\sigma_j} \,. \tag{28.3.81}$$

In this representation the effect of exchange is manifested in an induced charge density around the electrons. In the homogeneous electron gas, where the solutions are plane waves,

$$\rho_{\rm HF}(\boldsymbol{r}, \boldsymbol{r}') = \frac{e}{V} \sum_{|\boldsymbol{k}'| < k_{\rm F}} e^{i(\boldsymbol{k} - \boldsymbol{k}') \cdot (\boldsymbol{r} - \boldsymbol{r}')} \,.$$
(28.3.82)

Integration over the Fermi sphere gives

$$\rho_{\rm HF}(\boldsymbol{r},\boldsymbol{r}') = e \, e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \frac{k_{\rm F}^3}{2\pi^2} \frac{\sin k_{\rm F}|\boldsymbol{r}-\boldsymbol{r}'| - k_{\rm F}|\boldsymbol{r}-\boldsymbol{r}'|\cos k_{\rm F}|\boldsymbol{r}-\boldsymbol{r}'|}{(k_{\rm F}|\boldsymbol{r}-\boldsymbol{r}'|)^3} \\ = e \, e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \frac{k_{\rm F}^3}{2\pi^2} \frac{j_1(k_{\rm F}|\boldsymbol{r}-\boldsymbol{r}'|)}{k_{\rm F}|\boldsymbol{r}-\boldsymbol{r}'|} \,.$$
(28.3.83)

One can interpret this result by saying that the electrons create positively charged holes around themselves with an oscillatory charge density that dies off rather fast. We will return to this problem when correlations between electrons will be studied.

To calculate the dispersion curve of quasiparticles the sum in (28.3.77) is replaced by an integral over the Fermi sphere. The integral can be evaluated exactly using (C.2.31) with the result

$$\widetilde{\varepsilon}_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_{\rm e}} - 4\pi \widetilde{e}^2 \int_{|\mathbf{k}'| < k_{\rm F}} \frac{\mathrm{d}\mathbf{k}'}{(2\pi)^3} \frac{1}{|\mathbf{k} - \mathbf{k}'|^2}$$
$$= \frac{\hbar^2 k^2}{2m_{\rm e}} - \frac{2}{\pi} \widetilde{e}^2 k_{\rm F} F\left(\frac{k}{k_{\rm F}}\right)$$
$$= \left(\frac{k}{k_{\rm F}}\right)^2 \varepsilon_{\rm F} - \frac{2}{\pi} \widetilde{e}^2 k_{\rm F} F\left(\frac{k}{k_{\rm F}}\right), \qquad (28.3.84)$$

where

$$F(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1 + x}{1 - x} \right|.$$
 (28.3.85)

The function F(x), which will appear at various places, is plotted in Fig. 28.4. Note that F(x) is a smooth function, although its derivative is weakly, logarithmically singular at x = 1.



Fig. 28.4. Variation of F(x) as a function of x

Electronic energies are often given in the literature in hartree $(E_{\rm h})$ or rydberg (Ry),⁹

⁹ Hartree energy $(1 E_{\rm h} = \tilde{e}^2/a_0)$ is the atomic unit of energy. It is conveniently used in the atomic system of units, where the charge and mass of electron, \hbar , and

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$$1 E_{\rm h} = \frac{\tilde{e}^2}{a_0} = \frac{\hbar^2}{m_{\rm e}a_0^2} = 27.211 \,{\rm eV}\,,$$
 (28.3.86)

and 1 Ry = 13.606 eV. When the Fermi energy is expressed in terms of the Bohr radius,

$$\varepsilon_{\rm F} = \frac{\hbar^2 k_{\rm F}^2}{2m_{\rm e}} = \frac{1}{2} (k_{\rm F} a_0)^2 \frac{\tilde{e}^2}{a_0} ,$$
 (28.3.87)

and so

$$\widetilde{\varepsilon}_{\boldsymbol{k}} = \left[\frac{1}{2}(k_{\mathrm{F}}a_{0})^{2} \left(\frac{k}{k_{\mathrm{F}}}\right)^{2} - \frac{2}{\pi}k_{\mathrm{F}}a_{0}F\left(\frac{k}{k_{\mathrm{F}}}\right)\right]\frac{\widetilde{e}^{2}}{a_{0}}.$$
(28.3.88)

If the electron density is expressed in terms of the Wigner–Seitz radius r_0 ,¹⁰ or in terms of the dimensionless quantity $r_s = r_0/a_0$,

$$\varepsilon_{\rm F} = \frac{1}{2} \left(\frac{9\pi}{4}\right)^{2/3} \left(\frac{a_0}{r_0}\right)^2 \frac{\tilde{e}^2}{a_0} = \frac{1.842}{r_{\rm s}^2} E_{\rm h} ,$$
 (28.3.89)

and so

$$\widetilde{\varepsilon}_{\boldsymbol{k}} = \left[\frac{1.842}{r_{\rm s}^2} \left(\frac{k}{k_{\rm F}}\right)^2 - \frac{1.222}{r_{\rm s}} F\left(\frac{k}{k_{\rm F}}\right)\right] E_{\rm h} \,. \tag{28.3.90}$$

This dispersion curve is displayed in Fig. 28.5 for a relatively large density $(r_s = 2)$, which is close to the electron density in aluminum.



Fig. 28.5. The dispersion relation of quasiparticles in the Hartree–Fock approximation for an electron gas with density $r_{\rm s} = 2$. Dashed line shows the dispersion relation in the free electron gas

The energy correction is largest for the k = 0 state. Its value is

the Bohr radius are taken to be unity, and hence the Hartree energy is also unity. 1 Ry is the binding energy of the electron in the ground state of the hydrogen atom, it is half of the hartree energy.

¹⁰ The Wigner–Seitz radius, the radius of the sphere belonging to an electron, was introduced in Chapter 16. Its relationship to $k_{\rm F}$ is given in (16.2.31).

$$\Delta \varepsilon_{\boldsymbol{k}=0} = -\frac{2}{\pi} \tilde{e}^2 k_{\rm F} = -\frac{2}{\pi} k_{\rm F} a_0 \frac{\tilde{e}^2}{a_0} = -\frac{2}{\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{a_0}{r_0} \frac{\tilde{e}^2}{a_0} = -\frac{1.222}{r_{\rm s}} E_{\rm h} \,.$$
(28.3.91)

The shift is only half that much for electrons with wave number $k_{\rm F}$, whereas there is practically no energy shift for particles with large momentum. The energy spread of occupied states is thus

$$\widetilde{\varepsilon}_{k_{\rm F}} - \widetilde{\varepsilon}_{k=0} = \frac{\hbar^2 k_{\rm F}^2}{2m_{\rm e}} + \frac{1}{\pi} \widetilde{e}^2 k_{\rm F} = \left(\frac{1.842}{r_{\rm s}^2} + \frac{0.611}{r_{\rm s}}\right) E_{\rm h} = \left(\frac{50.111}{r_{\rm s}^2} + \frac{16.623}{r_{\rm s}}\right) eV.$$
(28.3.92)

The Hartree–Fock approximation of the electron–electron interaction gives a substantial increase of the bandwidth of occupied states in the uniform electron gas compared to the free electron model. For typical metallic electron densities, this width could easily double or increase by an even larger factor. We do not see any sign of such an increase in experiments. The bandwidth of occupied states is on the order of a few electron volts in the conduction band of simple metals, in rough agreement with free electron calculations.

It is even worse that the Hartree–Fock approximation yields an absolutely wrong result for the effective mass of electrons. To calculate the effective mass we redefine it in a somewhat different, though equivalent form. Taking a wave vector \mathbf{k}_0 on the Fermi surface, the quasiparticle energy $\tilde{\boldsymbol{\varepsilon}}_{\mathbf{k}}$ is expanded about the Fermi energy. For small deviations, to linear order

$$\widetilde{\varepsilon}_{\boldsymbol{k}} = \widetilde{\varepsilon}_{\boldsymbol{k}_0} + \left(\frac{\partial \widetilde{\varepsilon}_{\boldsymbol{k}}}{\partial \boldsymbol{k}}\right)_{\boldsymbol{k}_0} \cdot (\boldsymbol{k} - \boldsymbol{k}_0) \,. \tag{28.3.93}$$

In isotropic systems, where the energy depends only on the magnitude of k,

$$\widetilde{\varepsilon}_{k} = \widetilde{\varepsilon}_{k_{\rm F}} + \left(\frac{\partial \widetilde{\varepsilon}_{k}}{\partial k}\right)_{k_{\rm F}} (k - k_{\rm F}). \qquad (28.3.94)$$

For free electrons with a quadratic dispersion relation this expansion gives

$$\varepsilon_k = \varepsilon_{\rm F} + \frac{\hbar^2 k_{\rm F}}{m_{\rm e}} (k - k_{\rm F}) \,. \tag{28.3.95}$$

When the expansion of the quasiparticle energy is written in a similar form with an effective mass m^* , comparison of the two expressions gives

$$\frac{1}{m^*} = \frac{1}{\hbar^2 k_{\rm F}} \left(\frac{\partial \tilde{\varepsilon}_k}{\partial k}\right)_{k_{\rm F}}.$$
(28.3.96)

Due to the singular derivative of F(x) at x = 1, the derivative of the singleparticle energy $\partial \tilde{\epsilon}_k / \partial k$ diverges logarithmically at $k = k_{\rm F}$, and the effective mass vanishes on the Fermi surface in the Hartree–Fock approximation. The Sommerfeld expansion cannot be applied in this case and the electronic heat capacity would show a $T/\ln T$ temperature dependence instead of being proportional to T. These results are in contradiction with observations in metals. This is a consequence of treating the long-range Coulomb interaction in a mean-field approximation. Correlations beyond the Hartree–Fock approximation screen the Coulomb repulsion in metals making the electron–electron interaction effectively short ranged. This will be discussed in the next chapter.

28.3.9 Hartree–Fock Theory of the Hubbard Model

The Hamiltonian of the Hubbard model is chosen usually in the form

$$\mathcal{H} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U_{\rm H} \sum_{i} n_{i\uparrow} n_{i\downarrow} \qquad (28.3.97)$$

as given in (28.1.42). Only electrons with opposite spins interact in this model. They cannot be exchanged, so the Fock term gives no contribution. There is, however, a Hartree term. Employing the usual decoupling procedure the product of the number operators can be approximated by

$$n_{i\uparrow}n_{i\downarrow} \approx n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\uparrow} \rangle n_{i\downarrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle.$$
(28.3.98)

Thus

$$\mathcal{H} \approx \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U_{\rm H} \sum_{i\sigma} \langle n_{i,-\sigma} \rangle n_{i,\sigma} - U_{\rm H} \sum_{i} \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \,. \tag{28.3.99}$$

The energy of the electron at site *i* with spin σ is shifted by $U_{\rm H}\langle n_{i,-\sigma}\rangle$. If this energy shift is site dependent, e.g., it oscillates in space, the spin density may exhibit antiferromagnetic modulation. We will return to this problem in Chapter 33. In a translationally invariant solution, the one-particle energies $\varepsilon_{\mathbf{k}}$ (they are obtained by Fourier transformation from the hopping matrix elements) are shifted by the same amount. The quasiparticle energies are

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + U_{\mathrm{H}} \langle n_{i,-\sigma} \rangle \,. \tag{28.3.100}$$

If the average number of particles per unit volume

$$\langle n_{\sigma} \rangle = \frac{1}{V} \sum_{i} \langle n_{i,\sigma} \rangle = \frac{N}{V} \langle n_{i,\sigma} \rangle$$
 (28.3.101)

is used instead of the number of particles per site, we find

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + U\langle n_{-\sigma} \rangle, \qquad (28.3.102)$$

where the coupling constant U defined in (28.1.50) appears in place of $U_{\rm H}$ of the Hubbard model. The mean number of electrons with spin σ can be written in terms of the momentum distribution or Fermi distribution function in the form

$$\langle n_{i,\sigma} \rangle = \frac{1}{N} \sum_{\mathbf{k}} \langle n_{\mathbf{k}\sigma} \rangle = \frac{1}{N} \sum_{\mathbf{k}} f_0(\tilde{\varepsilon}_{\mathbf{k}\sigma}),$$

$$\langle n_{\sigma} \rangle = \frac{1}{V} \sum_{\mathbf{k}} \langle n_{\mathbf{k}\sigma} \rangle = \frac{1}{V} \sum_{\mathbf{k}} f_0(\tilde{\varepsilon}_{\mathbf{k}\sigma}),$$

(28.3.103)

where the shifted single-particle energies appear in the argument. This energy shift and the common chemical potential for up- and down-spin electrons have to be calculated self-consistently for a fixed total number $N_{\rm e}$ of electrons from

$$\widetilde{\varepsilon}_{\boldsymbol{k}\uparrow} = \varepsilon_{\boldsymbol{k}} + \frac{U}{V} \sum_{\boldsymbol{k}} f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\downarrow}),$$

$$\widetilde{\varepsilon}_{\boldsymbol{k}\downarrow} = \varepsilon_{\boldsymbol{k}} + \frac{U}{V} \sum_{\boldsymbol{k}} f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\uparrow}),$$
(28.3.104)

and from the requirement

$$\sum_{\boldsymbol{k}\sigma} \langle n_{\boldsymbol{k}\sigma} \rangle = \sum_{\boldsymbol{k}\sigma} f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}) = N_{\rm e} \,. \tag{28.3.105}$$

The unpolarized state in which $\tilde{\varepsilon}_{\mathbf{k}\uparrow} = \tilde{\varepsilon}_{\mathbf{k}\downarrow}$ is always a self-consistent solution of these equations. Later, in Chapter 33, we will return to these equations and will study the problem of when this unpolarized state becomes unstable.

28.4 Spatial and Temporal Correlations

Electrons fill the single-particle states independently in the Hartree approximation. There is no correlation between them. In the Hartree–Fock approximation, electrons still occupy single-particle states, but the requirement that the wavefunction has to be fully antisymmetric leads to an exchange interaction between electrons if their spins are parallel. The Pauli exclusion can be interpreted as an effective short-range repulsion through which electrons create a hole around themselves. This gives rise to spatial, distance-dependent correlations between electrons. We expect that dynamical, time-dependent correlations will also appear when we go beyond the Hartree–Fock approximation.

28.4.1 The *n*-Particle Density Matrix

An arbitrary one-particle operator, which is the sum of terms acting on individual electrons, can be expressed analogous to (28.1.8) as

$$\sum_{i=1}^{N_{e}} f(\boldsymbol{r}_{i}) = \int f(\boldsymbol{r}) n(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$
(28.4.1)

Its expectation value can be written in terms of the ground-state wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})$ of the many-particle system in the form

$$\left\langle \sum_{i=1}^{N_{\rm e}} f(\boldsymbol{r}_i) \right\rangle \equiv \sum_{i=1}^{N_{\rm e}} \iint \dots \int \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_{N_{\rm e}} \Psi^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_{N_{\rm e}}) \times f(\boldsymbol{r}_i) \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_{N_{\rm e}}) = \int f(\boldsymbol{r}) n_{\rm e}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} , \qquad (28.4.2)$$

where

$$n_{\rm e}(\boldsymbol{r}) = \sum_{i=1}^{N_{\rm e}} \iint \cdots \int \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_{N_{\rm e}} \boldsymbol{\Psi}^*(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_{N_{\rm e}})$$

$$\times \, \delta(\boldsymbol{r} - \boldsymbol{r}_i) \boldsymbol{\Psi}(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_{N_{\rm e}})$$
(28.4.3)

is the electron density defined in (28.3.5). Using the fully antisymmetric property of the wavefunction this expression reduces to

$$n_{\rm e}(\boldsymbol{r}) = N_{\rm e} \int \mathrm{d}\boldsymbol{r}_2 \cdots \int \mathrm{d}\boldsymbol{r}_{N_{\rm e}} \left| \boldsymbol{\Psi}(\boldsymbol{r}, \boldsymbol{r}_2, \dots, \boldsymbol{r}_{N_{\rm e}}) \right|^2.$$
(28.4.4)

In the Hartree–Fock approximation, where the many-particle wavefunction is a Slater determinant built up from single-particle functions $\phi_{\lambda_i}(\mathbf{r})$, the determinant can be expanded using the functions in the first column:

$$\Psi(\boldsymbol{r}, \boldsymbol{r}_2, \dots, \boldsymbol{r}_{n_{\rm e}}) = \frac{1}{\sqrt{N_{\rm e}}} \left[\phi_{\lambda_1}(\boldsymbol{r}) \Psi_1 - \phi_{\lambda_2}(\boldsymbol{r}) \Psi_2 + \cdots \right], \qquad (28.4.5)$$

where the subdeterminants Ψ_i defined in (28.3.64) describe the state of an $N_{\rm e}$ – 1-particle system. It is easily seen, using the orthonormality of these functions, that

$$n_{\rm e}(\boldsymbol{r}) = \sum_{i=1}^{N_{\rm e}} \phi_{\lambda_i}^*(\boldsymbol{r}) \phi_{\lambda_i}(\boldsymbol{r}) , \qquad (28.4.6)$$

in agreement with (28.3.11). Of course, the index λ_i includes here the spin quantum number as well.

When two-particle operators are considered and self-interaction is excluded, then in analogy to (28.1.11) we find

$$\frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{e}} f_{2}(\boldsymbol{r}_{i},\boldsymbol{r}_{j}) = \frac{1}{2} \left\{ \iint \mathrm{d}\boldsymbol{r}_{1} \, \mathrm{d}\boldsymbol{r}_{2} f_{2}(\boldsymbol{r}_{1},\boldsymbol{r}_{2}) n(\boldsymbol{r}_{1}) n(\boldsymbol{r}_{2}) - N_{e} f_{2}(\boldsymbol{r}_{1},\boldsymbol{r}_{1}) \right\}.$$
(28.4.7)

One has to be careful in taking the expectation value since – due to correlations – the expectation value of the product of the densities at positions r_1 and r_2 is not equal to the product of the mean values. Therefore, the expectation value of two-particle operators can be expressed in terms of the so-called two-particle density matrix as

$$\frac{1}{2} \left\langle \sum_{\substack{i,j=1\\i\neq j}}^{N_{e}} f_{2}(\boldsymbol{r}_{i},\boldsymbol{r}_{j}) \right\rangle = \iint f_{2}(\boldsymbol{r}_{1},\boldsymbol{r}_{2})\rho_{2}(\boldsymbol{r}_{1},\boldsymbol{r}_{2}) \,\mathrm{d}\boldsymbol{r}_{1} \,\mathrm{d}\boldsymbol{r}_{2} \,, \qquad (28.4.8)$$

where

$$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \binom{N_{\rm e}}{2} \int \mathrm{d}\boldsymbol{r}_3 \cdots \int \mathrm{d}\boldsymbol{r}_{N_{\rm e}} \left| \boldsymbol{\Psi}(\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_{N_{\rm e}}) \right|^2.$$
(28.4.9)

The density $n_{\rm e}(\mathbf{r})$ and the two-particle density matrix $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ are obtained from the absolute square of the many-body wavefunction by integrating over all its variables, except for one or two. The generalization of this prescription leads to the *n*-particle density matrix ρ_n . It is defined by

$$\rho_n(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n) = {N_{\rm e} \choose n} \int d\boldsymbol{r}_{n+1} \cdots \int d\boldsymbol{r}_{N_{\rm e}} \times \left| \Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n,\boldsymbol{r}_{n+1},\ldots,\boldsymbol{r}_{N_{\rm e}}) \right|^2, \qquad (28.4.10)$$

that is, the absolute square of the wavefunction of the many-body system is integrated over the variables of $N_{\rm e} - n$ particles. For the sake of brevity, only the integration over the spatial variables is explicitly displayed. For particles with spin, a summation over the spin variables is implied.

Although, following common usage, $\rho_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ was called *n*-particle density matrix, this quantity is in fact the diagonal element of the *n*-particle density matrix defined via

$$\rho_n(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n,\boldsymbol{r}'_1,\ldots,\boldsymbol{r}'_n) = {N_{\rm e} \choose n} \int \mathrm{d}\boldsymbol{r}_{n+1}\cdots \int \mathrm{d}\boldsymbol{r}_{N_{\rm e}} \\ \times \Psi^*(\boldsymbol{r}'_1,\boldsymbol{r}'_2,\ldots,\boldsymbol{r}'_n,\boldsymbol{r}_{n+1},\ldots,\boldsymbol{r}_{N_{\rm e}}) \qquad (28.4.11) \\ \times \Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n,\boldsymbol{r}_{n+1},\ldots,\boldsymbol{r}_{N_{\rm e}}),$$

where the variables which are not integrated over are different in Ψ^* and Ψ . The simplest case is the one-particle density matrix:

$$\rho_{1}(\boldsymbol{r},\boldsymbol{r}') = N_{e} \int d\boldsymbol{r}_{2} \dots \int d\boldsymbol{r}_{N_{e}} \Psi^{*}(\boldsymbol{r}',\boldsymbol{r}_{2},\boldsymbol{r}_{3},\dots,\boldsymbol{r}_{N_{e}}) \times \Psi(\boldsymbol{r},\boldsymbol{r}_{2},\boldsymbol{r}_{3},\dots,\boldsymbol{r}_{N_{e}}).$$
(28.4.12)

For a Slater-determinant wavefunction we get

$$\rho_1(\boldsymbol{r}, \boldsymbol{r}') = \sum_{i=1}^{N_{\rm e}} \phi_{\lambda_i}^*(\boldsymbol{r}') \phi_{\lambda_i}(\boldsymbol{r}) \,. \tag{28.4.13}$$

Note that if the system is in a mixed state and cannot be described by a wavefunction, the one-particle density matrix is defined as

$$\rho_1(\boldsymbol{r}, \boldsymbol{r}') = \sum_i p_{\lambda_i} \phi^*_{\lambda_i}(\boldsymbol{r}') \phi_{\lambda_i}(\boldsymbol{r}) , \qquad (28.4.14)$$

where the summation goes over a complete set of states and p_{λ_i} is the statistical weight of the state with index λ_i , i.e., the probability of finding the system in this particular state. The expectation value of a one-particle operator can be calculated by evaluating the integral

$$\left\langle \sum_{i} f(\boldsymbol{r}_{i}) \right\rangle = \int f(\boldsymbol{r}) \rho(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,,$$
 (28.4.15)

where $\rho(\mathbf{r})$ is the diagonal element of the one-particle density matrix,

$$\rho(\mathbf{r}) = \sum_{i} p_{\lambda_i} \phi^*_{\lambda_i}(\mathbf{r}) \phi_{\lambda_i}(\mathbf{r}) \,. \tag{28.4.16}$$

In the homogeneous electron gas, where all plane-wave states within the Fermi sphere $(|\mathbf{k}| < k_{\rm F})$ are filled with particles of both spin orientations,

$$\rho_1(\boldsymbol{r}, \boldsymbol{r}') = \frac{2}{V} \sum_{|\boldsymbol{k}| < k_{\rm F}} e^{i\boldsymbol{k} \cdot (\boldsymbol{r} - \boldsymbol{r}')} . \qquad (28.4.17)$$

This expression can readily be evaluated exactly by replacing the sum by an integral. Making use of (C.2.29) we get

$$\rho_{1}(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{\pi^{2}} \left[\frac{\sin k_{\rm F} |\boldsymbol{r} - \boldsymbol{r}'|}{|\boldsymbol{r} - \boldsymbol{r}'|^{3}} - \frac{k_{\rm F} \cos k_{\rm F} |\boldsymbol{r} - \boldsymbol{r}'|}{|\boldsymbol{r} - \boldsymbol{r}'|^{2}} \right]$$

= $3n_{\rm e} \frac{j_{1}(k_{\rm F} |\boldsymbol{r} - \boldsymbol{r}'|)}{k_{\rm F} |\boldsymbol{r} - \boldsymbol{r}'|}.$ (28.4.18)

Note that in second quantization the one-particle density matrix can be written in terms of the field operators

$$\hat{\psi}(\boldsymbol{r}) = \sum_{\sigma} \hat{\psi}_{\sigma}(\boldsymbol{r}), \qquad \hat{\psi}^{\dagger}(\boldsymbol{r}) = \sum_{\sigma} \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r})$$
(28.4.19)

as

$$\rho_1(\boldsymbol{r}, \boldsymbol{r}') = \left\langle \Psi \left| \hat{\psi}^{\dagger}(\boldsymbol{r}') \hat{\psi}(\boldsymbol{r}) \right| \Psi \right\rangle.$$
(28.4.20)

As a natural generalization of this expression one can define the spin-resolved one-particle density matrix via

$$\rho_{1\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \left\langle \Psi \left| \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}') \hat{\psi}_{\sigma}(\boldsymbol{r}) \right| \Psi \right\rangle.$$
(28.4.21)

When the spin quantum numbers are separated from the quantum numbers of the spatial part of the wavefunction and only the latter are denoted by λ_i ,

$$\rho_{1\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \sum_{i} \phi_{\lambda_{i}}^{*}(\boldsymbol{r}')\phi_{\lambda_{i}}(\boldsymbol{r})\delta_{\sigma\sigma'}, \qquad (28.4.22)$$

where the summation goes over the occupied single-particle states. For plane waves, we get the spin-dependent generalization of (28.4.18):

$$\rho_{1\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{2\pi^2} \frac{\sin k_{\rm F} |\boldsymbol{r} - \boldsymbol{r}'| - k_{\rm F} |\boldsymbol{r} - \boldsymbol{r}'| \cos k_{\rm F} |\boldsymbol{r} - \boldsymbol{r}'|}{|\boldsymbol{r} - \boldsymbol{r}'|^3} \delta_{\sigma\sigma'}.$$
 (28.4.23)

The two-particle density matrix is defined by

$$\rho_{2}(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}; \boldsymbol{r}_{1}', \boldsymbol{r}_{2}') = \frac{1}{2} N_{e}(N_{e} - 1) \int d\boldsymbol{r}_{3} \cdots \int d\boldsymbol{r}_{N_{e}}$$
(28.4.24)
 $\times \Psi^{*}(\boldsymbol{r}_{1}', \boldsymbol{r}_{2}', \boldsymbol{r}_{3}, \dots, \boldsymbol{r}_{N_{e}}) \Psi(\boldsymbol{r}_{1}, \boldsymbol{r}_{2}, \boldsymbol{r}_{3}, \dots, \boldsymbol{r}_{N_{e}}),$

where again the spin variables are not displayed for simplicity. The singleparticle density matrix is obtained from this expression by a further integration:

$$\int \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2) \,\mathrm{d}\boldsymbol{r}_2 = \frac{1}{2}(N_{\mathrm{e}} - 1)\rho_1(\boldsymbol{r}_1, \boldsymbol{r}_1') \,. \tag{28.4.25}$$

On the other hand, in the limit $\mathbf{r}_1 = \mathbf{r}'_1$ and $\mathbf{r}_2 = \mathbf{r}'_2$, we get back the quantity $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ used to calculate the expectation value of two-particle operators. We remark that the two-particle density matrix, too, can be given in terms of the field operators:

$$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1', \boldsymbol{r}_2') = \frac{1}{2} \left\langle \Psi \left| \hat{\psi}^{\dagger}(\boldsymbol{r}_2') \hat{\psi}^{\dagger}(\boldsymbol{r}_1') \hat{\psi}(\boldsymbol{r}_1) \hat{\psi}(\boldsymbol{r}_2) \right| \Psi \right\rangle.$$
(28.4.26)

One can show with the aid of the orthonormality of the single-particle functions $\phi_{\lambda_i}(\mathbf{r})$ that

$$\rho_{2}(\mathbf{r}_{1},\mathbf{r}_{2};\mathbf{r}_{1}',\mathbf{r}_{2}') = \frac{1}{2} \sum_{i,j=1}^{N_{e}} \left[\phi_{\lambda_{i}}^{*}(\mathbf{r}_{1}')\phi_{\lambda_{j}}^{*}(\mathbf{r}_{2}')\phi_{\lambda_{i}}(\mathbf{r}_{1})\phi_{\lambda_{j}}(\mathbf{r}_{2}) - \phi_{\lambda_{i}}^{*}(\mathbf{r}_{1}')\phi_{\lambda_{j}}^{*}(\mathbf{r}_{2}')\phi_{\lambda_{j}}(\mathbf{r}_{1})\phi_{\lambda_{i}}(\mathbf{r}_{2}) \right]$$

$$= \frac{1}{2} \left[\rho_{1}(\mathbf{r}_{1},\mathbf{r}_{1}')\rho_{1}(\mathbf{r}_{2},\mathbf{r}_{2}') - \rho_{1}(\mathbf{r}_{1},\mathbf{r}_{2}')\rho_{1}(\mathbf{r}_{2},\mathbf{r}_{1}') \right],$$
(28.4.27)

if the wavefunction has a Slater-determinant form. The diagonal elements can be written as

$$\rho_{2}(\boldsymbol{r}_{1},\boldsymbol{r}_{2}) = \frac{1}{2} \sum_{i,j=1}^{N_{e}} \left[\phi_{\lambda_{i}}^{*}(\boldsymbol{r}_{1})\phi_{\lambda_{j}}^{*}(\boldsymbol{r}_{2})\phi_{\lambda_{i}}(\boldsymbol{r}_{1})\phi_{\lambda_{j}}(\boldsymbol{r}_{2}) - \phi_{\lambda_{i}}^{*}(\boldsymbol{r}_{1})\phi_{\lambda_{j}}(\boldsymbol{r}_{2})\phi_{\lambda_{j}}(\boldsymbol{r}_{1})\phi_{\lambda_{i}}(\boldsymbol{r}_{2}) \right]$$

$$= \frac{1}{2} \sum_{i,j=1}^{N_{e}} \frac{1}{2!} \begin{vmatrix} \phi_{\lambda_{i}}^{*}(\boldsymbol{r}_{1}) \ \phi_{\lambda_{j}}^{*}(\boldsymbol{r}_{1}) \\ \phi_{\lambda_{i}}^{*}(\boldsymbol{r}_{2}) \ \phi_{\lambda_{j}}^{*}(\boldsymbol{r}_{2}) \end{vmatrix} \cdot \begin{vmatrix} \phi_{\lambda_{i}}(\boldsymbol{r}_{1}) \ \phi_{\lambda_{j}}(\boldsymbol{r}_{1}) \\ \phi_{\lambda_{i}}(\boldsymbol{r}_{2}) \ \phi_{\lambda_{j}}(\boldsymbol{r}_{2}) \end{vmatrix} .$$

$$(28.4.28)$$

Using the expression derived earlier for $\rho_1(\mathbf{r}, \mathbf{r}')$ for the homogeneous electron gas, an explicit expression can be obtained for $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$:

$$\rho_{2}(\boldsymbol{r}_{1},\boldsymbol{r}_{2}) = \frac{1}{2}n_{e}^{2} \left\{ 1 - \frac{9}{2} \left[\frac{\sin k_{F}|\boldsymbol{r}_{1} - \boldsymbol{r}_{2}| - k_{F}|\boldsymbol{r}_{1} - \boldsymbol{r}_{2}| \cos k_{F}|\boldsymbol{r}_{1} - \boldsymbol{r}_{2}|}{(k_{F}|\boldsymbol{r}_{1} - \boldsymbol{r}_{2}|)^{3}} \right]^{2} \right\}.$$
(28.4.29)

A factor 1/2 in front of the second term in the brackets arises because only electrons with identical spins contribute.

28.4.2 Pair Distribution Functions

We have seen in Chapter 2 that the short- or long-range order appearing in the spatial arrangement of atoms can be characterized by the pair distribution function or the structure factor which is the Fourier transform of the density– density correlation function. Here, repeating partly what has been learned there, we will consider electronic correlations and will demonstrate that the two-particle density matrix can be related to the pair distribution function and the density–density correlation function.

Starting with the expression

$$\rho_2(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{2}N_{\rm e}(N_{\rm e}-1)\int \mathrm{d}\boldsymbol{r}_3 \cdots \int \mathrm{d}\boldsymbol{r}_{N_{\rm e}} \left|\Psi(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}_3,\ldots,\boldsymbol{r}_{N_{\rm e}})\right|^2 \quad (28.4.30)$$

for the two-particle density matrix it is easy to show that

$$\rho_2(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{2} \left\langle \sum_{\substack{i,j=1\\i\neq j}}^{N_e} \delta(\boldsymbol{r} - \boldsymbol{r}_i) \delta(\boldsymbol{r}' - \boldsymbol{r}_j) \right\rangle, \qquad (28.4.31)$$

which is the two-particle probability density function defined in (2.1.4) apart from a factor 1/2. Here $\langle \cdots \rangle$ denotes the ground-state average or thermal average, depending on whether the correlations are studied at T = 0 or at finite temperatures. For spatially homogeneous systems it can be written as

$$\rho_{2}(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{2V} \int \mathrm{d}\boldsymbol{r}'' \left\langle \sum_{\substack{i,j=1\\i\neq j}}^{N_{\mathrm{e}}} \delta(\boldsymbol{r} - \boldsymbol{r}'' - \boldsymbol{r}_{i}) \delta(\boldsymbol{r}' - \boldsymbol{r}'' - \boldsymbol{r}_{j}) \right\rangle$$

$$= \frac{1}{2V} \left\langle \sum_{\substack{i,j=1\\i\neq j}}^{N_{\mathrm{e}}} \delta(\boldsymbol{r} - \boldsymbol{r}' + \boldsymbol{r}_{j} - \boldsymbol{r}_{i}) \right\rangle.$$
(28.4.32)

Following the approach outlined in Chapter 2 one can introduce the pair distribution function, which is the conditional probability of finding a particle at position r' provided that there is already a particle at position r. Defined according to (2.1.13) by

$$g(\boldsymbol{r} - \boldsymbol{r}') = \frac{V}{N_{\rm e}^2} \left\langle \sum_{\substack{i,j=1\\i\neq j}}^{N_{\rm e}} \delta(\boldsymbol{r} - \boldsymbol{r}' + \boldsymbol{r}_j - \boldsymbol{r}_i) \right\rangle, \qquad (28.4.33)$$

the pair distribution function is normalized in such a way that it tends to unity for large distances. It differs from the two-particle density matrix precisely in this normalization:

$$\rho_2(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{2} \left(\frac{N_e}{V}\right)^2 g(\boldsymbol{r} - \boldsymbol{r}'). \qquad (28.4.34)$$

The pair correlation function is obtained from the pair distribution function by subtracting unity, to express the fact that there are no correlations at large distances.¹¹

The density-density correlation function is defined by

$$\Gamma(\mathbf{r}, \mathbf{r}') = \frac{V}{N_{\rm e}} \langle n(\mathbf{r}) n(\mathbf{r}') \rangle, \qquad (28.4.35)$$

where $n(\mathbf{r})$ is given in (28.1.7). In a spatially homogeneous system, where correlations depend only on the distance between \mathbf{r} and \mathbf{r}' , it is more convenient to use the equivalent form

$$\Gamma(\boldsymbol{r}-\boldsymbol{r}') = \frac{1}{N_{\rm e}} \int \left\langle n(\boldsymbol{r}-\boldsymbol{r}'')n(\boldsymbol{r}'-\boldsymbol{r}'') \right\rangle \mathrm{d}\boldsymbol{r}'' \,. \tag{28.4.36}$$

Substitution of (28.1.7) into this expression gives

$$\Gamma(\boldsymbol{r} - \boldsymbol{r}') = \frac{1}{N_{\rm e}} \int \sum_{i,j=1}^{N_{\rm e}} \left\langle \delta(\boldsymbol{r} - \boldsymbol{r}'' - \boldsymbol{r}_i) \delta(\boldsymbol{r}' - \boldsymbol{r}'' - \boldsymbol{r}_j) \right\rangle \mathrm{d}\boldsymbol{r}''$$

$$= \frac{1}{N_{\rm e}} \sum_{i,j=1}^{N_{\rm e}} \left\langle \delta(\boldsymbol{r} - \boldsymbol{r}' + \boldsymbol{r}_j - \boldsymbol{r}_i) \right\rangle.$$
(28.4.37)

It is in this form that the density-density correlation function was defined in (2.1.16). It differs from the pair distribution function not only in the normalization factor but also in the inclusion of the terms i = j. To derive their relationship we separate the terms i = j in (28.4.37). This gives

$$\Gamma(\boldsymbol{r} - \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}') + \frac{1}{N_{e}} \left\langle \sum_{i \neq j} \delta(\boldsymbol{r} - \boldsymbol{r}' + \boldsymbol{r}_{j} - \boldsymbol{r}_{i}) \right\rangle$$

$$= \delta(\boldsymbol{r} - \boldsymbol{r}') + \frac{N_{e}}{V} g(\boldsymbol{r} - \boldsymbol{r}') .$$
(28.4.38)

¹¹ The pair distribution function itself is often called pair correlation function in the literature.

The same relationship could have been derived simply by expressing both $\Gamma(\mathbf{r} - \mathbf{r}')$ and $g(\mathbf{r} - \mathbf{r}')$ in terms of the field operators. Substituting (28.1.23) into (28.4.35) we have

$$\Gamma(\boldsymbol{r}-\boldsymbol{r}') = \frac{V}{N_{\rm e}} \sum_{\sigma\sigma'} \left\langle \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) \hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}') \hat{\psi}_{\sigma'}(\boldsymbol{r}') \right\rangle.$$
(28.4.39)

Moving the operator $\hat{\psi}_{\sigma}(\mathbf{r})$ to the right of the operators standing behind it, taking into account the anticommutation rules of fermion operators given in (28.1.21), and using the fact that

$$\sum_{\sigma} \left\langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) \right\rangle = \frac{N_{\rm e}}{V} \,, \qquad (28.4.40)$$

we get

$$\Gamma(\boldsymbol{r}-\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') + \frac{V}{N_{\rm e}} \sum_{\sigma\sigma'} \left\langle \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}') \hat{\psi}_{\sigma'}(\boldsymbol{r}') \hat{\psi}_{\sigma}(\boldsymbol{r}) \right\rangle.$$
(28.4.41)

The second term on the right-hand side describes the correlation between two different particles, since the two annihilation operators stand next to each other. It is proportional to the diagonal element of the two-particle density matrix [see (28.4.26)] which is related to the two-particle distribution function via (28.4.34). Hence

$$g(\boldsymbol{r} - \boldsymbol{r}') = \frac{\sum_{\sigma\sigma'} \left\langle \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}') \hat{\psi}_{\sigma'}(\boldsymbol{r}') \hat{\psi}_{\sigma}(\boldsymbol{r}) \right\rangle}{\left\langle n(\boldsymbol{r}) \right\rangle \left\langle n(\boldsymbol{r}') \right\rangle}$$
(28.4.42)

and (28.4.38) is indeed recovered.

Sometimes it is of interest to study the probability of finding an electron with identical or opposite spin around an electron with spin σ . The spin-resolved density-density correlations are described by the quantities

$$\Gamma_{\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \frac{V}{N_{\rm e}} \langle n_{\sigma}(\boldsymbol{r}) n_{\sigma'}(\boldsymbol{r}') \rangle, \qquad (28.4.43)$$

where the number-density operator for electrons with spin σ is

$$n_{\sigma}(\mathbf{r}) = \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})\hat{\psi}_{\sigma}(\mathbf{r}), \qquad (28.4.44)$$

while the properly normalized spin-resolved pair distribution functions are defined by

$$g_{\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \frac{\left\langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r})\hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}')\hat{\psi}_{\sigma'}(\boldsymbol{r}')\hat{\psi}_{\sigma}(\boldsymbol{r})\right\rangle}{\left\langle n_{\sigma}(\boldsymbol{r})\right\rangle \left\langle n_{\sigma'}(\boldsymbol{r}')\right\rangle} \,. \tag{28.4.45}$$

The relationship between these functions can be obtained by an appropriate reordering of the operators using the anticommutation rules. It is readily seen that

$$\Gamma_{\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}') = \frac{\langle n_{\sigma}(\boldsymbol{r}) \rangle}{n_{\rm e}} \delta_{\sigma\sigma'} \delta(\boldsymbol{r}-\boldsymbol{r}') + \frac{\langle n_{\sigma}(\boldsymbol{r}) \rangle \langle n_{\sigma'}(\boldsymbol{r}') \rangle}{n_{\rm e}} g_{\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}') \,. \tag{28.4.46}$$

In unpolarized systems where $N_{\uparrow} = N_{\downarrow} = N_{\rm e}/2$, only the relative spin matters. The correlations between electrons with identical or opposite spins are described by

$$\Gamma_{\parallel}(\boldsymbol{r},\boldsymbol{r}') = \frac{V}{N_{\rm e}} \sum_{\sigma} \left\langle n_{\sigma}(\boldsymbol{r}) n_{\sigma}(\boldsymbol{r}') \right\rangle,
\Gamma_{\perp}(\boldsymbol{r},\boldsymbol{r}') = \frac{V}{N_{\rm e}} \sum_{\sigma} \left\langle n_{\sigma}(\boldsymbol{r}) n_{-\sigma}(\boldsymbol{r}') \right\rangle,$$
(28.4.47)

and

$$\Gamma(\boldsymbol{r},\boldsymbol{r}') = \Gamma_{\parallel}(\boldsymbol{r},\boldsymbol{r}') + \Gamma_{\perp}(\boldsymbol{r},\boldsymbol{r}'). \qquad (28.4.48)$$

The pair distribution functions for electrons with identical and opposite spins are

$$g_{\uparrow\uparrow}(\boldsymbol{r},\boldsymbol{r}') = g_{\downarrow\downarrow}(\boldsymbol{r},\boldsymbol{r}') \equiv g_{\parallel}(\boldsymbol{r},\boldsymbol{r}'), g_{\uparrow\downarrow}(\boldsymbol{r},\boldsymbol{r}') = g_{\downarrow\uparrow}(\boldsymbol{r},\boldsymbol{r}') \equiv g_{\perp}(\boldsymbol{r},\boldsymbol{r}').$$
(28.4.49)

In a homogeneous system we then find

$$\Gamma_{\parallel}(\boldsymbol{r}-\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') + \frac{N_{\rm e}}{2V}g_{\parallel}(\boldsymbol{r}-\boldsymbol{r}'),$$

$$\Gamma_{\perp}(\boldsymbol{r}-\boldsymbol{r}') = \frac{N_{\rm e}}{2V}g_{\perp}(\boldsymbol{r}-\boldsymbol{r}'),$$
(28.4.50)

and

$$g(\mathbf{r} - \mathbf{r}') = \frac{1}{2} \left[g_{\parallel}(\mathbf{r} - \mathbf{r}') + g_{\perp}(\mathbf{r} - \mathbf{r}') \right].$$
(28.4.51)

Since the volume integral of both $\Gamma_{\parallel}(\mathbf{r}-\mathbf{r}')$ and $\Gamma_{\perp}(\mathbf{r}-\mathbf{r}')$ is equal to $N_{\rm e}/2$, the pair distribution functions satisfy the relations

$$\frac{N_{\rm e}}{2V} \int \left[1 - g_{\parallel}(\boldsymbol{r})\right] d\boldsymbol{r} = 1,$$

$$\frac{N_{\rm e}}{2V} \int \left[1 - g_{\perp}(\boldsymbol{r})\right] d\boldsymbol{r} = 0.$$
(28.4.52)

28.4.3 Correlations in the Homogeneous Electron Gas

The general expressions derived in the previous sections will now be applied to study correlations in the homogeneous electron gas at T = 0. In the Hartree approximation, where the self-energy due to electron–electron interaction is canceled exactly by the uniform positive background, there are no correlations between electrons; the pair distribution function is unity independently of the distance and the pair correlation function vanishes identically. Correlations first appear in the Fock approximation.

Our starting point is (28.4.34) that relates the pair distribution function to the two-particle density matrix:

$$g(\boldsymbol{r} - \boldsymbol{r}') = 2\left(\frac{V}{N_{\rm e}}\right)^2 \rho_2(\boldsymbol{r}, \boldsymbol{r}'). \qquad (28.4.53)$$

Since the Hartree–Fock wavefunction is a single Slater determinant, (28.4.27) can be applied. Displaying the spin variables explicitly in the single-particle functions for later convenience, the pair distribution function takes the form

$$g(\boldsymbol{r}-\boldsymbol{r}') = \left(\frac{V}{N_{\rm e}}\right)^2 \sum_{\lambda_i \sigma_i, \lambda_j \sigma_j} \left[\phi^*_{\lambda_i \sigma_i}(\boldsymbol{r}, s)\phi^*_{\lambda_j \sigma_j}(\boldsymbol{r}', s')\phi_{\lambda_i \sigma_i}(\boldsymbol{r}, s)\phi_{\lambda_j \sigma_j}(\boldsymbol{r}', s') -\phi^*_{\lambda_i \sigma_i}(\boldsymbol{r}, s)\phi^*_{\lambda_j \sigma_j}(\boldsymbol{r}', s')\phi_{\lambda_j \sigma_j}(\boldsymbol{r}, s)\phi_{\lambda_i \sigma_i}(\boldsymbol{r}', s')\right].$$
(28.4.54)

Here λ_i denotes the quantum numbers characterizing the spatial part of the wavefunction.

In an unpolarized electron gas the properly normalized pair distribution functions of electrons with identical or opposite spins take analogous forms

$$g_{\uparrow\uparrow}(\boldsymbol{r}-\boldsymbol{r}') = 4\left(\frac{V}{N_{\rm e}}\right)^2 \sum_{\lambda_i\lambda_j} \left[\phi_{\lambda_i,\uparrow}^*(\boldsymbol{r},s)\phi_{\lambda_j,\uparrow}^*(\boldsymbol{r}',s')\phi_{\lambda_i,\uparrow}(\boldsymbol{r},s)\phi_{\lambda_j,\uparrow}(\boldsymbol{r}',s')\right. \\ \left. - \phi_{\lambda_i,\uparrow}^*(\boldsymbol{r},s)\phi_{\lambda_j,\uparrow}^*(\boldsymbol{r}',s')\phi_{\lambda_j,\uparrow}(\boldsymbol{r},s)\phi_{\lambda_i,\uparrow}(\boldsymbol{r}',s')\right]$$
(28.4.55)

and

$$g_{\uparrow\downarrow}(\boldsymbol{r}-\boldsymbol{r}') = 4\left(\frac{V}{N_{\rm e}}\right)^2 \sum_{\lambda_i\lambda_j} \left[\phi_{\lambda_i,\uparrow}^*(\boldsymbol{r},s)\phi_{\lambda_j,\downarrow}^*(\boldsymbol{r}',s')\phi_{\lambda_i,\uparrow}(\boldsymbol{r},s)\phi_{\lambda_j,\downarrow}(\boldsymbol{r}',s')\right. \left. - \phi_{\lambda_i,\uparrow}^*(\boldsymbol{r},s)\phi_{\lambda_j,\downarrow}^*(\boldsymbol{r}',s')\phi_{\lambda_j,\downarrow}(\boldsymbol{r},s)\phi_{\lambda_i,\uparrow}(\boldsymbol{r}',s')\right].$$
(28.4.56)

The single-particle states being plane waves one finds

$$g_{\uparrow\uparrow}(\boldsymbol{r}-\boldsymbol{r}') = 4\left(\frac{V}{N_{\rm e}}\right)^2 \frac{1}{V^2} \sum_{\boldsymbol{k}_i \boldsymbol{k}_j} \left[1 - \mathrm{e}^{\mathrm{i}(\boldsymbol{k}_i - \boldsymbol{k}_j) \cdot (\boldsymbol{r}-\boldsymbol{r}')}\right]$$

$$= 1 - \left(\frac{2}{N_{\rm e}} \sum_{\boldsymbol{k}_i} \mathrm{e}^{\mathrm{i}\boldsymbol{k}_i \cdot (\boldsymbol{r}-\boldsymbol{r}')}\right)^2,$$
(28.4.57)

where naturally the summation goes over the $N_e/2$ wave vectors inside the Fermi sphere. The same sum appears here as in the one-particle density matrix. The relation between the two quantities should not surprise us. According to (28.4.27) the two-particle density matrix can be expressed through the

one-particle density matrix if the wavefunction is a single Slater determinant. Taking into account that the quantity in (28.4.17) is normalized by the volume whereas the number of electrons appears in (28.4.57), from (28.4.18) we get

$$\frac{2}{N_{\rm e}} \sum_{k_i} e^{ik_i \cdot r} = 3 \frac{j_1(k_{\rm F}r)}{k_{\rm F}r} \,. \tag{28.4.58}$$

Thus the spatial correlations between electrons with parallel spins are given in the Hartree–Fock approximation by the radial distribution function

$$g_{\uparrow\uparrow}(r) = 1 - 9 \left[\frac{\sin k_{\rm F} r - k_{\rm F} r \cos k_{\rm F} r}{(k_{\rm F} r)^3} \right]^2.$$
(28.4.59)

When $g_{\uparrow\downarrow}$ is calculated, the second term of (28.4.56) gives no contribution owing to the orthogonality of the spin functions and we find

$$g_{\uparrow\downarrow}(\boldsymbol{r} - \boldsymbol{r}') = 4\left(\frac{V}{N_{\rm e}}\right)^2 \frac{1}{V^2} \left(\frac{N_{\rm e}}{2}\right)^2 = 1.$$
 (28.4.60)

The spatial variations of the radial distribution functions are plotted in Fig. 28.6. The amplitude of the oscillatory term is so small that it can hardly be seen.



Fig. 28.6. Spatial variation of the radial distribution functions for electrons of parallel and antiparallel spin orientations in the Hartree–Fock approximation

The minimum appearing at r = 0 in the radial distribution function of electrons with identical spins is a consequence of the Pauli principle. Electrons occupying orthogonal states repel each other and

$$\lim_{r \to 0} g_{\uparrow\uparrow}(r) = 0, \qquad (28.4.61)$$

as can be shown mathematically rigorously. Moreover, for electrons interacting with the slowly decaying Coulomb repulsion, the Kimball relation¹²

$$\lim_{r \to 0} \frac{\mathrm{d}g_{\uparrow\uparrow}(r)}{\mathrm{d}r} = \frac{1}{a_0} \lim_{r \to 0} g_{\uparrow\uparrow}(r) \tag{28.4.62}$$

¹² J. C. KIMBALL, 1973.
holds, and hence also the derivative of the radial distribution function has to vanish at r = 0,

$$\lim_{r \to 0} \frac{\mathrm{d}g_{\uparrow\uparrow}(r)}{\mathrm{d}r} = 0.$$
(28.4.63)

This relationship is valid for spin-polarized systems as well. Since this is a consequence of quantum mechanical exchange between fermions, the dip in the radial distribution function at short distances is called an *exchange hole* or *Fermi hole*. The parallel-spin radial distribution function calculated with the Hartree–Fock wavefunction is in agreement with these exact results.

The radial distribution function for electrons with opposite spins has to satisfy the generalized Kimball relation

$$\lim_{r \to 0} \frac{\mathrm{d}g_{\uparrow\downarrow}(r)}{\mathrm{d}r} = \frac{1}{a_0} \lim_{r \to 0} g_{\uparrow\downarrow}(r) \,, \tag{28.4.64}$$

which follows from the slow 1/r dependence of the Coulomb repulsion. Although $g_{\uparrow\downarrow}(r)$ does not vanish at r = 0, the Coulomb repulsion leads to a dip around r = 0, known as the *Coulomb hole*. This relationship is not obeyed in the Hartree–Fock approximation and the Coulomb hole appears only when corrections beyond the Hartree–Fock approximation are taken into account. The Fermi and Coulomb holes are seen in Fig. 28.7 where the results of Monte Carlo simulations are plotted for the spin-resolved radial distribution functions at two different densities.



Fig. 28.7. "Exact" radial distribution functions of the homogeneous electron gas at two different densities calculated using Monte Carlo methods [Reprinted with permission from G. Ortiz and P. Ballone, *Phys. Rev. B* **50**, 1391 (1994). © (1994) by the American Physical Society]

In a dense electron gas, for small values of the dimensionless $r_{\rm s}$, where the kinetic energy is more important than the Coulomb repulsion, the Coulomb hole is smaller than the Fermi hole. On the other hand, in a dilute electron gas, for large values of $r_{\rm s}$, where the Coulomb repulsion is more important than the kinetic energy of electrons, the Coulomb and Fermi holes become comparable.

28.4.4 The Structure Factor

We know from Chapter 8 that the Fourier transform of the density–density correlation function, $\Gamma(\mathbf{q})$, can be directly measured by diffraction techniques. Taking (28.4.37) for the density–density correlation function, its Fourier transform with respect to $\mathbf{r} - \mathbf{r}'$ is

$$\Gamma(\boldsymbol{q}) = \int \Gamma(\boldsymbol{r} - \boldsymbol{r}') e^{-i\boldsymbol{q}\cdot(\boldsymbol{r} - \boldsymbol{r}')} d(\boldsymbol{r} - \boldsymbol{r}') \qquad (28.4.65)$$

$$= \frac{1}{N_{e}} \int \left\langle \sum_{i,j=1}^{N_{e}} \delta(\boldsymbol{r} - \boldsymbol{r}' + \boldsymbol{r}_{j} - \boldsymbol{r}_{i}) \right\rangle e^{-i\boldsymbol{q}\cdot(\boldsymbol{r} - \boldsymbol{r}')} d(\boldsymbol{r} - \boldsymbol{r}')$$

$$= \frac{1}{N_{e}} \left\langle \sum_{i,j=1}^{N_{e}} e^{-i\boldsymbol{q}\cdot(\boldsymbol{r}_{i} - \boldsymbol{r}_{j})} \right\rangle = \frac{1}{N_{e}} \left\langle \sum_{i=1}^{N_{e}} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_{i}} \sum_{j=1}^{N_{e}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}_{j}} \right\rangle.$$

This expression can be written as

$$\Gamma(\boldsymbol{q}) = \frac{1}{N_{\rm e}} \langle n(\boldsymbol{q})n(-\boldsymbol{q}) \rangle$$
(28.4.66)

where n(q) is the Fourier transform of the operator of the electron density.

If the ground state of the system is denoted by $|\Psi_0\rangle$ and a complete set of many-body states $|\Psi_m\rangle$ is inserted between the operators n(q) and $n(-q) = n^*(q)$, we get

$$\Gamma(\boldsymbol{q}) = \frac{1}{N_{\rm e}} \sum_{m} \left| \langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle \right|^2.$$
(28.4.67)

It is easily seen from (28.4.65) that $\Gamma(q)$ has a sharp peak at q = 0, since it is exactly true that

$$\Gamma(q=0) = N_{\rm e} \,.$$
 (28.4.68)

The static structure factor S(q) is defined by separating this peak:

$$\Gamma(\boldsymbol{q}) = N_{\rm e}\delta_{\boldsymbol{q},0} + S(\boldsymbol{q}). \qquad (28.4.69)$$

At finite temperatures, where the spectral representation of $\Gamma(q)$ is

$$\Gamma(\boldsymbol{q}) = \frac{1}{N_{\rm e}} \frac{1}{Z} \sum_{mn} \mathrm{e}^{-\beta E_n} \left| \langle \Psi_n | n(\boldsymbol{q}) | \Psi_m \rangle \right|^2, \qquad (28.4.70)$$

the peak at q = 0 is still a sharp Dirac delta peak.

As shown in Chapter 2, the structure factor and the pair correlation function are related via

$$S(\boldsymbol{q}) - 1 = \frac{N_{\rm e}}{V} \int \left[g(\boldsymbol{r} - \boldsymbol{r}') - 1 \right] e^{-\mathrm{i}\boldsymbol{q} \cdot (\boldsymbol{r} - \boldsymbol{r}')} \,\mathrm{d}(\boldsymbol{r} - \boldsymbol{r}') \tag{28.4.71}$$

or inverting the transformation,

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$$g(\mathbf{r} - \mathbf{r}') - 1 = \frac{1}{N_{\rm e}} \sum_{\mathbf{q}} \left[S(\mathbf{q}) - 1 \right] e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} .$$
(28.4.72)

In isotropic systems, after integration over the angles and using the relationship between the electron density and the Fermi wave number we find

$$S(q) - 1 = \frac{4k_{\rm F}^3}{3\pi} \int r^2 \big[g(r) - 1\big] \frac{\sin qr}{qr} \,\mathrm{d}r \tag{28.4.73}$$

 or

$$g(r) - 1 = \frac{3}{2k_{\rm F}^3} \int q^2 \left[S(q) - 1 \right] \frac{\sin qr}{qr} \,\mathrm{d}q \,. \tag{28.4.74}$$

The structure factor of the homogeneous electron gas can be computed in the Hartree–Fock approximation at T = 0 by inserting the expression derived earlier for the pair distribution function. We get

$$S_{\rm HF}(\boldsymbol{q}) = \begin{cases} \frac{3}{4} \frac{q}{k_{\rm F}} - \frac{1}{16} \left(\frac{q}{k_{\rm F}}\right)^3, & q < 2k_{\rm F}, \\ 1, & q > 2k_{\rm F}. \end{cases}$$
(28.4.75)

Since there is no correlation between electrons of opposite spins in the Hartree– Fock approximation, this form of the structure factor is due entirely to the Pauli exclusion of electrons with parallel spins.

An alternative derivation of this result starts from (28.4.66). Inserting

$$n(\boldsymbol{q}) = \sum_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}$$
(28.4.76)

for the Fourier transform of the electron density in second quantization we find

$$\Gamma(\boldsymbol{q}) = \frac{1}{N_{\rm e}} \left\langle \sum_{\boldsymbol{k}'\sigma'} \sum_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'+\boldsymbol{q}\sigma'} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}-\boldsymbol{q}\sigma} \right\rangle
= \frac{1}{N_{\rm e}} \left\langle \sum_{\boldsymbol{k}'\sigma'} \sum_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}'+\boldsymbol{q}\sigma'} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c_{\boldsymbol{k}\sigma} \right\rangle.$$
(28.4.77)

This gives, as it should, the total number of particles at q = 0. Separating this term, the remaining part is the static structure factor. Only the terms $\mathbf{k}' = \mathbf{k}$ and $\sigma' = \sigma$ contribute to it. The state with wave vector \mathbf{k} has to be occupied in the ground state, while the state with $\mathbf{k} + \mathbf{q}$ has to be empty originally. When the structure factor is evaluated for a noninteracting Fermi sea, the \mathbf{k} vectors have to be inside the Fermi sphere about the origin, but outside the Fermi sphere drawn about the tip of vector $-\mathbf{q}$. This region is displayed in Fig. 28.8.



Fig. 28.8. The region in k-space (shaded region) that gives nonvanishing contribution to the structure factor

The restrictions on the k vectors can be expressed in the form

$$S(\boldsymbol{q}) = \frac{2}{N_{\rm e}} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) \right].$$
(28.4.78)

The factor of 2 comes from the spin. When the sum is replaced by an integral, the volume of the nonoverlapping regions of the displaced Fermi spheres can easily be obtained using cylindrical coordinates with the axis fixed by the vector \boldsymbol{q} . The expression for $S(\boldsymbol{q})$ then reduces to (28.4.75).

28.4.5 Dynamical Correlations Between Electrons

The time-dependent density-density correlation function is a straightforward generalization of the static correlation function. It is defined by

$$\Gamma(\mathbf{r}, t, \mathbf{r}', t') = \frac{V}{N_{\rm e}} \langle n(\mathbf{r}, t) n(\mathbf{r}', t') \rangle, \qquad (28.4.79)$$

where

$$n(\mathbf{r},t) = \sum_{i=1}^{N_{e}} \delta(\mathbf{r} - \mathbf{r}_{i}(t)), \qquad (28.4.80)$$

and the time dependence of an operator $\mathcal O$ is defined as usual in the Heisenberg picture via

$$\mathcal{O}(t) = e^{i\mathcal{H}t/\hbar} \mathcal{O}e^{-i\mathcal{H}t/\hbar} . \qquad (28.4.81)$$

For electrons moving in a spatially uniform time-independent potential the correlation function depends on $\mathbf{r} - \mathbf{r}'$ and t - t', and so

$$\Gamma(\mathbf{r},t) = \frac{1}{N_{\rm e}} \left\langle \sum_{i,j=1}^{N_{\rm e}} \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle.$$
(28.4.82)

 $\Gamma(\mathbf{r}, t)$ can be decomposed into two parts:

$$\Gamma(\mathbf{r},t) = \Gamma_{\text{self}}(\mathbf{r},t) + \Gamma_{\text{pair}}(\mathbf{r},t). \qquad (28.4.83)$$

The first part, the self-correlation function, contains the terms i = j:

$$\Gamma_{\text{self}}(\boldsymbol{r},t) = \frac{1}{N_{\text{e}}} \left\langle \sum_{i=1}^{N_{\text{e}}} \delta(\boldsymbol{r} - \boldsymbol{r}_{i}(t) + \boldsymbol{r}_{i}(0)) \right\rangle$$
(28.4.84)

and describes how the position of an electron at time t correlates with its initial position. The terms $i \neq j$ describe the dynamical correlations between different particles:

$$\Gamma_{\text{pair}}(\boldsymbol{r},t) = \frac{1}{N_{\text{e}}} \left\langle \sum_{\substack{i,j=1\\i\neq j}}^{N_{\text{e}}} \delta(\boldsymbol{r} - \boldsymbol{r}_{i}(t) + \boldsymbol{r}_{j}(0)) \right\rangle.$$
(28.4.85)

The Fourier transform with respect to the spatial variable is

$$\Gamma(\boldsymbol{q},t) = \frac{1}{N_{\rm e}} \left\langle n(\boldsymbol{q},t)n(-\boldsymbol{q},0) \right\rangle$$
(28.4.86)

with

$$n(\boldsymbol{q},t) = \sum_{i=1}^{N_{e}} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_{i}(t)} . \qquad (28.4.87)$$

The time dependence can be given explicitly if a complete set of eigenstates of the total Hamiltonian are inserted between $n(\mathbf{q}, t)$ and $n(-\mathbf{q}, 0)$. We have

$$\Gamma(\boldsymbol{q},t) = \frac{1}{N_{\rm e}} \sum_{m} \langle \Psi_0 | n(\boldsymbol{q},t) | \Psi_m \rangle \langle \Psi_m | n(-\boldsymbol{q},0) | \Psi_0 \rangle$$

$$= \frac{1}{N_{\rm e}} \sum_{m} |\langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle|^2 \,\mathrm{e}^{-\mathrm{i}(E_m - E_0)t/\hbar} \,.$$
(28.4.88)

Taking the Fourier transform with respect to time we find

$$\Gamma(\boldsymbol{q},\omega) = \frac{2\pi\hbar}{N_{\rm e}} \sum_{m} |\langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle|^2 \,\delta(\hbar\omega - E_m + E_0) \,. \tag{28.4.89}$$

The dynamical structure factor $S(\mathbf{q}, \omega)$ is defined in analogy to the static structure factor by removing the forward scattering $(\mathbf{q} = 0)$, elastic $[\delta(\omega)]$ component from $\Gamma(\mathbf{q}, \omega)$:

$$\Gamma(\boldsymbol{q},\omega) = 2\pi N_{\rm e} \delta_{\boldsymbol{q},0} \delta(\omega) + S(\boldsymbol{q},\omega) \,. \tag{28.4.90}$$

 Thus^{13}

$$S(\boldsymbol{q},\omega) = \frac{2\pi\hbar}{N_{\rm e}} \sum_{m} |\langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle|^2 \,\delta(\hbar\omega - E_m + E_0) \,, \quad \boldsymbol{q} \neq 0 \,. \quad (28.4.91)$$

 $^{^{13}}$ Quite often in the literature, the dynamical structure factor is defined without the factor $2\pi/N_{\rm e}.$

At finite temperatures, where the thermal average has to be taken and not the ground-state expectation value,

$$S(\boldsymbol{q},\omega) = \frac{2\pi\hbar}{N_{\rm e}} \sum_{nm} \frac{1}{Z} e^{-\beta E_n} \left| \langle \boldsymbol{\Psi}_n | n(\boldsymbol{q}) | \boldsymbol{\Psi}_m \rangle \right|^2 \delta(\hbar\omega - E_m + E_n) \,. \quad (28.4.92)$$

The static structure factor is obtained by integrating over frequency:

$$S(\boldsymbol{q}) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} S(\boldsymbol{q}, \omega) \,. \tag{28.4.93}$$

The dynamical structure factor of the homogeneous electron gas can be calculated more conveniently by starting from the expression where the densities are written in terms of the field operators. As a natural generalization of (28.4.39) the dynamical density-density correlation function takes the form

$$\Gamma(\mathbf{r},t,\mathbf{r}',t') = \frac{V}{N_{\rm e}} \sum_{\sigma\sigma'} \left\langle \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r},t) \hat{\psi}_{\sigma}(\mathbf{r},t) \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}',t') \hat{\psi}_{\sigma'}(\mathbf{r}',t') \right\rangle.$$
(28.4.94)

When the field operators are expressed in terms of the creation and annihilation operators of plane-wave states we find

$$\Gamma(\boldsymbol{q},t) = \frac{1}{N_{\rm e}} \left\langle \sum_{\boldsymbol{k}\sigma} \sum_{\boldsymbol{k}'\sigma'} c^{\dagger}_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} \right\rangle$$
(28.4.95)

for the spatial Fourier transform of the dynamical density–density correlation function. It is a straightforward generalization of (28.4.77) and could have been obtained by using

$$n(\boldsymbol{q},t) = \sum_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \qquad (28.4.96)$$

in (28.4.86). We will evaluate it for the filled Fermi sea as the ground state. Although the Coulomb repulsion is neglected in this approximation, the quantum mechanical exchange is taken into account.

For free electrons the time dependence of the creation and annihilation operators is

$$c_{\boldsymbol{k}\sigma}^{\dagger}(t) = c_{\boldsymbol{k}\sigma}^{\dagger} \mathrm{e}^{\mathrm{i}\varepsilon_{\boldsymbol{k}\sigma}t/\hbar}, \qquad c_{\boldsymbol{k}\sigma}(t) = c_{\boldsymbol{k}\sigma} \mathrm{e}^{-\mathrm{i}\varepsilon_{\boldsymbol{k}\sigma}t/\hbar}.$$
(28.4.97)

Only the terms $\mathbf{k} = \mathbf{k}'$ and $\sigma = \sigma'$ give contribution for $\mathbf{q} \neq 0$, and so

$$S(\boldsymbol{q},t) = \frac{1}{N_{\rm e}} \sum_{\boldsymbol{k}\sigma} f_0(\varepsilon_{\boldsymbol{k}}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) \right] {\rm e}^{{\rm i}(\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}})t/\hbar} \,. \tag{28.4.98}$$

The Fourier transform with respect to time gives

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$$S(\boldsymbol{q},\omega) = \frac{1}{N_{\rm e}} \sum_{\boldsymbol{k}\sigma} f_0(\varepsilon_{\boldsymbol{k}}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) \right] \int_{-\infty}^{\infty} e^{\mathrm{i}(\hbar\omega + \varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}})t/\hbar} \,\mathrm{d}t$$

$$= \frac{2\pi\hbar}{N_{\rm e}} \sum_{\boldsymbol{k}\sigma} f_0(\varepsilon_{\boldsymbol{k}}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) \right] \delta(\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}) \,.$$
(28.4.99)

 \sim

At temperature T = 0, the state annihilated by $c_{\boldsymbol{k}\sigma}$ has to be inside the Fermi sphere, while the state created by $c_{\boldsymbol{k}+\boldsymbol{q}\sigma}$ has to be outside. Therefore, $\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} > \varepsilon_{\boldsymbol{k}}$ and the dynamical structure factor is finite only if $\omega > 0$. As long as $q \leq 2k_{\rm F}$, both the electron and the hole can be created in the neighborhood of the Fermi surface with vanishingly small excitation energies. The largest energy of the electron-hole pair for a fixed q is

$$\hbar\omega_{\rm max} = \frac{\hbar^2 (k_{\rm F} + q)^2}{2m_{\rm e}} - \frac{\hbar^2 k_{\rm F}^2}{2m_{\rm e}} = \frac{\hbar^2 k_{\rm F} q}{m_{\rm e}} + \frac{\hbar^2 q^2}{2m_{\rm e}} = \hbar v_{\rm F} q + \varepsilon_q \,. \tag{28.4.100}$$

This is attained when k is on the Fermi surface and q lies in the same direction as k. Hence, as shown in Fig. 28.9, in this range of wave vectors, the electron– hole pair excitations give a broad continuum that goes from zero to $\hbar\omega_{\rm max}$.



Fig. 28.9. The continuum of electron-hole pair excitations in a three-dimensional free electron gas

When $q > 2k_{\rm F}$, the continuum of excitations does not start at zero energy. The lower boundary is obtained when k is on the Fermi surface and q is oppositely oriented to k. We have

$$\hbar\omega_{\rm min} = \frac{\hbar^2 (k_{\rm F} - q)^2}{2m_{\rm e}} - \frac{\hbar^2 k_{\rm F}^2}{2m_{\rm e}} = \varepsilon_q - \hbar v_{\rm F} q \,. \tag{28.4.101}$$

The dynamical structure factor of the noninteracting electron gas can be calculated exactly at T = 0 if the sum over k is converted to an integral. Conveniently we choose cylindrical coordinates where the z-axis is in the direction of q. For $q < 2k_{\rm F}$ we find

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$$S(\boldsymbol{q},\omega) = \begin{cases} \frac{3\pi\hbar}{2\varepsilon_{\rm F}}\frac{\hbar\omega}{\hbar v_{\rm F}q} & 0 \le \hbar\omega < \hbar v_{\rm F}q - \varepsilon_{q} ,\\ \frac{3\pi\hbar}{4\varepsilon_{\rm F}}\frac{k_{\rm F}}{q} \left[1 - \left(\frac{\hbar\omega - \varepsilon_{q}}{\hbar v_{\rm F}q}\right)^{2}\right] & \hbar v_{\rm F}q - \varepsilon_{q} \le \hbar\omega \le \hbar v_{\rm F}q + \varepsilon_{q} ,\\ 0 & \hbar v_{\rm F}q + \varepsilon_{q} \le \hbar\omega , \end{cases}$$

$$(28.4.102)$$

while in the range $q > 2k_{\rm F}$

$$S(\boldsymbol{q},\omega) = \begin{cases} 0 & 0 \leq \hbar\omega < \varepsilon_{q} - \hbar v_{\mathrm{F}}q ,\\ \frac{3\pi\hbar}{4\varepsilon_{\mathrm{F}}} \frac{k_{\mathrm{F}}}{q} \left[1 - \left(\frac{\hbar\omega - \varepsilon_{q}}{\hbar v_{\mathrm{F}}q}\right)^{2} \right] & \varepsilon_{q} - \hbar v_{\mathrm{F}}q \leq \hbar\omega \leq \varepsilon_{q} + \hbar v_{\mathrm{F}}q ,\\ 0 & \varepsilon_{q} + \hbar v_{\mathrm{F}}q \leq \hbar\omega . \end{cases}$$

$$(28.4.103)$$

Figure 28.10 shows the ω dependence of the dynamical structure factor at a few fixed values of q. In all cases a broad, featureless maximum is seen.



Fig. 28.10. Frequency dependence of the dynamical structure factor of the noninteracting electron gas at four different q values. The density of the electron gas corresponds to $r_s = 3$

Expression (28.4.99) for the dynamical structure factor is valid also at finite temperatures if $f_0(\varepsilon_k)$ is the finite-temperature Fermi distribution function. $S(\mathbf{q}, \omega)$ is then nonvanishing for negative frequencies as well. It can be easily shown with the aid of (28.4.92) that

$$S(\boldsymbol{q}, -\omega) = e^{-\beta\hbar\omega} S(\boldsymbol{q}, \omega). \qquad (28.4.104)$$

The foregoing calculations were done for noninteracting electrons. All the results are still valid for isotropic electron systems characterized by an effective mass m^* , if the electron mass m_e is replaced with m^* in all expressions derived above.

28.4.6 Dynamical Structure Factor and Scattering Cross Section

It was shown in Chapter 8 that the intensity of the beam diffracted from a system of identical atoms is proportional to $|f_{\mathbf{K}}|^2$, where

$$f_{\boldsymbol{K}} = \sum_{m} \mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_{m}}, \qquad (28.4.105)$$

and $\mathbf{K} = \mathbf{k} - \mathbf{k}'$ is the change in the wave vector of the scattered particle (photons, neutrons, etc.).

Later, in Chapter 13 and in Appendix E, it was shown in connection with the study of lattice vibrations that the double differential cross section is proportional to

$$S(\boldsymbol{K},\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \sum_{m,n} \left\langle \mathrm{e}^{-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_m(t)} \mathrm{e}^{\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{r}_n(0)} \right\rangle, \qquad (28.4.106)$$

where $\mathbf{K} = \mathbf{k} - \mathbf{k}'$ and $\hbar \omega = E_{\rm i} - E_{\rm f}$, i.e., the \mathbf{K} and ω variables of the measured dynamical structure factor are related to the change in the wave vector and energy during the scattering process.

It follows from the Van Hove formula that this result is generally valid for scattering on solids whenever the interaction between the incoming radiation and the particles of the medium located at r_m can be given by a potential

$$\mathcal{H}_{\text{int}} = \sum_{m} V(\boldsymbol{r} - \boldsymbol{r}_{m}) \,. \tag{28.4.107}$$

Then the double differential cross section is proportional to the spatial and temporal Fourier transform of the density–density correlation function, which is exactly the dynamical structure factor discussed above:

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \,\mathrm{d}\varepsilon} \propto S(\boldsymbol{K}, \varepsilon/\hbar) \,. \tag{28.4.108}$$

If the system has sharply defined excitations, then sharp peaks appear at the corresponding energies in the dynamical structure factor, and hence in the scattering cross section. Conversely, sharp peaks in the dynamical structure factor imply the existence of well-defined excitations, as has been seen for phonons and magnons. In contrast to this behavior, when a beam is scattered by a noninteracting electron system, no sharp peaks appear in the energy dependence. The broad peak in the dynamical structure factor and in the energy distribution of the scattered beam is due to the fact that the energy of the created electron-hole pair can vary in a wide range for a fixed wave vector. We will see later that the dynamical structure factor is strongly modified by the interaction. When the interaction is strong enough a relatively sharp peak may appear indicating that relatively well-defined collective excitations are formed.

28.4.7 Magnetic Correlations

In an external magnetic field, the energy and the number of up- and down-spin electrons are no longer the same. Spin polarization also occurs when the spin-rotation symmetry is broken spontaneously. In such systems the spin-resolved density-density correlation functions defined in (28.4.43) or the spin-resolved pair distribution functions defined in (28.4.45) have to be studied. It follows from (28.4.46) that for spatially uniform systems

$$\Gamma_{\sigma\sigma}(\boldsymbol{r}-\boldsymbol{r}') = \delta_{\sigma\sigma'}\frac{n_{\sigma}}{n_{\rm e}}\delta(\boldsymbol{r}-\boldsymbol{r}') + \frac{n_{\sigma}n_{\sigma'}}{n_{\rm e}}g_{\sigma\sigma'}(\boldsymbol{r}-\boldsymbol{r}').$$
(28.4.109)

The polarization can be conveniently characterized by the quantity

$$\zeta = \frac{N_{\mathrm{e\uparrow}} - N_{\mathrm{e\downarrow}}}{N_{\mathrm{e\uparrow}} + N_{\mathrm{e\downarrow}}} = \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}}, \qquad (28.4.110)$$

that is

$$n_{\uparrow} = \frac{N_{\rm e}}{2V} (1+\zeta), \qquad n_{\downarrow} = \frac{N_{\rm e}}{2V} (1-\zeta).$$
 (28.4.111)

The spin-resolved density–density correlation functions can then be written as

$$\begin{split} \Gamma_{\uparrow\uparrow}(\boldsymbol{r}-\boldsymbol{r}') &= \frac{1+\zeta}{2}\delta(\boldsymbol{r}-\boldsymbol{r}') + \left(\frac{1+\zeta}{2}\right)^2 \frac{N_{\rm e}}{V} g_{\uparrow\uparrow}(\boldsymbol{r}-\boldsymbol{r}') \,, \\ \Gamma_{\downarrow\downarrow}(\boldsymbol{r}-\boldsymbol{r}') &= \frac{1-\zeta}{2}\delta(\boldsymbol{r}-\boldsymbol{r}') + \left(\frac{1-\zeta}{2}\right)^2 \frac{N_{\rm e}}{V} g_{\downarrow\downarrow}(\boldsymbol{r}-\boldsymbol{r}') \,, \\ \Gamma_{\uparrow\downarrow}(\boldsymbol{r}-\boldsymbol{r}') &= \frac{1-\zeta^2}{4} \frac{N_{\rm e}}{V} g_{\uparrow\downarrow}(\boldsymbol{r}-\boldsymbol{r}') \,, \\ \Gamma_{\downarrow\uparrow}(\boldsymbol{r}-\boldsymbol{r}') &= \frac{1-\zeta^2}{4} \frac{N_{\rm e}}{V} g_{\downarrow\uparrow}(\boldsymbol{r}-\boldsymbol{r}') \,, \end{split}$$
(28.4.112)

and

$$g(\boldsymbol{r} - \boldsymbol{r}') = \left(\frac{1+\zeta}{2}\right)^2 g_{\uparrow\uparrow}(\boldsymbol{r} - \boldsymbol{r}') + \left(\frac{1-\zeta}{2}\right)^2 g_{\downarrow\downarrow}(\boldsymbol{r} - \boldsymbol{r}') + \frac{1-\zeta^2}{4} \left[g_{\uparrow\downarrow}(\boldsymbol{r} - \boldsymbol{r}') + g_{\downarrow\uparrow}(\boldsymbol{r} - \boldsymbol{r}')\right].$$
(28.4.113)

In order to study dynamical correlations in a magnetically polarized system, the spin-resolved dynamical density–density correlation functions

$$\Gamma_{\sigma\sigma'}(\boldsymbol{r},t,\boldsymbol{r}',t') = \frac{V}{N_{\rm e}} \langle n_{\sigma}(\boldsymbol{r},t)n_{\sigma'}(\boldsymbol{r}',t') \rangle
= \frac{V}{N_{\rm e}} \left\langle \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r},t)\hat{\psi}_{\sigma}(\boldsymbol{r},t)\hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}',t')\hat{\psi}_{\sigma'}(\boldsymbol{r}',t') \right\rangle$$
(28.4.114)

have to be studied. In a spatially uniform system, the spatial Fourier transform is

$$\Gamma_{\sigma\sigma'}(\boldsymbol{q},t) = \frac{1}{N_{\rm e}} \left\langle n_{\sigma}(\boldsymbol{q},t) n_{\sigma'}(-\boldsymbol{q},0) \right\rangle$$
$$= \frac{1}{N_{\rm e}} \left\langle \sum_{\boldsymbol{k}\boldsymbol{k}'} c^{\dagger}_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} \right\rangle.$$
(28.4.115)

The dynamical structure factor is obtained by separating the term q = 0,

$$\Gamma_{\sigma\sigma'}(\boldsymbol{q},t) = N_{\rm e} \frac{N_{\rm e\sigma}}{N_{\rm e}} \frac{N_{\rm e\sigma'}}{N_{\rm e}} \delta_{\boldsymbol{q},0} + S_{\sigma\sigma'}(\boldsymbol{q},t) \,. \tag{28.4.116}$$

The $q \neq 0$ term describes the propagation of an electron-hole pair created at t = 0. It is the probability amplitude of finding the pair at a later time t. For noninteracting electrons, this contribution is finite only when the electrons have identical spins and $\mathbf{k} = \mathbf{k}'$. Taking into account that the hole is inside the Fermi sea while the electron is outside,

$$S_{\sigma\sigma'}(\boldsymbol{q},t) = \delta_{\sigma\sigma'} \frac{1}{N_{\rm e}} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}) \right] \mathrm{e}^{\mathrm{i}(\varepsilon_{\boldsymbol{k}\sigma} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma})t/\hbar}, \quad (28.4.117)$$

from which we get

$$S_{\sigma\sigma'}(\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{2\pi\hbar}{N_{\rm e}} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}) \right] \delta(\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma})$$
(28.4.118)

for the Fourier transform with respect to time.

Further Reading

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Electronic Response to External Perturbations

The transport and optical properties of solids are due primarily to the electron system and to a lesser extent to the ions. These properties were discussed in Chapters 24 and 25 without taking the interaction between electrons into account, although its role may be important in some cases. In this chapter we will study the response of the interacting electron system to external perturbations, to an applied electromagnetic field. We will consider first the effect of an external scalar potential and will derive general expressions that relate the dielectric function to the density-density response function and the dynamical structure factor introduced in the previous chapter. This will then allow us to get approximate expressions for the frequency and wave number dependence of the dielectric function. The study of the redistribution of electrons induced by an external charge will lead to a proper description of screening in metals. It will be shown that the optical conductivity can be calculated from the current–current correlation function. Finally, by studying the response of the electron system to an external magnetic field, we will be able to derive an approximate expression for the wave number- and frequency-dependent susceptibility which is the magnetic analog of the dielectric function.

29.1 The Dielectric Function

When a solid is exposed to an external electric field varying in space and time, the relationship between the electric displacement D and the electric field E is not local in space, though it is causal in time. The permittivity must then be expressed in an integral form. The relationship

$$D_{\alpha}(\boldsymbol{r},t) = \int \mathrm{d}\boldsymbol{r}' \int_{-\infty}^{t} \mathrm{d}t' \,\epsilon_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{r}',t-t') E_{\beta}(\boldsymbol{r}',t') \tag{29.1.1}$$

given in (16.1.50) is valid for isotropic systems. In a crystalline material we have

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$$D_{\alpha}(\boldsymbol{r},t) = \sum_{\beta} \int d\boldsymbol{r}' \int_{-\infty}^{t} dt' \epsilon_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t-t') E_{\beta}(\boldsymbol{r}',t'), \qquad (29.1.2)$$

where $\epsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t - t')$ depends on \mathbf{r} and \mathbf{r}' separately, not just on their difference. Hence its Fourier transform contains two momentum variables:

$$\epsilon_{\alpha\beta}(\boldsymbol{q},\boldsymbol{q}',t-t') = \iint \mathrm{d}\boldsymbol{r} \,\mathrm{d}\boldsymbol{r}' \epsilon_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t-t') \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}'\cdot\boldsymbol{r}'}.$$
 (29.1.3)

However, if the position vectors are written as $\mathbf{r} = \mathbf{R}_n + \mathbf{u}$ and $\mathbf{r}' = \mathbf{R}_m + \mathbf{u}'$ where \mathbf{u} and \mathbf{u}' are in the primitive cell around the lattice points \mathbf{R}_n and \mathbf{R}_m , respectively, the dielectric tensor depends on \mathbf{u} , \mathbf{u}' , and $\mathbf{R}_n - \mathbf{R}_m$ only, owing to the discrete translational invariance of the crystal, and \mathbf{q}' may differ from $-\mathbf{q}$ by a reciprocal-lattice vector \mathbf{G} . Taking the Fourier transform with respect to time the relationship

$$D_{\alpha}(\boldsymbol{q},\omega) = \sum_{\boldsymbol{G}} \sum_{\beta} \epsilon_{\alpha\beta}(\boldsymbol{q}, -\boldsymbol{q} - \boldsymbol{G}, \omega) E_{\beta}(\boldsymbol{q} + \boldsymbol{G}, \omega)$$
(29.1.4)

is obtained between the Fourier components of the fields. The terms with $G \neq 0$ take into account the variations of the fields over atomic distances and yield the so-called local-field corrections. These corrections are usually small and can be neglected, so that the system can be assumed to have full translational symmetry. We then arrive at the usual expression

$$D_{\alpha}(\boldsymbol{q},\omega) = \sum_{\beta} \epsilon_{\alpha\beta}(\boldsymbol{q},\omega) E_{\beta}(\boldsymbol{q},\omega) . \qquad (29.1.5)$$

But, even after this simplification the dielectric function depends on the direction of propagation of the electromagnetic field relative to the crystallographic axes. In what follows we will forget about this and will consider the properties of isotropic materials only.

Decomposing the electric field and the electric displacement into components parallel and perpendicular to the direction of q, their relationship in the general case can be written as

$$\boldsymbol{D}_{\parallel}(\boldsymbol{q},\omega) = \epsilon_{\parallel}(\boldsymbol{q},\omega)\boldsymbol{E}_{\parallel}(\boldsymbol{q},\omega), \quad \boldsymbol{D}_{\perp}(\boldsymbol{q},\omega) = \epsilon_{\perp}(\boldsymbol{q},\omega)\boldsymbol{E}_{\perp}(\boldsymbol{q},\omega), \quad (29.1.6)$$

which means that

$$\boldsymbol{D}(\boldsymbol{q},\omega) = \epsilon_{\parallel}(\boldsymbol{q},\omega) \frac{\boldsymbol{q} \cdot \boldsymbol{E}(\boldsymbol{q},\omega)}{q^2} \boldsymbol{q} + \epsilon_{\perp}(\boldsymbol{q},\omega) \frac{\boldsymbol{q} \times \boldsymbol{E}(\boldsymbol{q},\omega)}{q^2} \times \boldsymbol{q}, \qquad (29.1.7)$$

i.e., the permittivity tensor has the general form

$$\epsilon_{\alpha\beta}(\boldsymbol{q},\omega) = \epsilon_{\parallel}(\boldsymbol{q},\omega)\hat{q}_{\alpha}\hat{q}_{\beta} + \epsilon_{\perp}(\boldsymbol{q},\omega)\left(\delta_{\alpha\beta} - \hat{q}_{\alpha}\hat{q}_{\beta}\right), \qquad (29.1.8)$$

where \hat{q}_{α} is the α component of the unit vector \hat{q} that points in the direction of \boldsymbol{q} . The dielectric function is related to the longitudinal component $\epsilon_{\parallel}(\boldsymbol{q},\omega)$ by

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = \epsilon_{\parallel}(\boldsymbol{q},\omega)/\epsilon_0\,. \tag{29.1.9}$$

The dielectric function has been studied previously in Chapter 16 in the framework of the Drude model. The results derived there are, however, valid only in the long-wavelength limit, owing to the approximations inherent to that model. A better approximation will be applied here with the primary aim of studying the role of the electron–electron interaction. This will help us to get a better understanding of how electrons influence each other.

29.1.1 Dielectric Response of the Electron System

In order to obtain the dielectric function, we will study what happens in an originally homogeneous electron gas with a neutralizing background when external charges with a spatially inhomogeneous, time-dependent charge density $\rho_{\text{ext}}(\mathbf{r}, t)$ are introduced into it. The external charge is related to the electric displacement via Maxwell's third equation (Gauss's law):

$$\operatorname{div} \boldsymbol{D}(\boldsymbol{r}, t) = \rho_{\text{ext}}(\boldsymbol{r}, t) \,. \tag{29.1.10}$$

The Coulomb interaction between the external charges and the electrons of the system gives rise to a redistribution of the electrons and induces a charge density $\rho_{ind}(\mathbf{r}, t)$ in the originally homogeneous and neutral system. The electric field \mathbf{E} is generated by the total charge density, the sum of external and induced charges,

$$\rho(\boldsymbol{r},t) = \rho_{\text{ext}}(\boldsymbol{r},t) + \rho_{\text{ind}}(\boldsymbol{r},t), \qquad (29.1.11)$$

and their relationship is given by

$$\epsilon_0 \operatorname{div} \boldsymbol{E}(\boldsymbol{r}, t) = \rho(\boldsymbol{r}, t) \,. \tag{29.1.12}$$

This field is the negative gradient of the scalar potential $\varphi(\mathbf{r})$,

$$\boldsymbol{E}(\boldsymbol{r},t) = -\text{grad}\,\varphi(\boldsymbol{r},t)\,. \tag{29.1.13}$$

In analogy to this relationship an external potential $\varphi_{\text{ext}}(\mathbf{r})$ can be introduced that is generated by the external charge. It is defined by

$$\boldsymbol{D}(\boldsymbol{r},t) = -\epsilon_0 \operatorname{grad} \varphi_{\text{ext}}(\boldsymbol{r},t) \,. \tag{29.1.14}$$

Taking the Fourier transforms of the fields and potentials we find

$$\boldsymbol{E}(\boldsymbol{q},\omega) = -i\boldsymbol{q}\varphi(\boldsymbol{q},\omega), \qquad \boldsymbol{D}(\boldsymbol{q},\omega) = -i\epsilon_0 \boldsymbol{q}\varphi_{\text{ext}}(\boldsymbol{q},\omega).$$
(29.1.15)

It follows from (29.1.5) that a simple relationship exists between the two potentials:

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$$\varphi(\boldsymbol{q},\omega) = \frac{\epsilon_0}{\epsilon(\boldsymbol{q},\omega)} \varphi_{\text{ext}}(\boldsymbol{q},\omega) = \frac{1}{\epsilon_{\text{r}}(\boldsymbol{q},\omega)} \varphi_{\text{ext}}(\boldsymbol{q},\omega) \,. \tag{29.1.16}$$

Substitution of (29.1.13) and (29.1.14) into (29.1.12) and (29.1.10), respectively, gives

$$\epsilon_0 \nabla^2 \varphi(\mathbf{r}, t) = -\rho(\mathbf{r}, t),$$

$$\epsilon_0 \nabla^2 \varphi_{\text{ext}}(\mathbf{r}, t) = -\rho_{\text{ext}}(\mathbf{r}, t).$$
(29.1.17)

When these relationships are written for the Fourier transforms, they reduce to

$$\epsilon_0 q^2 \varphi(\boldsymbol{q}, \omega) = \rho(\boldsymbol{q}, \omega),$$

$$\epsilon_0 q^2 \varphi_{\text{ext}}(\boldsymbol{q}, \omega) = \rho_{\text{ext}}(\boldsymbol{q}, \omega).$$
(29.1.18)

Comparison of these equations with (29.1.16) yields

$$\rho(\boldsymbol{q},\omega) = \frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} \rho_{\rm ext}(\boldsymbol{q},\omega)$$
(29.1.19)

which can be written as

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = \frac{\rho(\boldsymbol{q},\omega)}{\rho_{\rm ext}(\boldsymbol{q},\omega)} = 1 + \frac{\rho_{\rm ind}(\boldsymbol{q},\omega)}{\rho_{\rm ext}(\boldsymbol{q},\omega)}.$$
(29.1.20)

If the external charge is expressed in terms of the external potential using (29.1.18), we find

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{1}{\epsilon_0 q^2} \frac{\rho_{\rm ind}(\boldsymbol{q},\omega)}{\varphi_{\rm ext}(\boldsymbol{q},\omega)}.$$
(29.1.21)

It is often more convenient to use the external, induced, and total number densities, $n_{\text{ext}}(\mathbf{r})$, $n_{\text{ind}}(\mathbf{r})$, and $n(\mathbf{r})$, respectively, instead of the corresponding charge densities, where $\rho_i(\mathbf{r}) = -en_i(\mathbf{r})$. Similarly, the quantity $V_i(\mathbf{r}) = -e\varphi_i(\mathbf{r})$ will be used instead of φ_i for both the external and the total potentials. When (29.1.17) is rewritten in terms of these quantities, the Fourier transforms satisfy the relations

$$V(\boldsymbol{q},\omega) = \frac{e^2}{\epsilon_0 q^2} n(\boldsymbol{q},\omega) = \frac{4\pi \tilde{e}^2}{q^2} n(\boldsymbol{q},\omega) ,$$

$$V_{\text{ext}}(\boldsymbol{q},\omega) = \frac{e^2}{\epsilon_0 q^2} n_{\text{ext}}(\boldsymbol{q},\omega) = \frac{4\pi \tilde{e}^2}{q^2} n_{\text{ext}}(\boldsymbol{q},\omega) .$$
(29.1.22)

The dielectric function can then be expressed as

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{e^2}{\epsilon_0 q^2} \frac{n_{\rm ind}(\boldsymbol{q},\omega)}{V_{\rm ext}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{n_{\rm ind}(\boldsymbol{q},\omega)}{V_{\rm ext}(\boldsymbol{q},\omega)} \,. \tag{29.1.23}$$

We introduce the quantity $\Pi(\boldsymbol{q},\omega)$ defined by

$$n_{\rm ind}(\boldsymbol{q},\omega) = \Pi(\boldsymbol{q},\omega) V_{\rm ext}(\boldsymbol{q},\omega) \,. \tag{29.1.24}$$

It has a simple physical interpretation. It tells how the electron system responds to the external perturbing potential and how the spatial distribution of electrons is modified in the presence of $V_{\text{ext}}(\boldsymbol{q},\omega)$. For this reason the quantity $\Pi(\boldsymbol{q},\omega)$ is called a response function. The inverse of the dielectric function can be written in terms of it as

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2}\Pi(\boldsymbol{q},\omega)\,. \tag{29.1.25}$$

Thus, the calculation of the dielectric function reduces to calculating this response function.

29.1.2 Density–Density Response Function

The function $\Pi(\mathbf{q}, \omega)$ was defined by (29.1.24) as the proportionality factor between the charge induced in an interacting electron system and the external perturbing potential. The Hamiltonian of this perturbation can be written in analogy to (28.1.8) in the form

$$\mathcal{H}_1(t) = \sum_i V_{\text{ext}}(\boldsymbol{r}_i, t) = \int V_{\text{ext}}(\boldsymbol{r}, t) n(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$
(29.1.26)

Hence the potential couples to the electron density. In terms of the Fourier transforms we have

$$\mathcal{H}_1(t) = \frac{1}{V} \sum_{\boldsymbol{q}} V_{\text{ext}}(\boldsymbol{q}, t) n(-\boldsymbol{q}) \,. \tag{29.1.27}$$

If the external perturbation is weak and the induced density $n_{ind}(\boldsymbol{q},\omega)$ is proportional to the external perturbation, $\Pi(\boldsymbol{q},\omega)$ can be calculated using linear response theory as a generalized susceptibility. Since the external potential couples to the density and the system responds by modifying its density, the quantity to be considered, $\Pi(\boldsymbol{q},\omega)$, is the Fourier transform of the density–density response function, also known as the retarded density–density correlation function,

$$\Pi(\boldsymbol{r},\boldsymbol{r}',t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\Big\langle \big[n(\boldsymbol{r},t),n(\boldsymbol{r}',t')\big]_{-}\Big\rangle,\qquad(29.1.28)$$

that is

$$\Pi(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')-\delta(t-t')} \frac{1}{V} \Big\langle \big[n(\boldsymbol{q},t), n(-\boldsymbol{q},t')\big]_{-} \Big\rangle,$$
(29.1.29)

where δ is a positive infinitesimal. As discussed in Appendix J [see (J.1.53), (J.1.54), (J.1.55), and (J.1.56)] it ensures the adiabatic switching on of the perturbation and hence the correct analytic properties.

The thermal average can be calculated in terms of the matrix elements between the complete set of many-body eigenstates $|\Psi_n\rangle$ of the Hamiltonian that includes the interaction between electrons but not the external perturbation. Using the completeness relation we obtain the spectral representation of the response function:

$$\Pi(\mathbf{r},\mathbf{r}',t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\sum_{mn}\frac{\mathrm{e}^{-\beta E_n}}{Z}\Big[\langle\Psi_n|n(\mathbf{r},t)|\Psi_m\rangle\langle\Psi_m|n(\mathbf{r}',t')|\Psi_n\rangle - \langle\Psi_n|n(\mathbf{r}',t')|\Psi_m\rangle\langle\Psi_m|n(\mathbf{r},t)|\Psi_n\rangle\Big].$$
(29.1.30)

The time dependence of the operators can be explicitly given in terms of the eigenvalues E_n . Interchanging the labels n and m in the second term, the Fourier transform of the response function is

$$\Pi(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \frac{\langle \boldsymbol{\Psi}_n | \boldsymbol{n}(\boldsymbol{q}) | \boldsymbol{\Psi}_m \rangle \langle \boldsymbol{\Psi}_m | \boldsymbol{n}(-\boldsymbol{q}) | \boldsymbol{\Psi}_n \rangle}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} = \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \frac{|\langle \boldsymbol{\Psi}_n | \boldsymbol{n}(\boldsymbol{q}) | \boldsymbol{\Psi}_m \rangle|^2}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} .$$
(29.1.31)

It will prove convenient to consider the spin-resolved response functions, i.e., the response of electrons with spin σ to a perturbation that couples to electrons with spin σ' . For this we define the response function

$$\Pi_{\sigma\sigma'}(\boldsymbol{r},\boldsymbol{r}',t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\Big\langle \big[n_{\sigma}(\boldsymbol{r},t),n_{\sigma'}(\boldsymbol{r}',t')\big]_{-}\Big\rangle$$
(29.1.32)

and its Fourier transform with respect to the spatial variable,

$$\Pi_{\sigma\sigma'}(\boldsymbol{q},t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\frac{1}{V}\left\langle \left[n_{\sigma}(\boldsymbol{q},t),n_{\sigma'}(-\boldsymbol{q},t')\right]_{-}\right\rangle,\qquad(29.1.33)$$

where the second-quantized form of the Fourier transform of the density of electrons with spin σ is

$$n_{\sigma}(\boldsymbol{q},t) = \sum_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) . \qquad (29.1.34)$$

Thus $\Pi_{\sigma\sigma'}(\mathbf{q}, t - t')$ describes the propagation of an electron-hole pair with momentum \mathbf{q} and spin σ' that is created at time t'. It gives the probability of finding this pair at a later time t with the same momentum and spin σ . This propagation can be represented pictorially by the diagram shown in Fig. 29.1.

In the simplest case, when the electron-hole pair does not interact with the other electrons of the Fermi sea during its propagation, we get the response function Π_0 of free electrons. In reality, the electron and the hole can take part in a variety of scattering processes due to electron-electron interaction. This is represented in the diagram by the shaded circle. Although strictly speaking the Feynman diagram technique can be used only for the causal Green



Fig. 29.1. Diagrammatic representation of the density–density response function as the propagation of an electron–hole pair

functions, diagrams can help to visualize the contributions to the retarded response function as well. Figure 29.2 shows a few low-order processes in the propagation of electron-hole pairs. The wavy lines represent the interaction.



Fig. 29.2. Low-order scattering processes that can occur during the propagation of an electron–hole pair

29.1.3 Relationship to the Dynamical Structure Factor

The dielectric function is related not only to the density–density response function but also to the dynamical structure factor via the fluctuation–dissipation theorem. To show this we start from (J.1.90). Applying this relation to the dynamical structure factor, taking into account that it is normalized by the number of particles and not by the volume, we obtain

$$S(\boldsymbol{q},\omega) = -\frac{2\hbar}{1 - \mathrm{e}^{-\beta\hbar\omega}} \frac{V}{N_{\mathrm{e}}} \mathrm{Im}\,\Pi(\boldsymbol{q},\omega)\,,\qquad(29.1.35)$$

or, if $\Pi(q,\omega)$ is expressed through the dielectric function via (29.1.25),

$$S(\boldsymbol{q},\omega) = -\frac{2\hbar}{1 - \mathrm{e}^{-\beta\hbar\omega}} \frac{V}{N_{\mathrm{e}}} \frac{q^2}{4\pi\tilde{e}^2} \mathrm{Im} \,\frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega)} \,. \tag{29.1.36}$$

The retarded response function \varPi being analytic in the upper half of the complex ω plane, the real and imaginary parts satisfy the Kramers–Kronig relation

$$\operatorname{Re} \Pi(\boldsymbol{q}, \omega) = \frac{1}{\pi} \operatorname{P} \int_{-\infty}^{\infty} \frac{\operatorname{Im} \Pi(\boldsymbol{q}, \omega')}{\omega' - \omega} \, \mathrm{d}\omega'$$

$$= \frac{1}{2\pi\hbar} \frac{N_{\mathrm{e}}}{V} \int_{-\infty}^{\infty} \frac{S(\boldsymbol{q}, \omega')}{\omega - \omega'} \left(1 - \mathrm{e}^{-\beta\hbar\omega'}\right) \, \mathrm{d}\omega' \,.$$
(29.1.37)

Taking both the real and imaginary parts, the full response function can be written in the form

$$\Pi(\boldsymbol{q},\omega) = \frac{1}{2\pi\hbar} \frac{N_{\rm e}}{V} \int_{-\infty}^{\infty} \frac{S(\boldsymbol{q},\omega')}{\omega - \omega' + \mathrm{i}\delta} \left(1 - \mathrm{e}^{-\beta\hbar\omega'}\right) \mathrm{d}\omega' \,. \tag{29.1.38}$$

Substituting (28.4.92) into this expression we recover the spectral representation of the response function given in (29.1.31).

Since $S(q, \omega)$ satisfies (28.4.104), the response function can be written as

$$\Pi(\boldsymbol{q},\omega) = \frac{1}{2\pi\hbar} \frac{N_{\rm e}}{V} \int_{0}^{\infty} S(\boldsymbol{q},\omega') \left(1 - \mathrm{e}^{-\beta\hbar\omega'}\right) \left[\frac{1}{\omega - \omega' + \mathrm{i}\delta} - \frac{1}{\omega + \omega' + \mathrm{i}\delta}\right] \mathrm{d}\omega'.$$
(29.1.39)

Inserting this into (29.1.25) we get

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{1}{2\pi\hbar} \frac{N_{\rm e}}{V} \int_0^\infty S(\boldsymbol{q},\omega') \left(1 - {\rm e}^{-\beta\hbar\omega'}\right) \\ \times \left[\frac{1}{\omega - \omega' + {\rm i}\delta} - \frac{1}{\omega + \omega' + {\rm i}\delta}\right] {\rm d}\omega' \,.$$
(29.1.40)

At T = 0, where the dynamical structure factor is given by (28.4.91), we find

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{1}{V} \sum_m |\langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle|^2 \\ \times \left[\frac{1}{\hbar\omega - E_m + E_0 + \mathrm{i}\delta} - \frac{1}{\hbar\omega + E_m - E_0 + \mathrm{i}\delta} \right] \qquad (29.1.41)$$
$$= 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{1}{V} \sum_m |\langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle|^2 \frac{2(E_m - E_0)}{(\hbar\omega + \mathrm{i}\delta)^2 - (E_m - E_0)^2}.$$

29.1.4 Self-Consistent Treatment of the Interaction

The response function $\Pi(q, \omega)$ has to be calculated for an unperturbed system, in which, however, the internal interactions between the constituents have to be taken into account in their full complexity. This requires to solve a complicated many-body problem. The difficulties can partially be circumvented by applying a self-consistent approach.

The full potential felt by the electrons is not the external potential φ_{ext} but $\varphi = \varphi_{\text{ext}}/\epsilon_{\text{r}}$ weakened by the dielectric function. Similarly, for the quantity $V = -e\varphi$ we have $V = V_{\text{ext}}/\epsilon_{\text{r}}$. The internal electric field is the negative gradient of this potential. Since ϵ_{r} is related to the internal dynamics of the electron system, the weakening of the external potential inside the system can be interpreted as arising from the screening effect of the dynamically rearranged charges. For this reason φ and V are called screened potentials.

When V_{ext} is replaced in (29.1.23) with $V\epsilon_{\text{r}}$, we have

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} \frac{n_{\rm ind}(\boldsymbol{q},\omega)}{V(\boldsymbol{q},\omega)}, \qquad (29.1.42)$$

from which after simple manipulations we obtain

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{n_{\rm ind}(\boldsymbol{q},\omega)}{V(\boldsymbol{q},\omega)} \,. \tag{29.1.43}$$

If the function $\widetilde{\Pi}(\boldsymbol{q},\omega)$ is defined by

$$n_{\rm ind}(\boldsymbol{q},\omega) = \widetilde{\Pi}(\boldsymbol{q},\omega)V(\boldsymbol{q},\omega)$$
(29.1.44)

as the response to the screened potential, the dielectric function is

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2}\tilde{H}(\boldsymbol{q},\omega)\,. \tag{29.1.45}$$

Comparison with (29.1.25) gives the following relationship between $\Pi(q, \omega)$ and $\widetilde{\Pi}(q, \omega)$:

$$\Pi(\boldsymbol{q},\omega) = \frac{\widetilde{\Pi}(\boldsymbol{q},\omega)}{1 - (4\pi \tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)} = \frac{\widetilde{\Pi}(\boldsymbol{q},\omega)}{\epsilon_{\rm r}(\boldsymbol{q},\omega)}, \qquad (29.1.46)$$

and the inverse dielectric function can be written as

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + U_{\rm eff}(\boldsymbol{q},\omega)\widetilde{\Pi}(\boldsymbol{q},\omega)$$
(29.1.47)

with

$$U_{\text{eff}}(\boldsymbol{q},\omega) = \frac{(4\pi\tilde{e}^2/q^2)}{1 - (4\pi\tilde{e}^2/q^2)\tilde{H}(\boldsymbol{q},\omega)} = \frac{1}{\epsilon_{\text{r}}(\boldsymbol{q},\omega)} \frac{4\pi\tilde{e}^2}{q^2}.$$
 (29.1.48)

Comparison of (29.1.25) with (29.1.47) shows that the dielectric properties of the interacting electron system can be described in two ways. Either the bare Coulomb coupling $4\pi \tilde{e}^2/q^2$ and the full response function Π is used, or the Coulomb interaction is assumed to be screened and then only the response $\tilde{\Pi}$ to the screened potential has to be considered. This latter approach is more convenient because the screened interaction is short ranged and does not contain the singularities characteristic of the Coulomb potential.

The self-consistent approach can be visualized by the diagrams used to represent the propagation of electron-hole pairs. Let us remark that some of the diagrams seen in Fig. 29.2 can be separated into two disjoint parts by removing a single interaction line. The initial point corresponding to the operator n(q, t) and the final point corresponding to n(-q, t') appear in the two distinct pieces. These are called reducible or improper diagrams. A diagram which cannot be broken into unconnected parts by cutting a single interaction line is called irreducible or proper. Such processes are shown in Fig. 29.3.



Fig. 29.3. Irreducible electron-hole propagation processes which do not fall into distinct parts by cutting a single interaction line

The reducible diagrams (some low-order ones can be seen in Fig. 29.2) can clearly be constructed by connecting irreducible diagrams by interaction lines in a sequence. If the sum of the contribution of all irreducible diagrams is denoted by $\widetilde{\Pi}(\boldsymbol{q},\omega)$, then the full response function is the sum of a geometric progression:

$$\Pi(\boldsymbol{q},\omega) = \widetilde{\Pi}(\boldsymbol{q},\omega) + \widetilde{\Pi}(\boldsymbol{q},\omega)\frac{4\pi\tilde{e}^2}{q^2}\widetilde{\Pi}(\boldsymbol{q},\omega) + \widetilde{\Pi}(\boldsymbol{q},\omega)\frac{4\pi\tilde{e}^2}{q^2}\widetilde{\Pi}(\boldsymbol{q},\omega)\frac{4\pi\tilde{e}^2}{q^2}\widetilde{\Pi}(\boldsymbol{q},\omega) + \cdots$$
(29.1.49)
$$= \frac{\widetilde{\Pi}(\boldsymbol{q},\omega)}{1 - (4\pi\tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)}.$$

Comparing this expression with (29.1.46) we see that $\tilde{\Pi}$ appearing in the selfconsistent approach is in fact the contribution of the irreducible diagrams.¹

A self-consistent potential can also be introduced for Bloch electrons interacting with a general potential U(q). The internal dynamics of the system gives rise to screening and the effective interaction between the particles is

$$U_{\text{eff}}(\boldsymbol{q},\omega) = \frac{U(\boldsymbol{q})}{1 - U(\boldsymbol{q})\widetilde{\Pi}(\boldsymbol{q},\omega)}.$$
(29.1.50)

 $^{^1}$ For this reason $\widetilde{\Pi}$ is sometimes called irreducible polarization function or irreducible polarization insertion.

The relation between the full response function and the irreducible one is then

$$\Pi(\boldsymbol{q},\omega) = \frac{\Pi(\boldsymbol{q},\omega)}{1 - U(\boldsymbol{q})\widetilde{\Pi}(\boldsymbol{q},\omega)}.$$
(29.1.51)

29.2 Dielectric Function of the Uniform Electron Gas

Having written down general expressions for the dielectric function and the response function $\Pi(\mathbf{q}, \omega)$ of an interacting electron system, we will now attempt to compute its explicit form, its \mathbf{q} and ω dependence. The full panoply of many-body theory would be needed if the electron–electron interaction is to be taken into account in its complexity. A reasonable approximate form can be obtained much simpler in the self-consistent treatment when the irreducible part of the response function, $\widetilde{\Pi}(\mathbf{q}, \omega)$, is approximated by $\Pi_0(\mathbf{q}, \omega)$, the response function of noninteracting electrons. This latter quantity can be evaluated exactly and can be written in a closed form. Before presenting this result it is useful to get acquainted with a simple semiclassical approach. Finally corrections beyond the self-consistent approach will be considered.

29.2.1 Thomas–Fermi Approximation

When the electron system is exposed to a static (time-independent), spatially slowly varying external potential, both the induced charge and the full (screened) potential $V(\mathbf{r})$ are also slowly varying in space. We may assume in the spirit of the semiclassical approximation that a local, spatially varying energy $\tilde{\varepsilon}_{\mathbf{k}}(\mathbf{r})$ can be defined, which is the bare energy of an electron shifted by the potential at the position \mathbf{r} of the electron:

$$\widetilde{\varepsilon}_{\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon_{\boldsymbol{k}} + V(\boldsymbol{r}).$$
 (29.2.1)

This is shown schematically in Fig. 29.4.



Fig. 29.4. Local displacement of the electron energy in the presence of a spatially slowly varying potential

Since the chemical potential is constant in space in thermal equilibrium, the Fermi momentum has to vary in space together with the spatial variation of the potential $V(\mathbf{r})$ in accordance with the relation

$$\mu = \frac{\hbar^2 k_{\rm F}^2(\boldsymbol{r})}{2m_{\rm e}} + V(\boldsymbol{r}). \qquad (29.2.2)$$

It then follows that

$$k_{\rm F}(\boldsymbol{r}) = \frac{\sqrt{2m_{\rm e}}}{\hbar} \left[\mu - V(\boldsymbol{r})\right]^{1/2} = k_{\rm F} \left[1 - \frac{V(\boldsymbol{r})}{\mu}\right]^{1/2}.$$
 (29.2.3)

The electron density has to exhibit a similar spatial variation since according to (16.2.25) there is a unique relationship between the electron density and the Fermi momentum:

$$n_{\rm e}(\boldsymbol{r}) = \frac{k_{\rm F}^3(\boldsymbol{r})}{3\pi^2} = \frac{k_{\rm F}^3}{3\pi^2} \left[1 - \frac{V(\boldsymbol{r})}{\mu} \right]^{3/2}.$$
 (29.2.4)

For weak external potentials a first-order expansion,

$$n_{\rm e}(\boldsymbol{r}) = \frac{k_{\rm F}^3}{3\pi^2} \left[1 - \frac{3}{2} \frac{V(\boldsymbol{r})}{\mu} \right] = \frac{k_{\rm F}^3}{3\pi^2} - \frac{m_{\rm e}k_{\rm F}}{\pi^2\hbar^2} V(\boldsymbol{r}) \,, \tag{29.2.5}$$

gives satisfactory results. One can recognize in the coefficient of $V(\mathbf{r})$ the electronic density of states at the Fermi energy, and so the induced electron density is given by

$$n_{\rm ind}(\boldsymbol{r}) = -\rho(\varepsilon_{\rm F})V(\boldsymbol{r})\,. \tag{29.2.6}$$

This result has a simple interpretation. When the external potential shifts locally and rigidly, by the same amount, all electron energies, the number of states that are pushed above the chemical potential and become empty is exactly equal to the number of states in a range of width $V(\mathbf{r})$ around the Fermi energy.

The foregoing calculation was done at temperature T = 0. The same result is valid at finite temperatures, too. To show this we make use of the fact that at finite temperature the occupation of electron states is given by the Fermi distribution function $f_0(\tilde{\varepsilon}_k(\mathbf{r}))$, and the local electron density is

$$n_{\rm e}(\boldsymbol{r}) = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} f_0(\widetilde{\varepsilon}_{\boldsymbol{k}}(\boldsymbol{r})). \qquad (29.2.7)$$

The change in the electron density due to the external perturbation, i.e., the induced electron density, is given by the difference

$$n_{\rm ind}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}\sigma} f_0(\tilde{\varepsilon}_{\mathbf{k}}(\mathbf{r})) - \frac{1}{V} \sum_{\mathbf{k}\sigma} f_0(\varepsilon_{\mathbf{k}})$$

$$= \frac{1}{(2\pi)^3} \sum_{\sigma} \int d\mathbf{k} [f_0(\tilde{\varepsilon}_{\mathbf{k}}(\mathbf{r})) - f_0(\varepsilon_{\mathbf{k}})].$$
(29.2.8)

If the external potential is weak compared to the Fermi energy, the function $f_0(\tilde{\varepsilon}_k(\boldsymbol{r})) = f_0(\varepsilon_k + V(\boldsymbol{r}))$ can be expanded in powers of $V(\boldsymbol{r})$. To linear order in the potential we find

$$n_{\rm ind}(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \sum_{\sigma} \int d\boldsymbol{k} \, \frac{\partial f_0(\varepsilon_{\boldsymbol{k}})}{\partial \varepsilon_{\boldsymbol{k}}} V(\boldsymbol{r}) \,. \tag{29.2.9}$$

If the integral over k is converted to an integral over energy and the temperature-dependent corrections in the Sommerfeld expansion [see (16.2.77)] are neglected, the leading term in the expansion gives precisely (29.2.6).

When the Fourier transforms are used,

$$n_{\rm ind}(\boldsymbol{q}) = -\rho(\varepsilon_{\rm F})V(\boldsymbol{q})\,. \tag{29.2.10}$$

Thus in this approximation, known as the *Thomas–Fermi approximation*,² a q-independent response function is obtained:

$$\widetilde{\Pi}(\boldsymbol{q},\omega) = -\rho(\varepsilon_{\rm F})\,,\tag{29.2.11}$$

which means that the electrons respond locally to the slowly varying external perturbation. By substituting this into (29.1.45) the dielectric function reduces to

$$\epsilon_{\rm r}(\boldsymbol{q}) = 1 + \frac{4\pi\tilde{e}^2}{q^2}\rho(\varepsilon_{\rm F}) = 1 + \frac{q_{\rm TF}^2}{q^2},$$
 (29.2.12)

where the Thomas–Fermi wave number $q_{\rm TF}$ has been introduced with the definition

$$q_{\rm TF}^2 = 4\pi \tilde{e}^2 \rho(\varepsilon_{\rm F}) \,. \tag{29.2.13}$$

Its physical meaning will become clear later on.

This result for the long-wavelength limit of the dielectric function is a good approximation for metals. The singularity at q = 0 is simply the consequence of the fact that a homogeneous electric field cannot be maintained in metals in thermal equilibrium.

29.2.2 The RPA

The Thomas–Fermi approach that relies on the semiclassical approximation is valid only for long-wavelength perturbations. It is in this limit that $\tilde{\Pi}$ is equal to the negative of the density of states at the Fermi energy. For shorter wavelengths a better approximation is needed. When working with the screened potential and the response to it, one might argue that screening takes into account at least in part the interaction between electrons; moreover, the screened interaction is much weaker than the bare Coulomb interaction and short ranged.³ Therefore, replacing $\tilde{\Pi}$ by its zeroth-order expression, Π_0 ,

² L. H. THOMAS, 1927 and E. FERMI, 1928.

 $^{^{3}}$ As we will see, the $1/q^{2}$ singularity of the Fourier transform of the Coulomb interaction vanishes when the screened interaction is considered.

might be justified. In this approximation, which for historical reasons is called the RPA,⁴ we have

$$\Pi(\boldsymbol{q},\omega) = \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - (4\pi\tilde{e}^2/q^2)\Pi_0(\boldsymbol{q},\omega)},$$
(29.2.14)

i.e., the full response is a geometric series whose first term, Π_0 , corresponds to the free propagation of an electron-hole pair, without scattering processes. The diagram corresponding to Π_0 is a simple bubble, also known as the polarization bubble. The higher order terms correspond to a special subset of all possible scattering processes. The electron-hole pair is annihilated in an interaction process creating another electron-hole pair. In the diagrammatic representation, the RPA corresponds to a series of bubbles shown in Fig. 29.5.



Fig. 29.5. Graphical representation of the propagation of an interacting electronhole pair in the RPA

The effective interaction obtained in this approximation,

$$U_{\text{eff}}(\boldsymbol{q},\omega) = \frac{U(\boldsymbol{q})}{1 - U(\boldsymbol{q})\Pi_0(\boldsymbol{q},\omega)}, \qquad (29.2.15)$$

can be represented by the diagrams depicted in Fig. 29.6. An infinite series of bubbles appears in the intermediate states. Thus, in the RPA, the effective interaction is mediated by subsequent electron-hole pairs.



Fig. 29.6. Processes contributing to the screening of the interaction U in the RPA

When this approximation is applied to the dielectric function, it follows from (29.1.44) and (29.1.45) that in the RPA

$$n_{\rm ind}(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega)V(\boldsymbol{q},\omega)$$
(29.2.16)

and

$$\epsilon_{\rm r}^{\rm RPA}(\boldsymbol{q},\omega) = 1 - \frac{4\pi \tilde{e}^2}{q^2} \Pi_0(\boldsymbol{q},\omega) \,.$$
 (29.2.17)

⁴ Acronym for **r**andom **p**hase **a**pproximation.

29.2.3 The Lindhard Dielectric Function

We will now show that Π_0 can be calculated exactly in closed form and a simple expression can be obtained for the dielectric function in the RPA. The formulas will be derived in two ways: first using elementary considerations of quantum mechanics and then applying the formalism of many-body theory. At a later stage, the results will be generalized to Bloch electrons moving through the periodic potential of the lattice.

Since the Fourier components belonging to different q and ω values are not mixed in the dielectric response, it is sufficient to consider the change in the electron density caused by a potential

$$V(\boldsymbol{r},t) = \frac{1}{V} \left[V(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t} + V^*(\boldsymbol{q}) \mathrm{e}^{-\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t} \right]$$
(29.2.18)

that varies periodically both in space and in time. The infinitesimally small positive δ ensures the adiabatic switching on of the perturbation.

We will consider a plane-wave state $\psi_{\mathbf{k}}^{(0)}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$ of the unperturbed system and study its time evolution due to the disturbance. The perturbed wavefunction $\psi_{\mathbf{k}}(\mathbf{r}, t)$ can be expanded in terms of a complete set of states. It is convenient to choose the eigenfunctions of the unperturbed Hamiltonian as this basis set, which in our case means an expansion in terms of plane waves:

$$\psi_{\mathbf{k}}(\mathbf{r},t) = \sum_{\mathbf{k}'} \alpha_{\mathbf{k}'}(t) \psi_{\mathbf{k}'}^{(0)}(\mathbf{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{\mathbf{k}'}t/\hbar} \,. \tag{29.2.19}$$

In the leading, linear order, the perturbing potential mixes the state $\psi_{\mathbf{k}}^{(0)}$ only with the states $\psi_{\mathbf{k}+\mathbf{q}}^{(0)}$ and $\psi_{\mathbf{k}-\mathbf{q}}^{(0)}$. The perturbed wavefunction can therefore be looked for in the form

$$\psi_{\mathbf{k}}(\mathbf{r},t) = \psi_{\mathbf{k}}^{(0)}(\mathbf{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{\mathbf{k}}t/\hbar} + \alpha_{\mathbf{k}+\mathbf{q}}(t)\psi_{\mathbf{k}+\mathbf{q}}^{(0)}(\mathbf{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{\mathbf{k}+\mathbf{q}}t/\hbar} + \alpha_{\mathbf{k}-\mathbf{q}}(t)\psi_{\mathbf{k}-\mathbf{q}}^{(0)}(\mathbf{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{\mathbf{k}-\mathbf{q}}t/\hbar} .$$
(29.2.20)

The coefficient of the first term was chosen to be unity, since the coefficients $\alpha_{\mathbf{k}'}(t)$ will be evaluated in lowest order of perturbation theory.

Using (G.2.7) we find

$$\alpha_{\boldsymbol{k}+\boldsymbol{q}}(t) = -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{t} \langle \psi_{\boldsymbol{k}+\boldsymbol{q}}^{(0)} | \mathcal{H}_{1}(t_{1}) | \psi_{\boldsymbol{k}}^{(0)} \rangle \mathrm{e}^{\mathrm{i}(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}-\varepsilon_{\boldsymbol{k}})t_{1}/\hbar} \, \mathrm{d}t_{1} \,, \qquad (29.2.21)$$

where the perturbing Hamiltonian $\mathcal{H}_1(t)$ has the same form as (29.1.26), except that here the screened potential V has to be used instead of V_{ext} .

If the space and time dependence of the perturbing potential is given by (29.2.18), the integration over the time variable t_1 can be performed. We get

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$$\alpha_{\mathbf{k}+\mathbf{q}}(t) = \frac{1}{V} \frac{V(\mathbf{q}) \mathrm{e}^{\mathrm{i}(\varepsilon_{\mathbf{k}+\mathbf{q}}-\varepsilon_{\mathbf{k}})t/\hbar} \mathrm{e}^{-\mathrm{i}\omega t} \mathrm{e}^{\delta t}}{\hbar\omega - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} + \mathrm{i}\delta} \,. \tag{29.2.22}$$

Similar calculation yields

$$\alpha_{\boldsymbol{k}-\boldsymbol{q}}(t) = -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{t} \left\langle \psi_{\boldsymbol{k}-\boldsymbol{q}}^{(0)} | \mathcal{H}_{1}(t_{1}) | \psi_{\boldsymbol{k}}^{(0)} \right\rangle \mathrm{e}^{\mathrm{i}(\varepsilon_{\boldsymbol{k}-\boldsymbol{q}}-\varepsilon_{\boldsymbol{k}})t_{1}/\hbar} \, \mathrm{d}t_{1}$$

$$= \frac{1}{V} \frac{V^{*}(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\varepsilon_{\boldsymbol{k}-\boldsymbol{q}}-\varepsilon_{\boldsymbol{k}})t/\hbar} \mathrm{e}^{\mathrm{i}\omega t} \mathrm{e}^{\delta t}}{-\hbar\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \,.$$
(29.2.23)

The perturbed wavefunction can thus be written as

$$\psi_{\mathbf{k}}(\mathbf{r},t) = \psi_{\mathbf{k}}^{(0)}(\mathbf{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{\mathbf{k}}t/\hbar} \left[1 + \frac{1}{V} \frac{V(\mathbf{q}) \mathrm{e}^{\mathrm{i}(\mathbf{q}\cdot\mathbf{r}-\omega t)} \mathrm{e}^{\delta t}}{\hbar\omega - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} + \mathrm{i}\delta} + \frac{1}{V} \frac{V^{*}(\mathbf{q}) \mathrm{e}^{-\mathrm{i}(\mathbf{q}\cdot\mathbf{r}-\omega t)} \mathrm{e}^{\delta t}}{-\hbar\omega - \varepsilon_{\mathbf{k}-\mathbf{q}} + \varepsilon_{\mathbf{k}} + \mathrm{i}\delta} \right].$$

$$(29.2.24)$$

The contribution of electrons with momentum $\hbar k$ to the induced electron density is

$$n_{\rm ind}(\boldsymbol{k}, \boldsymbol{r}, t) = \left[\left| \psi_{\boldsymbol{k}}(\boldsymbol{r}, t) \right|^2 - \left| \psi_{\boldsymbol{k}}^{(0)}(\boldsymbol{r}) \right|^2 \right].$$
(29.2.25)

The total induced electron density is obtained by summing over the occupied states

$$n_{\rm ind}(\boldsymbol{r},t) = 2 \sum_{|\boldsymbol{k}| < k_{\rm F}} \left[\left| \psi_{\boldsymbol{k}}(\boldsymbol{r},t) \right|^2 - \left| \psi_{\boldsymbol{k}}^{(0)}(\boldsymbol{r}) \right|^2 \right].$$
(29.2.26)

The factor 2 comes from the two spin orientations. Inserting (29.2.24) into this expression, taking into account the normalization factor $1/\sqrt{V}$ of plane waves and keeping only the terms linear in V(q), we find

$$n_{\rm ind}(\boldsymbol{r},t) = \frac{2}{V^2} \sum_{|\boldsymbol{k}| < k_{\rm F}} \left[\frac{V^*(\boldsymbol{q}) \mathrm{e}^{-\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} - \mathrm{i}\delta} + \frac{V(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{-\hbar\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} - \mathrm{i}\delta} + \frac{V(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} + \frac{V^*(\boldsymbol{q}) \mathrm{e}^{-\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{-\hbar\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \right]. \quad (29.2.27)$$

The Fourier components with both \boldsymbol{q} and $-\boldsymbol{q} [V^*(\boldsymbol{q}) = V(-\boldsymbol{q})]$ appear in the above expression due to our choice (29.2.18) of the potential. When only the terms proportional to $V(\boldsymbol{q}) \exp(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r})$ are collected,

$$n_{\rm ind}(\boldsymbol{r},t) = \frac{2}{V^2} \sum_{|\boldsymbol{k}| < k_{\rm F}} \left[\frac{V(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{-\hbar\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} - \mathrm{i}\delta} + \frac{V(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \right].$$
(29.2.28)

If the summation variable k is changed in the first term to k+q, the state with k+q has to be occupied. This condition can be expressed by an appropriately chosen Fermi distribution function. We then get

$$n_{\rm ind}(\boldsymbol{r},t) = \frac{2}{V^2} \sum_{\boldsymbol{k}} \left[\frac{f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})V(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{-\hbar\omega - \varepsilon_{\boldsymbol{k}} + \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \mathrm{i}\delta} + \frac{f_0(\varepsilon_{\boldsymbol{k}})V(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)} \mathrm{e}^{\delta t}}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \right].$$
(29.2.29)

It follows from this expression that the Fourier transform of the induced density is

$$n_{\rm ind}(\boldsymbol{q},\omega) = \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} V(\boldsymbol{q}) \,. \tag{29.2.30}$$

Comparison with (29.2.16) gives

$$\Pi_0(\boldsymbol{q},\omega) = \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \,. \tag{29.2.31}$$

Note that the term $i\delta$ in the denominator originates from the factor $e^{\delta t}$ describing the adiabatic switching on of the external perturbation, and it ensures the correct analytic properties of $\Pi_0(\mathbf{q},\omega)$ and of the dielectric function in the complex ω plane. By inserting this expression into (29.2.17) we find

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \,.$$
(29.2.32)

This is known as the *Lindhard dielectric function*,⁵ and the response function $\Pi_0(\mathbf{q}, \omega)$ itself is called the Lindhard function.

29.2.4 Alternative Derivation of the Lindhard Function

The response function Π_0 of the noninteracting electron system and hence the dielectric function can be calculated even more simply in second quantization. For this we evaluate the spin-resolved generalization of the response function, the quantity $\Pi_{\sigma\sigma'}$ defined in (29.1.33), for noninteracting electrons.

The first term of the commutator in (29.1.33),

$$\sum_{\boldsymbol{k}\boldsymbol{k}'} \left\langle c^{\dagger}_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'}(t') c_{\boldsymbol{k}'\sigma'}(t') \right\rangle, \qquad (29.2.33)$$

describes the propagation of an electron-hole pair from time t' when it is created until time t when the pair is annihilated. Apart from the trivial case

⁵ J. Lindhard, 1954.

q = 0, the hole with momentum \mathbf{k}' and spin σ' created at t' has to be filled at t by the electron with momentum \mathbf{k} and spin σ . Hence only the terms with $\mathbf{k}' = \mathbf{k}$ and $\sigma' = \sigma$ give finite contributions. The electron-hole pair can be created only if the state with wave vector \mathbf{k} is occupied in the ground state, while the state with $\mathbf{k} + \mathbf{q}$ has to be empty. These requirements can be written concisely by the Fermi distribution functions $f_0(\varepsilon_{\mathbf{k}\sigma})$ and $1 - f_0(\varepsilon_{\mathbf{k}+\mathbf{q}\sigma})$. The time dependence of the operators can be evaluated using (28.4.97). Thus we find that

$$\sum_{\boldsymbol{k}\boldsymbol{k}'} \left\langle c^{\dagger}_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t)c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'}(t')c_{\boldsymbol{k}'\sigma'}(t')\right\rangle$$
(29.2.34)
$$= \delta_{\sigma\sigma'} \sum_{\boldsymbol{k}} e^{i\varepsilon_{\boldsymbol{k}\sigma}(t-t')/\hbar} e^{-i\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t-t')/\hbar} f_0(\varepsilon_{\boldsymbol{k}\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma})\right].$$

As a retarded response function (the retardation is ensured by the Heaviside step function) the Fourier transform $\Pi^0(\boldsymbol{q},\omega)$ with respect to time has to be analytic in the upper complex half-plane. This can be achieved by incorporating a factor $\exp(-\delta|t-t'|)$ with infinitesimal δ , which is equivalent to switching on the perturbation adiabatically. The Fourier transform is then

$$\int_{-\infty}^{\infty} \theta(t-t') e^{i\omega(t-t')} e^{i(\varepsilon_{k\sigma} - \varepsilon_{k+q\sigma})(t-t')/\hbar} e^{-\delta|t-t'|} d(t-t')$$

$$= \int_{0}^{\infty} e^{i(\hbar\omega - \varepsilon_{k+q\sigma} + \varepsilon_{k\sigma} + i\delta)(t-t')/\hbar} d(t-t') \qquad (29.2.35)$$

$$= \frac{i\hbar}{\hbar\omega - \varepsilon_{k+q\sigma} + \varepsilon_{k\sigma} + i\delta}.$$

Since the response function is defined in (29.1.33) with a prefactor $-i/\hbar V$, the first term of the commutator yields

$$\frac{1}{V}\delta_{\sigma\sigma'}\sum_{\boldsymbol{k}}f_0(\varepsilon_{\boldsymbol{k}\sigma})\left[1-f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma})\right]\frac{1}{\hbar\omega-\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}+\varepsilon_{\boldsymbol{k}\sigma}+\mathrm{i}\delta}.$$
(29.2.36)

Analogously, the second term of the commutator,

$$\sum_{\boldsymbol{k}\boldsymbol{k}'} \left\langle c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'}(t')c_{\boldsymbol{k}'\sigma'}(t')c^{\dagger}_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \right\rangle , \qquad (29.2.37)$$

again gives finite contribution only if $\mathbf{k}' = \mathbf{k}$ and $\sigma' = \sigma$. However, now the state with quantum number \mathbf{k} has to be empty while the state with wave vector $\mathbf{k} + \mathbf{q}$ has to be occupied. Thus,

$$\sum_{\boldsymbol{k}\boldsymbol{k}'} \left\langle c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'}(t')c_{\boldsymbol{k}'\sigma'}(t')c^{\dagger}_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \right\rangle$$
(29.2.38)
$$= \delta_{\sigma\sigma'} \sum_{\boldsymbol{k}} e^{i\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t'-t)/\hbar} e^{-i\varepsilon_{\boldsymbol{k}\sigma}(t'-t)/\hbar} f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}\sigma})\right].$$

Multiplying it with the step function and incorporating the factor that describes the adiabatic turning on, the Fourier transform of this expression with respect to time gives

$$\delta_{\sigma\sigma'} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}\sigma}) \right] \frac{\mathrm{i}\hbar}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} \,. \tag{29.2.39}$$

Multiplying by the prefactor $-i/\hbar V$ and subtracting the contributions of the two terms of the commutator, we find

$$\Pi_{0\sigma\sigma'}(\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}\sigma}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} \,.$$
(29.2.40)

If the single-particle energies are spin independent, summation over the spin variables gives back the Lindhard function for the polarization bubble

$$\Pi_0(\boldsymbol{q},\omega) = \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta}, \qquad (29.2.41)$$

and the usual form of the Lindhard dielectric function is recovered:

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \,. \tag{29.2.42}$$

By a change of variables $k \to -k-q$ in (29.2.39) the second term of the commutator could be written in the form

$$\delta_{\sigma\sigma'} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}) \right] \frac{\mathrm{i}\hbar}{\hbar\omega + \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} , \qquad (29.2.43)$$

since the electron energy is an even function of the wave number. Multiplying this expression by $-i/\hbar V$ and combining it with (29.2.36) the spin-resolved response function can be written as

$$\Pi_{0\sigma\sigma'}(\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}) \right]$$

$$\times \left[\frac{1}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} - \frac{1}{\hbar\omega + \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} \right].$$
(29.2.44)

The term that contains the product of the two Fermi distribution functions gives vanishing contribution. This can again be shown by a change of variables $\mathbf{k} \rightarrow -\mathbf{k} - \mathbf{q}$. While the product of the Fermi distribution functions remains unchanged, the expression in the square bracket changes sign; thus, there is complete cancelation when the sum over \mathbf{k} is performed and the expression then simplifies to

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$$\Pi_{0\sigma\sigma'}(\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}\sigma})$$

$$\times \left[\frac{1}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} - \frac{1}{\hbar\omega + \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} \right],$$
(29.2.45)

while the Lindhard dielectric function can be written as

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{\epsilon}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}})$$

$$\times \left[\frac{1}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} - \frac{1}{\hbar\omega + \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \right].$$
(29.2.46)

29.2.5 Explicit Form of the Lindhard Dielectric Function

The dielectric function $\epsilon_{\rm r}(\boldsymbol{q},\omega)$ can be decomposed into real and imaginary parts:

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = \epsilon_1(\boldsymbol{q},\omega) + {\rm i}\,\epsilon_2(\boldsymbol{q},\omega). \tag{29.2.47}$$

Taking the expression given in (29.2.42) and using (C.3.3) we find

$$\epsilon_1(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}}$$
(29.2.48)

and

$$\epsilon_2(\boldsymbol{q},\omega) = \frac{4\pi^2 \tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} \left[f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) \right] \delta(\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}) \,. \tag{29.2.49}$$

On the other hand, if the form given in (29.2.46) is used, we obtain

$$\epsilon_{1}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{\epsilon}^{2}}{q^{2}} \frac{2}{V} \sum_{\boldsymbol{k}} f_{0}(\varepsilon_{\boldsymbol{k}})$$

$$\times \left[\frac{1}{\hbar\omega - (\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}})} - \frac{1}{\hbar\omega + (\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}})} \right]$$
(29.2.50)

and

$$\epsilon_2(\boldsymbol{q},\omega) = \frac{4\pi^2 \tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}}) \big[\delta(\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}) - \delta(\hbar\omega - \varepsilon_{\boldsymbol{k}} + \varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) \big].$$
(29.2.51)

It is readily seen from these expressions that the real part of the dielectric function is even in ω , while the imaginary part is an odd function of ω .

The summation can be performed exactly in both the real and the imaginary parts at temperature T = 0 if it is transformed into an integral in k-space. Using (29.2.50) for the real part and integrating first over the angle θ between k and q and then over the length of k, we find 29.2 Dielectric Function of the Uniform Electron Gas

$$\epsilon_{1}(\boldsymbol{q},\omega) = 1 + \frac{q_{\mathrm{TF}}^{2}}{q^{2}} \left\{ \frac{1}{2} + \frac{k_{\mathrm{F}}}{4q} \left\{ \left[1 - \left(\frac{\hbar\omega + \varepsilon_{q}}{\hbar v_{\mathrm{F}}q} \right)^{2} \right] \ln \left(\frac{\hbar\omega + \hbar v_{\mathrm{F}}q + \varepsilon_{q}}{\hbar\omega - \hbar v_{\mathrm{F}}q + \varepsilon_{q}} \right) + \left[1 - \left(\frac{\hbar\omega - \varepsilon_{q}}{\hbar v_{\mathrm{F}}q} \right)^{2} \right] \ln \left(\frac{\hbar\omega - \hbar v_{\mathrm{F}}q - \varepsilon_{q}}{\hbar\omega + \hbar v_{\mathrm{F}}q - \varepsilon_{q}} \right) \right\} \right\}$$
(29.2.52)

with $\varepsilon_q = \hbar^2 q^2 / 2m_e$, and $q_{\rm TF}$ is the Thomas–Fermi wave number defined in (29.2.13).

In the static case the dielectric function simplifies to

$$\epsilon_{\rm r}(\boldsymbol{q}) = 1 + \frac{q_{\rm TF}^2}{q^2} \left[\frac{1}{2} + \frac{k_{\rm F}}{2q} \left(1 - \frac{q^2}{4k_{\rm F}^2} \right) \ln \left| \frac{q + 2k_{\rm F}}{q - 2k_{\rm F}} \right| \right].$$
(29.2.53)

For later convenience this is written in the form

$$\epsilon_{\rm r}(\boldsymbol{q}) = 1 + \frac{q_{\rm TF}^2}{q^2} F(q/2k_{\rm F}) = 1 + \frac{4\pi\tilde{\epsilon}^2}{q^2} \rho(\varepsilon_{\rm F}) F(q/2k_{\rm F}) , \qquad (29.2.54)$$

where the function F(x) is defined in (28.3.85). Here it appears with the argument $x = q/2k_{\rm F}$. Making use of the fact that $F(x) \approx 1$ for small values of x, as can be seen in Fig. 28.4, the result of the Thomas–Fermi approximation is recovered in the long-wavelength limit. This is not surprising since we know that the Thomas–Fermi approximation is applicable for spatially slowly varying potentials. Recalling that the derivative of F(x) is logarithmically singular at x = 1, it follows that the derivative of the dielectric function is also logarithmically singular at $q = 2k_{\rm F}$. This has – as will be seen – serious implications. Among others this gives rise to the Friedel oscillations of the screening charge.

According to (29.2.49) the imaginary part is finite only at those ω values for which $\hbar\omega$ is equal to the excitation energy of an electron-hole pair, i.e.,

$$\hbar\omega = \varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} = \frac{\hbar^2}{m_{\rm e}} \mathbf{q} \cdot \mathbf{k} + \frac{\hbar^2 q^2}{2m_{\rm e}}.$$
 (29.2.55)

This is quite natural since the imaginary part is related to the energy dissipation and the electron system can absorb energy from the external field through electron-hole pair excitations. We saw already in Fig. 28.9 that these excitations form a broad continuum. Knowing that $\epsilon_2(\mathbf{q}, \omega)$ is an odd function of ω , we list the results for $\omega > 0$ only. One has to distinguish three frequency ranges. For $\mathbf{q} < 2k_{\rm F}$

$$\epsilon_{2}(\boldsymbol{q},\omega) = \begin{cases} \frac{\pi}{2} \frac{\hbar\omega}{\hbar v_{\mathrm{F}} q} \frac{q_{\mathrm{TF}}^{2}}{q^{2}} & 0 \leq \hbar\omega < \hbar v_{\mathrm{F}} q - \varepsilon_{q}, \\ \frac{\pi}{4} \frac{k_{\mathrm{F}}}{q} \left[1 - \left(\frac{\hbar\omega - \varepsilon_{q}}{\hbar v_{\mathrm{F}} q} \right)^{2} \right] \frac{q_{\mathrm{TF}}^{2}}{q^{2}} & \hbar v_{\mathrm{F}} q - \varepsilon_{q} \leq \hbar\omega \leq \hbar v_{\mathrm{F}} q + \varepsilon_{q}, \\ 0 & \hbar v_{\mathrm{F}} q + \varepsilon_{q} \leq \hbar\omega, \end{cases}$$

$$(29.2.56)$$

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while for $q > 2k_{\rm F}$

$$\epsilon_{2}(\boldsymbol{q},\omega) = \begin{cases} 0 & 0 \leq \hbar\omega < \varepsilon_{q} - \hbar v_{\mathrm{F}}q, \\ \frac{\pi}{4} \frac{k_{\mathrm{F}}}{q} \left[1 - \left(\frac{\hbar\omega - \varepsilon_{q}}{\hbar v_{\mathrm{F}}q}\right)^{2} \right] \frac{q_{\mathrm{TF}}^{2}}{q^{2}} & \varepsilon_{q} - \hbar v_{\mathrm{F}}q \leq \hbar\omega \leq \varepsilon_{q} + \hbar v_{\mathrm{F}}q, \\ 0 & \varepsilon_{q} + \hbar v_{\mathrm{F}}q \leq \hbar\omega . \end{cases}$$

$$(29.2.57)$$

Figure 29.7 shows the frequency dependence of the real and imaginary parts of the dielectric function for positive ω for small, intermediate, and large values of $q/k_{\rm F}$.



Fig. 29.7. Frequency dependence of the real and imaginary parts of the dielectric function of the electron gas for small, intermediate, and large values of the wave number. The results are shown for a typical metallic electron density, $r_s = 3$

As a retarded function, $\Pi(q, \omega)$ is analytic in the upper half-plane. Hence, it has to satisfy the Kramers–Kronig relations given in (J.1.70):

$$\operatorname{Re}\frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega)} - 1 = \frac{1}{\pi} \operatorname{P} \int_{-\infty}^{\infty} \mathrm{d}\omega' \operatorname{Im}\frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega')} \frac{1}{\omega' - \omega}$$
(29.2.58)

and

$$\operatorname{Im} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega)} = \frac{1}{\pi} \operatorname{P} \int_{-\infty}^{\infty} \mathrm{d}\omega' \left[1 - \operatorname{Re} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega')} \right] \frac{1}{\omega' - \omega} \,. \tag{29.2.59}$$

We also note that since the dielectric function establishes a causal relationship between the electric displacement and the electric field, the Kramers– Kronig relations are valid between the real and imaginary parts of the dielectric function as well. These relations were given in (16.1.65).

29.2.6 Corrections Beyond the RPA

If we wish to go beyond the RPA, the methods of many-body theory have to be used. There are several possibilities for that. One of them is to calculate $\widetilde{H}(\boldsymbol{q},\omega)$ up to a given order of perturbation theory. Another is to select an infinite set of irreducible diagrams for the two-particle Green function according to some physical considerations and to sum up their contributions. For this let us notice that there is a large class of processes in which the electron and the hole of the pair propagate independently of one another in the sense that although they interact with the other electrons of the Fermi sea, there are no intermediate scattering processes that would couple the electron to the hole either directly or indirectly. Such processes are displayed in Fig. 29.8.



Fig. 29.8. Scattering processes during the propagation of the electron-hole pair that lead to the renormalization of the energy of the electron and the hole separately

These processes have a simple physical interpretation: the electron and the hole propagating in the system are not bare particles but quasiparticles. Their energy is not $\varepsilon_{\mathbf{k}+\mathbf{q}}$ and $\varepsilon_{\mathbf{k}}$, respectively; it is renormalized by the interaction with the rest of the electron system. The first two diagrams correspond to the simplest Hartree and Fock corrections to the energy, but higher order processes should also be taken into account. When only such self-energy corrections are considered, the dielectric function still has a Lindhard-like form; however the energy of quasiparticles $\tilde{\varepsilon}_{\mathbf{k}}$ appears in place of $\varepsilon_{\mathbf{k}}$, the energy of free electrons. We then have

$$\epsilon_{\mathbf{r}}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\tilde{\varepsilon}_{\boldsymbol{k}}) - f_0(\tilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \tilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}} + \tilde{\varepsilon}_{\boldsymbol{k}} + \mathrm{i}\delta}.$$
 (29.2.60)

This approximation is called the *renormalized RPA*.

A further possibility is to use the equation-of-motion method explained briefly in Appendix J. That method relies on solving the equation of motion

$$\frac{\mathrm{d}n(\boldsymbol{q},t)}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar} \big[\mathcal{H}, n(\boldsymbol{q},t) \big]_{-}$$
(29.2.61)

for the Fourier transform of the operator of electron density given in secondquantized form in (28.4.96), where \mathcal{H} denotes the total Hamiltonian of the system that includes, besides the kinetic energy and the interaction given in (28.1.34), the external potential $V_{\text{ext}}(\mathbf{r},t)$. This last term, which is treated as a perturbation, is used in one of the equivalent forms. It is written either in real space in terms of the field operators or in momentum space in terms of the Fourier transforms of the potential and density. The Fourier transform of the density can also be expressed in terms of the creation and annihilation operators. Thus we have

$$\mathcal{H}_{1}(t) = \sum_{\sigma} \int \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) V_{\text{ext}}(\boldsymbol{r}, t) \hat{\psi}_{\sigma}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}$$

$$= \frac{1}{V} \sum_{\boldsymbol{q}} V_{\text{ext}}(\boldsymbol{q}, t) n(-\boldsymbol{q})$$

$$= \frac{1}{V} \sum_{\boldsymbol{k} \boldsymbol{q} \sigma} V_{\text{ext}}(\boldsymbol{q}, t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \,.$$
(29.2.62)

Once the equation of motion is solved for n(q, t), the induced charge is its expectation value:

$$n_{\text{ind}}(\boldsymbol{q},t) = \langle n(\boldsymbol{q},t) \rangle. \tag{29.2.63}$$

As known from our earlier calculations, and it follows also from the derivation given in Appendix J, in a noninteracting system the electron density induced by the external potential is

$$n_{\rm ind}(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega) V_{\rm ext}(\boldsymbol{q},\omega)$$
(29.2.64)

with the known Π_0 . If the external potential is generated by an external charge,

$$n_{\rm ind}(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega) \frac{4\pi\tilde{e}^2}{q^2} n_{\rm ext}(\boldsymbol{q},\omega) \,. \tag{29.2.65}$$

New, more complicated terms appear on the right-hand side of the equation of motion when the electron–electron interaction is taken into account. Depending on the treatment of these terms different approximation schemes are obtained; some details of which can be found in Appendix J. Here we present only the results, motivating them by using a simple approach.

If the interacting electron system is treated in the RPA,

$$n_{\rm ind}(\boldsymbol{q},\omega) = \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - (4\pi\tilde{e}^2/q^2)\Pi_0(\boldsymbol{q},\omega)} V_{\rm ext}(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega)V(\boldsymbol{q},\omega) , \quad (29.2.66)$$

where $V(\boldsymbol{q},\omega) = V_{\text{ext}}(\boldsymbol{q},\omega)/\epsilon_{\text{r}}(\boldsymbol{q},\omega)$ is the screened potential. Combining this expression with the first equation of (29.1.22) we have

$$n_{\text{ind}}(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega) \frac{4\pi\tilde{e}^2}{q^2} n(\boldsymbol{q},\omega)$$

= $\Pi_0(\boldsymbol{q},\omega) \frac{4\pi\tilde{e}^2}{q^2} \left[n_{\text{ext}}(\boldsymbol{q},\omega) + n_{\text{ind}}(\boldsymbol{q},\omega) \right].$ (29.2.67)

This expression is similar to (29.2.65) which is valid for noninteracting electrons except that the induced electron density is found to be proportional to the total density. We know that owing to exchange and correlations, electrons repel other electrons from their close vicinity creating Fermi and Coulomb holes around themselves. Therefore, a presumably better approximation can be achieved by assuming that the electron system does not react to the full charge, but to a charge corrected by the local field. If so, then only an effective particle density

$$n_{\text{eff}}(\boldsymbol{q},\omega) = n_{\text{ext}}(\boldsymbol{q},\omega) + [1 - G(\boldsymbol{q})]n_{\text{ind}}(\boldsymbol{q},\omega)$$
(29.2.68)

should appear on the right-hand side of (29.2.67). The quantity $G(\mathbf{q})$ is the so-called *local-field factor* and accounts for the short-range exchange and correlation effects not present in the RPA. With this assumption the dielectric function takes the form

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - (4\pi\tilde{e}^2/q^2) [1 - G(\boldsymbol{q})] \Pi_0(\boldsymbol{q},\omega)} \,. \tag{29.2.69}$$

This expression shows that G(q) weakens the screening.

The local-field factor has to be determined using physical considerations. Depending on its choice different approximation schemes are obtained. Using the equation-of-motion method for the screening charge, as explained in Appendix J, J. HUBBARD (1957) proposed the expression

$$G(\boldsymbol{q}) = \frac{1}{2} \frac{q^2}{q^2 + k_{\rm F}^2} \,. \tag{29.2.70}$$

Somewhat later K. S. SINGWI and A. SJÖLANDER (1967) have shown that a better approximation can be achieved if G(q) is chosen in the form

$$G(q) = q \int_{0}^{\infty} \mathrm{d}r \left[1 - g(r) \right] j_1(qr) \,, \qquad (29.2.71)$$

where g(r) is the pair distribution function and j_1 is the first-order spherical Bessel function. The RPA corresponds to completely neglecting this local-field correction.
29.2.7 Effect of Finite Relaxation Time

Until now the electron states have been assumed to have infinite lifetime. Although the states near the Fermi energy have a rather long lifetime if only the electron–electron interaction is taken into account, impurities that are unavoidably present in the sample or interaction with phonons can give rise to a substantial shortening of the lifetime. Here, we will consider the effect of the finite lifetime on the dielectric function in the semiclassical approximation. The induced charge will be determined using the nonstationary Boltzmann equation in an improved relaxation-time approximation.

We assume a space- and time-dependent external perturbation described by a periodically varying scalar potential

$$\varphi(\mathbf{r}, t) = \varphi(\mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} . \qquad (29.2.72)$$

The force acting on the electron is

$$\boldsymbol{F} = -e\boldsymbol{E} = e \operatorname{grad} \varphi(\boldsymbol{r}) = i e \boldsymbol{q} \varphi(\boldsymbol{q}) e^{i(\boldsymbol{q} \cdot \boldsymbol{r} - \omega t)}, \qquad (29.2.73)$$

or, when expressed in terms of $V(q) = -e\varphi(q)$,

$$\boldsymbol{F} = -\mathrm{i}\boldsymbol{q}V(\boldsymbol{q})\mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)}.$$
(29.2.74)

This perturbation gives rise to a periodically varying term in the distribution function which can be written as

$$f(\mathbf{k}, \mathbf{r}, t) = f_0(n_0) + f_1(\mathbf{k}) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)},$$
 (29.2.75)

where $f_0(n_0)$ is the distribution function corresponding to the uniform charge density n_0 . However, when the effect of collisions is treated in the relaxationtime approximation of the Boltzmann equation, we should take into account that the electron density relaxes to its local equilibrium value $n(\mathbf{r}, t)$ and not to its uniform equilibrium value n_0 . Thus, when the explicit time dependence of the distribution function is kept in the Boltzmann equation [see (24.2.16)] and this improved relaxation-time approximation is used for the collision integral, we have

$$\frac{\partial f}{\partial t} + \boldsymbol{v}_{\boldsymbol{k}} \frac{\partial f}{\partial \boldsymbol{r}} + \frac{1}{\hbar} \boldsymbol{F}(\boldsymbol{r}, t) \frac{\partial f}{\partial \boldsymbol{k}} = -\frac{f - f_0[n(\boldsymbol{r}, t)]}{\tau} \,. \tag{29.2.76}$$

If the difference between distribution functions belonging to the local equilibrium density and the uniform density is denoted by

$$\delta_n f_0 = f_0(n) - f_0(n_0), \qquad (29.2.77)$$

the Boltzmann equation linearized in f_1 takes the form

$$\frac{\partial f_1}{\partial t} + \boldsymbol{v}_{\boldsymbol{k}} \frac{\partial f_1}{\partial \boldsymbol{r}} + \frac{1}{\hbar} \boldsymbol{F}(\boldsymbol{r}, t) \frac{\partial f_0}{\partial \boldsymbol{k}} = -\frac{f_1}{\tau} + \frac{\delta_n f_0}{\tau} \,. \tag{29.2.78}$$

The equilibrium distribution function f_0 depends on \mathbf{k} through the energy only. Making use of the periodic spatial and temporal variation of the distribution function and using (29.2.74) for the force we have

$$-\mathrm{i}\omega f_1 + \mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} f_1 - \mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} V(\boldsymbol{q}) \frac{\partial f_0}{\partial \varepsilon} = -\frac{f_1}{\tau} + \frac{\delta_n f_0}{\tau} \,. \tag{29.2.79}$$

The formal solution of this equation yields

$$f_1 = \frac{\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} \tau V(\boldsymbol{q}) \frac{\partial f_0}{\partial \varepsilon} + \delta_n f_0}{1 - \mathrm{i}\omega\tau + \mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}}\tau} \,. \tag{29.2.80}$$

The induced number density is obtained by summing the contributions of all occupied states, that is by summing f_1 over the k vectors within the Fermi sphere:

$$n_{\rm ind} = \frac{2}{V} \sum_{|\mathbf{k}| < k_{\rm F}} f_1(\mathbf{k}).$$
 (29.2.81)

The distribution function changes significantly, however, only in the neighborhood of the Fermi energy. This is seen when the second term in the numerator of (29.2.80) is rewritten using the expansion

$$\delta_n f_0 = f_0(n) - f_0(n_0) = \frac{\partial f_0}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial n} \delta n, \qquad (29.2.82)$$

where δn is the induced particle density. We know from the Thomas–Fermi approximation that for long-wavelength disturbances

$$\frac{\partial n}{\partial \varepsilon} = -\rho(\varepsilon_{\rm F})\,,\tag{29.2.83}$$

and thus

$$\delta_n f_0 = -\frac{1}{\rho(\varepsilon_{\rm F})} \frac{\partial f_0}{\partial \varepsilon} n_{\rm ind} \,. \tag{29.2.84}$$

Averaging first over the angle between q and v_k on the Fermi surface yields

$$\langle f_1 \rangle_{\text{ave}} = V(\boldsymbol{q}) \frac{\partial f_0(\boldsymbol{k})}{\partial \varepsilon} \left[1 + \frac{\omega + i/\tau}{2v_F q} \ln \left(\frac{\omega - v_F q + i/\tau}{\omega + v_F q + i/\tau} \right) \right] - \frac{n_{\text{ind}}}{\rho(\varepsilon_F)} \frac{\partial f_0(\boldsymbol{k})}{\partial \varepsilon} \frac{1}{2iqv_F \tau} \ln \left(\frac{\omega - v_F q + i/\tau}{\omega + v_F q + i/\tau} \right).$$

$$(29.2.85)$$

Then the integral over the length of k is performed by converting it to an integral over energy. It is readily obtained that

$$n_{\rm ind} = -V(\boldsymbol{q})\rho(\varepsilon_{\rm F}) \left[1 + \frac{\omega + \mathrm{i}/\tau}{2v_{\rm F}q} \ln\left(\frac{\omega - v_{\rm F}q + \mathrm{i}/\tau}{\omega + v_{\rm F}q + \mathrm{i}/\tau}\right) \right] + \frac{n_{\rm ind}}{2\mathrm{i}qv_{\rm F}\tau} \ln\left(\frac{\omega - v_{\rm F}q + \mathrm{i}/\tau}{\omega + v_{\rm F}q + \mathrm{i}/\tau}\right).$$
(29.2.86)

The solution of this equation for n_{ind} leads to the following expression for the response function $\widetilde{\Pi}$:

$$\widetilde{\Pi}(\boldsymbol{q},\omega) = -\rho(\varepsilon_{\rm F}) \frac{1 + \frac{\omega + \mathrm{i}/\tau}{2v_{\rm F}q} \ln\left(\frac{\omega - v_{\rm F}q + \mathrm{i}/\tau}{\omega + v_{\rm F}q + \mathrm{i}/\tau}\right)}{1 + \frac{\mathrm{i}/\tau}{2v_{\rm F}q} \ln\left(\frac{\omega - v_{\rm F}q + \mathrm{i}/\tau}{\omega + v_{\rm F}q + \mathrm{i}/\tau}\right)}.$$
(29.2.87)

The dielectric function then takes the form

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 + \frac{4\pi\tilde{e}^2}{q^2}\rho(\varepsilon_{\rm F})\frac{1 + \frac{\omega + \mathrm{i}/\tau}{2v_{\rm F}q}\ln\left(\frac{\omega - v_{\rm F}q + \mathrm{i}/\tau}{\omega + v_{\rm F}q + \mathrm{i}/\tau}\right)}{1 + \frac{\mathrm{i}/\tau}{2v_{\rm F}q}\ln\left(\frac{\omega - v_{\rm F}q + \mathrm{i}/\tau}{\omega + v_{\rm F}q + \mathrm{i}/\tau}\right)}.$$
(29.2.88)

In the static, $\omega \to 0$ limit the semiclassical Thomas–Fermi result is recovered, while in the long-wavelength, $q \to 0$ limit we find

$$\widetilde{\Pi}(\boldsymbol{q},\omega) = \frac{n_{\rm e}q^2}{m_{\rm e}\omega(\omega+{\rm i}/\tau)}\,,\tag{29.2.89}$$

where $n_{\rm e} = k_{\rm F}^3/3\pi^2$ is the electron density. It then follows that

$$\epsilon_{\rm r}(\omega) = 1 - \frac{4\pi n_{\rm e}\tilde{e}^2}{m_{\rm e}\omega(\omega + {\rm i}/\tau)} \,. \tag{29.2.90}$$

This expression is identical to the result derived for the frequency-dependent dielectric function in the Drude model [see (16.1.68)]. This has been used in Chapter 25 to study the optical properties of metals. To get a more accurate expression with a better q dependence than the Thomas–Fermi result, a quantum mechanical treatment is needed. We note that the naive approximation in which the polarization bubble of the RPA is calculated for an electron and a hole with finite lifetime τ would yield a Lindhard-like expression where $\omega + i\delta$ is replaced with $\omega + i/\tau$, i.e.,

$$\widetilde{\Pi}(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega + \mathrm{i}/\tau) = \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}/\tau} \,.$$
(29.2.91)

We know from our earlier considerations that this approach does not give a physically correct result since in a periodically driven system relaxation is toward local equilibrium and not toward thermodynamic equilibrium. When this is taken into account, one finds the so-called Lindhard–Mermin⁶ form for the dielectric function

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{\left[1 + {\rm i}/(\omega\tau)\right]\Pi_0(\boldsymbol{q},\omega + {\rm i}/\tau)}{1 + {\rm i}/(\omega\tau)\left[\Pi_0(\boldsymbol{q},\omega + {\rm i}/\tau)/\Pi_0(\boldsymbol{q},0)\right]} \,. \tag{29.2.92}$$

In the $\tau \to \infty$ limit the Lindhard form of the dielectric function (29.2.32) is recovered. This expression also yields the correct static limit and the known expression for the frequency-dependent conductivity.

⁶ N. D. MERMIN, 1970.

29.3 Static Screening

One essential feature of the above-derived result for the dielectric function is its $1/q^2$ divergence in the long-wavelength $(\boldsymbol{q} \to 0)$ limit. As a consequence of that, the electronic charge distribution is drastically modified if an external charge is introduced into a simple metal. We show below that the induced charge screens completely the external charge.

The potential created by a pointlike external charge Q is

$$\varphi_{\text{ext}}(r) = \frac{Q}{4\pi\epsilon_0 r} \,. \tag{29.3.1}$$

Equation (C.1.63) implies that the Fourier transform of the potential is

$$\varphi_{\text{ext}}(\boldsymbol{q}) = \frac{Q}{\epsilon_0 q^2}.$$
 (29.3.2)

This potential gives rise to an inhomogeneous charge distribution in the vicinity of the external charge. In the static case, the Fourier transform of the induced number density is given according to (29.1.24) by

$$n_{\rm ind}(\boldsymbol{q}) = \Pi(\boldsymbol{q}) V_{\rm ext}(\boldsymbol{q}) = -e\Pi(\boldsymbol{q})\varphi_{\rm ext}(\boldsymbol{q}) = -\frac{eQ}{\epsilon_0 q^2} \Pi(\boldsymbol{q}).$$
(29.3.3)

If the density–density response function is expressed in terms of the dielectric function using (29.1.25) we get

$$n_{\rm ind}(\boldsymbol{q}) = \frac{Q}{e} \left[1 - \frac{1}{\epsilon_{\rm r}(\boldsymbol{q})} \right]$$
(29.3.4)

or, if the irreducible polarization function is used,

$$n_{\rm ind}(\boldsymbol{q}) = -\frac{eQ}{\epsilon_0 q^2} \frac{\Pi(\boldsymbol{q})}{1 - \frac{e^2}{\epsilon_0 q^2} \widetilde{\Pi}(\boldsymbol{q})} \,. \tag{29.3.5}$$

The total induced charge, the volume integral of the induced charge density $\rho_{\text{ind}}(\mathbf{r}) = -en_{\text{ind}}(\mathbf{r})$, is equal to the $\mathbf{q} = 0$ Fourier component of the induced charge density. If $\widetilde{\Pi}(\mathbf{q})$ remains finite in the limit $\mathbf{q} \to 0$, which is the case in the homogeneous electron gas and in metals as well,

$$Q_{\rm ind} = -e \lim_{\boldsymbol{q} \to 0} n_{\rm ind}(\boldsymbol{q}) = Q \lim_{\boldsymbol{q} \to 0} \frac{\frac{e^2}{\epsilon_0 q^2} \widetilde{\boldsymbol{\Pi}}(\boldsymbol{q})}{1 - \frac{e^2}{\epsilon_0 q^2} \widetilde{\boldsymbol{\Pi}}(\boldsymbol{q})} = -Q.$$
(29.3.6)

The sign of the total induced charge is opposite to that of the external charge and they are equal in magnitude; hence, screening is indeed complete in metals. In semiconductors, where there are mobile carriers, but $\widetilde{\Pi}(q)$ vanishes at q = 0 owing to the absence of low-energy electron-hole pair excitations, screening is not complete.

In what follows we will show, calculating the spatial variation of the screening charge and the screened potential, that in metals, where screening is complete, screening of the long-range Coulomb potential leads to a short-range effective interaction.

29.3.1 Thomas–Fermi Screening

It follows from (29.1.16) that the Fourier transform of the screened potential around a charge Q introduced into a metal is

$$\varphi(\boldsymbol{q}) = \frac{1}{\epsilon_{\rm r}(\boldsymbol{q})} \varphi_{\rm ext}(\boldsymbol{q}) = \frac{1}{\epsilon_{\rm r}(\boldsymbol{q})} \frac{Q}{\epsilon_0 q^2}.$$
 (29.3.7)

The Thomas–Fermi approximation for the dielectric function [see (29.2.12)] gives

$$\varphi(\boldsymbol{q}) = \frac{Q}{\epsilon_0 (q^2 + q_{\rm TF}^2)}, \qquad (29.3.8)$$

which shows that the $1/q^2$ singularity of the Coulomb potential is removed by the screening effect of the electrons.

The spatial variation of the screened potential can be obtained by taking the inverse Fourier transform. According to (C.1.62)

$$\varphi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} \frac{Q}{\epsilon_0 (q^2 + q_{\rm TF}^2)} e^{\mathbf{i}\mathbf{q}\cdot\mathbf{r}} = \frac{Q}{4\pi\epsilon_0 r} e^{-q_{\rm TF}r}.$$
(29.3.9)

This is the well-known Yukawa potential of nuclear physics. The spatial variation of the induced charge is given according to (29.2.6) by

$$\rho_{\rm ind}(\boldsymbol{r}) = -en_{\rm ind}(\boldsymbol{r}) = -e^2 \rho(\varepsilon_{\rm F})\varphi(\boldsymbol{r}) = -e^2 \rho(\varepsilon_{\rm F}) \frac{Q}{4\pi\epsilon_0 r} e^{-q_{\rm TF}r} \,. \quad (29.3.10)$$

If the prefactor is expressed in terms of the Thomas–Fermi wave number, we find

$$\rho_{\rm ind}(\mathbf{r}) = -\frac{Q}{4\pi} \frac{q_{\rm TF}^2}{r} e^{-q_{\rm TF}r} \,. \tag{29.3.11}$$

The total induced charge is its volume integral

$$Q_{\rm ind} = \int_{V} \rho_{\rm ind}(\mathbf{r}) \,\mathrm{d}\mathbf{r} = -\frac{Q}{4\pi} \int_{0}^{\infty} \frac{q_{\rm TF}^2}{r} \mathrm{e}^{-q_{\rm TF}r} 4\pi r^2 \,\mathrm{d}r$$
$$= -Q \int_{0}^{\infty} x \mathrm{e}^{-x} \,\mathrm{d}x = -Q, \qquad (29.3.12)$$

as has already been demonstrated generally. The redistribution of the electric charge is so drastic that the screened potential decreases exponentially fast. The characteristic screening length is $1/q_{\rm TF}$; the external charge is practically not felt at distances larger than a few times $1/q_{\rm TF}$.

Before estimating the screening length for metals we note that this type of exponential screening of external charges is well known in the *Debye–Hückel* theory of electrolytes, which are classical, nondegenerate charged systems, but their screening length is essentially different from that in degenerate systems. According to the classical Maxwell–Boltzmann distribution applicable to electrolytes and also to nondegenerate semiconductors, the density of particles varies as

$$n(\mathbf{r}) = n_{\rm e} {\rm e}^{-V(\mathbf{r})/k_{\rm B}T}$$
 (29.3.13)

when the energy is changed locally by an amount $V(\mathbf{r})$. This expression can be expanded to linear order if the potential is weak, and the change in the particle density is given by

$$n_{\rm ind}(\mathbf{r}) = -\frac{n_{\rm e}}{k_{\rm B}T}V(\mathbf{r}).$$
 (29.3.14)

Comparison of this expression with (29.2.6) shows that the response of classical particles is given by $n_{\rm e}/k_{\rm B}T$ instead of the density of states $\rho(\varepsilon_{\rm F})$. Using this in the dielectric function an expression similar to the Thomas–Fermi approximation is obtained, where screening is characterized by the *Debye–Hückel* wave number defined via

$$q_{\rm DH}^2 = \frac{n_{\rm e}e^2}{\epsilon_0 k_{\rm B}T} = \frac{4\pi n_{\rm e}\tilde{e}^2}{k_{\rm B}T} \,. \tag{29.3.15}$$

The inverse of this wave number is the Debye length which was introduced and used already in Chapter 27 where the properties of semiconductors were studied.

For the degenerate electron gas, where the Fermi distribution function applies, the density of states of the three-dimensional free electron gas is used in (29.2.13) to estimate the screening length. Comparing $q_{\rm TF}$ to the Fermi momentum and expressing $k_{\rm F}$ with the radius r_0 of the Wigner–Seitz sphere available for an electron or with the dimensionless $r_{\rm s}$, we find

$$\frac{q_{\rm TF}^2}{k_{\rm F}^2} = \frac{4\pi\tilde{e}^2}{k_{\rm F}^2} \frac{m_{\rm e}k_{\rm F}}{\hbar^2\pi^2} = \left(\frac{16}{3\pi^2}\right)^{2/3} \frac{r_0}{a_0} = \left(\frac{16}{3\pi^2}\right)^{2/3} r_{\rm s}\,,\qquad(29.3.16)$$

from which

$$q_{\rm TF} = 0.815 \, k_{\rm F} r_{\rm s}^{1/2} \,. \tag{29.3.17}$$

The typical range for $r_{\rm s}$ is between 1.8 and 6 in metals. This implies that $q_{\rm TF}$ is of the same order as $k_{\rm F}$. Since the inverse of $k_{\rm F}$ is on the order of atomic distances, screening occurs on the same length scale in metals.

29.3.2 Friedel Oscillations

The Thomas–Fermi approximation gives only a crude picture of the spatial variation of the screening charge since screening occurs on the atomic scale while the approximation is applicable for long-wavelength variations only. We have therefore to consider how the result changes when the Lindhard function with its correct \boldsymbol{q} dependence is used for Π_0 and not its $\boldsymbol{q} \to 0$ limit.

For that one would have to repeat the calculation of the induced charge by inserting the Lindhard form of the dielectric function into (29.3.4), and then taking the inverse Fourier transform of $n_{ind}(q)$. Unfortunately, this inverse Fourier transform cannot be calculated exactly. Therefore, we apply a different procedure used already in Chapter 16 when we studied the scattering of electrons by an impurity. Equation (16.4.44) shows already that at distances far from the impurity, outside the range of the atomic potential, the induced density decays as $1/r^3$ and it is modulated by an oscillatory function. These oscillations will be discussed further here.

When the incoming particle is described by a plane wave and the scattering center by a potential $V(\mathbf{r})$, it follows from (16.4.4) that the wavefunction satisfies the equation

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} + \int d\mathbf{r}' G(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}'), \qquad (29.3.18)$$

where

$$G(\boldsymbol{r} - \boldsymbol{r}') = -\frac{m_{\rm e}}{2\pi\hbar^2} \frac{\mathrm{e}^{ik|\boldsymbol{r} - \boldsymbol{r}'|}}{|\boldsymbol{r} - \boldsymbol{r}'|}$$
(29.3.19)

is the Green function of free electrons. The first iteration gives

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \left[1 + \int d\mathbf{r}' G(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') e^{i\mathbf{k}\cdot(\mathbf{r}' - \mathbf{r})} \right].$$
(29.3.20)

When the change in the electron density is calculated from this expression up to first order in the potential, we get

$$n_{\text{ind}}(\boldsymbol{r}) = \frac{2}{V} \sum_{|\boldsymbol{k}| < k_{\text{F}}} \int d\boldsymbol{r}' V(\boldsymbol{r}')$$

$$\times \left[G(\boldsymbol{r} - \boldsymbol{r}') e^{i\boldsymbol{k} \cdot (\boldsymbol{r}' - \boldsymbol{r})} + G^{*}(\boldsymbol{r} - \boldsymbol{r}') e^{-i\boldsymbol{k} \cdot (\boldsymbol{r}' - \boldsymbol{r})} \right],$$
(29.3.21)

where the factor 2 comes from the two spin orientations. Using (29.3.19) for the Green function, replacing the sum by an integral, and performing first the integration over the angular variable, we have

$$n_{\rm ind}(\mathbf{r}) = -\frac{m_{\rm e}}{2\pi^3\hbar^2} \int d\mathbf{r}' \, V(\mathbf{r}') \int_0^{k_{\rm F}} dk \, k^2 \left[\frac{\sin k|\mathbf{r} - \mathbf{r}'|}{k|\mathbf{r} - \mathbf{r}'|} \cdot \frac{2\cos k|\mathbf{r} - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}'|} \right].$$
(29.3.22)

Performing then the integral over k gives

$$n_{\rm ind}(\boldsymbol{r}) = \frac{2m_{\rm e}k_{\rm F}^4}{\pi^3\hbar^2} \int \mathrm{d}\boldsymbol{r}' V(\boldsymbol{r}') g(2k_{\rm F}|\boldsymbol{r}-\boldsymbol{r}'|), \qquad (29.3.23)$$

where

$$g(x) = \frac{x \cos x - \sin x}{x^4} \,. \tag{29.3.24}$$

If the potential $V(\mathbf{r})$ varies slowly in space compared to the inverse of $2k_{\rm F}$ over which this oscillatory function decays, then the local relationship (29.2.6) found in the Thomas–Fermi approximation holds true between the induced charge density and the perturbing potential. If, on the other hand, the screened potential is short ranged, as is the case in metals, then asymptotically, beyond the screening length, the induced charge density decays as

$$n_{\rm ind}(\mathbf{r}) \sim \frac{\cos 2k_{\rm F}r}{(2k_{\rm F}r)^3},$$
 (29.3.25)

as has already been seen in (16.4.44). This slowly decaying oscillation is the consequence of the weak (logarithmic) singularity in the derivative of the Lindhard function at $q = 2k_{\rm F}$. Physically it is due to the sharp Fermi edge in the momentum distribution of electrons. The wavelength of the oscillation is determined by $1/2k_{\rm F}$.

It can be shown using a somewhat more rigorous calculation that asymptotically, far from the impurity, only the $q = 2k_{\rm F}$ Fourier components of the bare external potential $V_{\rm ext} = -e\varphi_{\rm ext}$ and of the dielectric function play a role, and the induced charge density is given by the expression

$$\rho_{\rm ind}(\boldsymbol{r}) \approx -\frac{e^2}{4\pi} \rho(\varepsilon_{\rm F}) \,\frac{\varphi_{\rm ext}(2k_{\rm F})}{\epsilon_{\rm r}^2(2k_{\rm F})} \,\frac{\cos 2k_{\rm F}r}{r^3} \,. \tag{29.3.26}$$

It is interesting to note that the induced charge is not proportional to the $2k_{\rm F}$ Fourier component of the screened potential; the square of the dielectric function appears in the denominator. Inserting the Fourier transform of the Coulomb potential of the localized charge Q and using the Lindhard function, we find

$$\rho_{\rm ind}(\mathbf{r}) \approx -\frac{Q}{4\pi} \frac{\xi^2}{(1+\xi^2/2)^2} \frac{\cos 2k_{\rm F}r}{r^3}$$
(29.3.27)

with $\xi = q_{\rm TF}/2k_{\rm F}$.

29.4 Dielectric Function of Metals and Semiconductors

In the foregoing, the Lindhard function and the dielectric function have been calculated for electrons moving in a uniform background. Plane-wave wavefunctions and a quadratic dispersion relation have been assumed. The result obtained may be valid for simple metals where the contribution of the fully occupied bands lying deep below and the completely empty bands lying far above the Fermi energy can be neglected, and the main contribution to the dielectric function comes from electrons of a single partially filled conduction band. If the states of this band can be characterized by a scalar effective mass m^* , then the results derived above are still valid with the proviso that m^* and the corresponding Fermi velocity are used instead of $m_{\rm e}$ and $v_{\rm F}$ of free electrons.

The calculations can be extended to solids with more complicated, realistic band structure. We will see that metals, where the Fermi energy lies inside the conduction bands, and semiconductors, where the Fermi energy lies inside the gap between the valence and conduction bands, have essentially different dielectric functions.

29.4.1 Dielectric Function of Bloch Electrons

To calculate the dielectric function of the system of Bloch electrons we repeat our earlier derivation of the Lindhard function but now we start with a Bloch state $\psi_{nk}^{(0)}(\mathbf{r})$ of wave vector \mathbf{k} in the *n*th band. The periodically varying external field (29.2.18) couples this state only to those states whose wave vector is $\mathbf{k} + \mathbf{q}$ or $\mathbf{k} - \mathbf{q}$, though they may be in any band. For this reason, generalizing the trial function given in (29.2.20), the perturbed state is sought in the form

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r},t) = \psi_{n\boldsymbol{k}}^{(0)}(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{n\boldsymbol{k}}t/\hbar} + \sum_{n'} \alpha_{nn'\boldsymbol{k}+\boldsymbol{q}}(t) \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)}(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}}t/\hbar} + \sum_{n'} \alpha_{nn'\boldsymbol{k}-\boldsymbol{q}}(t) \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)}(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\varepsilon_{n'\boldsymbol{k}-\boldsymbol{q}}t/\hbar} \,.$$
(29.4.1)

The coefficient $\alpha_{nn'\mathbf{k}+\mathbf{q}}(t)$ can be determined using the formulas of perturbation theory. To lowest order we find

$$\alpha_{nn'\boldsymbol{k}+\boldsymbol{q}}(t) = \frac{1}{V} \frac{V(\boldsymbol{q}) \langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} | \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} | \psi_{n\boldsymbol{k}}^{(0)} \rangle \mathrm{e}^{\mathrm{i}(\varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}}-\varepsilon_{n\boldsymbol{k}})t/\hbar} \mathrm{e}^{-\mathrm{i}\omega t} \mathrm{e}^{\delta t}}{\hbar \omega - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{n\boldsymbol{k}} + \mathrm{i}\delta}$$
(29.4.2)

and

$$\alpha_{nn'\boldsymbol{k}-\boldsymbol{q}}(t) = \frac{1}{V} \frac{V^*(\boldsymbol{q}) \langle \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} | \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} | \psi_{n\boldsymbol{k}}^{(0)} \rangle \mathrm{e}^{\mathrm{i}(\varepsilon_{n'\boldsymbol{k}-\boldsymbol{q}}-\varepsilon_{n\boldsymbol{k}})t/\hbar} \mathrm{e}^{\mathrm{i}\omega t} \mathrm{e}^{\delta t}}{-\hbar\omega - \varepsilon_{n'\boldsymbol{k}-\boldsymbol{q}} + \varepsilon_{n\boldsymbol{k}} + \mathrm{i}\delta} . \quad (29.4.3)$$

Thus, the perturbed wavefunction is

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r},t) = e^{-i\varepsilon_{\boldsymbol{k}}t/\hbar} \left[\psi_{n\boldsymbol{k}}^{(0)}(\boldsymbol{r})$$

$$+ \frac{1}{V} \sum_{n'} \frac{V(\boldsymbol{q}) \langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} | \psi_{n\boldsymbol{k}}^{(0)} \rangle e^{-i\omega t} e^{\delta t}}{\hbar\omega - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{n\boldsymbol{k}} + i\delta} \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)}(\boldsymbol{r})$$

$$+ \frac{1}{V} \sum_{n'} \frac{V^{*}(\boldsymbol{q}) \langle \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} | e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} | \psi_{n\boldsymbol{k}}^{(0)} \rangle e^{i\omega t} e^{\delta t}}{-\hbar\omega - \varepsilon_{n'\boldsymbol{k}-\boldsymbol{q}} + \varepsilon_{n\boldsymbol{k}} + i\delta} \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)}(\boldsymbol{r}) \right].$$
(29.4.4)

The essential difference compared to the earlier result for plane waves is that an extra factor appears besides $V(\mathbf{q})$, the matrix element of $e^{\pm i\mathbf{q}\cdot\mathbf{r}}$ between $\psi_{n\mathbf{k}}^{(0)}$ and $\psi_{n'\mathbf{k}\pm\mathbf{q}}^{(0)}$. Using the Bloch form of the electron wavefunction and the lattice periodicity of $u_{n\mathbf{k}}(\mathbf{r})$, the matrix element can be written as

$$\left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \middle| e^{\mathbf{i}\boldsymbol{q}\cdot\boldsymbol{r}} \middle| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle = \frac{1}{v} \int_{v} u_{n'\boldsymbol{k}+\boldsymbol{q}}^{*}(\boldsymbol{r}) u_{n\boldsymbol{k}}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,, \tag{29.4.5}$$

where the integration goes over the volume v of the elementary cell.

The induced density is obtained by summing the absolute square of the wavefunction over all occupied states. Taking its Fourier transform and keeping only the terms proportional to V(q), the expression for the polarization function is rather similar to (29.2.41) and the dielectric function has a Lindhard-like form,

$$\epsilon_{\mathbf{r}}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}nn'} \frac{f_0(\varepsilon_{n\boldsymbol{k}}) - f_0(\varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{n\boldsymbol{k}} + \mathrm{i}\delta} \left| \left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right| \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} |\psi_{n\boldsymbol{k}}^{(0)} \right\rangle \right|^2;$$
(29.4.6)

however, it contains the absolute square of the matrix element (29.4.5) and besides the summation over k one has to sum over the band indices.

In the extended-zone scheme, the states belonging to different zones can be distinguished by an appropriate vector G of the reciprocal lattice. Then the dielectric function can be written in the form

$$\epsilon_{\mathbf{r}}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{G}\boldsymbol{G}'\sigma} \frac{f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{G}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G}'})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G}'} + \varepsilon_{\boldsymbol{k}+\boldsymbol{G}} + \mathrm{i}\delta} \times \left| \left\langle \psi_{\boldsymbol{k}+\boldsymbol{q}+\boldsymbol{G}'} | \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} | \psi_{\boldsymbol{k}+\boldsymbol{G}} \right\rangle \right|^2.$$
(29.4.7)

29.4.2 Dielectric Constant of Semiconductors

Expression (29.4.6) derived for arbitrary band structure will now be used to calculate the dielectric constant of semiconductors. As has been mentioned already, transitions between the valence and conduction bands play an important role in their optical properties. When their dielectric function is calculated, the states of at least two bands have to be considered. Those terms give a finite contribution in (29.4.6), where the state $\psi_{nk}^{(0)}$ is in the valence band and

 $\psi_{n'\bm k+\bm q}^{(0)}$ in the conduction band or vice versa. To evaluate the matrix element we consider the double commutator

$$\left[\left[\mathcal{H}, e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \right]_{-}, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \right]_{-}.$$
(29.4.8)

The lattice-periodic potential in \mathcal{H} commutes with $e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$, but the operator of kinetic energy does not. Writing explicitly $-(\hbar^2/2m_e)\nabla^2$ for the kinetic energy it is readily seen that

$$\left[\left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \right]_{-}, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \right]_{-} = -\frac{\hbar^2 q^2}{m_{\rm e}} = -2\varepsilon_q \,. \tag{29.4.9}$$

Alternatively, the diagonal matrix element of the double commutator for state $\psi_{n\mathbf{k}}^{(0)}$ with energy $\varepsilon_{n\mathbf{k}}$ can be calculated by inserting a complete set of intermediate states $\psi_{n'\mathbf{k}'}^{(0)}$. Due to quasimomentum conservation the matrix elements appearing in this expression are nonvanishing only for those intermediate states whose wave vector is equivalent to $\mathbf{k} \pm \mathbf{q}$. We get

$$\left\langle \psi_{n\boldsymbol{k}}^{(0)} \right| \left[\left[\mathcal{H}, e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \right]_{-}, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \right]_{-} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle$$

$$= \sum_{n'} \left\langle \psi_{n\boldsymbol{k}}^{(0)} \right| \mathcal{H}e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} \right\rangle \left\langle \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} \right| e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle$$

$$- \sum_{n'} \left\langle \psi_{n\boldsymbol{k}}^{(0)} \right| e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \mathcal{H} \left| \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} \right\rangle \left\langle \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} \right| e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle$$

$$- \sum_{n'} \left\langle \psi_{n\boldsymbol{k}}^{(0)} \right| e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right\rangle \left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right| \mathcal{H}e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle$$

$$+ \sum_{n'} \left\langle \psi_{n\boldsymbol{k}}^{(0)} \right| e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right\rangle \left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right| e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \mathcal{H} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle$$

$$= \sum_{n'} (\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}}) \left| \left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right| e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle \right|^{2}$$

$$+ \sum_{n'} (\varepsilon_{n\boldsymbol{k}} - \varepsilon_{n'\boldsymbol{k}-\boldsymbol{q}}) \left| \left\langle \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} \right| e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle \right|^{2}.$$

Comparison of the two expressions yields

$$\sum_{n'} \left[\left(\varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{n\boldsymbol{k}} \right) \left| \left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right| e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle \right|^{2} + \left(\varepsilon_{n'\boldsymbol{k}-\boldsymbol{q}} - \varepsilon_{n\boldsymbol{k}} \right) \left| \left\langle \psi_{n'\boldsymbol{k}-\boldsymbol{q}}^{(0)} \right| e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle \right|^{2} \right] = 2\varepsilon_{q} .$$

$$(29.4.11)$$

When the dielectric constant, the value of the dielectric function at $q \approx 0$, is considered, the energy difference in the direct transitions between the valence and conduction bands can be approximated by the direct gap,

$$\varepsilon_{n'\boldsymbol{k}\pm\boldsymbol{q}} - \varepsilon_{n\boldsymbol{k}} \approx \varepsilon_{\mathrm{g}}, \qquad (29.4.12)$$

when k is in the valence band and $k \pm q$ in the conduction band. This is used both in (29.4.11) and in the energy denominator of (29.4.6). The sum over the k vectors in the valence and conduction bands gives

$$\epsilon_{\rm r}(\boldsymbol{q},0) \approx 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{2n_{\rm e}}{\varepsilon_{\rm g}} \frac{\varepsilon_q}{\varepsilon_{\rm g}} = 1 + \frac{4\pi n_{\rm e}\tilde{e}^2\hbar^2}{m^*\varepsilon_{\rm g}^2}$$
(29.4.13)

for the dielectric constant where $n_{\rm e}$ is the electron density in the valence band. When the density is expressed in terms of the plasma frequency with the help of (16.1.69), we obtain

$$\epsilon_{\rm r}(\boldsymbol{q},0) = 1 + \left(\frac{\hbar\omega_{\rm p}}{\varepsilon_{\rm g}}\right)^2. \tag{29.4.14}$$

The $1/q^2$ singularity characteristic for metals does not appear in semiconductors and the dielectric constant is finite in the limit $q \to 0$ owing to the finite gap, the forbidden region around the Fermi energy. As a consequence screening is not complete in semiconductors.

The direct gap is about 4 eV in both Ge and Si, and the plasmon energy is about $\hbar\omega_{\rm p} \approx 16 \,\text{eV}$. This would give $\epsilon_{\rm r} \approx 17$ for the dielectric constant in good agreement with the experimental values. As mentioned already in Chapter 20, $\epsilon_{\rm r} \approx 12$ in silicon and $\epsilon_{\rm r} \approx 16$ in germanium.

29.5 Dielectric Function in Special Cases

A very interesting development of the last decades was the discovery of a large class of materials – some of them exist in nature, others could only be synthesized artificially – in which the motion of electrons is confined by the overlap of the wavefunctions of neighboring atoms to only one or two spatial dimensions. This is equivalent to saying that ε_{k} depends in fact on only one or two components of the wave vector. For simplicity we will consider systems where a scalar effective mass can be used, i.e., the dispersion relation has the form

$$\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2 k_x^2}{2m^*} \quad \text{or} \quad \varepsilon_{\boldsymbol{k}} = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m^*}. \quad (29.5.1)$$

The dielectric function will be computed for such systems in the RPA. The response function Π_0 is still defined by (29.2.41), but its value, which can be given in closed form for both one- and two-dimensional systems,⁷ depends strongly on the dimensionality of the phase space. Finally we will discuss the case when the Fermi surface has a nesting property. Even though the motion of the electrons is not restricted to one or two directions, a singularity characteristic of one-dimensional systems appears in the dielectric function.

 $^{^{7}}$ The results will be given by replacing the effective mass with the electron mass.

29.5.1 Dielectric Function of the Two-Dimensional Electron Gas

The dielectric function of the two-dimensional electron gas will be written in analogy to (29.2.54) in the form

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 + \frac{4\pi\tilde{e}^2}{q^2}\rho_{\rm 2d}(\varepsilon_{\rm F})F_{\rm 2d}(q,\omega)\,,\qquad(29.5.2)$$

where $\rho_{2d}(\varepsilon_F) = m_e/\pi\hbar^2$ is the density of states of the two-dimensional electron gas. In a strictly two-dimensional system, solution of the Poisson equation gives $U(q) = 2\pi\tilde{e}^2/q$ for the Fourier transform of the Coulomb potential. Nonetheless, we use the choice given above since we are considering a truly three-dimensional system, in which, however, the electrons can propagate with high probability in two directions only. We first consider the region of momenta $q < 2k_F$ where $\hbar v_F q > \varepsilon_q$. One has to distinguish again three frequency ranges. Separating $F_{2d}(q,\omega)$ into real and imaginary parts in the form F' + iF'', in the low-frequency range $0 \leq \hbar\omega < \hbar v_F q - \varepsilon_q$ we have

$$F'_{2d}(q,\omega) = 1 \tag{29.5.3}$$

and

$$F_{\rm 2d}^{\prime\prime}(q,\omega) = \frac{\left[\left(\hbar q v_{\rm F}\right)^2 - \left(\varepsilon_q - \hbar \omega\right)^2\right]^{1/2}}{2\varepsilon_q} - \frac{\left[\left(\hbar q v_{\rm F}\right)^2 - \left(\varepsilon_q + \hbar \omega\right)^2\right]^{1/2}}{2\varepsilon_q}.$$
(29.5.4)

For intermediate frequencies satisfying $\hbar v_{\rm F}q - \varepsilon_q \leq \hbar \omega \leq \hbar v_{\rm F}q + \varepsilon_q$ we find

$$F'_{\rm 2d}(q,\omega) = 1 - \frac{\left[\left(\varepsilon_q + \hbar\omega\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q}$$
(29.5.5)

and

$$F_{\rm 2d}^{\prime\prime}(q,\omega) = \frac{\left[\left(\hbar q v_{\rm F}\right)^2 - \left(\varepsilon_q - \hbar \omega\right)^2\right]^{1/2}}{2\varepsilon_q} \,. \tag{29.5.6}$$

Finally, at high frequencies where $\hbar v_{\rm F} q + \varepsilon_q \leq \hbar \omega$ we have

$$F_{\rm 2d}'(q,\omega) = 1 - \frac{\left[\left(\varepsilon_q + \hbar\omega\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q} + \frac{\left[\left(\hbar\omega - \varepsilon_q\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q}$$
(29.5.7)

and

$$F_{\rm 2d}''(q,\omega) = 0.$$
 (29.5.8)

Similar expressions are obtained for $q > 2k_{\rm F}$ where $\varepsilon_q > \hbar v_{\rm F} q$. At low frequencies, in the range $0 \leq \hbar \omega < \varepsilon_q - \hbar v_{\rm F} q$,

$$F'_{\rm 2d}(q,\omega) = 1 - \frac{\left[\left(\varepsilon_q + \hbar\omega\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q} - \frac{\left[\left(\varepsilon_q - \hbar\omega\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q}$$
(29.5.9)

and

$$F_{\rm 2d}^{\prime\prime}(q,\omega) = 0, \qquad (29.5.10)$$

in the intermediate frequency range $\varepsilon_q - \hbar v_{\rm F} q \leq \hbar \omega \leq \varepsilon_q + \hbar v_{\rm F} q$ we find

$$F'_{\rm 2d}(q,\omega) = 1 - \frac{\left[\left(\varepsilon_q + \hbar\omega\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q}$$
(29.5.11)

and

$$F_{\rm 2d}^{\prime\prime}(q,\omega) = \frac{\left[\left(\hbar q v_{\rm F}\right)^2 - \left(\varepsilon_q - \hbar \omega\right)^2\right]^{1/2}}{2\varepsilon_q},\qquad(29.5.12)$$

while in the high-frequency range $\varepsilon_q + \hbar v_{\rm F} q \leq \hbar \omega$

$$F'_{\rm 2d}(q,\omega) = 1 - \frac{\left[\left(\varepsilon_q + \hbar\omega\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q} + \frac{\left[\left(\varepsilon_q - \hbar\omega\right)^2 - (\hbar q v_{\rm F})^2\right]^{1/2}}{2\varepsilon_q}$$
(29.5.13)

and

$$F_{\rm 2d}^{\prime\prime}(q,\omega) = 0. \qquad (29.5.14)$$

In the static limit, the function F(q) takes the form

$$F_{\rm 2d}(q) = \begin{cases} 1 & \text{for } q < 2k_{\rm F}, \\ 1 - \sqrt{1 - (2k_{\rm F}/q)^2} & \text{for } q > 2k_{\rm F}. \end{cases}$$
(29.5.15)

29.5.2 Dielectric Function of the One-Dimensional Electron Gas

The polarization function of a one-dimensional electron gas is again given by (29.2.31). If $q < 2k_{\rm F}$, two regions, $k_{\rm F} - q \leq k \leq k_{\rm F}$ and $-k_{\rm F} - q \leq k \leq -k_{\rm F}$ (see Fig. 29.9), give finite contribution in the integral. Otherwise either both Fermi distribution functions take unit value or both vanish.



Fig. 29.9. The "Fermi spheres" belonging to the wave numbers k and k + q. Only the regions covered once give finite contributions to the Lindhard function

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We get

$$\operatorname{Re} \Pi_{0}(q,\omega) = \frac{1}{\pi} \int_{k_{\mathrm{F}}-q}^{k_{\mathrm{F}}} \mathrm{d}k \frac{1}{\hbar\omega - \hbar^{2}qk/m_{\mathrm{e}} - \varepsilon_{q}} - \frac{1}{\pi} \int_{-k_{\mathrm{F}}-q}^{-k_{\mathrm{F}}} \mathrm{d}k \frac{1}{\hbar\omega - \hbar^{2}qk/m_{\mathrm{e}} - \varepsilon_{q}}$$
$$= -\frac{1}{\pi} \frac{m_{\mathrm{e}}}{\hbar^{2}q} \left\{ \ln \left| \frac{\hbar v_{\mathrm{F}}q + \varepsilon_{q} - \hbar\omega}{\hbar v_{\mathrm{F}}q - \varepsilon_{q} - \hbar\omega} \right| - \ln \left| \frac{\hbar v_{\mathrm{F}}q - \varepsilon_{q} + \hbar\omega}{\hbar v_{\mathrm{F}}q + \varepsilon_{q} + \hbar\omega} \right| \right\}$$
$$= -\frac{1}{\pi} \frac{m_{\mathrm{e}}}{\hbar^{2}q} \ln \left| \frac{(\hbar v_{\mathrm{F}}q + \varepsilon_{q})^{2} - (\hbar\omega)^{2}}{(\hbar v_{\mathrm{F}}q - \varepsilon_{q})^{2} - (\hbar\omega)^{2}} \right|$$
(29.5.16)

for the real part. If $q>2k_{\rm F},$ the integration goes over two full "Fermi spheres". We then have

$$\operatorname{Re}\Pi_{0}(q,\omega) = \frac{1}{\pi} \int_{-k_{\mathrm{F}}}^{k_{\mathrm{F}}} \mathrm{d}k \frac{1}{\hbar\omega - \hbar^{2}qk/m_{\mathrm{e}} - \varepsilon_{q}} - \frac{1}{\pi} \int_{-k_{\mathrm{F}}-q}^{k_{\mathrm{F}}-q} \mathrm{d}k \frac{1}{\hbar\omega - \hbar^{2}qk/m_{\mathrm{e}} - \varepsilon_{q}}$$
$$= -\frac{1}{\pi} \frac{m_{\mathrm{e}}}{\hbar^{2}q} \left\{ \ln \left| \frac{\hbar v_{\mathrm{F}}q + \varepsilon_{q} - \hbar\omega}{-\hbar v_{\mathrm{F}}q + \varepsilon_{q} - \hbar\omega} \right| - \ln \left| \frac{\hbar v_{\mathrm{F}}q - \varepsilon_{q} - \hbar\omega}{-\hbar v_{\mathrm{F}}q - \varepsilon_{q} - \hbar\omega} \right| \right\}$$
$$= -\frac{1}{\pi} \frac{m_{\mathrm{e}}}{\hbar^{2}q} \ln \left| \frac{(\hbar v_{\mathrm{F}}q + \varepsilon_{q})^{2} - (\hbar\omega)^{2}}{(\hbar v_{\mathrm{F}}q - \varepsilon_{q})^{2} - (\hbar\omega)^{2}} \right|.$$
(29.5.17)

The imaginary part, too, can be easily calculated yielding

$$\operatorname{Im} \Pi_{0}(q,\omega) = \begin{cases} 0 & \text{for } 0 \leq \hbar\omega < \hbar v_{\mathrm{F}}q - \varepsilon_{q} ,\\ -\frac{m_{\mathrm{e}}}{\hbar^{2}k_{\mathrm{F}}} & \text{for } \hbar v_{\mathrm{F}}q - \varepsilon_{q} \leq \hbar\omega \leq \hbar v_{\mathrm{F}}q + \varepsilon_{q} ,\\ 0 & \text{for } \hbar v_{\mathrm{F}}q + \varepsilon_{q} \leq \hbar\omega . \end{cases}$$
(29.5.18)

We can write again the response function in the form

$$\Pi_0(q,\omega) = -\rho_{\rm 1d}(\varepsilon_{\rm F})F_{\rm 1d}(q,\omega), \qquad (29.5.19)$$

where

$$\rho_{\rm 1d}(\varepsilon_{\rm F}) = \frac{2m_{\rm e}}{\pi\hbar^2 k_{\rm F}} \tag{29.5.20}$$

is the density of states of the one-dimensional electron gas at the Fermi energy and $(t_{1}, t_{2}, t_{3})^{2}$

$$\operatorname{Re} F_{1d}(q,\omega) = \frac{k_{\rm F}}{2q} \ln \left| \frac{(\hbar v_{\rm F} q + \varepsilon_q)^2 - (\hbar \omega)^2}{(\hbar v_{\rm F} q - \varepsilon_q)^2 - (\hbar \omega)^2} \right|.$$
(29.5.21)

In the static limit, this quantity reduces to

$$F_{\rm 1d}(q) = \frac{k_{\rm F}}{q} \ln \left| \frac{2k_{\rm F} + q}{2k_{\rm F} - q} \right|.$$
(29.5.22)

The results obtained for F(x) with $x = q/2k_{\rm F}$ for the one-, two-, and threedimensional cases are plotted in Fig. 29.10.



Fig. 29.10. q dependence of the static density–density response function in the one-, two-, and three-dimensional electron gas

The function F(x) displays stronger and stronger singularities at x = 1 $(q = 2k_{\rm F})$ as the dimensionality decreases. It is continuous in the two- and three-dimensional cases and only its derivative is singular at x = 1. The function F itself is singular at this point in the one-dimensional case. The reason for this singular behavior is easy to find when we look at (29.2.31). As described by the Fermi distribution functions, the hole with wave vector \mathbf{k} has to be created inside the Fermi sphere and the electron with $\mathbf{k} + \mathbf{q}$ outside or the role of the electron and the hole can be interchanged. When two Fermi spheres shifted by a vector $-\mathbf{q}$ are drawn as in Fig. 29.11, the integrand vanishes outside the shaded region. The region inside the Fermi sphere around the origin appears with weight +1 in the integrand, whereas the region inside the Fermi sphere around the tip of the vector $-\mathbf{q}$ with weight -1.



Fig. 29.11. The regions of integration giving nonvanishing contribution to the Lindhard function

Taking $\omega = 0$ at a fixed value of q the energy denominator in the Lindhard function vanishes at those k vectors for which $\varepsilon_{k+q} = \varepsilon_k$. This condition is satisfied in a tiny portion of the region of integration in the three-dimensional case, along the intersection of the two displaced Fermi spheres, where both the electron and the hole are on the Fermi surface. The integrand is large in the neighborhood of this circle, but only in a tiny portion of the phase space.

The response function is thus a continuous function and only its derivative shows a weak, logarithmic singularity at $q = 2k_{\rm F}$.

In two-dimensional systems the energy denominator vanishes at two points, at the intersection of the two Fermi circles. The integral itself remains finite; however, the derivative of the response function displays a stronger singularity, it is discontinuous at $q = 2k_{\rm F}$. The integrand is singular at two points of the phase space in the one-dimensional case as well, but this singularity is not compensated by the smallness of the corresponding phase space. The response function itself is singular at $q = 2k_{\rm F}$.

29.5.3 Materials with Nested Fermi Surface

We may ask what happens when the electron system is three dimensional, but the shape of the Fermi surface deviates significantly from the sphere. We consider as an example a crystal with orthorhombic structure where the energy of electron states in the tight-binding approximation is given by

$$\varepsilon_{\mathbf{k}} = \varepsilon_0 + \varepsilon_1 \cos k_x a + \varepsilon_2 \cos k_y b + \varepsilon_3 \cos k_z c \,. \tag{29.5.23}$$

It may occur that in two of the crystallographic directions (say in the y- and z-directions) the overlap of the wavefunctions of neighboring atoms is much weaker than in the third direction, $|\varepsilon_1| \gg |\varepsilon_2|$, $|\varepsilon_3|$, and also that $|\varepsilon_2| \gg |\varepsilon_3|$. In such systems there is a preferred direction of propagation. Electrons move in one direction with much higher probability than in the other directions. The system can be considered electronically quasi-one-dimensional. If the term proportional to ε_1 is approximated by a linear spectrum near the Fermi energy and the smallest term proportional to ε_3 is neglected, the dispersion relation becomes

$$\varepsilon_{\mathbf{k}} = \varepsilon_0 + \hbar v_{\mathrm{F}} (\pm k_x - k_{\mathrm{F}}) + \varepsilon_2 \cos k_y b \,, \qquad (29.5.24)$$

where the + sign has to be chosen for k_x close to k_F and the - sign when k_x is close to $-k_F$. Figure 29.12 shows the Fermi surface corresponding to this spectrum. It is seen that the Fermi surface consists of two parts, which appear as two sheets.

It is easy to verify that if the left sheet of the Fermi surface is shifted by the vector

$$\boldsymbol{q}_0 = (2k_{\rm F}, \, \pi/b) \,,$$
 (29.5.25)

it will exactly coincide with the right sheet, provided that, if necessary, the wave vectors are reduced to the first Brillouin zone. Evaluating the response function at this q_0 , the energy denominator vanishes for all k vectors lying on the left sheet of the Fermi surface and the response function is singular at $q = q_0$. The same logarithmic singularity appears as in one-dimensional systems.

Such a divergence may appear not only in quasi-one-dimensional systems. As has been seen already in Fig. 18.23, the "Fermi sphere" is distorted to a



Fig. 29.12. Fermi surface of a quasi-one-dimensional system with the nesting vector

square in the tight-binding approximation for a two-dimensional square lattice if the band is half filled. Opposite edges of the Fermi surface are separated by one of the vectors $\mathbf{q}_0 = (\pm \pi/a, \pm \pi/a)$. If the response function is calculated at this \mathbf{q}_0 , the energy denominator vanishes for every vector \mathbf{k} of the edge of the Fermi surface under consideration and therefore the response function exhibits similar logarithmic singularities.

These examples show that the divergence is the consequence of the special shape of the Fermi surface, namely, when the Fermi surface is displaced by an appropriately chosen wave vector q_0 , an extended region of the Fermi surface has to coincide (nest) with another portion of the Fermi surface. Such Fermi surfaces are said to have the property of *nesting*. Figure 29.13 shows two further examples of nested Fermi surfaces.



Fig. 29.13. Nested Fermi surfaces with the nesting vector

When the dielectric response of such systems is calculated at the nesting vector \boldsymbol{q}_0 , the energy denominator vanishes along the whole nesting region, and therefore the response function has the same kind of logarithmic singularity as the one-dimensional model at $2k_{\rm F}$. This singularity may lead to the appearance of a new state, a static charge-density-wave or spin-density-wave state. This problem will be treated in Chapter 33.

29.6 Response to Electromagnetic Field

In the foregoing the response of the electron system to an external charge or scalar potential was studied. This could have been described equivalently as the response to a longitudinal vector potential, since according to (29.1.15)both the electric field and the electric displacement are parallel to the wave vector \boldsymbol{q} . The dielectric function and the conductivity determined in this way are thus responses to longitudinal perturbations. A different situation is encountered when the optical properties are considered, since in a radiating electromagnetic field the vectors E and H are perpendicular to the direction of propagation. The ratio of the perpendicular components of D and Egives the transverse dielectric function $\epsilon_{\perp r} = \epsilon_{\perp}/\epsilon_0$, where ϵ_{\perp} was defined in (29.1.6) and (29.1.8). This quantity is not necessarily the same as the longitudinal dielectric function even if the medium is isotropic. More importantly, the transverse electromagnetic field couples to the current and therefore the response of the electron system to such perturbations can be described by the current–current response function. We will derive the Kubo formula that expresses the conductivity in terms of the retarded current-current correlation function and will specify it for the optical and DC conductivities.

29.6.1 Interaction with the Electromagnetic Field

The interaction between the electron system and an electromagnetic field can be derived from the Hamiltonian of the interacting electron system in the presence of an electromagnetic field. If the field is described by a scalar potential $\varphi(\mathbf{r})$ and a vector potential $\mathbf{A}(\mathbf{r})$, we have

$$\mathcal{H} = \frac{1}{2m_{\rm e}} \sum_{i=1}^{N_{\rm e}} \left[\boldsymbol{p}_i + e\boldsymbol{A}(\boldsymbol{r}_i) \right]^2 - e \sum_{i=1}^{N_{\rm e}} \varphi(\boldsymbol{r}_i) + \frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{\rm e}} \frac{\tilde{e}^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \quad (29.6.1)$$

where the kinetic energy is given in terms of the kinetic momentum p + eAinstead of the canonical momentum p. Subtracting from this expression the terms not related to the electromagnetic field, the remaining terms collected into

$$\mathcal{H}_{1} = \sum_{i} \left\{ \frac{e}{2m_{e}} \left[\boldsymbol{A}(\boldsymbol{r}_{i}) \cdot \boldsymbol{p}_{i} + \boldsymbol{p}_{i} \cdot \boldsymbol{A}(\boldsymbol{r}_{i}) \right] + \frac{e^{2}}{2m_{e}} \boldsymbol{A}^{2}(\boldsymbol{r}_{i}) - e\varphi(\boldsymbol{r}_{i}) \right\}$$

$$= \sum_{i} \left\{ \frac{e\hbar}{2im_{e}} \left[\boldsymbol{A}(\boldsymbol{r}_{i}) \cdot \boldsymbol{\nabla}_{i} + \boldsymbol{\nabla}_{i} \cdot \boldsymbol{A}(\boldsymbol{r}_{i}) \right] + \frac{e^{2}}{2m_{e}} \boldsymbol{A}^{2}(\boldsymbol{r}_{i}) - e\varphi(\boldsymbol{r}_{i}) \right\}$$

$$(29.6.2)$$

describe the interaction. It is convenient to work in Coulomb (transverse) gauge, where div $\mathbf{A} = 0$, i.e., the vector potential is perpendicular to the propagation vector \mathbf{q} and the scalar potential vanishes. When only the terms

linear in the vector potential are kept, the interaction Hamiltonian can be written in the simple form

$$\mathcal{H}_1 = -\int \hat{\boldsymbol{j}}(\boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r}, t) \,\mathrm{d}\boldsymbol{r} \,, \qquad (29.6.3)$$

where $\hat{j}(\mathbf{r})$ is the operator of the current density. To substantiate this statement we recall that the quantum mechanical expression for the operator of the particle-current density is

$$\hat{\boldsymbol{j}}_{n}(\boldsymbol{r}) = \frac{1}{2m_{\rm e}} \sum_{i} \left[\boldsymbol{p}_{i} \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) + \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) \boldsymbol{p}_{i} \right]$$
(29.6.4)

and the electric-current operator is

$$\hat{\boldsymbol{j}}(\boldsymbol{r}) = -e\hat{\boldsymbol{j}}_n(\boldsymbol{r}) = -\frac{e}{2m_{\rm e}}\sum_i \left[\boldsymbol{p}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i) + \delta(\boldsymbol{r}-\boldsymbol{r}_i)\boldsymbol{p}_i\right].$$
(29.6.5)

This shows that the perturbing vector potential couples indeed to the current. Expressing the vector potential and the current in terms of their Fourier components, one readily finds

$$\mathcal{H}_1 = -\frac{1}{V} \sum_{\boldsymbol{q}} \hat{\boldsymbol{j}}(-\boldsymbol{q}) \cdot \boldsymbol{A}(\boldsymbol{q}, t), \qquad (29.6.6)$$

where

$$\hat{\boldsymbol{j}}(\boldsymbol{q}) = -\frac{e}{2m_{\rm e}}\frac{\hbar}{{\rm i}}\sum_{i} \left[\boldsymbol{\nabla}_{i}{\rm e}^{-{\rm i}\boldsymbol{q}\cdot\boldsymbol{r}_{i}} + {\rm e}^{-{\rm i}\boldsymbol{q}\cdot\boldsymbol{r}_{i}}\boldsymbol{\nabla}_{i}\right], \qquad (29.6.7)$$

or in second-quantized form

$$\hat{\boldsymbol{j}}(\boldsymbol{q}) = -\frac{e\hbar}{m_{\rm e}} \sum_{\boldsymbol{k}\sigma} (\boldsymbol{k} + \frac{1}{2}\boldsymbol{q}) c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}+\boldsymbol{q}\sigma} = -\frac{e\hbar}{m_{\rm e}} \sum_{\boldsymbol{k}\sigma} \boldsymbol{k} c_{\boldsymbol{k}-\boldsymbol{q}/2\sigma}^{\dagger} c_{\boldsymbol{k}+\boldsymbol{q}/2\sigma}.$$
 (29.6.8)

Before going on we have to recognize that the expression given above for the current density is valid in the absence of electromagnetic field. In its presence it has to be modified to make it gauge invariant. The correct expression should contain the kinetic momentum

$$\hat{\boldsymbol{j}}(\boldsymbol{r}) = -\frac{e}{2m_{\rm e}} \sum_{i} \left\{ \left[\boldsymbol{p}_{i} + e\boldsymbol{A}(\boldsymbol{r}_{i}) \right] \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) + \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) \left[\boldsymbol{p}_{i} + e\boldsymbol{A}(\boldsymbol{r}_{i}) \right] \right\}$$

$$= -\frac{e}{2m_{\rm e}} \sum_{i} \left[\boldsymbol{p}_{i} \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) + \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) \boldsymbol{p}_{i} \right] - \frac{e^{2}}{m_{\rm e}} \sum_{i} \boldsymbol{A}(\boldsymbol{r}_{i}) \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) .$$

$$(29.6.9)$$

The total current operator can be decomposed naturally into two terms:

$$\hat{j} = \hat{j}_{\rm p} + \hat{j}_{\rm d},$$
 (29.6.10)

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where

$$\hat{\boldsymbol{j}}_{\mathrm{p}}(\boldsymbol{r}) = -\frac{e}{2m_{\mathrm{e}}} \sum_{i} \left[\boldsymbol{p}_{i} \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) + \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) \boldsymbol{p}_{i} \right]$$
(29.6.11)

is the so-called paramagnetic current; it is the current component that appears in the interaction with the electromagnetic field to lowest order in the field, while the second term,

$$\hat{\boldsymbol{j}}_{\rm d}(\boldsymbol{r}) = -\frac{e^2}{m_{\rm e}} \sum_i \boldsymbol{A}(\boldsymbol{r}_i) \delta(\boldsymbol{r} - \boldsymbol{r}_i) , \qquad (29.6.12)$$

is the diamagnetic current. This term can be written in terms of the electron density as

$$\hat{j}_{\rm d}(\mathbf{r}) = -\frac{e^2}{m_{\rm e}} \mathbf{A}(\mathbf{r}) n(\mathbf{r}) \,.$$
 (29.6.13)

29.6.2 Current–Current Correlations and the Kubo Formula

The total current density is the expectation value of the current operator. In what follows the notation j will be used for the total current density and \hat{j} for the operator of the paramagnetic current. We then have

$$\boldsymbol{j}(\boldsymbol{r},t) = \left\langle \hat{\boldsymbol{j}}(\boldsymbol{r},t) \right\rangle - \frac{n_{\rm e}e^2}{m_{\rm e}} \boldsymbol{A}(\boldsymbol{r},t) \,, \qquad (29.6.14)$$

if the electric field is time dependent, and the particle density has been replaced with its unperturbed mean value. Assuming a periodically varying space and time dependence for the vector potential with a fixed frequency and wave vector,

$$\boldsymbol{A}(\boldsymbol{r},t) = \boldsymbol{A}(\boldsymbol{q},t) \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} = \boldsymbol{A}(\boldsymbol{q}) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)}, \qquad (29.6.15)$$

the current varies with the same periodicity, and the spatial Fourier transform of the current density is

$$\boldsymbol{j}(\boldsymbol{q},t) = \left\langle \hat{\boldsymbol{j}}(\boldsymbol{q},t) \right\rangle - \frac{n_{\rm e}e^2}{m_{\rm e}} \boldsymbol{A}(\boldsymbol{q},t) \,. \tag{29.6.16}$$

The current at a given frequency is the Fourier transform of this quantity, that is

$$\boldsymbol{j}(\boldsymbol{q},\omega) = \left\langle \hat{\boldsymbol{j}}(\boldsymbol{q},\omega) \right\rangle - \frac{n_{\rm e}e^2}{m_{\rm e}} \boldsymbol{A}(\boldsymbol{q},\omega) \,. \tag{29.6.17}$$

For weak external perturbations the current is proportional to the internal electric field. In the most general case

$$j_{\alpha}(\boldsymbol{r},t) = \sum_{\beta} \int \mathrm{d}\boldsymbol{r}' \int_{-\infty}^{t} \mathrm{d}t' \sigma_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t-t') E_{\beta}(\boldsymbol{r}',t') , \qquad (29.6.18)$$

where $\sigma_{\alpha\beta}$ is the conductivity tensor. In a homogeneous system the relationship is algebraic between the Fourier components:

$$\boldsymbol{j}(\boldsymbol{q},\omega) = \boldsymbol{\sigma}(\boldsymbol{q},\omega)\boldsymbol{E}(\boldsymbol{q},\omega)\,. \tag{29.6.19}$$

Note that the relationship between current and electric field is causal; hence, the Kramers–Kronig relations are satisfied by the real and imaginary parts of the conductivity:

$$\operatorname{Re} \sigma(\boldsymbol{q}, \omega) = \frac{1}{\pi} \operatorname{P} \int_{-\infty}^{\infty} d\omega' \frac{\operatorname{Im} \sigma(\boldsymbol{q}, \omega')}{\omega' - \omega} = \frac{2}{\pi} \operatorname{P} \int_{0}^{\infty} d\omega' \frac{\omega' \operatorname{Im} \sigma(\boldsymbol{q}, \omega')}{\omega'^{2} - \omega^{2}},$$
(29.6.20)
$$\operatorname{Im} \sigma(\boldsymbol{q}, \omega) = -\frac{1}{\pi} \operatorname{P} \int_{-\infty}^{\infty} d\omega' \frac{\operatorname{Re} \sigma(\boldsymbol{q}, \omega')}{\omega' - \omega} = -\frac{2\omega}{\pi} \operatorname{P} \int_{0}^{\infty} d\omega' \frac{\operatorname{Re} \sigma(\boldsymbol{q}, \omega')}{\omega'^{2} - \omega^{2}}.$$

To derive the conductivity, the paramagnetic current has to be calculated as a linear response to the perturbing electromagnetic field. Since the mean value of the paramagnetic current has to be calculated and the vector potential couples to the same paramagnetic component of the current, the response function that connects the current to the vector potential in the expression

$$\langle \hat{j}_{\alpha}(\boldsymbol{r},t) \rangle = -\int_{-\infty}^{t} \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' P_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t-t') A_{\beta}(\boldsymbol{r}',t')$$
(29.6.21)

is the current–current response function:

$$P_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\Big\langle \left[\hat{j}_{\alpha}(\boldsymbol{r},t),\hat{j}_{\beta}(\boldsymbol{r}',t')\right]_{-}\Big\rangle.$$
(29.6.22)

In a homogeneous system where the response depends only on r - r', the Fourier transform of the paramagnetic current density is

$$\langle \hat{j}_{\alpha}(\boldsymbol{q},\omega) \rangle = -P_{\alpha\beta}(\boldsymbol{q},\omega)A_{\beta}(\boldsymbol{q},\omega),$$
 (29.6.23)

where

$$P_{\alpha\beta}(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{-\infty}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \theta(t-t') \Big\langle \left[\hat{j}_{\alpha}(\boldsymbol{q},t), \hat{j}_{\beta}(-\boldsymbol{q},t')\right]_{-} \Big\rangle$$
$$= -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \Big\langle \left[\hat{j}_{\alpha}(\boldsymbol{q},t), \hat{j}_{\beta}(-\boldsymbol{q},0)\right]_{-} \Big\rangle.$$
(29.6.24)

The retarded response function has to be analytic in the upper complex ω half-plane. This is achieved by inserting a factor $\exp(-\delta t)$ with a positive

infinitesimal δ in the last integrand. This factor corresponds to switching on the perturbation adiabatically. We thus have

$$P_{\alpha\beta}(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t - \delta t} \left\langle \left[\hat{j}_{\alpha}(\boldsymbol{q},t), \hat{j}_{\beta}(-\boldsymbol{q},0) \right]_{-} \right\rangle.$$
(29.6.25)

When the average is calculated at finite temperatures in terms of the matrix elements between the complete set of eigenstates of the unperturbed Hamiltonian, we find

$$P_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \frac{\langle \Psi_n | \hat{j}_\alpha(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | \hat{j}_\beta(-\boldsymbol{q}) | \Psi_n \rangle}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} \,.$$
(29.6.26)

The current–current correlation function appears in response to the vector potential, while the conductivity is defined through the response to the electric field. We make use of the relationship

$$\boldsymbol{E}(\boldsymbol{r},t) = -\frac{\partial \boldsymbol{A}(\boldsymbol{r},t)}{\partial t}$$
(29.6.27)

valid in that gauge where the scalar potential vanishes. For fields varying with frequency $\omega,$ this leads to

$$\boldsymbol{E}(\boldsymbol{r},\omega) = i\omega \boldsymbol{A}(\boldsymbol{r},\omega) \,. \tag{29.6.28}$$

Substituting this into (29.6.23) and adding the paramagnetic and diamagnetic contributions we have

$$\sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\omega} \left[P_{\alpha\beta}(\boldsymbol{q},\omega) + \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}} \delta_{\alpha\beta} \right].$$
(29.6.29)

With the explicit form of the current–current response function $P_{\alpha\beta}$ we find the relationship

$$\sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{1}{\hbar\omega} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \Big\langle \left[\hat{j}_{\alpha}(\boldsymbol{q},t),\hat{j}_{\beta}(-\boldsymbol{q},0)\right]_{-} \Big\rangle + \frac{\mathrm{i}n_{\mathrm{e}}e^{2}}{m_{\mathrm{e}}\omega} \delta_{\alpha\beta}$$
(29.6.30)

known as the Kubo formula.⁸ In real-space representation

⁸ R. KUBO, 1957. The name Kubo formula refers more generally to the formula that expresses the generalized susceptibility as a retarded correlation function. This is discussed in more detail in Appendix J. The expression for transport coefficients is often referred to as Green–Kubo formula (M. S. GREEN, 1952, 1954), while the expression for the conductivity is sometimes referred to as Kubo–Nakano formula (H. NAKANO. 1956).

$$\sigma_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{1}{\hbar\omega} \int_{0}^{\infty} dt \, \mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \left\langle \left[\hat{j}_{\alpha}(\boldsymbol{r},t), \hat{j}_{\beta}(\boldsymbol{r}',0) \right]_{-} \right\rangle + \frac{\mathrm{i}n_{\mathrm{e}}(\boldsymbol{r})e^{2}}{m_{\mathrm{e}}\omega} \delta_{\alpha\beta}\delta(\boldsymbol{r}-\boldsymbol{r}') \,.$$

$$(29.6.31)$$

If the thermal average is written in terms of the matrix elements between a complete set of states $|\Psi_n\rangle$ of energy E_n , as in (29.6.26), we find

$$\sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\omega} \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \frac{\langle \Psi_n | \hat{j}_{\alpha}(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | \hat{j}_{\beta}(-\boldsymbol{q}) | \Psi_n \rangle}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} + \frac{\mathrm{i}n_{\mathrm{e}}e^2}{m_{\mathrm{e}}\omega} \delta_{\alpha\beta} \,.$$
(29.6.32)

The real part of the frequency-dependent conductivity can then be written as

$$\operatorname{Re} \sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{\pi}{\omega} \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \left\langle \Psi_n | \hat{j}_{\alpha}(\boldsymbol{q}) | \Psi_m \right\rangle$$

$$\times \left\langle \Psi_m | \hat{j}_{\beta}(-\boldsymbol{q}) | \Psi_n \right\rangle \delta(\hbar\omega - E_m + E_n)$$

$$= \frac{\pi}{\omega} \left(1 - \mathrm{e}^{-\beta\hbar\omega} \right) \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \left\langle \Psi_n | \hat{j}_{\alpha}(\boldsymbol{q}) | \Psi_m \right\rangle$$

$$\times \left\langle \Psi_m | \hat{j}_{\beta}(-\boldsymbol{q}) | \Psi_n \right\rangle \delta(\hbar\omega - E_m + E_n) .$$

$$(29.6.33)$$

Alternatively this expression could have been derived by making use of the fact that the real part of the conductivity is proportional to the imaginary part of the current–current response function

$$\operatorname{Re} \sigma_{\alpha\beta}(\boldsymbol{q},\omega) = -\frac{1}{\omega} \operatorname{Im} P_{\alpha\beta}(\boldsymbol{q},\omega), \qquad (29.6.34)$$

which in turn can be expressed in terms of the current-current correlation function using the fluctuation-dissipation theorem outlined in Appendix J:

$$\frac{1}{V} \int_{-\infty}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \left\langle \hat{j}_{\alpha}(\boldsymbol{q},t) \hat{j}_{\beta}(-\boldsymbol{q},0) \right\rangle = -\frac{2\hbar}{1 - \mathrm{e}^{-\beta\hbar\omega}} \,\mathrm{Im} \, P_{\alpha\beta}(\boldsymbol{q},\omega) \,. \tag{29.6.35}$$

We then find that

$$\operatorname{Re}\sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{1}{2\hbar\omega} \left(1 - \mathrm{e}^{-\beta\hbar\omega}\right) \frac{1}{V} \int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} \left\langle \hat{j}_{\alpha}(\boldsymbol{q},t)\hat{j}_{\beta}(-\boldsymbol{q},0) \right\rangle. \quad (29.6.36)$$

If the thermal average is written in terms of the matrix elements between a complete set of states with the appropriate weight factor, the time integral can be performed using

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$$\int_{-\infty}^{\infty} e^{i\omega t} dt = 2\pi \delta(\omega)$$
(29.6.37)

and we find precisely (29.6.33).

29.6.3 Transverse and Longitudinal Response

In the derivation of the Kubo formula the response to an external electric field was considered. When the conductivity is calculated, we have to take into account that the current is the response to the internal field E. We show that this leads to the expression

$$\sigma_{\alpha\beta}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\omega} \left[\widetilde{P}_{\alpha\beta}(\boldsymbol{q},\omega) + \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}} \delta_{\alpha\beta} \right]$$
(29.6.38)

for the conductivity tensor instead of (29.6.29), where $\tilde{P}_{\alpha\beta}(\boldsymbol{q},\omega)$ is the irreducible part of $P_{\alpha\beta}(\boldsymbol{q},\omega)$.

First, we show that this makes no difference for the transverse response since transverse fields are not screened. This can be best seen when the current–current response function is visualized by diagrams. These diagrams have the same form as the diagrams for the density-density response function; their analytic expression is, however, different. The current vertex (its analytic form can be inferred from the second-quantized expression for the current operator) appears at the two end points, where the electron-hole pair is created and annihilated. Analogous to the density-density response function, one can distinguish irreducible and reducible processes in the current–current response function, too. The reducible diagrams can be separated into two unconnected parts by cutting a single appropriately chosen interaction line. The diagrams for the full response function form again a geometric progression, in which irreducible polarization bubbles are coupled to each other by interaction lines, similar to the diagrammatic representation of the density-density correlation function, except that the first and last bubbles have a current vertex; they represent the irreducible part of the current-density and the density-current response functions

$$S_{\alpha}(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t - \delta t} \left\langle \left[\hat{j}_{\alpha}(\boldsymbol{q},t), n(-\boldsymbol{q},0) \right]_{-} \right\rangle$$
(29.6.39)

and

$$\overline{S}_{\alpha}(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t - \delta t} \left\langle \left[n(\boldsymbol{q},t), \hat{j}_{\alpha}(-\boldsymbol{q},0) \right]_{-} \right\rangle.$$
(29.6.40)

Denoting their irreducible parts by $\widetilde{S}_{\alpha}(\boldsymbol{q},\omega)$ and $\overline{\widetilde{S}}_{\alpha}(\boldsymbol{q},\omega)$, respectively, and the irreducible part of the current–current response function by $\widetilde{P}_{\alpha\beta}$, we have

$$P_{\alpha\beta}(\boldsymbol{q},\omega) = \widetilde{P}_{\alpha\beta}(\boldsymbol{q},\omega) + \widetilde{S}_{\alpha}(\boldsymbol{q},\omega) \frac{4\pi \widetilde{e}^2/q^2}{1 - (4\pi \widetilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)} \overline{\widetilde{S}}_{\beta}(\boldsymbol{q},\omega) \,. \quad (29.6.41)$$

The current–density response function being a vector, its components perpendicular to q vanish by symmetry in an isotropic system,

$$S_{\perp}(\boldsymbol{q},\omega) = \widetilde{S}_{\perp}(\boldsymbol{q},\omega) = 0, \qquad (29.6.42)$$

and therefore

$$P_{\perp}(\boldsymbol{q},\omega) = P_{\perp}(\boldsymbol{q},\omega). \qquad (29.6.43)$$

This shows that there are no polarization corrections to the transverse response; the transverse vector potential and transverse fields are not screened. Thus

$$\sigma_{\perp}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\omega} \left[P_{\perp}(\boldsymbol{q},\omega) + \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}} \right] = \frac{\mathrm{i}}{\omega} \left[\widetilde{P}_{\perp}(\boldsymbol{q},\omega) + \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}} \right].$$
(29.6.44)

The situation is different for the longitudinal response. To see that we rewrite the interaction of the electron system with an external potential,

$$\mathcal{H}_{1} = \int n(\boldsymbol{r}) V_{\text{ext}}(\boldsymbol{r}, t) \, \mathrm{d}\boldsymbol{r} = -e \int n(\boldsymbol{r}) \varphi_{\text{ext}}(\boldsymbol{r}, t) \, \mathrm{d}\boldsymbol{r}$$

$$= -\frac{e}{V} \sum_{\boldsymbol{q}} n(-\boldsymbol{q}) \varphi_{\text{ext}}(\boldsymbol{q}, t) \,, \qquad (29.6.45)$$

in terms of a longitudinal vector potential by making use of the gauge invariance of electrodynamics. The same longitudinal electric field is obtained from the longitudinal vector potential defined by

$$-\operatorname{grad}\varphi_{\mathrm{ext}}(\boldsymbol{r},t) = -\frac{\partial \boldsymbol{A}_{\mathrm{ext}}(\boldsymbol{r},t)}{\partial t}.$$
 (29.6.46)

Assuming that the longitudinal field varies periodically in space and time we have the relationship

$$\boldsymbol{q}\varphi_{\mathrm{ext}}(\boldsymbol{q},\omega) = -\omega \boldsymbol{A}_{\mathrm{ext}}(\boldsymbol{q},\omega)$$
 (29.6.47)

between the Fourier components. On the other hand, the number density and the particle-current density have to satisfy the continuity equation

$$\frac{\partial n(\boldsymbol{r},t)}{\partial t} + \operatorname{div} \hat{\boldsymbol{j}}_n(\boldsymbol{r},t) = 0$$
(29.6.48)

that follows from the particle-number (charge) conservation. This implies

$$\omega n(\boldsymbol{q}, t) = \boldsymbol{q} \cdot \hat{\boldsymbol{j}}_n(\boldsymbol{q}, t). \qquad (29.6.49)$$

Substituting these relations into (29.6.45) we see that in the longitudinal case as well

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$$\mathcal{H}_{1} = \frac{e}{V} \sum_{\boldsymbol{q}} \hat{\boldsymbol{j}}_{n}(-\boldsymbol{q}) \cdot \boldsymbol{A}(\boldsymbol{q},t) = -\frac{1}{V} \sum_{\boldsymbol{q}} \hat{\boldsymbol{j}}(-\boldsymbol{q}) \cdot \boldsymbol{A}(\boldsymbol{q},t)$$

$$= -\int \hat{\boldsymbol{j}}(\boldsymbol{r}) \boldsymbol{A}(\boldsymbol{r},t) \, \mathrm{d}\boldsymbol{r} \,.$$
(29.6.50)

If the vector potential and the current are parallel to q, the relationship

$$\langle \hat{j}(\boldsymbol{q},\omega) \rangle = -P_{\parallel}(\boldsymbol{q},\omega)A_{\mathrm{ext}}(\boldsymbol{q},\omega)$$
 (29.6.51)

defines the longitudinal current–current response function, and the total current is given by

$$\boldsymbol{j}(\boldsymbol{q},\omega) = -\left[P_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\rm e}e^2}{m_{\rm e}}\right]\boldsymbol{A}_{\rm ext}(\boldsymbol{q},\omega)\,.$$
(29.6.52)

As we know, the longitudinal field (potential) is screened and the physically relevant internal vector potential and field are

$$\boldsymbol{A}(\boldsymbol{q},\omega) = \frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} \boldsymbol{A}_{\rm ext}(\boldsymbol{q},\omega), \qquad \boldsymbol{E}(\boldsymbol{q},\omega) = \frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} \boldsymbol{E}_{\rm ext}(\boldsymbol{q},\omega). \quad (29.6.53)$$

Using (29.6.28) that relates the vector potential to the electric field we get

$$\boldsymbol{j}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\omega} \epsilon_{\mathrm{r}}(\boldsymbol{q},\omega) \left[P_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}} \right] \boldsymbol{E}(\boldsymbol{q},\omega) , \qquad (29.6.54)$$

from which

$$\sigma_{\parallel}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\omega} \epsilon_{\mathrm{r}}(\boldsymbol{q},\omega) \left[P_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}} \right].$$
(29.6.55)

The effect of screening appears in the factor $\epsilon_{\rm r}(\boldsymbol{q},\omega)$.

To get a simpler expression we rewrite the longitudinal conductivity in terms of the density–density response function. For that we multiply both sides of (29.6.52) by q, rewrite the left-hand side in terms of the number density, and express the vector potential on the right-hand side by the scalar potential using (29.6.47). This leads to

$$-e\omega \langle n(\boldsymbol{q},\omega) \rangle = \left[P_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\rm e}e^2}{m_{\rm e}} \right] \frac{q^2}{\omega} \varphi_{\rm ext}(\boldsymbol{q},\omega) \,. \tag{29.6.56}$$

On the other hand, the induced charge density and the external potential are related by the density-density response function $\Pi(q, \omega)$. Comparing the above expression with (29.1.24) we find

$$P_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\rm e}e^2}{m_{\rm e}} = \frac{\omega^2 e^2}{q^2} \Pi(\boldsymbol{q},\omega) \,. \tag{29.6.57}$$

This relationship can be readily checked alternatively by evaluating the response functions directly. Using (29.1.31) and (29.6.26) and

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$$\langle \Psi_n | \boldsymbol{q} \cdot \hat{\boldsymbol{j}}(\boldsymbol{q}) | \Psi_m \rangle = \frac{e}{\hbar} (E_n - E_m) \langle \Psi_n | n(\boldsymbol{q}) | \Psi_m \rangle$$
(29.6.58)

that follows from the continuity equation, we find

$$\frac{\omega^2 e^2}{q^2} \Pi(\boldsymbol{q}, \omega) - P_{\parallel}(\boldsymbol{q}, \omega) = \frac{e^2}{\hbar^2 q^2} \frac{1}{V} \sum_{mn} \left(\frac{e^{-\beta E_n}}{Z} - \frac{e^{-\beta E_m}}{Z} \right)$$
(29.6.59)

$$\times \left(\hbar \omega + E_m - E_n \right) \left| \langle \Psi_n | n(\boldsymbol{q}) | \Psi_m \rangle \right|^2$$
$$= \frac{e^2}{\hbar^2 q^2} \frac{1}{V} \sum_{mn} 2 \frac{e^{-\beta E_n}}{Z} (E_m - E_n) \left| \langle \Psi_n | n(\boldsymbol{q}) | \Psi_m \rangle \right|^2.$$

On the other hand, the dynamical structure factor $S(q, \omega)$ is known to satisfy the sum rule [see (J.2.20)]

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \omega S(\boldsymbol{q}, \omega) \mathrm{d}\omega = \frac{\hbar q^2}{2m_{\mathrm{e}}} \,. \tag{29.6.60}$$

Substituting the spectral representation (28.4.92) into this equation, we find

$$\frac{1}{\hbar N_{\rm e}} \sum_{mn} \frac{{\rm e}^{-\beta E_n}}{Z} (E_m - E_n) \left| \langle \Psi_n | n(\boldsymbol{q}) | \Psi_m \rangle \right|^2 = \frac{\hbar^2 q^2}{2m_{\rm e}} \,. \tag{29.6.61}$$

Combining this with (29.6.59) we in fact recover (29.6.57).

Inserting now (29.6.57) into (29.6.52) and using (29.6.28) valid for the longitudinal component, we find

$$\boldsymbol{j}(\boldsymbol{q},\omega) = -\frac{\omega^2 e^2}{q^2} \Pi(\boldsymbol{q},\omega) \boldsymbol{A}_{\text{ext}}(\boldsymbol{q},\omega) = -\frac{\omega^2 e^2}{q^2} \Pi(\boldsymbol{q},\omega) \epsilon_{\text{r}}(\boldsymbol{q},\omega) \boldsymbol{A}(\boldsymbol{q},\omega)$$
$$= \frac{\mathrm{i}\omega e^2}{q^2} \Pi(\boldsymbol{q},\omega) \epsilon_{\text{r}}(\boldsymbol{q},\omega) \boldsymbol{E}(\boldsymbol{q},\omega), \qquad (29.6.62)$$

from which we get

$$\sigma_{\parallel}(\boldsymbol{q},\omega) = \frac{\mathrm{i}\omega e^2}{q^2} \Pi(\boldsymbol{q},\omega) \epsilon_{\mathrm{r}} = \frac{\mathrm{i}\omega e^2}{q^2} \widetilde{\Pi}(\boldsymbol{q},\omega) \,. \tag{29.6.63}$$

When (29.6.41) is applied to the longitudinal component,

$$P_{\parallel}(\boldsymbol{q},\omega) = \widetilde{P}_{\parallel}(\boldsymbol{q},\omega) + \widetilde{S}_{\parallel}(\boldsymbol{q},\omega) \frac{4\pi\tilde{e}^2/q^2}{1 - (4\pi\tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)} \overline{\widetilde{S}}_{\parallel}(\boldsymbol{q},\omega) \,. \tag{29.6.64}$$

The longitudinal current–density response function appearing here can be expressed using the continuity equation via the density–density response. We readily find

$$S_{\parallel}(\boldsymbol{q},\omega) = -\frac{e\,\omega}{q}\Pi(\boldsymbol{q},\omega)\,. \tag{29.6.65}$$

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When it is written in terms of the irreducible parts, we have

$$S_{\parallel}(\boldsymbol{q},\omega) = \widetilde{S}_{\parallel}(\boldsymbol{q},\omega) + \widetilde{S}_{\parallel}(\boldsymbol{q},\omega) \frac{4\pi \tilde{e}^2/q^2}{1 - (4\pi \tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)} \widetilde{\Pi}(\boldsymbol{q},\omega)$$

$$= \frac{\widetilde{S}_{\parallel}(\boldsymbol{q},\omega)}{1 - (4\pi \tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)},$$
(29.6.66)

and hence

$$\widetilde{S}_{\parallel}(\boldsymbol{q},\omega) = -\frac{e\,\omega}{q}\widetilde{\Pi}(\boldsymbol{q},\omega)\,. \tag{29.6.67}$$

Similar relations hold for the density–current response function. To check them we have to recognize that

$$\overline{S}_{\alpha}(\boldsymbol{q},\omega) = S^*_{\alpha}(\boldsymbol{q},\omega)|_{\delta \to -\delta}, \qquad (29.6.68)$$

which follows from the spectral representations

$$S_{\alpha}(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \frac{\langle \Psi_n | \hat{j}_{\alpha}(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | n(-\boldsymbol{q}) | \Psi_n \rangle}{\hbar \omega - E_m + E_n + \mathrm{i}\delta}$$
(29.6.69)

and

$$\overline{S}_{\alpha}(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \frac{\langle \Psi_n | n(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | \hat{j}_{\alpha}(-\boldsymbol{q}) | \Psi_n \rangle}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} \,.$$
(29.6.70)

Since $\Pi(\pmb{q},\omega)$ itself satisfies the relation

$$\Pi(\boldsymbol{q},\omega) = \Pi^*(\boldsymbol{q},\omega)|_{\delta \to -\delta}, \qquad (29.6.71)$$

which can be best seen from the spectral representation in (29.1.31), we have

$$\overline{S}_{\parallel}(\boldsymbol{q},\omega) = -\frac{e\,\omega}{q}\Pi(\boldsymbol{q},\omega)\,. \tag{29.6.72}$$

When this is written in terms of the irreducible parts we find

$$\overline{S}_{\parallel}(\boldsymbol{q},\omega) = \overline{\widetilde{S}}_{\parallel}(\boldsymbol{q},\omega) + \widetilde{\Pi}(\boldsymbol{q},\omega) \frac{4\pi \tilde{e}^2/q^2}{1 - (4\pi \tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)} \overline{\widetilde{S}}_{\parallel}(\boldsymbol{q},\omega)
= \frac{\widetilde{S}_{\parallel}(\boldsymbol{q},\omega)}{1 - (4\pi \tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)},$$
(29.6.73)

and hence

$$\widetilde{\overline{S}}_{\parallel}(\boldsymbol{q},\omega) = -\frac{e\,\omega}{q}\widetilde{\Pi}(\boldsymbol{q},\omega)\,.$$
(29.6.74)

Combining these expressions with (29.6.64) we find

$$\widetilde{P}_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\rm e}e^2}{m_{\rm e}} = \frac{\omega^2 e^2}{q^2} \widetilde{\Pi}(\boldsymbol{q},\omega)$$

$$= \epsilon_{\rm r}(\boldsymbol{q},\omega) \left[P_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\rm e}e^2}{m_{\rm e}} \right],$$
(29.6.75)

which is equivalent to the statement that the longitudinal field is screened. When this relationship is used for the conductivity in (29.6.55) we get

$$\sigma_{\parallel}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\omega} \left[\widetilde{P}_{\parallel}(\boldsymbol{q},\omega) + \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}} \right].$$
(29.6.76)

Thus, indeed, it is the irreducible part of the current–current response that appears in the Kubo formula for the longitudinal conductivity.

29.6.4 Dielectric Tensor and Conductivity

It was mentioned in Chapter 16 that the conductivity and the dielectric constant are not independent of each other. Indeed (29.6.63) shows that the longitudinal conductivity can be expressed in terms of the irreducible density–density response function, which in turn is simply related to the dielectric function. We thus find

$$\epsilon_{\parallel \mathbf{r}}(\boldsymbol{q},\omega) = 1 + \frac{\mathrm{i}}{\epsilon_0 \omega} \sigma_{\parallel}(\boldsymbol{q},\omega) \,, \qquad (29.6.77)$$

which is exactly the relationship we have found in (16.1.64).

A similar equation holds for the transverse components. To derive it we combine Maxwell's first equation (Ampère's law) with Ohm's law. The Maxwell equation is written either as

$$\operatorname{curl} \boldsymbol{B} = \mu_0 \left(\epsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} + \boldsymbol{j} \right)$$
(29.6.78)

with the full electric-current density or as

$$\operatorname{curl} \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t} + \boldsymbol{j}_{\text{ext}},$$
 (29.6.79)

where only the external current appears on the right-hand side. The difference between the electric displacement and the electric field is due to the current j_{ind} induced by the electromagnetic field

$$\frac{\partial \boldsymbol{D}}{\partial t} = \epsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} + \boldsymbol{j}_{\text{ind}} \,. \tag{29.6.80}$$

Inserting (29.6.19) into (29.6.80) and using (29.1.5) we find

$$\epsilon_{\alpha\beta}(\boldsymbol{q},\omega) = \epsilon_0 \delta_{\alpha\beta} + \frac{\mathrm{i}}{\omega} \sigma_{\alpha\beta}(\boldsymbol{q},\omega) \,, \qquad (29.6.81)$$

which is nothing else than the generalization of (16.1.64). Thus the transverse component of the dielectric function and the transverse conductivity are related by

$$\epsilon_{\perp r}(\boldsymbol{q},\omega) = 1 + \frac{i}{\epsilon_0 \omega} \sigma_{\perp}(\boldsymbol{q},\omega) \,. \tag{29.6.82}$$

29.6.5 Transverse Dielectric Function of the Electron Gas

An explicit expression can be derived for the transverse dielectric function by substituting (29.6.29) into (29.6.81). When the spectral representation of the current–current response function is used,

$$\begin{aligned} \epsilon_{\alpha\beta}(\boldsymbol{q},\omega) &= \epsilon_0 \delta_{\alpha\beta} - \frac{1}{\omega^2} \left[P_{\alpha\beta}(\boldsymbol{q},\omega) + \frac{n_{\rm e}e^2}{m_{\rm e}} \delta_{\alpha\beta} \right] \\ &= \epsilon_0 \left(1 - \frac{\omega_{\rm p}}{\omega^2} \right) \delta_{\alpha\beta} + \frac{\mathrm{i}}{\omega^2} \frac{1}{V} \sum_{mn} \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \\ &\times \frac{\langle \Psi_n | \hat{j}_\alpha(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | \hat{j}_\beta(-\boldsymbol{q}) | \Psi_n \rangle}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} \,. \end{aligned}$$
(29.6.83)

Choosing the propagation vector q of the radiation field in the z-direction and calculating the response in the x-direction for free electrons, the transverse dielectric function has a form similar to the Lindhard function

$$\epsilon_{\perp r}(\boldsymbol{q},\omega) = 1 - \frac{\omega_{\rm p}^2}{\omega^2} - \frac{e^2}{\epsilon_0 m_{\rm e}^2 \omega^2} \frac{2}{V} \sum_{\boldsymbol{k}} \hbar^2 k_x^2 \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \,. \tag{29.6.84}$$

Comparison with (29.4.6) shows two differences between the formulas for the longitudinal and transverse components of the dielectric function. One is an extra term in the transverse component due to the diamagnetic current. The other is that the matrix element of the current appears in place of the dipole matrix element. We note that if the calculation is done for Bloch electrons, we find

$$\epsilon_{\perp \mathbf{r}}(\boldsymbol{q},\omega) = 1 - \frac{n_{\mathrm{e}}e^2}{\epsilon_0 m_{\mathrm{e}}\omega^2} - \frac{e^2}{\epsilon_0 m_{\mathrm{e}}^2\omega^2} \frac{2}{V} \sum_{\boldsymbol{k}nn'} \frac{f_0(\varepsilon_{n\boldsymbol{k}}) - f_0(\varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{n'\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{n\boldsymbol{k}} + \mathrm{i}\delta} \\ \times \left| \left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \right| \frac{1}{2} \left(p_x \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} + \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} p_x \right) \left| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle \right|^2, \qquad (29.6.85)$$

where the matrix element is

$$\left\langle \psi_{n'\boldsymbol{k}+\boldsymbol{q}}^{(0)} \middle| \frac{1}{2} \left(\boldsymbol{p} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} + \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \boldsymbol{p} \right) \middle| \psi_{n\boldsymbol{k}}^{(0)} \right\rangle = \frac{1}{v_0} \int_{v_0} u_{n'\boldsymbol{k}+\boldsymbol{q}}^*(\boldsymbol{r})$$

$$\times \left[\frac{\hbar}{\mathrm{i}} \boldsymbol{\nabla} + \hbar \boldsymbol{k} + \frac{1}{2} \hbar \boldsymbol{q} \right] u_{n,\boldsymbol{k}}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$

$$(29.6.86)$$

The transverse dielectric function can be calculated for free electrons in closed form. For the real part we have

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$$\epsilon_{1\perp}(\boldsymbol{q},\omega) = 1 - \frac{q_{\mathrm{TF}}^2}{q^2} \left\{ \frac{1}{8} \left(\frac{\hbar v_{\mathrm{F}} q}{\hbar \omega} \right)^2 \left[\left(\frac{\varepsilon_q}{\hbar v_{\mathrm{F}} q} \right)^2 + 3 \left(\frac{\hbar \omega}{\hbar v_{\mathrm{F}} q} \right)^2 + 1 \right] \quad (29.6.87)$$
$$- \frac{q}{4k_{\mathrm{F}}} \left(\frac{\varepsilon_{\mathrm{F}}}{\hbar \omega} \right)^2 \left(\left[1 - \left(\frac{\hbar \omega + \varepsilon_q}{\hbar v_{\mathrm{F}} q} \right)^2 \right] \ln \left(\frac{\hbar \omega + \hbar v_{\mathrm{F}} q + \varepsilon_q}{\hbar \omega - \hbar v_{\mathrm{F}} q + \varepsilon_q} \right) + \left[1 - \left(\frac{\hbar \omega - \varepsilon_q}{\hbar v_{\mathrm{F}} q} \right)^2 \right] \ln \left(\frac{\hbar \omega - \hbar v_{\mathrm{F}} q - \varepsilon_q}{\hbar \omega + \hbar v_{\mathrm{F}} q - \varepsilon_q} \right) \right\}.$$

The imaginary part is

$$\epsilon_{2\perp}(\boldsymbol{q},\omega) = \begin{cases} \frac{\pi}{4} \frac{\hbar v_{\mathrm{F}} q}{\hbar \omega} \frac{q_{\mathrm{TF}}^2}{q^2} \left[1 - \left(\frac{\hbar \omega}{\hbar v_{\mathrm{F}} q}\right)^2 - \left(\frac{\varepsilon_q}{\hbar v_{\mathrm{F}} q}\right)^2 \right] \\ \text{for} \quad 0 \le \hbar \omega < \hbar v_{\mathrm{F}} q - \varepsilon_q, \\ \\ \frac{\pi}{4} \frac{q}{k_{\mathrm{F}}} \left(\frac{\varepsilon_{\mathrm{F}}}{\hbar \omega}\right)^2 \left[1 - \left(\frac{\hbar \omega - \varepsilon_q}{\hbar v_{\mathrm{F}} q}\right)^2 \right] \frac{q_{\mathrm{TF}}^2}{q^2} \\ \text{for} \quad \hbar v_{\mathrm{F}} q - \varepsilon_q \le \hbar \omega \le \hbar v_{\mathrm{F}} q + \varepsilon_q, \\ \\ 0 \qquad \text{for} \qquad \hbar v_{\mathrm{F}} q + \varepsilon_q \le \hbar \omega, \end{cases}$$
(29.6.88)

if $q < 2k_{\rm F}$, while for $q > 2k_{\rm F}$

$$\epsilon_{2\perp}(\boldsymbol{q},\omega) = \begin{cases} 0 & \text{for} \quad 0 \le \hbar\omega < \varepsilon_q - \hbar v_{\rm F} q, \\ \frac{\pi}{4} \frac{k_{\rm F}}{q} \left(\frac{\varepsilon_{\rm F}}{\hbar\omega}\right)^2 \left[1 - \left(\frac{\hbar\omega - \varepsilon_q}{\hbar v_{\rm F} q}\right)^2\right] \frac{q_{\rm TF}^2}{q^2} \\ & \text{for} \quad \varepsilon_q - \hbar v_{\rm F} q \le \hbar\omega \le \varepsilon_q + \hbar v_{\rm F} q, \\ 0 & \text{for} \quad \varepsilon_q + \hbar v_{\rm F} q \le \hbar\omega . \end{cases}$$
(29.6.89)

29.7 Optical and DC Conductivity

The formulas derived above will now be applied to calculate the conductivity in two special cases, at optical frequencies and in the limit $\omega = 0$, to get the optical and the DC conductivity, respectively.

29.7.1 Optical Conductivity

Since the momentum transfer during the emission or absorption of an optical photon is much less than the typical momenta of electrons in solids, the relevant quantities in the description of optical properties are the $q \to 0$ limits of the dielectric function and the conductivity. The real part of the quantity

$$\sigma_{\perp}(\omega) = \lim_{\boldsymbol{q} \to 0} \sigma_{\perp}(\boldsymbol{q}, \omega) \tag{29.7.1}$$

is called *optical conductivity*. It characterizes the response of the electron system to an electromagnetic radiation of frequency ω . From the spectral representation of the Kubo formula [see (29.6.33)] we find

$$\operatorname{Re} \sigma_{\perp}(\omega) = \frac{\pi}{\omega} \left(1 - e^{-\beta\omega}\right) \frac{1}{V} \sum_{mn} \frac{e^{-\beta E_n}}{Z} \left| \left\langle \Psi_n \right| \hat{j}_x |\Psi_m \rangle \right|^2 \delta(\hbar\omega - E_m + E_n) \,.$$
(29.7.2)

This form allows a simple physical interpretation of the optical conductivity: It is the power absorbed from the electromagnetic field at frequency ω .

An alternative, much used form of the Kubo formula, can be derived for the q = 0 component in uniform systems, if the current is written as the time derivative of the operator

$$\boldsymbol{Q} = -e\sum_{i} \boldsymbol{r}_{i} \,, \qquad (29.7.3)$$

since

$$\dot{\boldsymbol{Q}} = \frac{\mathrm{i}}{\hbar} [\mathcal{H}_0, \boldsymbol{Q}]_- = -\frac{e}{m_{\mathrm{e}}} \sum_i \boldsymbol{p}_i = \hat{\boldsymbol{j}}. \qquad (29.7.4)$$

Using this in (29.6.30) we find

$$\sigma_{\alpha\beta}(\omega) = \frac{1}{\hbar\omega} \frac{1}{V} \int_{0}^{\infty} dt \, \mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \frac{\mathrm{d}}{\mathrm{d}t} \Big\langle \left[Q_{\alpha}(t), \hat{j}_{\beta}(0)\right]_{-} \Big\rangle + \frac{\mathrm{i}n_{\mathrm{e}}e^{2}}{m_{\mathrm{e}}\omega} \delta_{\alpha\beta} \,, \qquad (29.7.5)$$

which after integration by parts yields

$$\sigma_{\alpha\beta}(\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \left\langle \left[Q_{\alpha}(t), \hat{j}_{\beta}(0)\right]_{-} \right\rangle - \frac{1}{\hbar\omega} \frac{1}{V} \left\langle \left[Q_{\alpha}(0), \hat{j}_{\beta}(0)\right]_{-} \right\rangle + \frac{\mathrm{i}n_{\mathrm{e}}e^{2}}{m_{\mathrm{e}}\omega} \delta_{\alpha\beta} \,.$$

$$(29.7.6)$$

Making use of the canonical commutation relations we find

$$\left[Q_{\alpha}(0), \hat{j}_{\beta}(0)\right]_{-} = \frac{i\hbar e^2 N_{\rm e}}{m_{\rm e}}.$$
(29.7.7)

Hence the second and third terms cancel each other exactly. The thermal average in the first term can be written in terms of the equilibrium density matrix $\rho_0 = e^{-\beta \mathcal{H}}/Z$ of the unperturbed system. After a cyclic permutation of the operators in the trace

$$\sigma_{\alpha\beta}(\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \, \mathrm{Tr}\left(\rho_0 \left[Q_\alpha(t), \hat{j}_\beta(0)\right]_{-}\right) = \frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \, \mathrm{Tr}\left(\left[Q_\alpha(t), \rho_0\right]_{-} \hat{j}_\beta(0)\right).$$
(29.7.8)

This expression can be further manipulated by using the operator identity

$$e^{\beta \mathcal{H}_{0}} \mathcal{A}(t) e^{-\beta \mathcal{H}_{0}} - \mathcal{A}(t) = \frac{1}{\hbar} \int_{0}^{\beta \hbar} d\lambda e^{\lambda \mathcal{H}_{0}/\hbar} [\mathcal{H}_{0}, \mathcal{A}(t)]_{-} e^{-\lambda \mathcal{H}_{0}/\hbar}$$

$$= \frac{1}{\hbar} \int_{0}^{\beta \hbar} d\lambda [\mathcal{H}_{0}, \mathcal{A}(t - i\lambda)]_{-}, \qquad (29.7.9)$$

which is equivalent to

$$\left[\mathcal{A}(t),\rho_{0}\right]_{-}=-\mathrm{i}\rho_{0}\int_{0}^{\beta\hbar}\mathrm{d}\lambda\dot{\mathcal{A}}(t-\mathrm{i}\lambda)\,,\qquad(29.7.10)$$

where $\dot{\mathcal{A}}$ denotes the time derivative of \mathcal{A} . Applying this transformation in (29.7.8) and taking into account that the derivative of \boldsymbol{Q} is the current, we find

$$\sigma_{\alpha\beta}(\omega) = \frac{1}{\hbar} \frac{1}{V} \int_{0}^{\infty} dt \int_{0}^{\beta\hbar} d\lambda \, \mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \left\langle \hat{j}_{\alpha}(t-\mathrm{i}\lambda)\hat{j}_{\beta}(0) \right\rangle, \qquad (29.7.11)$$

or after a rearrangement of the operators

$$\sigma_{\alpha\beta}(\omega) = \frac{1}{\hbar} \frac{1}{V} \int_{0}^{\infty} dt \int_{0}^{\beta\hbar} d\lambda \, \mathrm{e}^{\mathrm{i}(\omega+\mathrm{i}\delta)t} \left\langle \hat{j}_{\beta}(-\mathrm{i}\lambda)\hat{j}_{\alpha}(t) \right\rangle. \tag{29.7.12}$$

29.7.2 Optical Conductivity of the Electron Gas

We note that in the long-wavelength $(q \rightarrow 0)$ limit, when there is no preferred direction in an isotropic system, the longitudinal and transverse components of the dielectric function and of the conductivity become identical,

$$\epsilon_{\parallel}(0,\omega) = \epsilon_{\perp}(0,\omega) \quad \text{and} \quad \sigma_{\parallel}(0,\omega) = \sigma_{\perp}(0,\omega). \quad (29.7.13)$$

We will therefore use the expressions derived for the longitudinal component of the conductivity tensor given in (29.6.63), although, strictly speaking, the optical conductivity is related to the transverse response. In the RPA $\tilde{\Pi}$ is replaced with Π_0 . Looking at (29.2.46) we see that

$$\Pi_0(\boldsymbol{q},\omega) = \frac{2}{V} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}}) \frac{2(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}})}{(\hbar\omega + \mathrm{i}\delta)^2 - (\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}})^2}, \qquad (29.7.14)$$

from which in the $v_{\rm F}q \ll \omega$ limit we obtain

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$$\Pi_0(\boldsymbol{q},\omega) \approx \frac{n_{\rm e}q^2}{m_{\rm e}\omega^2}.$$
(29.7.15)

Inserting this expression into (29.6.63) gives

$$\sigma(\omega) = i \frac{n_e e^2}{m_e \omega} \,. \tag{29.7.16}$$

As it stands, a purely imaginary conductivity with no real part cannot be true; it does not satisfy the Kramers–Kronig relations. Assuming that the above form is valid for the imaginary part, the Kramers–Kronig relations give vanishing real part at nonzero frequencies, but a finite, singularly large value at $\omega = 0$:

$$\operatorname{Re}\sigma(\omega) = \pi \frac{n_{\rm e}e^2}{m_{\rm e}}\delta(\omega). \qquad (29.7.17)$$

This sharp peak in the real part of the conductivity is the Drude peak. The real and imaginary parts can be combined into the expression

$$\sigma(\omega) = i \frac{n_e e^2}{m_e(\omega + i\delta)}.$$
(29.7.18)

One can show that this expression is valid more generally whenever scattering by lattice vibrations or by impurities can be neglected, and only the electron– electron interaction is taken into account since then energy is not dissipated in the system.

The finite lifetime of electron states due to scattering by impurities or lattice vibrations will modify this situation. According to (29.2.89) $\tilde{\Pi}$ can be approximated by

$$\widetilde{\Pi}(\boldsymbol{q},\omega) = \frac{n_{\rm e}q^2}{m_{\rm e}\omega(\omega+{\rm i}/\tau)}\,,\tag{29.7.19}$$

which leads to the result known from the Drude model

$$\sigma(\omega) = i \frac{n_e e^2}{m_e(\omega + i/\tau)} = \frac{n_e e^2 \tau}{m_e(1 - i\omega\tau)}$$
(29.7.20)

and

$$\operatorname{Re}\sigma(\omega) = \frac{n_{\rm e}e^2\tau}{m_{\rm e}} \frac{1}{1+(\omega\tau)^2} = \frac{\sigma_0}{1+(\omega\tau)^2} \,. \tag{29.7.21}$$

The Drude peak is broadened by the scattering processes, the width is proportional to $1/\tau$, and the optical conductivity decays as $1/\omega^2$ for high frequencies:

$$\operatorname{Re}\sigma(\omega) \approx \frac{n_{\mathrm{e}}e^2}{m_{\mathrm{e}}\omega^2\tau}$$
. (29.7.22)

This form of frequency-dependent conductivity satisfies the $\mathit{conductivity}\ sum$ rule

$$\int_{0}^{\infty} d\omega \operatorname{Re} \sigma(\omega) = \frac{\pi n_{e} e^{2}}{2m_{e}}$$
(29.7.23)

derived in (J.2.11).

When a more realistic band structure is considered, photons can be absorbed or emitted in association with interband transitions in the electron system. Thus, as has been discussed in Chapter 25, the imaginary part of the dielectric function and hence the optical conductivity gives information about the joint density of states of the bands between which the transition takes place. The Van Hove singularities of the joint density of states produce sharp structures in $\sigma(\omega)$. Similar sharp features may appear in the dielectric function and optical conductivity at frequencies corresponding to the absorption or emission of optical phonons. Nevertheless, the optical *f*-sum rule has to be satisfied.

Note that if the transverse response is studied, the contribution given in (29.7.16) and hence the Drude peak arises from the diamagnetic term. Its contribution to the real part of the conductivity is singular and proportional to $\delta(\omega)$, even when scattering processes are taken into account. This singularity is, however, unphysical. By considering the properties of the irreducible current-current response function one can show that its real part cancels exactly the contribution of the diamagnetic term in the $\omega \to 0$ limit, and the imaginary part is proportional to ω . This then leads to a finite conductivity even at $\omega = 0$.

29.7.3 DC Conductivity

The DC conductivity is obtained by taking the limit $\mathbf{q} \to 0$ first and the limit $\omega \to 0$ afterward in (29.6.33).⁹ Using the relationship

$$\lim_{\omega \to 0} \frac{1}{\omega} \left(1 - e^{-\beta\hbar\omega} \right) = \beta\hbar, \qquad (29.7.24)$$

we have

$$\operatorname{Re} \sigma_{\alpha\beta} = \frac{1}{2k_{\mathrm{B}}T} \frac{1}{V} \int_{-\infty}^{\infty} \mathrm{d}t \left\langle \hat{j}_{\alpha}(t)\hat{j}_{\beta} \right\rangle$$

$$= \frac{\pi\hbar}{k_{\mathrm{B}}T} \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_{n}}}{Z} \left\langle \Psi_{n} \right| \hat{j}_{\alpha} \left| \Psi_{m} \right\rangle \left\langle \Psi_{m} \right| \hat{j}_{\beta} \left| \Psi_{n} \right\rangle \delta(E_{m} - E_{n}) \,.$$

$$(29.7.25)$$

⁹ We note that the order of the limits is different when the static dielectric constant or the static magnetic susceptibility is calculated. The limit $\omega \to 0$ has to be performed first for finite q, and only after that we can take the limit $q \to 0$. Otherwise the Lindhard function gives zero, because the number of particles and the magnetization are conserved quantities.
Although (29.7.25) is a seemingly simple expression, the explicit calculation of the conductivity using this formula is not easy and has only been done in a few simple cases. The difficulties, which are related to the fact that it does not suffice to carry out the calculations in some low orders of perturbation theory, can be readily seen when scattering by impurities is considered.

According to the lowest order Born approximation the inverse collision time is proportional to the absolute square of the matrix element of the scattering potential $V_{\rm imp}$:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} n_{\rm i} \rho(\varepsilon_{\rm F}) \left| V_{\rm imp} \right|^2, \qquad (29.7.26)$$

where n_i is the concentration of impurities. Thus, a second-order calculation of the current–current response would give a conductivity that is inversely proportional to the collision time. We know, however, that according to the celebrated Drude formula

$$\sigma = \frac{n_{\rm e}e^2\tau}{m_{\rm e}} \tag{29.7.27}$$

the conductivity is proportional to the collision time of electrons. This result can be obtained in a perturbative treatment of the response function only if the contribution of the scattering processes are summed up to infinite order. A partial summation can be achieved by including a finite lifetime for the propagating electrons and holes when calculating the current–current response function. This approximation corresponds to taking into account the so-called self-energy corrections, but neglecting the processes that would directly or indirectly couple the electron and the hole. When the form

$$G^{\rm R}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \varepsilon_{\boldsymbol{k}} + \mathrm{i}\hbar/2\tau}$$
(29.7.28)

is used for the retarded Green function, we obtain

$$\widetilde{P}_{\alpha\alpha} = -\frac{n_{\rm e}}{m_{\rm e}} \frac{1}{1 - \mathrm{i}\omega/\tau} \tag{29.7.29}$$

for the response function. This would yield a Drude-like expression for the conductivity with this τ as the relaxation time. This result is, however, still not correct. To describe the contribution of the scattering processes to the conductivity properly, the so-called vertex corrections have to be taken into account as well. To understand their role we recall that the correct expression for the conductivity contains the so-called transport relaxation time, which differs from the usual lifetime of electrons. The scattering processes are weighted by a factor $1 - \cos \theta$, where θ is the change in the direction of the scattered electron, when the transport relaxation time is calculated. This factor takes into account the effectiveness of losing current due to scattering.

29.7.4 The Kubo–Greenwood Formula

A more convenient, simpler, and, in some cases, more easily applicable expression can be obtained by the following considerations: We neglect the diamagnetic term since it gives contribution only to the imaginary part and

$$\hat{\boldsymbol{j}} = -e \frac{\hbar}{\mathrm{i}m_{\mathrm{e}}V} \sum_{i=1}^{N_{\mathrm{e}}} \boldsymbol{\nabla}_i$$
(29.7.30)

is used for the current operator, while the interaction with the electromagnetic field is expressed in terms of the electric field instead of the vector potential in the form

$$\mathcal{H}_{\text{ext}} = -\frac{\hbar e}{m_{\text{e}}\omega} \sum_{i=1}^{N_{\text{e}}} \boldsymbol{E} \cdot \boldsymbol{\nabla}_{i} \,. \tag{29.7.31}$$

To calculate the expectation value of the current we start from

$$\boldsymbol{j} = \langle \hat{\boldsymbol{j}} \rangle = \operatorname{Tr} \{ \rho^{(1)} \hat{\boldsymbol{j}} \},$$
 (29.7.32)

where $\rho^{(1)}$ is the first-order correction to the density matrix due to the interaction with the electromagnetic field. According to (J.1.35)

$$\rho^{(1)}(t) = \frac{i}{\hbar} \int_{-\infty}^{t} e^{-i\mathcal{H}_{0}(t-t')/\hbar} [\rho_{0}, \mathcal{H}_{ext}(t')]_{e} e^{i\mathcal{H}_{0}(t-t')/\hbar} dt'.$$
(29.7.33)

The trace in (29.7.32) is evaluated using a complete set of many-body eigenstates $|\Psi_n\rangle$. Insertion of a complete set of intermediate states gives

$$\boldsymbol{j} = \sum_{mn} \langle \Psi_n | \hat{\boldsymbol{j}} | \Psi_m \rangle \langle \Psi_m | \rho^{(1)} | \Psi_n \rangle .$$
(29.7.34)

The matrix elements of the current are obtained from (29.7.30), while the matrix elements of the density matrix can be evaluated using (29.7.33). For its temporal Fourier transform we find

$$\langle \Psi_m | \rho^{(1)} | \Psi_n \rangle = \left(\frac{\mathrm{e}^{-\beta E_n}}{Z} - \frac{\mathrm{e}^{-\beta E_m}}{Z} \right) \frac{\langle \Psi_m | \mathcal{H}_{\mathrm{ext}} | \Psi_n \rangle}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} \,. \tag{29.7.35}$$

In the one-electron approximation the many-body states are Slater determinants built up from single-particle functions φ_n of energy ε_n . The real part of the conductivity then takes the form

$$\operatorname{Re} \sigma_{\alpha\beta} = \frac{\pi e^2 \hbar^2}{m_e^2 \omega} \frac{1}{V} \sum_{mn} \left[f_0(\varepsilon_m) - f_0(\varepsilon_n) \right]$$

$$\times \langle \varphi_n | \nabla_\alpha | \varphi_m \rangle \langle \varphi_m | \nabla_\beta | \varphi_n \rangle \delta(\varepsilon_m - \varepsilon_n - \hbar \omega) ,$$
(29.7.36)

where f_0 is the Fermi distribution function. Assuming that the matrix element can be approximated by an average matrix element depending only on the energy of the state, the summation over the states can be converted to an integral over energy where the density of states appears in the integrand:

$$\operatorname{Re} \sigma_{\alpha\beta} = \frac{\pi e^2 \hbar^2}{m_{\rm e}^2 \omega} \int \mathrm{d}\varepsilon \,\rho(\varepsilon)\rho(\varepsilon + \hbar\omega) \left[f_0(\varepsilon + \hbar\omega) - f_0(\varepsilon) \right] \\ \times \langle \varphi_{\varepsilon} | \nabla_{\alpha} | \varphi_{\varepsilon + \hbar\omega} \rangle \langle \varphi_{\varepsilon + \hbar\omega} | \nabla_{\beta} | \varphi_{\varepsilon} \rangle \,.$$

$$(29.7.37)$$

In the static, $\omega \to 0$ limit, the difference between the Fermi distribution functions is replaced by the derivative $\partial f_0 / \partial \varepsilon$. Finally, in isotropic systems, the DC conductivity can be written in the form

$$\sigma = -\int \sigma_{\varepsilon}(0) \frac{\partial f_0}{\partial \varepsilon} \,\mathrm{d}\varepsilon \,, \qquad (29.7.38)$$

where

$$\sigma_{\varepsilon}(0) = \frac{\pi e^2 \hbar^2}{m_{\rm e}^2} \left[\rho(\varepsilon) \right]^2 \left| \left\langle \varphi_{\varepsilon} \left| \frac{\partial}{\partial x} \right| \varphi_{\varepsilon} \right\rangle \right|^2.$$
(29.7.39)

This is the Kubo–Greenwood formula.¹⁰ Besides the density of states the conductivity is determined by the matrix element of the operator $\partial/\partial x$. As expected on physical grounds and expressed mathematically by the factor $-\partial f_0/\partial \varepsilon$, only electrons lying in the neighborhood of the Fermi energy in a range of width $k_{\rm B}T$ contribute to the integral. Thus it suffices to know the wavefunction of states near the Fermi energy.

The situation is different in semiconductors. The states responsible for conduction are at the bottom of the conduction band or at the top of the valence band, typically much farther away from the chemical potential than $k_{\rm B}T$, i.e., $\varepsilon - \mu \gg k_{\rm B}T$ for electrons in the conduction band. In this limit classical statistics can be used instead of Fermi statistics and

$$\frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \approx -\frac{f_0(\varepsilon)}{k_{\rm B}T} \,. \tag{29.7.40}$$

The conductivity can then be written in the form

$$\sigma = e \int \mu(\varepsilon) n(\varepsilon) \,\mathrm{d}\varepsilon \,, \qquad (29.7.41)$$

where

$$\mu(\varepsilon) = \frac{\sigma_{\varepsilon}(0)}{ek_{\rm B}T\rho(\varepsilon)} \tag{29.7.42}$$

is the mobility and

$$n(\varepsilon) = \rho(\varepsilon) f_0(\varepsilon) \tag{29.7.43}$$

¹⁰ D. A. Greenwood, 1958.

is the density of electrons. If σ_{ε} vanishes for $\varepsilon < \varepsilon_{\rm c}$, and this is the case for extrinsic *n*-type semiconductors, there are no mobile charge carriers below the conduction band. The conductivity then has an activated form

$$\sigma \approx \sigma_{\varepsilon_c} \mathrm{e}^{-(\varepsilon_c - \mu)/k_{\mathrm{B}}T} \,. \tag{29.7.44}$$

A similar activated form is obtained for disordered systems if the electron states near the Fermi energy are localized and do not contribute to the conduction.

29.8 Response to Magnetic Perturbations

The external perturbations considered until now couple identically to electrons of both spin orientations and give rise to a change in the electronic density or generate a current. An external magnetic field couples to the magneticmoment density acting oppositely on electrons of opposite spin and results in a net magnetization when the field is homogeneous in space. For weak enough disturbance the response to the magnetic field is linear in the field strength, and the proportionality factor is the magnetic susceptibility. Because this response depends on the internal dynamics of the system, the magnetic susceptibility, like the dielectric function, is sensitive to the electron–electron interaction. We will first calculate how, in a simple Hubbard model of interacting electrons, the Pauli susceptibility is modified by this interaction. Then the dynamical susceptibility will be studied. Finally, the Ruderman–Kittel oscillations, the magnetic analog of the Friedel oscillations, will be considered.

29.8.1 Stoner Enhancement of the Susceptibility

The dielectric response of the electron gas was calculated analytically for electrons moving in a uniform neutralizing background, interacting with each other by Coulomb repulsion. In this model, as will be seen in Chapter 30, magnetic fluctuations are weak at the usual metallic densities. Magnetic instability may appear only at very low densities, for large values of r_s . To get a more realistic picture of the magnetic properties of metals we should consider electrons in d or f states rather than free electrons. Such electrons can reasonably be described in the tight-binding approximation, and a Hubbard-like model may be more appropriate. We will therefore study the influence of electron–electron interaction on the susceptibility in the Hubbard model.

The Hartree–Fock theory of the Hubbard model was presented in the previous chapter. We saw that the quasiparticle energies are

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + U\langle n_{-\sigma} \rangle, \qquad (29.8.1)$$

where the average number of particles with spin σ and per unit volume has to be determined self-consistently from 126 29 Electronic Response to External Perturbations

$$\langle n_{\sigma} \rangle = \frac{1}{V} \sum_{\boldsymbol{k}} \langle n_{\boldsymbol{k}\sigma} \rangle = \frac{1}{V} \sum_{\boldsymbol{k}} f_0(\tilde{\varepsilon}_{\boldsymbol{k}\sigma}) \,.$$
 (29.8.2)

When an external field H is applied, an additional spin-dependent shift appears in the single-particle energies. Choosing the quantization axis in the direction of the field, the quasiparticle energies are modified to

$$\widetilde{\varepsilon}_{\boldsymbol{k}\uparrow} = \varepsilon_{\boldsymbol{k}} + U\langle n_{\downarrow}\rangle - \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}H, \quad \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow} = \varepsilon_{\boldsymbol{k}} + U\langle n_{\uparrow}\rangle + \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}H, \quad (29.8.3)$$

where the densities $\langle n_{\uparrow} \rangle$ and $\langle n_{\downarrow} \rangle$ have to be determined self-consistently for a fixed total electron density

$$n_{\rm e} = \frac{N_{\rm e}}{V} = \langle n_{\uparrow} \rangle + \langle n_{\downarrow} \rangle \,. \tag{29.8.4}$$

The magnetization is obtained from the difference of the number of particles with up- and down-spin orientations:

$$M = \frac{1}{2} g_{e} \mu_{B} \left[\langle n_{\uparrow} \rangle - \langle n_{\downarrow} \rangle \right] = \frac{1}{2} g_{e} \mu_{B} \frac{1}{V} \sum_{\boldsymbol{k}} \left[\langle n_{\boldsymbol{k}\uparrow} \rangle - \langle n_{\boldsymbol{k}\downarrow} \rangle \right]$$

$$= \frac{1}{2} g_{e} \mu_{B} \frac{1}{V} \sum_{\boldsymbol{k}} \left[f_{0}(\tilde{\varepsilon}_{\boldsymbol{k}\uparrow}) - f_{0}(\tilde{\varepsilon}_{\boldsymbol{k}\downarrow}) \right].$$
(29.8.5)

For weak magnetic fields the Fermi distribution functions can be expanded to linear order in the energy correction yielding

$$M = \frac{1}{2} g_{\rm e} \mu_{\rm B} \frac{1}{V} \sum_{\boldsymbol{k}} \frac{\partial f_0(\varepsilon_{\boldsymbol{k}})}{\partial \varepsilon_{\boldsymbol{k}}} \left[U \langle n_{\downarrow} \rangle - \frac{1}{2} g_{\rm e} \mu_{\rm B} \mu_0 H - U \langle n_{\uparrow} \rangle - \frac{1}{2} g_{\rm e} \mu_{\rm B} \mu_0 H \right].$$
(29.8.6)

Replacing the summation by an integral, we find

$$M = \frac{1}{2} g_{\rm e} \mu_{\rm B} \int \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \left[U \langle n_{\downarrow} \rangle - U \langle n_{\uparrow} \rangle - g_{\rm e} \mu_{\rm B} \mu_0 H \right] \rho_{\sigma}(\varepsilon) \,\mathrm{d}\varepsilon \,, \qquad (29.8.7)$$

where $\rho_{\sigma}(\varepsilon)$ is the density of states for one spin orientation. At low temperatures, where the thermal corrections in the Sommerfeld expansion can be neglected, the leading term gives

$$M = -\frac{1}{2}g_{\rm e}\mu_{\rm B} \left[U\langle n_{\downarrow} \rangle - U\langle n_{\uparrow} \rangle - g_{\rm e}\mu_{\rm B}\mu_0 H \right] \rho_{\sigma}(\varepsilon_{\rm F}) \,. \tag{29.8.8}$$

The quantity $\langle n_{\uparrow} \rangle - \langle n_{\downarrow} \rangle$ on the right-hand side can be expressed by the magnetization using (29.8.5). We then find

$$M = U\rho_{\sigma}(\varepsilon_{\rm F})M + \frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\rho_{\sigma}(\varepsilon_{\rm F})H, \qquad (29.8.9)$$

from which

$$M = \frac{\frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\rho_{\sigma}(\varepsilon_{\rm F})}{1 - U\rho_{\sigma}(\varepsilon_{\rm F})}H.$$
(29.8.10)

The susceptibility is then

$$\chi = \frac{\frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\rho_{\sigma}(\varepsilon_{\rm F})}{1 - U\rho_{\sigma}(\varepsilon_{\rm F})}.$$
(29.8.11)

The expression in the numerator is just the Pauli susceptibility of the freeelectron gas derived in (16.2.113). Coulomb repulsion gives rise to its increase through the factor $S = 1/[1 - U\rho_{\sigma}(\varepsilon_{\rm F})]$ which is known as the *Stoner en*hancement factor.¹¹

The unpolarized, paramagnetic state, where $\tilde{\epsilon}_{\mathbf{k}\uparrow} = \tilde{\epsilon}_{\mathbf{k}\downarrow}$ and $\langle n_{\uparrow} \rangle = \langle n_{\downarrow} \rangle$, is stable without external magnetic field, if $U\rho_{\sigma}(\varepsilon_{\rm F}) < 1$. The Stoner factor is positive and the susceptibility is indeed enhanced. When the interaction is strong enough or the density of states is large, the paramagnetic state becomes unstable even without external magnetic field. A polarized, ferromagnetic state may appear in which the equality of the number of electrons with opposite spin orientations is broken spontaneously. The condition $U\rho_{\sigma}(\varepsilon_{\rm F}) = 1$ obtained for this transition in the mean-field approximation is, however, only a rough estimate. Transition to a homogeneous magnetic state cannot so easily occur when correlations between electrons are taken into account. Without going into these details we will study the properties of the broken-symmetry state in Chapter 33.

Materials in which the symmetry is not broken spontaneously but $U\rho_{\sigma}(\varepsilon_{\rm F})$ is close to the instability threshold are of particular interest. Being close to the threshold where the system becomes ferromagnetic, these metals are called *nearly ferromagnetic*. As indicated by the large Stoner enhancement factor, magnetic fluctuations are strongly enhanced in them and they give rise to modifications in the thermodynamic properties (e.g., the temperature dependence of the specific heat) compared to ordinary metals. Among the elemental metals platinum and palladium fall into this class. The best estimate for palladium is $U\rho_{\sigma}(\varepsilon_{\rm F}) \approx 0.9$.

29.8.2 Dynamical Susceptibility

Having determined the static susceptibility we now turn to the problem where a weak, spatially and temporarily varying magnetic field $\boldsymbol{H}_{\text{ext}}(\boldsymbol{r},t)$ is applied to the system in addition to a stronger uniform, static magnetic field H. The uniform field shifts the one-particle energies of up- and down-spin electrons oppositely and gives rise to a spatially uniform magnetization. We will study how the magnetization is modified by the weak oscillating field.

Assuming that the weak field can be treated as a perturbation, the perturbation Hamiltonian is

¹¹ E. C. STONER, 1938.

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$$\mathcal{H}_{1}(t) = -\mu_{0} \int \boldsymbol{H}_{\text{ext}}(\boldsymbol{r}, t) \cdot \boldsymbol{m}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}$$

$$= -\frac{\mu_{0}}{V} \sum_{\boldsymbol{q}} \boldsymbol{H}_{\text{ext}}(\boldsymbol{q}, t) \cdot \boldsymbol{m}(-\boldsymbol{q}) , \qquad (29.8.12)$$

where $\boldsymbol{m}(\boldsymbol{r})$ is the operator of the magnetic-moment density, its expectation value is the local magnetization, and $\boldsymbol{m}(\boldsymbol{q})$ is its Fourier transform. For simplicity we assume that the perturbing field varies in space and time with wave vector \boldsymbol{q} and frequency $\boldsymbol{\omega}$. In response to this perturbation a magnetization component appears that has the same wave vector and frequency:

$$\langle \boldsymbol{m}(\boldsymbol{q},\omega) \rangle = \chi(\boldsymbol{q},\omega) \boldsymbol{H}_{\mathrm{ext}}(\boldsymbol{q},\omega),$$
 (29.8.13)

where $\chi(\mathbf{q}, \omega)$ is the dynamical susceptibility. It follows from linear response theory that apart from a factor μ_0 the components of the susceptibility tensor are the temporal Fourier transforms of the magnetization–magnetization response function:

$$\chi_{\alpha\beta}(\boldsymbol{q},t-t') = \frac{\mathrm{i}}{\hbar} \mu_0 \theta(t-t') \frac{1}{V} \left\langle \left[m^{\alpha}(\boldsymbol{q},t), m^{\beta}(-\boldsymbol{q},t') \right]_{-} \right\rangle.$$
(29.8.14)

This equation is the analog of the relationship between the electrical polarizability and the density–density response function.

Choosing the weak frequency-dependent field in the same (z) direction as the uniform field, the parallel (longitudinal) susceptibility is defined by

$$\chi_{\parallel}(\boldsymbol{q},\omega) = \frac{\langle m^{z}(\boldsymbol{q},\omega)\rangle}{H_{\mathrm{ext}}^{z}(\boldsymbol{q},\omega)}.$$
(29.8.15)

This response function is obtained by using the z-component of the magneticmoment density in (29.8.14):

$$\chi_{\parallel}(\boldsymbol{q},t-t') = \frac{\mathrm{i}}{\hbar} \mu_0 \theta(t-t') \frac{1}{V} \left\langle \left[m^z(\boldsymbol{q},t), m^z(-\boldsymbol{q},t') \right]_{-} \right\rangle.$$
(29.8.16)

When the spin density is used instead of the magnetic-moment density, we have $(\tilde{z}(x_{1}))$

$$\chi_{\parallel}(\boldsymbol{q},\omega) = \frac{g_{\mathrm{e}}\mu_{\mathrm{B}}\langle s^{z}(\boldsymbol{q},\omega)\rangle}{H_{\mathrm{ext}}^{z}(\boldsymbol{q},\omega)},$$
(29.8.17)

and accordingly

$$\chi_{\parallel}(\boldsymbol{q},\omega) = g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \Sigma_{\parallel}(\boldsymbol{q},\omega) \,, \qquad (29.8.18)$$

where $\Sigma_{\parallel}(\boldsymbol{q},\omega)$ is the Fourier transform of the spin-density response function:

$$\Sigma_{\parallel}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')-\delta(t-t')} \frac{1}{V} \left\langle \left[s^{z}(\boldsymbol{q},t), s^{z}(-\boldsymbol{q},t') \right]_{-} \right\rangle.$$
(29.8.19)

The magnetization–magnetization response function is a retarded Green function and as such it can be calculated using the methods of many-body theory. In principle, one should sum up all processes to all orders of perturbation theory. Here we will apply the much simpler equation-of-motion method described in Appendix J. We will study how the expectation value of $s^{z}(\boldsymbol{q},\omega)$ changes due to the external perturbation.

If the magnetization is written in second-quantized form using (H.2.62), its Fourier transform is

$$\boldsymbol{m}(\boldsymbol{q}) = \frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \sum_{\boldsymbol{k}\alpha\beta} c^{\dagger}_{\boldsymbol{k}\alpha} \boldsymbol{\sigma}_{\alpha\beta} c_{\boldsymbol{k}+\boldsymbol{q}\beta} , \qquad (29.8.20)$$

where σ is the Pauli matrix and the spin density is

$$\boldsymbol{s}(\boldsymbol{q}) = \frac{1}{2} \sum_{\boldsymbol{k}\alpha\beta} c^{\dagger}_{\boldsymbol{k}\alpha} \boldsymbol{\sigma}_{\alpha\beta} c_{\boldsymbol{k}+\boldsymbol{q}\beta} \,. \tag{29.8.21}$$

The component along the quantization axis is

$$s^{z}(\boldsymbol{q},t) = \frac{1}{2} \left[n_{\uparrow}(\boldsymbol{q},t) - n_{\downarrow}(\boldsymbol{q},t) \right]$$

=
$$\frac{1}{2} \sum_{\boldsymbol{k}} \left[c^{\dagger}_{\boldsymbol{k}\uparrow}(t) c_{\boldsymbol{k}+\boldsymbol{q}\uparrow}(t) - c^{\dagger}_{\boldsymbol{k}\downarrow}(t) c_{\boldsymbol{k}+\boldsymbol{q}\downarrow}(t) \right].$$
(29.8.22)

The equation of motion will be written separately for $n_{\uparrow}(q,t)$ and $n_{\downarrow}(q,t)$ using

$$\mathcal{H}_{1} = -\frac{1}{2}g_{e}\mu_{B}\mu_{0}\frac{1}{V}\sum_{\boldsymbol{k}\boldsymbol{q}}H^{z}_{ext}(\boldsymbol{q},t)\left[c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}c_{\boldsymbol{k}\uparrow} - c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\downarrow}c_{\boldsymbol{k}\downarrow}\right]$$
(29.8.23)

as perturbation.

If, for the sake of simplicity, the on-site Coulomb repulsion of the Hubbard model is used to describe the interaction between electrons, then

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}+\varepsilon_{\boldsymbol{k}\uparrow}\right)c_{\boldsymbol{k}\uparrow}^{\dagger}(t) = -\frac{U}{V}\sum_{\boldsymbol{k}'\boldsymbol{q}'}c_{\boldsymbol{k}+\boldsymbol{q}'\uparrow}^{\dagger}(t)c_{\boldsymbol{k}'-\boldsymbol{q}'\downarrow}(t)c_{\boldsymbol{k}'\downarrow}(t) \quad (29.8.24)$$
$$+\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\frac{1}{V}\sum_{\boldsymbol{q}'}H_{\mathrm{ext}}^{z}(\boldsymbol{q}',t)c_{\boldsymbol{k}+\boldsymbol{q}'\uparrow}^{\dagger}(t),$$

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}+\varepsilon_{\boldsymbol{k}\downarrow}\right)c_{\boldsymbol{k}\downarrow}^{\dagger}(t) = -\frac{U}{V}\sum_{\boldsymbol{k}'\boldsymbol{q}'}c_{\boldsymbol{k}+\boldsymbol{q}'\downarrow}^{\dagger}(t)c_{\boldsymbol{k}'-\boldsymbol{q}'\uparrow}(t)c_{\boldsymbol{k}'\uparrow}(t) \quad (29.8.25)$$
$$-\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\frac{1}{V}\sum_{\boldsymbol{q}'}H_{\mathrm{ext}}^{z}(\boldsymbol{q}',t)c_{\boldsymbol{k}+\boldsymbol{q}'\downarrow}^{\dagger}(t),$$

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$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t} - \varepsilon_{\mathbf{k}+\mathbf{q}\uparrow}\right)c_{\mathbf{k}+\mathbf{q}\uparrow}(t) = \frac{U}{V}\sum_{\mathbf{k}'\mathbf{q}'}c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\downarrow}(t)c_{\mathbf{k}'\downarrow}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\uparrow}(t) \ (29.8.26)$$
$$-\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\frac{1}{V}\sum_{\mathbf{q}'}H^{z}_{\mathrm{ext}}(\mathbf{q}',t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\uparrow}(t) \ ,$$

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t} - \varepsilon_{\mathbf{k}+\mathbf{q}\downarrow}\right)c_{\mathbf{k}+\mathbf{q}\downarrow}(t) = \frac{U}{V}\sum_{\mathbf{k}'\mathbf{q}'}c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\uparrow}(t)c_{\mathbf{k}'\uparrow}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\downarrow}(t) \ (29.8.27)$$
$$+\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\frac{1}{V}\sum_{\mathbf{q}'}H^{z}_{\mathrm{ext}}(\mathbf{q}',t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\downarrow}(t) \ .$$

These equations can be linearized if the product $c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma}(t)c_{\mathbf{k}'\sigma}(t)$ appearing on the right-hand side in the terms containing three operators is replaced with its expectation value. In doing so we have to take into account that the quantity $\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma}(t)c_{\mathbf{k}'\sigma}(t)\rangle$ is finite only if $\mathbf{q}' = 0$ or \mathbf{q}' is equal to the wave vector of the external perturbing field. The term with $\mathbf{q}' = 0$ gives the Hartree correction of the one-particle energies. That is why $\tilde{\varepsilon}_{\mathbf{k}\sigma}$ and $\tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\sigma}$ appear in the equations below instead of $\varepsilon_{\mathbf{k}\sigma}$ and $\varepsilon_{\mathbf{k}+\mathbf{q}\sigma}$. By a change of variables $\mathbf{k}' \to \mathbf{k}' + \mathbf{q}$ in the summation and combining the above equations we find

$$\begin{pmatrix}
-\frac{\hbar}{i}\frac{d}{dt} - \tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\uparrow} + \tilde{\varepsilon}_{\mathbf{k}\uparrow} \\
= -\frac{U}{V}\sum_{\mathbf{k}'} \langle c_{\mathbf{k}'\downarrow}^{\dagger}(t)c_{\mathbf{k}+\mathbf{q}\downarrow}(t) \rangle [f_{0}(\tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\uparrow}) - f_{0}(\tilde{\varepsilon}_{\mathbf{k}\uparrow})] \\
+ \frac{1}{2}g_{e}\mu_{B}\mu_{0}H_{ext}^{z}(\mathbf{q},t)\frac{1}{V} [f_{0}(\tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\uparrow}) - f_{0}(\tilde{\varepsilon}_{\mathbf{k}\uparrow})], \\
\begin{pmatrix}
-\frac{\hbar}{i}\frac{d}{dt} - \tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\downarrow} + \tilde{\varepsilon}_{\mathbf{k}\downarrow} \\
V \\
= -\frac{U}{V}\sum_{\mathbf{k}'} \langle c_{\mathbf{k}'\uparrow}^{\dagger}(t)c_{\mathbf{k}'+\mathbf{q}\uparrow}(t) \rangle [f_{0}(\tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\downarrow}) - f_{0}(\tilde{\varepsilon}_{\mathbf{k}\downarrow})] \\
- \frac{1}{2}g_{e}\mu_{B}H_{ext}^{z}(\mathbf{q},t)\frac{1}{V} [f_{0}(\tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\downarrow}) - f_{0}(\tilde{\varepsilon}_{\mathbf{k}\downarrow})] .
\end{cases}$$
(29.8.28)
$$(29.8.29)$$

Dividing the temporal Fourier transform by the energy factor and summing over the momentum ${\boldsymbol k}$ gives

$$\langle n_{\uparrow}(\boldsymbol{q},\omega) \rangle = \left[\frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} H_{\mathrm{ext}}^{z}(\boldsymbol{q},\omega) - U \langle n_{\downarrow}(\boldsymbol{q},\omega) \rangle \right] \\ \times \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}) - f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}\uparrow})}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} + \widetilde{\varepsilon}_{\boldsymbol{k}\uparrow}}$$
(29.8.30)

and

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$$\langle n_{\downarrow}(\boldsymbol{q},\omega) \rangle = \left[-\frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} H_{\mathrm{ext}}^{z}(\boldsymbol{q},\omega) - U \langle n_{\uparrow}(\boldsymbol{q},\omega) \rangle \right]$$

$$\times \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\downarrow}) - f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}\downarrow})}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\downarrow} + \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow}} .$$

$$(29.8.31)$$

We introduce the notation

$$\Sigma_{0\sigma}(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_0(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\sigma}) - f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma})}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \widetilde{\varepsilon}_{\boldsymbol{k}\sigma}}.$$
 (29.8.32)

The solution of (29.8.30) and (29.8.31) then takes the form

$$\langle n_{\uparrow}(\boldsymbol{q},\omega) \rangle = \frac{\frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} \Sigma_{0\uparrow}(\boldsymbol{q},\omega) \left[1 + U \Sigma_{0\downarrow}(\boldsymbol{q},\omega) \right]}{1 - U^{2} \Sigma_{0\uparrow}(\boldsymbol{q},\omega) \Sigma_{0\downarrow}(\boldsymbol{q},\omega)} H^{z}_{\mathrm{ext}}(\boldsymbol{q},\omega) ,$$

$$\langle n_{\downarrow}(\boldsymbol{q},\omega) \rangle = -\frac{\frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} \Sigma_{0\downarrow}(\boldsymbol{q},\omega) \left[1 + U \Sigma_{0\uparrow}(\boldsymbol{q},\omega) \right]}{1 - U^{2} \Sigma_{0\uparrow}(\boldsymbol{q},\omega) \Sigma_{0\downarrow}(\boldsymbol{q},\omega)} H^{z}_{\mathrm{ext}}(\boldsymbol{q},\omega) ,$$

$$(29.8.33)$$

and the longitudinal susceptibility can be written as

$$\chi_{\parallel}(\boldsymbol{q},\omega) = \left(\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\right)^{2}\mu_{0}\left[\frac{\Sigma_{0\uparrow}(\boldsymbol{q},\omega)\left[1+U\Sigma_{0\downarrow}(\boldsymbol{q},\omega)\right]}{1-U^{2}\Sigma_{0\uparrow}(\boldsymbol{q},\omega)\Sigma_{0\downarrow}(\boldsymbol{q},\omega)} + \frac{\Sigma_{0\downarrow}(\boldsymbol{q},\omega)\left[1+U\Sigma_{0\uparrow}(\boldsymbol{q},\omega)\right]}{1-U^{2}\Sigma_{0\uparrow}(\boldsymbol{q},\omega)\Sigma_{0\downarrow}(\boldsymbol{q},\omega)}\right].$$
(29.8.34)

To interpret this result we rewrite the interaction with the perturbing magnetic field in terms of $n_{\sigma}(q)$:

$$\mathcal{H}_{1} = -\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\frac{1}{V}\sum_{\boldsymbol{q}}H_{\mathrm{ext}}^{z}(\boldsymbol{q},t)\left[n_{\uparrow}(-\boldsymbol{q})-n_{\downarrow}(-\boldsymbol{q})\right].$$
(29.8.35)

Since the magnetization is proportional to the difference of $n_{\uparrow}(q, \omega)$ and $n_{\downarrow}(q, \omega)$, the parallel susceptibility consists of four terms:

$$\chi_{\parallel}(\boldsymbol{q},\omega) = (\frac{1}{2}g_{\rm e}\mu_{\rm B})^2\mu_0 \big[\Sigma_{\uparrow\uparrow}(\boldsymbol{q},\omega) - \Sigma_{\uparrow\downarrow}(\boldsymbol{q},\omega) - \Sigma_{\downarrow\uparrow}(\boldsymbol{q},\omega) + \Sigma_{\downarrow\downarrow}(\boldsymbol{q},\omega) \big],$$
(29.8.36)

where

$$\Sigma_{\sigma\sigma'}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')-\delta(t-t')} \frac{1}{V} \Big\langle \big[n_{\sigma}(\boldsymbol{q},t), n_{\sigma'}(-\boldsymbol{q},t') \big]_{-} \Big\rangle.$$
(29.8.37)

These quantities are known already from the dielectric function. They are equal to the negative of the temporal Fourier transform of $\Pi_{\sigma\sigma'}(\boldsymbol{q},t-t')$ defined in (29.1.33):

$$\Sigma_{\sigma\sigma'}(\boldsymbol{q},\omega) = -\Pi_{\sigma\sigma'}(\boldsymbol{q},\omega). \qquad (29.8.38)$$

The \uparrow spin and \downarrow spin electrons contribute with equal weight to the density; therefore, the dielectric function contains the sum of the spin-resolved response

functions. On the other hand, they appear in (29.8.36) with signs depending on the spin orientation. The RPA for the density–density response function could be visualized (see Fig. 29.5) as an infinite series of diagrams containing consecutive polarization bubbles. When a similar approximation is made for the susceptibility, we have to take into account that the dielectric function was calculated for the spin-independent Coulomb repulsion, while here we consider a Hubbard model in which only electrons of opposite spins interact. Therefore, when the spin-resolved response function is calculated in the RPA for the Hubbard model and the propagation of the electron–hole pair is visualized by diagrams, the subsequent bubbles have to have opposite spin orientations as shown pictorially in Fig. 29.14.



Fig. 29.14. The simplest processes contributing to the longitudinal susceptibility

Owing to this spin restriction, the sum of the bubble series gives

$$\Sigma_{\uparrow\uparrow}(\boldsymbol{q},\omega) = \frac{\Sigma_{0\uparrow}(\boldsymbol{q},\omega)}{1 - U^2 \Sigma_{0\uparrow}(\boldsymbol{q},\omega) \Sigma_{0\downarrow}(\boldsymbol{q},\omega)}$$
(29.8.39)

and

$$\Sigma_{\uparrow\downarrow}(\boldsymbol{q},\omega) = \frac{-\Sigma_{0\uparrow}(\boldsymbol{q},\omega)U\Sigma_{0\downarrow}(\boldsymbol{q},\omega)}{1 - U^2\Sigma_{0\uparrow}(\boldsymbol{q},\omega)\Sigma_{0\downarrow}(\boldsymbol{q},\omega)}.$$
(29.8.40)

Summing up these expressions with the signs given in (29.8.36) we recover exactly the expression derived earlier for the longitudinal susceptibility. Thus the result of the equation-of-motion method is a straightforward extension of the renormalized RPA to the Hubbard model.

If the material is unpolarized, $\Sigma_{0\uparrow}$ and $\Sigma_{0\downarrow}$ are equal. Denoting their common value by Σ_0 , we have

$$\langle n_{\uparrow}(\boldsymbol{q},\omega)\rangle = -\langle n_{\downarrow}(\boldsymbol{q},\omega)\rangle = \frac{\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\Sigma_{0}(\boldsymbol{q},\omega)}{1 - U\Sigma_{0}(\boldsymbol{q},\omega)}H_{\mathrm{ext}}^{z}(\boldsymbol{q},\omega).$$
(29.8.41)

Thus we get

$$\langle m^{z}(\boldsymbol{q},\omega)\rangle = \frac{\frac{1}{2}g_{e}^{2}\mu_{B}^{2}\mu_{0}\Sigma_{0}(\boldsymbol{q},\omega)}{1 - U\Sigma_{0}(\boldsymbol{q},\omega)}H_{ext}^{z}(\boldsymbol{q},\omega)$$
(29.8.42)

for the z-component of the magnetic-moment density, and the longitudinal magnetic susceptibility becomes

$$\chi_{\parallel}(\boldsymbol{q},\omega) = \frac{\frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\Sigma_0(\boldsymbol{q},\omega)}{1 - U\Sigma_0(\boldsymbol{q},\omega)}.$$
(29.8.43)

When taking the limit $\omega \to 0$ first and then $q \to 0$, $\Sigma_0(0,0)$ is just the density of states for a single spin orientation. We then recover (29.8.11) derived for the static susceptibility. This expression can thus be considered as its generalization to the dynamical susceptibility.

Equation (29.8.43) for the susceptibility is formally very similar to the density-density response function (29.2.14) derived in the RPA. There is, however, an important difference. Π_0 appearing in the denominator of (29.2.14) is equal to the negative of the density of states in the static, long-wavelength limit. This is due to the sign difference in (29.8.38). Thus, the Coulomb repulsion leads to a weakening of density fluctuations, but enhances magnetic fluctuations. Charge fluctuations can be enhanced by attractive interactions. Such an interaction can be mediated between electrons by long-wavelength acoustic phonons, as we have seen in Chapter 23, and the enhanced density fluctuations may give rise to the formation of static charge-density waves. This will be further discussed in Chapter 33.

29.8.3 Transverse Dynamical Susceptibility

In certain resonance experiments the weak high-frequency field H_{ext} is perpendicular to the homogeneous magnetic field H. Choosing again the direction of the homogeneous field as the z-axis, it is convenient to use the linear combinations

$$H_{\text{ext}}^{\pm} = H_{\text{ext}}^{x} \pm \mathrm{i}H_{\text{ext}}^{y} \tag{29.8.44}$$

for the perturbing field. The magnetic-moment density and the spin density will be expressed similarly by the linear combinations

$$m^{\pm} = m^x \pm i m^y, \qquad s^{\pm} = s^x \pm i s^y, \qquad (29.8.45)$$

instead of the x- and y-components of the m and s operators. The Hamiltonian describing the interaction with the perturbing field is then

$$\begin{aligned} \mathcal{H}_{1}(t) &= -\frac{1}{2}\mu_{0}\frac{1}{V}\sum_{\boldsymbol{q}}\left[H_{\text{ext}}^{+}(\boldsymbol{q},t)m^{-}(-\boldsymbol{q}) + H_{\text{ext}}^{-}(\boldsymbol{q},t)m^{+}(-\boldsymbol{q})\right] \quad (29.8.46) \\ &= -\frac{1}{2}g_{\text{e}}\mu_{\text{B}}\mu_{0}\frac{1}{V}\sum_{\boldsymbol{q}}\left[H_{\text{ext}}^{+}(\boldsymbol{q},t)s^{-}(-\boldsymbol{q}) + H_{\text{ext}}^{-}(\boldsymbol{q},t)s^{+}(-\boldsymbol{q})\right] \\ &= -\frac{1}{2}g_{\text{e}}\mu_{\text{B}}\mu_{0}\frac{1}{V}\sum_{\boldsymbol{k}\boldsymbol{q}}\left[H_{\text{ext}}^{+}(\boldsymbol{q},t)c_{\boldsymbol{k}+\boldsymbol{q}\downarrow}^{\dagger}c_{\boldsymbol{k}\uparrow} + H_{\text{ext}}^{-}(\boldsymbol{q},t)c_{\boldsymbol{k}+\boldsymbol{q}\uparrow}^{\dagger}c_{\boldsymbol{k}\downarrow}\right],\end{aligned}$$

where we used the second-quantized expressions

$$s^{+}(\boldsymbol{q}) = \sum_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}+\boldsymbol{q}\downarrow}, \qquad s^{-}(\boldsymbol{q}) = \sum_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\downarrow} c_{\boldsymbol{k}+\boldsymbol{q}\uparrow}.$$
(29.8.47)

The response to the transverse field can be characterized by the transverse susceptibility:

$$\chi_{\perp}(\boldsymbol{q},\omega) = \frac{\langle m^{+}(\boldsymbol{q},\omega) \rangle}{H_{\mathrm{ext}}^{+}(\boldsymbol{q},\omega)} = \frac{g_{\mathrm{e}}\mu_{\mathrm{B}}\langle s^{+}(\boldsymbol{q},\omega) \rangle}{H_{\mathrm{ext}}^{+}(\boldsymbol{q},\omega)} \,.$$
(29.8.48)

To calculate the expectation value $\langle s^+(\boldsymbol{q},\omega)\rangle$ we use again the equation-ofmotion method. Here the quantity $\left\langle c^{\dagger}_{\boldsymbol{k}\uparrow}(t)c_{\boldsymbol{k}+\boldsymbol{q}\downarrow}(t)\right\rangle$ has to be studied. The equations for the creation and annihilation operators are

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}+\varepsilon_{\mathbf{k}\uparrow}\right)c^{\dagger}_{\mathbf{k}\uparrow}(t) = -\frac{U}{V}\sum_{\mathbf{k}'\mathbf{q}'}c^{\dagger}_{\mathbf{k}+\mathbf{q}'\uparrow}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\downarrow}(t)c_{\mathbf{k}'\downarrow}(t) \quad (29.8.49)$$
$$+\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\frac{1}{V}\sum_{\mathbf{q}'}H^{+}_{\mathrm{ext}}(\mathbf{q}',t)c^{\dagger}_{\mathbf{k}+\mathbf{q}'\downarrow}(t)$$

and

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t} - \varepsilon_{\mathbf{k}+\mathbf{q}\downarrow}\right)c_{\mathbf{k}+\mathbf{q}\downarrow}(t) = \frac{U}{V}\sum_{\mathbf{k}'\mathbf{q}'}c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\uparrow}(t)c_{\mathbf{k}'\uparrow}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\downarrow}(t) \ (29.8.50)$$
$$-\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\frac{1}{V}\sum_{\mathbf{q}'}H^{+}_{\mathrm{ext}}(\mathbf{q}',t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\uparrow}(t) \ .$$

When the three-operator terms are linearized (decoupled) by replacing the product of two operators by its expectation value, as was done in calculating the longitudinal susceptibility, these equations lead to

$$\langle s^+(\boldsymbol{q},\omega)\rangle = \left[\frac{1}{2}g_{\rm e}\mu_{\rm B}\mu_0 H_{\rm ext}^+(\boldsymbol{q},\omega) + U\langle s^+(\boldsymbol{q},\omega)\rangle\right]\Sigma_{\perp}^0(\boldsymbol{q},\omega),$$
 (29.8.51)

where

$$\Sigma_{\perp}^{0}(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}) - f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}\downarrow})}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} + \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow}}.$$
(29.8.52)

The solution of this equation yields

$$\left\langle s^{+}(\boldsymbol{q},\omega)\right\rangle = \frac{\frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\Sigma_{\perp}^{0}(\boldsymbol{q},\omega)}{1-U\Sigma_{\perp}^{0}(\boldsymbol{q},\omega)}H_{\mathrm{ext}}^{+}(\boldsymbol{q},\omega),\qquad(29.8.53)$$

from which we find

$$\chi_{\perp}(\boldsymbol{q},\omega) = \frac{\frac{1}{2}g_{e}^{2}\mu_{B}^{2}\mu_{0}\Sigma_{\perp}^{0}(\boldsymbol{q},\omega)}{1 - U\Sigma_{\perp}^{0}(\boldsymbol{q},\omega)}$$
(29.8.54)

for the transverse susceptibility. This quantity will be considered in Chapter 33 when spin-density fluctuations will be studied. Notice that this expression is identical to that obtained earlier for the longitudinal susceptibility when the system is unpolarized.

It is interesting to see which processes contribute to the transverse susceptibility in this approximation. For that we recall that according to linear response theory the transverse susceptibility is the temporal Fourier transform of the retarded response function

$$\chi_{\perp}(\boldsymbol{q}, t - t') = \frac{1}{2}\mu_0 \frac{\mathrm{i}}{\hbar} \theta(t - t') \frac{1}{V} \left\langle \left[m^+(\boldsymbol{q}, t), m^-(-\boldsymbol{q}, t') \right]_- \right\rangle.$$
(29.8.55)

When the spin density is used instead of the magnetic moment, we have

$$\chi_{\perp}(\boldsymbol{q},\omega) = \frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\Sigma_{\perp}(\boldsymbol{q},\omega)\,,\qquad(29.8.56)$$

where

$$\Sigma_{\perp}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')-\delta(t-t')} \frac{1}{V} \Big\langle \big[s^{+}(\boldsymbol{q},t), s^{-}(-\boldsymbol{q},t')\big]_{-} \Big\rangle.$$
(29.8.57)

When s^+ and s^- are written in the second-quantized form, one sees that this response function describes the propagation of an electron-hole pair with opposite spins. The electron and the hole created at time t' interact with each other and with the other electrons of the Fermi sea before being annihilated at time t. The susceptibility derived from the equation of motion is just the contribution of the processes shown diagrammatically in Fig. 29.15, when the series is continued up to infinity. Since the analytic contributions of these diagrams form a geometric progression, the summed-up form is easily obtained.



Fig. 29.15. The simplest processes taken into account in the transverse susceptibility

29.8.4 Ruderman–Kittel Oscillations

We know from Chapter 16 and from our earlier discussions in this chapter that a charged impurity distorts the electron states around itself. The external charge is fully screened in metals by the accumulated charge density. The spatial oscillations of this decaying charge density are called Friedel oscillations. Similar spatial oscillations may appear in the spin density of electrons when the impurity has a magnetic moment, as mentioned already in Chapter 14. We rederive here this oscillating spin density.

We saw in Chapter 24, in connection with the Kondo effect, that the interaction between conduction electrons and localized magnetic moments (spins) of a magnetic impurity can be described by the so-called s-d interaction. When a single localized moment is placed into the system at the origin and the quantization axis is in the z-direction, then

$$\mathcal{H}_{s-d} = -J\hat{\psi}^{\dagger}_{\alpha}(0)\boldsymbol{S}\cdot\boldsymbol{\sigma}_{\alpha\beta}\hat{\psi}_{\beta}(0) \tag{29.8.58}$$
$$= -\frac{J}{V}\sum_{\boldsymbol{k}\boldsymbol{k}'} \left[S^{+}c^{\dagger}_{\boldsymbol{k}'\downarrow}c_{\boldsymbol{k}\uparrow} + S^{-}c^{\dagger}_{\boldsymbol{k}'\uparrow}c_{\boldsymbol{k}\downarrow} + S^{z} \left(c^{\dagger}_{\boldsymbol{k}'\uparrow}c_{\boldsymbol{k}\uparrow} - c^{\dagger}_{\boldsymbol{k}'\downarrow}c_{\boldsymbol{k}\downarrow} \right) \right].$$

Let us assume that the system of electrons is in thermal equilibrium, the charge and spin densities are homogeneous, and the localized spin is originally in state $|M\rangle$ for which $S^z|M\rangle = M|M\rangle$. We are interested in the modification of the electronic wavefunction and the spatial distribution of the spin density around the localized spin. Technically it is easier to determine this spatial variation of the spin density than to derive the Friedel oscillations in the charge density since the interaction with the magnetic impurities is short ranged, while the Coulomb interaction is long ranged.

The wavefunction of the perturbed electron system can be written in Slater-determinant form, where the single-particle states are perturbed plane waves obtained by taking the interaction with the localized spin into account. If the electron has wave vector \mathbf{k} and spin \uparrow , and the localized spin is in state $|M\rangle$, the unperturbed state is

$$|\boldsymbol{k}\uparrow, M\rangle = c_{\boldsymbol{k}\uparrow}^{\dagger}|0\rangle|M\rangle, \qquad (29.8.59)$$

where $|0\rangle$ denotes the vacuum of electrons. This state will be mixed by the s-d interaction to states $|\mathbf{k}'\sigma', M'\rangle$ in which both the wave vector and the spin of the electron as well as the orientation of the impurity spin can differ from that in the initial state. In first order of perturbation theory, the perturbed wavefunction is

$$|\boldsymbol{k}\uparrow, M\rangle^{(1)} = |\boldsymbol{k}\uparrow, M\rangle + \sum_{\boldsymbol{k}'\sigma'} |\boldsymbol{k}'\sigma', M'\rangle \frac{\langle \boldsymbol{k}'\sigma', M'| \mathcal{H}_{\text{s-d}} |\boldsymbol{k}\uparrow, M\rangle}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}'}}.$$
 (29.8.60)

There is no summation over M'; it cannot be chosen arbitrarily, because the z-component of the total spin is conserved. Taking the matrix elements of the interaction Hamiltonian we find

$$|\boldsymbol{k}\uparrow, M\rangle^{(1)} = |\boldsymbol{k}\uparrow, M\rangle - \frac{1}{V} \sum_{\boldsymbol{k}'} \frac{J}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}'}} \left[\langle M+1|S^+|M\rangle |\boldsymbol{k}'\downarrow, M+1 \rangle + \langle M|S^z|M\rangle |\boldsymbol{k}'\uparrow, M\rangle \right].$$
(29.8.61)

Similarly

$$|\boldsymbol{k}\downarrow, M\rangle^{(1)} = |\boldsymbol{k}\downarrow, M\rangle - \frac{1}{V} \sum_{\boldsymbol{k}'} \frac{J}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}'}} \left[\langle M - 1 | S^- | M \rangle | \boldsymbol{k}' \uparrow, M - 1 \rangle - \langle M | S^z | M \rangle | \boldsymbol{k}' \downarrow, M \rangle \right].$$
(29.8.62)

In an isotropic system, where the unperturbed states are plane waves, we obtain

$$|\boldsymbol{k}\uparrow, M\rangle^{(1)} = \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}|\uparrow, M\rangle - \frac{J}{V^{3/2}} \sum_{\boldsymbol{k}'} \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}}}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}'}}$$
(29.8.63)
$$\times \left[\langle M+1|S^+|M\rangle|\downarrow, M+1\rangle + \langle M|S^z|M\rangle|\uparrow, M\rangle \right]$$

and

$$|\boldsymbol{k}\downarrow, M\rangle^{(1)} = \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}|\downarrow, M\rangle - \frac{J}{V^{3/2}} \sum_{\boldsymbol{k}'} \frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}}}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}'}}$$
(29.8.64)
$$\times \left[\langle M - 1|S^{-}|M\rangle|\uparrow, M - 1\rangle - \langle M|S^{z}|M\rangle|\downarrow, M\rangle \right].$$

The integration over k' can be done using (C.1.66) yielding

$$|\boldsymbol{k}\uparrow, M\rangle^{(1)} = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}|\uparrow, M\rangle - \frac{1}{\sqrt{V}} \frac{m_{e}J\cos kr}{2\pi r\hbar^{2}}$$
(29.8.65)
$$\times \left(\sqrt{S(S+1) - M(M+1)}|\downarrow, M+1\rangle + M|\uparrow, M\rangle\right)$$

and

$$|\boldsymbol{k}\downarrow, M\rangle^{(1)} = \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}|\downarrow, M\rangle - \frac{1}{\sqrt{V}} \frac{m_{\mathrm{e}}J\cos kr}{2\pi r\hbar^{2}}$$
(29.8.66)
$$\times \left(\sqrt{S(S+1) - M(M-1)}|\uparrow, M-1\rangle - M|\downarrow, M\rangle\right).$$

The density due to electrons occupying these states is obtained by calculating the quantities ${}^{(1)}\langle M, \mathbf{k} \uparrow | \mathbf{k} \uparrow, M \rangle^{(1)}$ and ${}^{(1)}\langle M, \mathbf{k} \downarrow | \mathbf{k} \downarrow, M \rangle^{(1)}$. We find

$$n_{\uparrow}(\boldsymbol{k},\boldsymbol{r}) = \frac{1}{V} \left[1 - \frac{m_{\rm e}J\cos kr}{\pi r\hbar^2} M\cos(\boldsymbol{k}\cdot\boldsymbol{r}) \right],$$

$$n_{\downarrow}(\boldsymbol{k},\boldsymbol{r}) = \frac{1}{V} \left[1 + \frac{m_{\rm e}J\cos kr}{\pi r\hbar^2} M\cos(\boldsymbol{k}\cdot\boldsymbol{r}) \right].$$
(29.8.67)

The total density of the up- and down-spin electrons is obtained by summing the contribution of all occupied states. At temperature T = 0, this is equivalent to integrating over all k vectors inside the Fermi sphere. This gives

$$n_{\uparrow}(r) = \frac{k_{\rm F}^3}{6\pi^2} \left[1 + \frac{6m_{\rm e}JMk_{\rm F}}{\pi\hbar^2} g(2k_{\rm F}r) \right],$$

$$n_{\downarrow}(r) = \frac{k_{\rm F}^3}{6\pi^2} \left[1 - \frac{6m_{\rm e}JMk_{\rm F}}{\pi\hbar^2} g(2k_{\rm F}r) \right],$$
(29.8.68)

where g(x) is the decaying oscillatory function given in (29.3.24).

This shows that the localized moment perturbs the spatial distribution of conduction electrons in such a way that the number density $n(r) = n_{\uparrow}(r) + n_{\downarrow}(r)$, and hence the charge density, remains uniform, but a spatially varying spin density $\sigma(r) = n_{\uparrow}(r) - n_{\downarrow}(r)$ appears in the originally unpolarized system. This spin density oscillates in space and decays with the third power of the distance from the impurity. These oscillations are known as the Ruderman–Kittel oscillations. The periodicity of the oscillations, their wavelength λ , is determined by the relation $2k_{\rm F}\lambda = 2\pi$. As has been mentioned already and derived in Appendix I, this oscillating-induced spin density gives rise to the spatially oscillating RKKY interaction between magnetic moments placed at a distance r in a metal.

The results derived above are modified at finite temperatures for two reasons. On the one hand, the Fermi distribution function is smeared out over an interval of width $k_{\rm B}T$ around the Fermi energy, and this leads to a factor $\exp(-\pi k_{\rm F} r k_{\rm B} T/\varepsilon_{\rm F})$ in the charge distribution. On the other hand, an extra factor $\exp(-r/l)$ may appear due to the finite mean free path l of electrons.

This oscillating spin density around a magnetic impurity can be observed experimentally, e.g., in the shift of the resonance frequency of nuclear magnetic resonance.

Further Reading

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Cohesive Energy of the Electron System

When the types of bonds that hold solids together were discussed in Chapter 4, only a few sentences were devoted to the metallic bond. It was emphasized that this type of bond can be understood only if electron–electron interactions are taken into account. After the study of a few simple consequences of these interactions in the previous chapters we can now turn to the problem of the cohesive energy of metals. The total binding energy is the sum of electronic and ionic contributions. Here we will consider the portion due to electrons.

We will first treat an electron gas moving in a uniform positive background. Then we present the density-functional theory which can be used to calculate the cohesive energy of real metals.

30.1 Total Energy of the Dense Electron Gas

According to the rules of quantum mechanics the total energy of the electron system is obtained from

$$E = \frac{\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \qquad (30.1.1)$$

where $|\Psi_0\rangle$ is the ground-state wavefunction. If the interaction can be treated in perturbation theory, the contributions of the most important interaction processes have to be summed up. We will see that the perturbative approach gives convergent result only for the dense electron gas.

30.1.1 Total Energy in the Hartree–Fock Approximation

We know from Chapter 28 that there is no self-energy correction to the oneparticle energies if the homogeneous electron gas is treated in the Hartree approximation since the interaction with the homogeneous background precisely cancels the q = 0 component of the electron–electron interaction. The total energy is the sum of the energies of the filled one-particle states. In the

J. Sólyom, Fundamentals of the Physics of Solids, DOI 10.1007/978-3-642-04518-9 3, © Springer-Verlag Berlin Heidelberg 2010 ground state of an unpolarized electron gas, where the k vectors of the occupied states fill the Fermi sphere of radius $k_{\rm F}$ and each state is doubly occupied with electrons of both spin orientations, the total energy of the electron system is

$$E_{\rm H} = 2 \sum_{|\mathbf{k}| < k_{\rm F}} \frac{\hbar^2 k^2}{2m_{\rm e}} = 2 \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| < k_{\rm F}} \frac{\hbar^2 k^2}{2m_{\rm e}} \,\mathrm{d}\mathbf{k} \,. \tag{30.1.2}$$

The integration gives

$$E_{\rm H} = 2 \frac{V}{(2\pi)^3} \int_0^{k_{\rm F}} \frac{\hbar^2 k^2}{2m_{\rm e}} 4\pi k^2 \,\mathrm{d}k = \frac{V}{\pi^2} \frac{\hbar^2}{2m_{\rm e}} \frac{k_{\rm F}^5}{5} \,. \tag{30.1.3}$$

By the use of (16.2.24) that relates the Fermi wave number to the number $N_{\rm e}$ of electrons we have

$$E_{\rm H} = N_{\rm e} \frac{3}{5} \frac{\hbar^2 k_{\rm F}^2}{2m_{\rm e}} = N_{\rm e} \frac{3}{5} \varepsilon_{\rm F} \,. \tag{30.1.4}$$

The average energy of electrons filling the Fermi sphere is three-fifths of the Fermi energy. When the Fermi wave number is expressed in terms of the Wigner–Seitz radius r_0 using (16.2.31) and then by the dimensionless $r_s = r_0/a_0$, we get

$$\varepsilon_{\rm F} = \frac{(9\pi/4)^{2/3}}{r_{\rm s}^2} \frac{\hbar^2}{2m_{\rm e}a_0^2} = \frac{8.029}{r_{\rm s}^2} \times 10^{-18} \,{\rm J}\,.$$
 (30.1.5)

If the electron volt is used as the unit of energy, $\varepsilon_{\rm F}=50.112/r_{\rm s}^2\,{\rm eV}$ and

$$\frac{E_{\rm H}}{N_{\rm e}} = \frac{30.067}{r_{\rm s}^2} \,\text{eV}\,. \tag{30.1.6}$$

Quite often the cohesive energy of the electron system is given in rydberg $(1 \text{ Ry} = \tilde{e}^2/2a_0)$ or – using atomic units – in hartree $(1 E_{\rm h} = \tilde{e}^2/a_0)$. Since the energy per particle can be written with the help of (28.3.86) in the form

$$\frac{E_{\rm H}}{N_{\rm e}} = \frac{3}{5} \frac{\tilde{e}^2}{2a_0} \left(k_{\rm F} a_0\right)^2, \qquad (30.1.7)$$

we find

$$\frac{E_{\rm H}}{N_{\rm e}} = \frac{3}{5} \left(\frac{(9\pi/4)^{1/3} a_0}{r_0} \right)^2 \frac{\tilde{e}^2}{2a_0} = \frac{1.105}{r_{\rm s}^2} \frac{\tilde{e}^2}{a_0} \,. \tag{30.1.8}$$

In the Hartree–Fock approximation, where exchange gives rise to a selfenergy correction, the total energy is not equal to the sum of the energies of quasiparticles. The interaction modifies the energy of both interacting partners, but this correction has to appear in the total energy only once. It follows from (28.3.71) that in the homogeneous electron gas

$$E_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \widetilde{\varepsilon}_{\boldsymbol{k}\sigma} f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}) + \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma} U(\boldsymbol{k}' - \boldsymbol{k}) f_0(\widetilde{\varepsilon}_{\boldsymbol{k}'\sigma}) f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma})$$

$$= \sum_{\boldsymbol{k}\sigma} \widetilde{\varepsilon}_{\boldsymbol{k}\sigma} f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}) + \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} U(\boldsymbol{q}) f_0(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q},\sigma}) f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}), \qquad (30.1.9)$$

where the Fermi function f_0 gives the occupation probability of the quasiparticle state, and \mathbf{k}' was replaced with $\mathbf{k} + \mathbf{q}$ in the second line. The second term on the right-hand side corrects the double counting of the contribution due to the interaction.

To evaluate the total energy, it is more convenient to use (28.3.70), where the Hartree–Fock energy is given in terms of the bare electron energies. The quasiparticles fill the same Fermi sphere as without interaction, so we have

$$E_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} f_0(\varepsilon_{\boldsymbol{k}\sigma}) - \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} U(\boldsymbol{q}) f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q},\sigma}) f_0(\varepsilon_{\boldsymbol{k}\sigma}) \,. \tag{30.1.10}$$

The summation over k in the second term goes over the overlapping region of two displaced Fermi spheres. The integration over k and then over q can be carried out using (C.2.34) and (16.2.24) for Coulomb interaction and we get

$$E_{\rm HF} = N_{\rm e} \left[\frac{3}{5} \varepsilon_{\rm F} - \frac{3}{4\pi} \tilde{e}^2 k_{\rm F} \right].$$
 (30.1.11)

When the dimensionless parameter r_s characterizing the density of the electron gas is used instead of the Fermi energy and Fermi momentum, we find

$$\frac{E_{\rm HF}}{N_{\rm e}} = \left[\frac{30.067}{r_{\rm s}^2} - \frac{12.467}{r_{\rm s}}\right] \,\text{eV}\,. \tag{30.1.12}$$

The correction compared to the Hartree approximation is called *exchange* energy. When both terms are expressed in the atomic energy unit \tilde{e}^2/a_0 , we have

$$\frac{E_{\rm HF}}{N_{\rm e}} = \frac{\tilde{e}^2}{2a_0} \left[\frac{3}{5} \left(k_{\rm F} a_0 \right)^2 - \frac{3}{2\pi} \left(k_{\rm F} a_0 \right) \right]
= \left[\frac{1.105}{r_{\rm s}^2} - \frac{0.458}{r_{\rm s}} \right] \frac{\tilde{e}^2}{a_0}.$$
(30.1.13)

The dependence on $r_{\rm s}$ of the total energy per particle is displayed in Fig. 30.1.

The total electronic energy has a minimum at $r_{\rm s} = 4.825$ and its value is $-0.0475 \,\tilde{e}^2/a_0$. This is the first indication that metallic bonding exists. The system of electrons can be in thermal equilibrium at a finite density notwithstanding the Coulomb repulsion provided that the entire system is neutral; the charge of electrons is compensated by a positive background. The equilibrium value of $r_{\rm s}$ is reasonably close to the value calculated from the number of conduction electrons and the lattice constant for alkali metals as seen from Table 16.6.



Fig. 30.1. $r_{\rm s}$ dependence of the energy per particle in the Hartree–Fock approximation

30.1.2 The Exchange Potential

The previous considerations are valid for a uniform electron gas. The calculation is much more difficult in the inhomogeneous case. We know that if the Fock term in the Hartree–Fock equations is written in terms of an exchange potential, this potential is nonlocal, and the energy correction due to exchange can be calculated only approximately. A simple approximation scheme was proposed by J. C. SLATER in 1951. For this he rewrote the Fock term

$$-\tilde{e}^{2}\sum_{j=1}^{N_{e}}\int \mathrm{d}\boldsymbol{r}'\frac{\phi_{\lambda_{j}}^{*}(\boldsymbol{r}')\phi_{\lambda_{i}}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\phi_{\lambda_{j}}(\boldsymbol{r})$$
(30.1.14)

of the Hartree–Fock equations given in (28.3.36) in the equivalent form

$$-\tilde{e}^{2} \frac{\sum_{j=1}^{N_{\mathrm{e}}} \int \mathrm{d}\boldsymbol{r}' \phi_{\lambda_{i}}^{*}(\boldsymbol{r}) \phi_{\lambda_{i}}(\boldsymbol{r}') \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \phi_{\lambda_{j}}^{*}(\boldsymbol{r}') \phi_{\lambda_{j}}(\boldsymbol{r})}{\phi_{\lambda_{i}}^{*}(\boldsymbol{r}) \phi_{\lambda_{i}}(\boldsymbol{r})} \phi_{\lambda_{i}}(\boldsymbol{r}) \qquad (30.1.15)$$

and proposed to approximate the effective, nonlocal potential felt by an electron in orbital λ_i , the factor multiplying $\phi_{\lambda_i}(\mathbf{r})$ in the Hartree–Fock equations,

$$-\tilde{e}^{2}\frac{\sum_{j=1}^{N_{e}}\int \mathrm{d}\mathbf{r}'\phi_{\lambda_{i}}^{*}(\mathbf{r})\phi_{\lambda_{i}}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{\lambda_{j}}^{*}(\mathbf{r}')\phi_{\lambda_{j}}(\mathbf{r})}{\phi_{\lambda_{i}}^{*}(\mathbf{r})\phi_{\lambda_{i}}(\mathbf{r})},\qquad(30.1.16)$$

by a weighted average with weight

$$\frac{\phi_{\lambda_i}^*(\boldsymbol{r})\phi_{\lambda_i}(\boldsymbol{r})}{\sum_{i=1}^{N_{\rm e}}\phi_{\lambda_i}^*(\boldsymbol{r})\phi_{\lambda_i}(\boldsymbol{r})}$$
(30.1.17)

corresponding to the probability of finding an electron in state λ_i at the position r. The average Slater exchange potential is

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$$V_{\rm x}^{\rm S}(\mathbf{r}) = -\tilde{e}^2 \frac{\sum_{i,j=1}^{N_{\rm e}} \int d\mathbf{r}' \phi_{\lambda_i}^*(\mathbf{r}) \phi_{\lambda_i}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{\lambda_j}^*(\mathbf{r}') \phi_{\lambda_j}(\mathbf{r})}{\sum_{i=1}^{N_{\rm e}} \phi_{\lambda_i}^*(\mathbf{r}) \phi_{\lambda_i}(\mathbf{r})} .$$
 (30.1.18)

When written in terms of the pair distribution function,

$$V_{\rm x}^{\rm S}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \frac{\tilde{e}^2}{|\boldsymbol{r} - \boldsymbol{r}'|} n_{\rm e}(\boldsymbol{r}') [g(\boldsymbol{r}, \boldsymbol{r}') - 1] . \qquad (30.1.19)$$

Using this local potential in the Hartree–Fock equations, they reduce to

$$-\frac{\hbar^2}{2m_{\rm e}}\boldsymbol{\nabla}^2\phi^{\rm S}_{\lambda_i}(\boldsymbol{r}) + V_{\rm ion}(\boldsymbol{r})\phi^{\rm S}_{\lambda_i}(\boldsymbol{r}) + \tilde{e}^2\int \mathrm{d}\boldsymbol{r}' \frac{n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\phi^{\rm S}_{\lambda_i}(\boldsymbol{r}) + V^{\rm S}_{\rm x}(\boldsymbol{r})\phi^{\rm S}_{\lambda_i}(\boldsymbol{r}) = \hat{\varepsilon}^{\rm S}_{\lambda_i}\phi^{\rm S}_{\lambda_i}(\boldsymbol{r}), \qquad (30.1.20)$$

where the exchange potential and the density

$$n_{\rm e}(\boldsymbol{r}) = \sum_{i} \left| \phi_{\lambda_i}^{\rm S}(\boldsymbol{r}) \right|^2 \tag{30.1.21}$$

have to be determined self-consistently. These equations are referred to as the *Hartree–Fock–Slater equations*. Instead of the integro-differential equation of the Hartree–Fock approximation, only a differential equation has to be solved in this approach, a technically much simpler task. The ground-state energy is the expectation value of the Hamiltonian taken with respect to the Slater determinant of the one-particle functions $\phi_{\lambda_i}^{\rm S}(\boldsymbol{r})$.

When the local exchange potential is calculated for plane-wave wavefunctions, we get a constant value

$$V_{\rm x}^{\rm S}(\boldsymbol{r}) = -\frac{3\tilde{e}^2}{2\pi}k_{\rm F} = -\frac{3\tilde{e}^2}{2\pi}\left(3\pi^2 n_{\rm e}\right)^{1/3}\,.\tag{30.1.22}$$

Assuming that this expression is valid at each point of an inhomogeneous electron gas with the local value of the density $n_{\rm e}(\mathbf{r})$, we have

$$V_{\rm x}^{\rm S}(\boldsymbol{r}) = -\frac{3\tilde{e}^2}{2\pi} \left[3\pi^2 n_{\rm e}(\boldsymbol{r})\right]^{1/3} \,. \tag{30.1.23}$$

Due to the ambiguity in the approximation scheme and with the aim to account for correlation effects, SLATER proposed to multiply this potential by a factor α . The procedure using the local potential

$$V_{\rm xc}^{\rm S}(\boldsymbol{r}) = -\alpha \frac{3\tilde{e}^2}{2} \left[\frac{3}{\pi} n_{\rm e}(\boldsymbol{r})\right]^{1/3}$$
(30.1.24)

is referred to as the $X\alpha$ method. The optimal value of α is obtained by minimizing the ground-state energy with respect to this parameter.

30.1.3 Higher Order Corrections to the Energy

After this detour we return to the uniform electron gas. It was seen earlier that the cohesive energy as a function of $r_{\rm s}$ varies rather slowly in the neighborhood of the minimum found in the Hartree–Fock approximation. To get a more precise location of the minimum a better treatment of the electron–electron interaction is needed. Corrections beyond the Fock term that collectively bear the name *correlation energy* have to be calculated. The task, to get reliable results for the correlation energy, is made difficult by the fact that if the electron–electron interaction is treated as a perturbation, then – as will be seen – it is not sufficient to go to some finite order of perturbation theory, but the contributions of certain classes of processes have to be summed up to infinite order in the interaction. This requires the use of methods of the manybody problem, although the summation of the contributions of an infinite series of processes can partially be avoided if screening is taken into account.

According to the Brueckner–Goldstone linked-cluster expansion¹ of perturbation theory, the corrections to the ground-state energy can be written in a simple form

$$\Delta E = \sum_{n=0}^{\infty} \left\langle \Psi_{\rm FS} \left| \mathcal{H}_{\rm int} \left(\frac{1}{E_0 - \mathcal{H}_0} \mathcal{H}_{\rm int} \right)^n \right| \Psi_{\rm FS} \right\rangle_{\rm connected}, \qquad (30.1.25)$$

where $|\Psi_{\rm FS}\rangle$ denotes the ground state of the unperturbed electron system, the free Fermi sea. The subscript *connected* indicates that – if the individual processes are visualized by diagrams – only the contributions of the connected diagrams have to be taken into account.

The first-order correction is simply the expectation value of the interaction Hamiltonian:

$$\Delta E^{(1)} = \left\langle \Psi_{\rm FS} \middle| \frac{1}{2V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}\\\sigma\sigma'}} U(\boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma} \middle| \Psi_{\rm FS} \right\rangle.$$
(30.1.26)

Starting from the filled Fermi sea the scattering event takes two electrons out of the filled Fermi sea and scatters them into empty states, but the system has to return to the unperturbed ground state at the end. There are two possibilities: The electrons with wave vectors \mathbf{k} and \mathbf{k}' are scattered either back into their initial states or into the initial state of the other electron. These processes are depicted in Fig. 30.2.

There is no momentum transfer in the first type of process. Its contribution is proportional to $U(\mathbf{q} = 0)$. Such processes are excluded in the homogeneous electron gas, and the Hartree term gives no contribution to the total energy. In the second type of process, corresponding to the Fock term, two electrons are exchanged by the scattering. The electron with wave vector \mathbf{k} is scattered into

¹ K. A. Brueckner, 1955, J. Goldstone, 1957.



Fig. 30.2. First-order scattering processes contributing to the ground-state energy. The corresponding Feynman diagrams are shown at the bottom of the figure

the hole left behind by the electron of wave vector \mathbf{k}' . A nonzero contribution is obtained only if $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ and $\sigma' = \sigma$. Thus the first-order correction to the ground-state energy is

$$\Delta E^{(1)} = \left\langle \Psi_{\rm FS} \left| \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} U(\boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma} c_{\boldsymbol{k}\sigma} \right| \Psi_{\rm FS} \right\rangle$$

$$= -\frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} U(\boldsymbol{q}) \langle c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma} \rangle \langle c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \rangle, \qquad (30.1.27)$$

where the negative sign comes from the interchange of the order of the fermion operators. This energy correction is exactly the one obtained in the Hartree– Fock approximation.

Two processes are possible in second order, too. They are shown in Fig. 30.3. In the first step, in both processes, the electrons with wave vectors \mathbf{k} and \mathbf{k}' are scattered into empty states outside the Fermi sphere with quantum numbers $\mathbf{k} + \mathbf{q}$ and $\mathbf{k}' - \mathbf{q}$, respectively. The two processes differ in the second step. Either both electrons scatter back into their initial states, this is the direct process, or the electrons are scattered from the states $\mathbf{k} + \mathbf{q}$



Fig. 30.3. Second-order processes contributing to the ground-state energy. The numbers indicate the sequence of the scattering processes. The corresponding Feynman diagrams are shown at the bottom of the figure

and k' - q into the holes left behind by the other electron. The change of the wave vector is then k + q - k'. This is the exchange process. It can occur only if the two electrons have the same spin orientation.

The energy of the intermediate state is $\varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}'-\mathbf{q}} - \varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}$ in both cases. Taking into account the minus sign coming from the change of the order of the fermion operators, the two processes yield a contribution

$$\Delta E^{(2)} = \frac{1}{2} \left(\frac{1}{V}\right)^2 \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q}\\\sigma\sigma'}} \frac{U(\mathbf{q})U(\mathbf{q})}{\varepsilon_{\mathbf{k}} + \varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}'-\mathbf{q}}} - \frac{1}{2} \left(\frac{1}{V}\right)^2 \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q}\\\sigma}} \frac{U(\mathbf{q})U(\mathbf{k}+\mathbf{q}-\mathbf{k}')}{\varepsilon_{\mathbf{k}} + \varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}'-\mathbf{q}}}.$$
(30.1.28)

The summation (integration) has to be performed over the region where k and k' are inside the Fermi sphere, while k + q and k' - q are outside.

The second term, the exchange process, is considered first. Using the quadratic dispersion relation of free electrons and the $1/q^2$ behavior of the Fourier transform of the Coulomb interaction, the integral to be evaluated is

$$V \frac{\left(4\pi\tilde{e}^2\right)^2}{(2\pi)^9} \int \frac{\mathrm{d}\boldsymbol{q}}{q^2} \int_{|\boldsymbol{k}| < k_{\mathrm{F}}} \mathrm{d}\boldsymbol{k} \int_{|\boldsymbol{k}'| < k_{\mathrm{F}}} \frac{\mathrm{d}\boldsymbol{k}'}{(\boldsymbol{k} + \boldsymbol{q} - \boldsymbol{k}')^2} \frac{m_{\mathrm{e}}}{\hbar^2 [\boldsymbol{q} \cdot (\boldsymbol{k} - \boldsymbol{k}') + q^2]},$$
(30.1.29)

where the constraints $|\mathbf{k}+\mathbf{q}| > k_{\rm F}$ and $|\mathbf{k}'-\mathbf{q}| > k_{\rm F}$ have to be imposed on the range of integration over the variable \mathbf{q} . These requirements can be satisfied if both \mathbf{k} and \mathbf{k}' are in the neighborhood of the Fermi surface, in a range of width \mathbf{q} if \mathbf{q} is small. The integrals over \mathbf{k} and \mathbf{k}' lead to a term proportional to \mathbf{q} , and the energy correction per particle due to the exchange process is

$$\left[\frac{1}{6}\ln 2 - \frac{1}{4\pi^2}\zeta(3)\right]\frac{\tilde{e}^2}{a_0} = 0.02418\,\tilde{e}^2/a_0\,. \tag{30.1.30}$$

The contribution of the direct process contains the integral

$$V \frac{\left(4\pi\tilde{e}^2\right)^2}{(2\pi)^9} \int \frac{\mathrm{d}\boldsymbol{q}}{q^4} \int_{|\boldsymbol{k}| < k_\mathrm{F}} \mathrm{d}\boldsymbol{k} \int_{|\boldsymbol{k}'| < k_\mathrm{F}} \mathrm{d}\boldsymbol{k}' \frac{m_\mathrm{e}}{\hbar^2 [\boldsymbol{q} \cdot (\boldsymbol{k} - \boldsymbol{k}') + q^2]} \,. \tag{30.1.31}$$

Even though the integration over k and k' gives again a result proportional to q, the strong singularity of the $1/q^4$ prefactor for small q values, which comes from the slow decay (long range) of the Coulomb interaction, leads to a divergent result. M. GELL-MANN and K. A. BRUECKNER (1957) have shown that further divergent contributions appear in higher orders of perturbation theory. It can be shown that the strongest divergence is due to those processes in which in each elementary scattering process an electron-hole pair with total wave vector q is scattered into another electron-hole pair with the same total wave vector. The ring diagrams corresponding to these processes are displayed in Fig. 30.4.



Fig. 30.4. The so-called ring diagrams

The momentum transfer being equal in each interaction process, the interactions give a factor $U^n(q) \propto q^{-2n}$ in *n*th order. This strong singularity of the integrand at small q makes the contribution of these processes divergent. However, when the contributions of all these processes are summed up, the divergences cancel out due to the alternating signs and a finite correction is obtained.

This can be easily understood if we notice that these processes can be generated from the second-order direct process by replacing the Coulomb interaction by the effective, screened interaction shown in Fig. 29.6. Screening transforms the long-range Coulomb potential into a short-range one, eliminates the $1/q^2$ singularity of the Fourier transform, and eliminates the divergence in the total energy. In the Thomas–Fermi approximation the Fourier transform of the screened potential can be approximated by the form

$$\frac{4\pi\tilde{e}^2}{\epsilon_{\rm r}(q)q^2} = \frac{4\pi\tilde{e}^2}{q^2 + q_{\rm TF}^2} \,. \tag{30.1.32}$$

As a rough estimate of the effect of screening, the $1/q^2$ dependence can be cut off at a value on the order of $q_{\rm TF}$ when the energy correction is calculated. The value of the integral depends logarithmically on this cutoff. Expressing the Thomas–Fermi wave number in terms of $r_{\rm s}$ with the help of (29.3.17), the correction to the ground-state energy per particle is proportional to the logarithm of $r_{\rm s}$,

$$\frac{1}{\pi^2} (1 - \ln 2) \ln r_{\rm s} \,\tilde{e}^2 / a_0 = 0.0311 \ln r_{\rm s} \,\tilde{e}^2 / a_0 \,. \tag{30.1.33}$$

By calculating the contribution of the diagrams more accurately Gell-MANN and BRUECKNER could obtain also a constant term independent of $r_{\rm s}$. Later W. J. CARR JR. and A. A. MARADUDIN (1964) determined the coefficient of the term proportional to $r_{\rm s} \ln r_{\rm s}$. Collecting all these corrections we find 148 30 Cohesive Energy of the Electron System

$$\frac{E}{N_{\rm e}} = \left[\frac{1.105}{r_{\rm s}^2} - \frac{0.458}{r_{\rm s}} - 0.047 + 0.0311 \ln r_{\rm s} + 0.009 r_{\rm s} \ln r_{\rm s} + \mathcal{O}(r_{\rm s})\right] \frac{\tilde{e}^2}{a_0}.$$
(30.1.34)

As can be seen from Fig. 30.5, the perturbative corrections to the Hartree– Fock approximation are not small when $r_{\rm s} > 2.5$. Since the terms proportional to $r_{\rm s}$ or its higher powers are not known, this expression is valid only for small values of $r_{\rm s}$, i.e., for a dense electron gas.



Fig. 30.5. Ground-state energy obtained in perturbation theory (solid line) compared to the result of the Hartree–Fock approximation

30.1.4 Relationship Between Energy and Correlation Function

The two-particle interaction can be written according to (28.1.11) or (28.1.12) as a product of electron densities, and thus the expectation value of the interaction energy can be expressed in terms of the Fourier transform of the density–density correlation function $\Gamma(\mathbf{r} - \mathbf{r}')$. Using (28.4.66) we obtain

$$\langle \mathcal{H}_{\text{int}} \rangle = \frac{N_{\text{e}}}{2V} \sum_{\boldsymbol{q}} \frac{4\pi \tilde{e}^2}{q^2} \left[\Gamma(\boldsymbol{q}) - 1 \right].$$
(30.1.35)

The q = 0 term is missing from the sum for the homogeneous electron gas, thus the interaction energy is related to the static structure factor via

$$\langle \mathcal{H}_{\text{int}} \rangle = \frac{N_{\text{e}}}{2V} \sum_{\boldsymbol{q}} \frac{4\pi \tilde{e}^2}{q^2} \left[S(\boldsymbol{q}) - 1 \right].$$
(30.1.36)

The interaction modifies the expectation value of \mathcal{H}_0 , too, compared to the free electron value, since the expectation value has to be determined using the wavefunction of the perturbed ground state. The total change of the ground-state energy due to the interaction can be determined using a formula originating from PAULI, which can be considered as a special case of the *Hellmann–Feynman theorem.*² The theorem states that if the Hamiltonian

² H. Hellmann, 1936, R. P. Feynman, 1939.

depends on a continuous parameter λ and $|\varPsi_n\rangle$ is an eigenstate with energy $E_n,$

$$\mathcal{H}|\Psi_n\rangle = E_n|\Psi_n\rangle, \qquad (30.1.37)$$

then

$$\frac{\mathrm{d}E_n}{\mathrm{d}\lambda} = \left\langle \Psi_n \left| \frac{\mathrm{d}\mathcal{H}}{\mathrm{d}\lambda} \right| \Psi_n \right\rangle. \tag{30.1.38}$$

To prove this theorem one has to take into account that $|\Psi_n\rangle$ itself depends on λ and therefore

$$\frac{\mathrm{d}E_n}{\mathrm{d}\lambda} = \left\langle \left. \frac{\mathrm{d}\Psi_n}{\mathrm{d}\lambda} \right| \mathcal{H} \right| \Psi_n \right\rangle + \left\langle \Psi_n \left| \frac{\mathrm{d}\mathcal{H}}{\mathrm{d}\lambda} \right| \Psi_n \right\rangle + \left\langle \Psi_n \left| \mathcal{H} \right| \frac{\mathrm{d}\Psi_n}{\mathrm{d}\lambda} \right\rangle.$$
(30.1.39)

Making use of the eigenvalue equation and the fact that the function $|\Psi_n\rangle$ is normalized to unity,

$$\frac{\mathrm{d}E_n}{\mathrm{d}\lambda} = E_n \frac{\mathrm{d}}{\mathrm{d}\lambda} \left\langle \Psi_n | \Psi_n \right\rangle + \left\langle \Psi_n \left| \frac{\mathrm{d}\mathcal{H}}{\mathrm{d}\lambda} \right| \Psi_n \right\rangle = \left\langle \Psi_n \left| \frac{\mathrm{d}\mathcal{H}}{\mathrm{d}\lambda} \right| \Psi_n \right\rangle, \qquad (30.1.40)$$

as stated above.

We will apply this theorem to the case when λ is the coupling constant of the interaction:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int} = \mathcal{H}_0 + \lambda \mathcal{H}_1, \qquad (30.1.41)$$

and thus

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}\lambda} = \mathcal{H}_1 = \frac{\mathcal{H}_{\mathrm{int}}(\lambda)}{\lambda} \,. \tag{30.1.42}$$

Then the ground-state energy $E_0(\lambda)$ satisfies the differential equation

$$\frac{\mathrm{d}E_0}{\mathrm{d}\lambda} = \frac{1}{\lambda} \langle \Psi_0 | \mathcal{H}_{\mathrm{int}}(\lambda) | \Psi_0 \rangle. \qquad (30.1.43)$$

Integration of this equation gives

$$E_0(\lambda) = E_0(\lambda = 0) + \int_0^\lambda \frac{\mathrm{d}\lambda'}{\lambda'} \langle \Psi_0(\lambda') | \mathcal{H}_{\mathrm{int}}(\lambda') | \Psi_0(\lambda') \rangle . \qquad (30.1.44)$$

If the expectation value of the interaction Hamiltonian is expressed in terms of the structure factor using (30.1.36) and \tilde{e}^2 is chosen as the coupling constant of the Coulomb interaction, we have

$$E_{0}(\lambda) = E_{0}(\lambda = 0) + \frac{N_{e}}{2V} \int_{0}^{\tilde{e}^{2}} \frac{d\lambda'}{\lambda'} \sum_{q} \frac{4\pi\lambda'}{q^{2}} \left[S(q) - 1 \right].$$
(30.1.45)

This shows that the total energy of the interacting electron system can be calculated if the density-density correlation function or the static structure factor is known. S(q) itself depends on the coupling constant in general, hence performing the integral is not a simple task.

At finite temperatures, a similar expression can be derived for the free energy. For this we write the free energy in terms of the partition function,

$$F = -k_{\rm B}T\ln Z = -k_{\rm B}T\ln \operatorname{Tr} e^{-(\mathcal{H}_0 + \mathcal{H}_{\rm int})/k_{\rm B}T}$$
(30.1.46)

and take its derivative with respect to λ . This gives

$$\frac{\partial F}{\partial \lambda} = -\frac{k_{\rm B}T}{Z(\lambda)} \frac{\partial Z(\lambda)}{\partial \lambda} = \frac{1}{Z(\lambda)} \operatorname{Tr} \frac{\mathrm{d}\mathcal{H}_{\rm int}(\lambda)}{\mathrm{d}\lambda} \mathrm{e}^{-(\mathcal{H}_0 + \mathcal{H}_{\rm int})/k_{\rm B}T} \,. \tag{30.1.47}$$

By the use of (30.1.42) we find

$$\frac{\partial F}{\partial \lambda} = \frac{\langle \mathcal{H}_{\text{int}}(\lambda) \rangle}{\lambda}, \qquad (30.1.48)$$

where $\langle \cdots \rangle$ denotes the thermodynamic average. Integration of this equation gives

$$F(\lambda) = F(\lambda = 0) + \int_{0}^{\lambda} \frac{\mathrm{d}\lambda'}{\lambda'} \langle \mathcal{H}_{\mathrm{int}}(\lambda') \rangle, \qquad (30.1.49)$$

from which

$$F(\lambda) = F(\lambda = 0) + \frac{N_{\rm e}}{2V} \int_{0}^{\tilde{e}^2} \frac{\mathrm{d}\lambda'}{\lambda'} \sum_{\boldsymbol{q}} \frac{4\pi\lambda'}{q^2} \left[S(\boldsymbol{q}) - 1 \right].$$
(30.1.50)

Thus the free energy can be obtained if the structure factor (or equivalently the density–density correlation function) is known at finite temperatures.

30.1.5 Correlation Energy in the RPA

When the static structure factor calculated in the Hartree–Fock approximation [see Eq. (28.4.75)] is used in (30.1.36), we have

$$\langle \mathcal{H}_{\rm int} \rangle = -\frac{3}{4\pi} \tilde{e}^2 k_{\rm F} N_{\rm e} \,. \tag{30.1.51}$$

Since \tilde{e}^2 appears only as a multiplicative factor, this expression gives at the same time the correction to the ground-state energy, in agreement with (30.1.11).

To get a better result we make use of the fluctuation-dissipation theorem that relates the structure factor and the density-density response function. Applying (J.1.93) which is valid at T = 0 we have

$$\Gamma(\boldsymbol{q}) = -2\hbar \frac{V}{N_{\rm e}} \int_{0}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{Im} \,\Pi(\boldsymbol{q},\omega) \,. \tag{30.1.52}$$

Substitution of this expression into (30.1.35) gives

$$\langle \mathcal{H}_{\text{int}} \rangle = \frac{1}{2} \sum_{\boldsymbol{q}} \frac{4\pi \tilde{e}^2}{q^2} \left[-2\hbar \int_0^\infty \frac{\mathrm{d}\omega}{2\pi} \mathrm{Im} \,\Pi(\boldsymbol{q},\omega) - \frac{N_{\text{e}}}{V} \right].$$
(30.1.53)

Note that if $\Pi(\boldsymbol{q}, \omega)$ is approximated by $\Pi_0(\boldsymbol{q}, \omega)$, the result of the Hartree– Fock approximation is recovered. A more natural choice is to use the RPA result for $\Pi(\boldsymbol{q}, \omega)$. Its imaginary part can be written in terms of the real and imaginary parts of $\Pi_0(\boldsymbol{q}, \omega)$ as

$$\operatorname{Im} \Pi(\boldsymbol{q}, \omega) = \frac{\operatorname{Im} \Pi_0(\boldsymbol{q}, \omega)}{\left[1 - (4\pi \tilde{e}^2/q^2) \operatorname{Re} \Pi_0(\boldsymbol{q}, \omega)\right]^2 + \left[(4\pi \tilde{e}^2/q^2) \operatorname{Im} \Pi_0(\boldsymbol{q}, \omega)\right]^2}.$$
(30.1.54)

Inserting this into (30.1.53) and then into (30.1.44), \tilde{e}^2 appears both in the numerator and in the denominator; nevertheless, the integration over the coupling constant can be performed yielding

$$E = E_0 - \frac{1}{2} \sum_{\boldsymbol{q}} \left[\frac{\hbar}{\pi} \int_0^\infty d\omega \arctan \frac{(4\pi \tilde{e}^2/q^2) \operatorname{Im} \Pi_0(\boldsymbol{q}, \omega)}{1 - (4\pi \tilde{e}^2/q^2) \operatorname{Re} \Pi_0(\boldsymbol{q}, \omega)} + \frac{N_{\rm e}}{V} \frac{4\pi \tilde{e}^2}{q^2} \right].$$
(30.1.55)

Using the known form for the Lindhard function the integration yields

$$\frac{E}{N_{\rm e}} = \left[\frac{1.105}{r_{\rm s}^2} - \frac{0.458}{r_{\rm s}} + 0.0311\ln r_{\rm s} - 0.071 + \cdots\right]\frac{\tilde{e}^2}{a_0}$$
(30.1.56)

for small $r_{\rm s}$. The constant term differs from the one given in (30.1.34) which was obtained by summing the contribution of the ring diagrams. The difference is just the contribution of the second-order exchange process given in (30.1.30) which is missing in the RPA. The RPA misses some other processes, too, but their contributions are of higher order in $r_{\rm s}$.

30.2 The Total Energy at Lower Densities

We know that the Hartree–Fock approximation or the perturbative approach to calculate the total energy of the electron gas is reasonable for small values of $r_{\rm s}$ ($r_{\rm s} < 1$), i.e., for a dense electron gas. On the other hand we also know that in most metals the electronic density – if expressed in terms of $r_{\rm s}$ – falls into the range $1.8 \leq r_{\rm s} \leq 6$. If we want to understand the metallic bond, it is necessary to compute the cohesive energy of the electron gas more accurately. First – following E. P. WIGNER (1934) – we will consider the lowdensity electron gas, and then – since in real metals the density is between the two limits – interpolation formulas will be presented that allow a smooth interpolation between the low- and high-density limits.

30.2.1 The Low-Density Electron Gas, Wigner Crystal

The kinetic energy of electrons goes as $1/r_s^2$, while the exchange energy is proportional to $1/r_s$, hence the interaction is dominant in the low-density, large r_s limit. WIGNER assumed that a minimum energy configuration can be achieved if electrons get localized as far apart as possible, i.e., they occupy the lattice sites of a close-packed lattice, which gives the largest interparticle spacing for a given density. This electron crystal is called the *Wigner crystal*.

To estimate the energy of this electron crystal, the Wigner–Seitz cells around the lattice sites are replaced with spheres of radius r_0 and it is assumed that there is exactly one electron in each sphere. The positive background of the ions has been assumed to be uniform. Although the spheres necessarily overlap, the tesselation of space by spheres probably gives a small error, since the Wigner–Seitz cells of face-centered and body-centered cubic lattices can be well approximated by spheres.

If the electron is in the center of the sphere and the charge of the ions is smeared out uniformly in the sphere, the electric field vanishes outside the sphere. Each electron feels only the positive background of its respective sphere, and there is no electric interaction between the spheres. The potential created at \mathbf{r} relative to the center of the sphere by the smeared positive charge of density $3e/(4r_0^3\pi)$ is

$$\varphi(\mathbf{r}) = \frac{e}{4\pi\epsilon_0} \frac{3}{4r_0^3 \pi} \int_{|\mathbf{r}'| < r_0} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \,\mathrm{d}\mathbf{r}' = \frac{e}{4\pi\epsilon_0} \left[\frac{3}{2r_0} - \frac{r^2}{2r_0^3} \right]. \tag{30.2.1}$$

Hence the electron sitting at the center of the sphere feels a potential $\varphi(0) = (e/4\pi\epsilon_0)(3/2r_0)$ and the electrostatic energy per particle is

$$\frac{E^{(-)}}{N_{\rm e}} = -e\varphi(0) = -\frac{e^2}{4\pi\epsilon_0}\frac{3}{2r_0} = -\frac{3\tilde{e}^2}{2r_0}\,. \tag{30.2.2}$$

The same potential can be used to get the energy of interaction of the positive background with itself. This energy is

$$\frac{E^{(+)}}{N_{\rm e}} = \frac{1}{2} \tilde{e}^2 \frac{3}{4r_0^3 \pi} \frac{3}{4r_0^3 \pi} \int_{|\boldsymbol{r}| < r_0} \mathrm{d}\boldsymbol{r} \int_{|\boldsymbol{r}'| < r_0} \mathrm{d}\boldsymbol{r}' \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|}
= \frac{1}{2} \tilde{e}^2 \frac{3}{4r_0^3 \pi} \int_{|\boldsymbol{r}| < r_0} \left(\frac{3}{2r_0} - \frac{r^2}{2r_0^3}\right) \mathrm{d}\boldsymbol{r} = \frac{6}{5} \frac{\tilde{e}^2}{2r_0}$$
(30.2.3)

for each cell. Thus the total energy due to the Coulomb interaction between the positive and negative charges inside the sphere is

$$\frac{E_{\rm C}}{N_{\rm e}} = \frac{E^{(+)} + E^{(-)}}{N_{\rm e}} = \frac{\tilde{e}^2}{2r_0} \left[\frac{6}{5} - 3\right] = -\frac{9}{5} \frac{\tilde{e}^2}{2r_0} = -\frac{0.9}{r_{\rm s}} \frac{\tilde{e}^2}{a_0} \,. \tag{30.2.4}$$

However rough it might be, this estimate is quite reasonable as can be shown by comparing it with the Madelung energy of the electron crystal. This latter has been calculated numerically for simple crystal structures whose lattice constant a was chosen in such a way that the volume belonging to every electron be equal to the volume of the sphere with radius $r_0 = a_0 r_s$. Expressing the Madelung energy in terms of r_s , and not in terms of the nearest-neighbor distance as is done usually, it takes the form

$$\frac{E_{\text{Mad}}}{N_{\text{e}}} = -\frac{\alpha}{r_{\text{s}}} \frac{\tilde{e}^2}{a_0} \,. \tag{30.2.5}$$

The Madelung constant α is 0.880 for the simple cubic lattice, while $\alpha \approx 0.896$ for the body-centered cubic lattice, and nearly the same value is found for the face-centered cubic and hexagonal close-packed lattices. The largest value, although only by a slight margin, is $\alpha = 0.89593$, for the body-centered cubic lattice. Later numerical works on the conditions for the existence of the Wigner crystal concentrated therefore on this lattice type.

If the electron is displaced from the center of the sphere, its electrostatic energy is

$$\frac{E^{(-)}}{N_{\rm e}} = -e\varphi(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0} \left[\frac{3}{2r_0} - \frac{r^2}{2r_0^3}\right] = -\frac{\tilde{e}^2}{2r_0} \left[3 - \left(\frac{r}{r_0}\right)^2\right], \quad (30.2.6)$$

and the total Coulomb energy of the positive and negative charges inside the sphere is

$$\frac{E_{\rm C}}{N_{\rm e}} = \frac{E^{(+)} + E^{(-)}}{N_{\rm e}} = \frac{\tilde{e}^2}{2r_0} \left[\frac{6}{5} - 3 + \left(\frac{r}{r_0}\right)^2 \right] = \frac{\tilde{e}^2}{2r_0} \left[-\frac{9}{5} + \left(\frac{r}{r_0}\right)^2 \right].$$
(30.2.7)

This can be interpreted as the energy of a particle in a harmonic potential. Adding it to the kinetic energy, the total energy of an electron in a Wigner crystal is

$$\frac{E_{\rm W}}{N_{\rm e}} = \frac{p^2}{2m_{\rm e}} + \frac{\tilde{e}^2}{2r_0} \left[-\frac{9}{5} + \left(\frac{r}{r_0}\right)^2 \right].$$
 (30.2.8)

Comparing it with the Hamiltonian of a harmonic oscillator of frequency ω ,

$$\mathcal{H} = \frac{p^2}{2m_{\rm e}} + \frac{1}{2}m_{\rm e}\omega^2 r^2 \,, \qquad (30.2.9)$$

one finds

$$\frac{1}{2}m_{\rm e}\omega^2 = \frac{\tilde{e}^2}{2r_0^3}\,.\tag{30.2.10}$$

The frequency of oscillations of electrons in the Wigner crystal has to be determined from this relation. When the frequency is expressed in terms of the electron density $n_{\rm e} = 3/(4\pi r_0^3)$, we have

$$\omega^2 = \frac{4\pi n_{\rm e}\tilde{e}^2}{3m_{\rm e}} = \frac{1}{3}\omega_{\rm p}^2, \qquad (30.2.11)$$

where $\omega_{\rm p}$ is the frequency of plasma oscillations given in (16.1.69).

There are three degenerate modes corresponding to the three directions of oscillation. Their zero-point oscillations give a finite contribution to the ground-state energy. Adding the zero-point energy to the energy due to the Coulomb repulsion, we get

$$\frac{E_{\rm W}}{N_{\rm e}} = -\frac{9}{5}\frac{\tilde{e}^2}{2r_0} + \frac{3}{2}\hbar\omega = -\frac{9}{5}\frac{\tilde{e}^2}{2r_0} + \frac{\sqrt{3}}{2}\hbar\omega_{\rm p}\,,\qquad(30.2.12)$$

for the energy per particle. In atomic energy units, where the plasma frequency is given by

$$\hbar\omega_{\rm p} = \left(\frac{3}{(r_0/a_0)^3}\right)^{1/2} \frac{\tilde{e}^2}{a_0} = \left(\frac{3}{r_{\rm s}^3}\right)^{1/2} \frac{\tilde{e}^2}{a_0}, \qquad (30.2.13)$$

we have

$$\frac{E_{\rm W}}{N_{\rm e}} = \left[-\frac{0.9}{r_{\rm s}} + \frac{1.5}{r_{\rm s}^{3/2}} \right] \frac{\tilde{e}^2}{a_0} \,. \tag{30.2.14}$$

When the energy of vibrations is calculated more accurately, one finds 1.325 instead of 1.5 for the coefficient of the term proportional to $r_{\rm s}^{-3/2}$. If anharmonicity is taken into account, corrections proportional to $r_{\rm s}^{-2}$ and to higher powers of $1/r_{\rm s}$ are found. The leading perturbative correction is $-0.365/r_{\rm s}^2$. Writing the total energy of the electron system at low densities, in the Wigner-crystal state, in the form

$$\frac{E_{\rm WC}}{N_{\rm e}} = \left[\frac{c_1}{r_{\rm s}} + \frac{c_{3/2}}{r_{\rm s}^{3/2}} + \frac{c_2}{r_{\rm s}^2} + \cdots\right] \frac{\tilde{e}^2}{a_0}, \qquad (30.2.15)$$

the best values for the expansion coefficients are obtained from fitting the total energy calculated by quantum Monte Carlo methods to this form. Fixing c_1 to the value calculated for the Madelung constant α of the body-centered cubic lattice, we get

$$\frac{E_{\rm WC}}{N_{\rm e}} = \left[-\frac{0.896}{r_{\rm s}} + \frac{1.338}{r_{\rm s}^{3/2}} - \frac{0.553}{r_{\rm s}^2} \right] \frac{\tilde{e}^2}{a_0} \,. \tag{30.2.16}$$

The physical picture used to derive this energy allows us to get an estimate of the validity of this approximation. Provided the vibrations of the Wigner crystal are harmonic, the mean-square displacement of the electron from its equilibrium position is

$$\langle r^2 \rangle = 3 \frac{\hbar}{2m_{\rm e}\omega} = \frac{3}{2} \frac{\hbar}{m_{\rm e}} \left(\frac{m_{\rm e} r_0^3}{\tilde{e}^2}\right)^{1/2} = \frac{3}{2} \left(a_0 r_0^3\right)^{1/2},$$
 (30.2.17)

where we have taken into account that each electron can participate in three independent vibrational modes. Our assumption about the localization of the electrons to lattice sites becomes meaningless if $\langle r^2 \rangle^{1/2}$ is comparable to the radius of the sphere in which the electron oscillates. We know from Chapter 12 that a crystal melts according to the Lindemann criterion when the root-mean-square displacement of the atoms reaches about one quarter of the lattice parameter,

$$\frac{\langle \boldsymbol{u}^2 \rangle^{1/2}}{a} \approx \frac{1}{4} \,. \tag{30.2.18}$$

If r_0 is identified with the lattice constant, the relative mean displacement is

$$\frac{\langle r^2 \rangle^{1/2}}{r_0} = \sqrt{\frac{3}{2}} \frac{(a_0 r_0^3)^{1/4}}{r_0} = \sqrt{\frac{3}{2}} \left(\frac{1}{r_{\rm s}}\right)^{1/4}.$$
 (30.2.19)

Applying this criterion to the Wigner crystal we find that it can be stable at very low densities only, for $r_{\rm s} > 20$.

A better treatment of the interacting electron system gives a much stricter bound: Wigner crystal can be formed in a three-dimensional homogeneous electron gas only at much lower densities. If the energy of the low-density electron system is calculated numerically by using quantum Monte Carlo methods, one finds that the body-centered cubic Wigner crystal is the stable ground state for $r_{\rm s} \geq 106$. We will see in Chapter 33 that the homogeneous paramagnetic fluid phase does not go over directly to the Wigner-crystal phase as the density is lowered. The electron system becomes magnetically polarized, the occupation of states with opposite spin orientations becoming unequal, for densities $r_{\rm s} > 50$. The typical values of $r_{\rm s}$ in normal metals being much smaller than this limit, no three-dimensional Wigner crystals have been observed in nature.

The limits for the existence of the Wigner crystal are not so extreme in a two-dimensional homogeneous electron gas. The best numerical estimates give $r_{\rm s} \approx 35$ –38 beyond which the triangular Wigner-crystal phase is the stable ground state. Modern semiconductor technology allows us to produce two-dimensional electron gases with such densities. Figure 30.6 shows the temperature dependence of the resistivity of a high purity GaAs/AlGaAs heterostructure for several concentrations of carriers. The change from metalliclike to semiconductor-like behavior, the metal–insulator transition in the ground state can be interpreted as being due to the localization of electrons in the Wigner crystal.



Fig. 30.6. Temperature dependence of the resistivity of a two-dimensional hole system in a GaAs/AlGaAs heterostructure for different hole densities. The system behaves as a metal at higher densities and as an insulator at lower densities. The critical density is 7.7×10^9 cm⁻², corresponding to $r_s = 35$ [Reprinted with permission from J. Yoon et al., *Phys. Rev. Lett.* 82, 1744 (1999). \bigcirc (1999) by the American Physical Society]

30.2.2 Parametrization of the Correlation Energy

The results obtained in the low- and high-density limits are not valid for densities characteristic of most metals. Since we have analytic expressions in these limits, it seems natural to attempt to find smooth interpolation formulas for intermediate densities.

Subtracting the Hartree–Fock result from (30.2.16) we find

$$\frac{E_{\rm c}}{N_{\rm e}} = \left[-\frac{0.438}{r_{\rm s}} + \frac{1.338}{r_{\rm s}^{3/2}} - \frac{1.658}{r_{\rm s}^2} \right] \frac{\tilde{e}^2}{a_0}$$
(30.2.20)

for the correlation energy of the low-density electron gas. On the other hand, taking (30.1.34) for the dense electron gas, we have

$$\frac{E_{\rm c}}{N_{\rm e}} = \left[-0.047 + 0.0311 \ln r_{\rm s} + 0.009 \, r_{\rm s} \ln r_{\rm s} + \mathcal{O}(r_{\rm s}) \right] \tilde{e}^2 / a_0 \,. \qquad (30.2.21)$$

WIGNER derived a somewhat different expression for the dense electron gas and proposed the interpolation formula

$$\frac{E_{\rm c}^{\rm W}}{N_{\rm e}} = -\frac{0.44}{r_{\rm s} + 7.8} \,\frac{\tilde{e}^2}{a_0} \tag{30.2.22}$$

for intermediate values of $r_{\rm s}$. The applicability of this formula is doubtful, since it connects the energy of two regions by a smooth function between which, if a Wigner crystal exists, a first-order phase transition takes place, and the derivative of the energy is discontinuous at the transition point. Nevertheless, as seen in Fig. 30.7, the total energy is quite close to the values obtained in the better approximations discussed below, when this expression is used for the correlation energy.



Fig. 30.7. Ground-state energy of the electron gas as a function of r_s in the Hartree– Fock approximation (HF) and using the expressions for the correlation energy proposed by WIGNER (W); NOZIÈRES and PINES (NP); VOSKO, WILK, and NUSAIR (VWN); or PERDEW and ZUNGER (PZ)

Using the result derived in the RPA, P. NOZIÈRES and D. PINES (1958) proposed a somewhat different interpolation formula:

$$\frac{E_{\rm c}^{\rm NP}}{N_{\rm e}} = \left[-0.057 + 0.015 \ln r_{\rm s}\right] \tilde{e}^2 / a_0 \,. \tag{30.2.23}$$

Taking a completely different approach, D. M. CEPERLEY and B. J. ALDER (1980) calculated the correlation energy of the homogeneous electron gas at various densities by a Monte Carlo method. Using these results as well as the expansions valid for low and high densities, S. H. VOSKO, L. WILK, and M. NUSAIR (1980) proposed the analytic expression

$$\begin{aligned} \frac{E_{\rm c}^{\rm VWN}}{N_{\rm e}} &= 0.0311 \left\{ \ln \left(\frac{r_{\rm s}}{r_{\rm s} + 3.7274 \sqrt{r_{\rm s}} + 12.9352} \right) \\ &+ 1.2474 \arctan \left(\frac{6.1520}{2\sqrt{r_{\rm s}} + 3.7274} \right) \\ &+ 0.0312 \ln \left[\frac{(\sqrt{r_{\rm s}} + 0.1050)^2}{r_{\rm s} + 3.7274 \sqrt{r_{\rm s}} + 12.9352} \right] \right\} \frac{\tilde{e}^2}{a_0} \,. \end{aligned}$$

Using the same data but assuming a different analytic form, J. P. PERDEW and A. ZUNGER (1981) proposed a slightly modified form of the perturbative expression,
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$$\frac{E_{\rm c}^{\rm PZ}}{N_{\rm e}} = \left[0.0311 \ln r_{\rm s} - 0.048 + 0.0020 r_{\rm s} \ln r_{\rm s} - 0.0116 r_{\rm s}\right] \tilde{e}^2 / a_0 \,, \quad (30.2.25)$$

for a dense electron gas, in the range $0 \le r_s \le 1$, and

$$\frac{E_{\rm c}^{\rm PZ}}{N_{\rm e}} = -\frac{0.1423}{1+1.0529\sqrt{r_{\rm s}}+0.3334r_{\rm s}}\frac{\tilde{e}^2}{a_0} \tag{30.2.26}$$

when $r_{\rm s} \ge 1$. The two expressions join smoothly at $r_{\rm s} = 1$. The total energies calculated with these expressions are also shown in Fig. 30.7.

A numerically even simpler parametrization of the correlation energy is due to J. P. PERDEW and Y. WANG (1992). They assumed the same analytical form

$$\frac{E_{\rm c}^{\rm PW}}{N_{\rm e}} = -2A(1+\alpha_1 r_{\rm s})\ln\left[1+\frac{1}{2A\left(\beta_1 r_{\rm s}^{1/2}+\beta_2 r_{\rm s}+\beta_3 r_{\rm s}^{3/2}+\beta_4 r_{\rm s}^2\right)}\right]\frac{\tilde{e}^2}{a_0}$$
(30.2.27)

both at low and high densities and found good matching to the numerical values if A = 0.0311, $\alpha_1 = 0.2137$, $\beta_1 = 7.5957$, $\beta_2 = 3.5876$, $\beta_3 = 1.6382$, and $\beta_4 = 0.4929$.

30.3 The Density-Functional Theory

The energy of the homogeneous electron gas could be expressed as a function of r_s , i.e., as a function of the electron density. The electronic density is inhomogeneous in a realistic model of solids owing to the presence of the inhomogeneous potential $V_{\rm ion}(\mathbf{r})$ of the ions, and we might not expect a unique functional relationship between the local electronic density and the total energy. The Thomas–Fermi approximation seems to be an exception. When electrons propagate in a slowly varying external one-particle potential $V_{\rm ext}(\mathbf{r})$, a local Fermi wave number can be defined which is related to the local electron density via (29.2.4). Using (30.1.4) for the average kinetic energy of an electron in a uniform system, the kinetic energy of the inhomogeneous electron gas is

$$E_{\rm kin} = \frac{3}{5} \frac{\hbar^2}{2m_{\rm e}} \int k_{\rm F}^2(\boldsymbol{r}) n_{\rm e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} = \frac{3\hbar^2}{10m_{\rm e}} (3\pi^2)^{2/3} \int n_{\rm e}^{5/3}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$
(30.3.1)

Adding to this the energy due to the external potential $V_{\text{ext}}(\mathbf{r})$ and the term due to the Coulomb interaction,

$$\int V_{\text{ext}}(\boldsymbol{r}) n_{\text{e}}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} + \frac{\tilde{e}^2}{2} \iint \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' \frac{n_{\text{e}}(\boldsymbol{r}) n_{\text{e}}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \,, \qquad (30.3.2)$$

the total energy is a unique functional of the density.

Although the kinetic energy cannot be written in such a simple form when we go beyond the semiclassical Thomas–Fermi approximation, it is still true that the local density $n_{\rm e}(\mathbf{r})$ determines uniquely the solutions of the Hartree equations. The exchange correction of the Hartree–Fock approximation could be derived from the density only when the generically nonlocal exchange potential was approximated by a density-dependent local exchange potential. Quite generally we could only show that the total energy can be calculated only if the density–density correlation function, which contains the two-particle correlations, as well as the density are known.

It might be surprising then that P. HOHENBERG and W. KOHN³ (1964) have shown that there is a unique relationship between the ground-state energy of an interacting electron system and the density $n_{\rm e}(\mathbf{r})$ of the electrons. Further developments of the theory have led to well-defined procedures to calculate the correlation energy.

30.3.1 Hohenberg–Kohn Theorems

Assume that we know the solutions of the Schrödinger equation of the manybody system where the particles move in an external potential $V_{\text{ext}}(\mathbf{r}_i)$ and the electrons interact with each other via a two-particle potential $U(\mathbf{r}_i - \mathbf{r}_j)$. The ground-state energy is denoted by E_0 and the corresponding wavefunction is $\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e})$. Introducing the short-hand notation

$$T = \sum_{i=1}^{N_{\rm e}} \left(-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}_i^2 \right), \qquad U = \frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{N_{\rm e}} U(\boldsymbol{r}_i - \boldsymbol{r}_j), \qquad (30.3.3)$$

for the kinetic energy and the interparticle interaction, respectively, and

$$V = \sum_{i=1}^{N_{\rm e}} V_{\rm ext}(\boldsymbol{r}_i) \tag{30.3.4}$$

for the external potential, the Schrödinger equation can be written in the concise form

$$\mathcal{H}|\Psi_0\rangle \equiv (T+U+V)|\Psi_0\rangle = E_0|\Psi_0\rangle. \tag{30.3.5}$$

For a fixed particle–particle interaction, the ground-state wavefunction and the corresponding energy eigenvalue are determined by the external potential. Provided the many-body wavefunction is known, the one-particle density can be calculated unequivocally using (28.4.4). Thus the external potential is mapped uniquely on the density.

The first Hohenberg-Kohn theorem states that this map is unique not only in this direction, but in the opposite sense as well. More precisely, the

³ WALTER KOHN (1923–) was awarded the Nobel Prize in chemistry in 1998 "for his development of the density-functional theory".

ground-state wavefunction and consequently the ground-state expectation value of any observable physical quantity – among others the ground-state energy – is a unique functional of the ground-state electron density. Moreover, if the ground-state wavefunctions of two systems are identical, the potentials can differ only by a constant. We will assume in the proof that the ground state is nondegenerate. It can be shown, although the proof is more involved, that the theorem is true for degenerate ground states as well.

First, we prove that if two systems have identical electronic densities, then their many-particle wavefunctions have to be necessarily identical. To show this we consider two systems with different one-particle potentials:

$$V = \sum_{i} V_{\text{ext}}(\boldsymbol{r}_i) \tag{30.3.6}$$

in one of them and

$$V' = \sum_{i} V'_{\text{ext}}(\boldsymbol{r}_i) \tag{30.3.7}$$

in the other, but the same electron–electron interaction acts in both of them. If the ground-state wavefunction of the latter problem is denoted by $|\Psi'_0\rangle$ and the ground-state energy by E'_0 , the corresponding Schrödinger equation is

$$\mathcal{H}'|\Psi_0'\rangle \equiv (T+U+V')|\Psi_0'\rangle = E_0'|\Psi_0'\rangle.$$
(30.3.8)

According to the variational principle of quantum mechanics if $|\Psi_0\rangle$ is the ground-state wavefunction of \mathcal{H} , then

$$\langle \Psi | \mathcal{H} | \Psi \rangle > \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = E_0 \tag{30.3.9}$$

for any other state $|\Psi\rangle$. If $|\Psi\rangle$ is chosen to be the ground state of \mathcal{H}' , that is $|\Psi'_0\rangle$, the left-hand side is

$$\langle \Psi_0' | \mathcal{H} | \Psi_0' \rangle = \langle \Psi_0' | \mathcal{H}' + V - V' | \Psi_0' \rangle = E_0' + \langle \Psi_0' | V - V' | \Psi_0' \rangle, \qquad (30.3.10)$$

and the inequality yields

$$E'_{0} + \langle \Psi'_{0} | V - V' | \Psi'_{0} \rangle > E_{0}. \qquad (30.3.11)$$

On the other hand, starting from the inequality

$$\langle \Psi | \mathcal{H}' | \Psi \rangle > \langle \Psi_0' | \mathcal{H}' | \Psi_0' \rangle = E_0' \tag{30.3.12}$$

valid for the ground-state energy of Hamiltonian \mathcal{H}' provided $|\Psi\rangle$ is different from $|\Psi'_0\rangle$ and applying it to $|\Psi\rangle = |\Psi_0\rangle$, similar steps lead to the inequality

$$E_0 + \langle \Psi_0 | V' - V | \Psi_0 \rangle = E_0 - \langle \Psi_0 | V - V' | \Psi_0 \rangle > E'_0.$$
 (30.3.13)

Combining the two inequalities we find

$$E'_{0} + \langle \Psi'_{0} | V - V' | \Psi'_{0} \rangle > E'_{0} + \langle \Psi_{0} | V - V' | \Psi_{0} \rangle.$$
(30.3.14)

The contribution of the one-particle potentials depends only on the electron density and we have

$$\langle \Psi_0 | V - V' | \Psi_0 \rangle = \int n_{\rm e}(\boldsymbol{r}) \left[V_{\rm ext}(\boldsymbol{r}) - V'_{\rm ext}(\boldsymbol{r}) \right] \mathrm{d}\boldsymbol{r} \,. \tag{30.3.15}$$

Similarly

$$\langle \Psi'_0 | V - V' | \Psi'_0 \rangle = \int n'_{\rm e}(\mathbf{r}) \left[V_{\rm ext}(\mathbf{r}) - V'_{\rm ext}(\mathbf{r}) \right] \mathrm{d}\mathbf{r} \,.$$
 (30.3.16)

If the densities corresponding to the two wavefunctions are identical,

$$\langle \Psi_0' | V - V' | \Psi_0' \rangle = \langle \Psi_0 | V - V' | \Psi_0 \rangle. \qquad (30.3.17)$$

Inequality (30.3.14) thus reduces to

$$E_0' > E_0' \,. \tag{30.3.18}$$

This contradiction can be resolved only if we assume that the wavefunctions $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ are in fact identical and in all previous relations equality holds instead of inequality. This proves that the densities $n_{\rm e}(\mathbf{r})$ and $n'_{\rm e}(\mathbf{r})$ calculated from $|\Psi_0\rangle$ and $|\Psi'_0\rangle$, respectively, can be equal only if the wavefunctions are identical, which means that the wavefunction is a unique functional of the density.

Assume now that the same wavefunctions appear in (30.3.5) and (30.3.8). Subtracting the two equations gives

$$(V - V')|\Psi_0\rangle = (E_0 - E'_0)|\Psi_0\rangle.$$
 (30.3.19)

It then follows that – apart from singular potentials for which the wavefunction vanishes on finite regions – V and V' may only differ in an additive constant, which is the energy difference ΔE_0 of the two ground states.

Application of the two steps one after the other leads to the following result: if the density $n_{\rm e}(\mathbf{r})$ calculated in the presence of $V_{\rm ext}(\mathbf{r})$ is equal to the density $n'_{\rm e}(\mathbf{r})$ calculated for $V'_{\rm ext}(\mathbf{r})$, then the two potentials may differ in an additive constant only. This statement is valid for degenerate ground states as well.

Thus far we have seen that the external potential, the ground-state wavefunction, and the ground-state density of the electrons are uniquely related. Since the wavefunction is a unique functional of the density and the electron–electron interaction was taken to be fixed, the sum of the kinetic energy and the energy due to electron–electron interaction,

$$F[n_{\rm e}(\boldsymbol{r})] \equiv \langle \Psi_0 | T + U | \Psi_0 \rangle, \qquad (30.3.20)$$

is also a unique functional of the density. Furthermore, since the density determines the one-particle potential, too, apart from an additive constant, the total energy

$$E[n_{\rm e}(\boldsymbol{r})] = F[n_{\rm e}(\boldsymbol{r})] + \int V_{\rm ext}(\boldsymbol{r})n_{\rm e}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} \qquad (30.3.21)$$

is a unique functional of the density, as the first Hohenberg–Kohn theorem stated.

Another, equally important property of the functional relationship between the ground-state energy and density is stated by the second Hohenberg-Kohn theorem: the energy as a functional of the density takes its minimum at the true ground-state density. Stated otherwise, the ground-state energy for a given external potential $V_{\text{ext}}(\mathbf{r})$ is obtained by minimizing the total energy functional $E[n_{\text{e}}(\mathbf{r})]$ with respect to the density, provided the total number of particles N_{e} is fixed, i.e.,

$$\int n_{\rm e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} = N_{\rm e} \,. \tag{30.3.22}$$

When this condition is taken into account by a Lagrange multiplier μ , the minimum of the functional

$$E[n_{\rm e}(\boldsymbol{r})] - \mu \left[\int n_{\rm e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} - N_{\rm e} \right]$$
(30.3.23)

has to be found, that is, the ground-state density satisfies the equation

$$\frac{\delta E[n_{\rm e}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})} \equiv \frac{\delta F[n_{\rm e}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})} + V_{\rm ext}(\boldsymbol{r}) = \mu, \qquad (30.3.24)$$

and the value of the functional at the minimum is the ground-state energy. It can be shown that the Lagrange multiplier μ is equal to the chemical potential.

The second theorem is the consequence of the Rayleigh–Ritz variational principle of quantum mechanics which states that the expectation value of the Hamiltonian is minimal if it is calculated with the true ground-state wavefunction, provided the particle number is fixed, and the value of the minimum is the ground-state energy:

$$E_0 = \min E[n_e(\mathbf{r})].$$
 (30.3.25)

An interesting generalization of these theorems to finite temperatures has been proved by N. D. MERMIN (1965). He has shown that the grand canonical potential

$$\Omega = E - \mu N - TS \tag{30.3.26}$$

is a unique functional of the density and it takes its minimum at the physical density of the finite-temperature system.

30.3.2 Kohn–Sham Equations

The many-body problem is thus reduced to finding the functional $F[n_{\rm e}(\mathbf{r})]$ that contains the kinetic energy and the contribution of the electron–electron interaction and to solving the corresponding variational problem. The Hohenberg–Kohn theorems only state the existence of this functional but give no hint about its form. The density-functional theory can be applied for the calculation of physical quantities only if some assumptions can be made about this functional. This difficult task could be simplified if the many-body problem could be reduced to an effective one-body problem with an appropriately chosen potential. Such a procedure has been proposed by W. KOHN and L. J. SHAM (1965).

Consider an interacting system with a physical $V_{\text{ext}}(\mathbf{r})$ one-particle potential and density $n_{\text{e}}(\mathbf{r})$. KOHN and SHAM supposed that one can find a fictitious noninteracting system that produces the same density in the presence of an effective one-particle potential $V_{\text{s}}(\mathbf{r})$. The question whether an effective potential can necessarily be found to a given smooth density is a fundamental problem of the mathematical foundation of density-functional theory. This is the problem of *v*-representability. Without going into mathematical details we assume that such an effective potential exists. Then it follows from the first Hohenberg–Kohn theorem that $V_{\text{s}}(\mathbf{r})$ is uniquely defined.

The particles of this noninteracting auxiliary problem satisfy the oneparticle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_{\rm e}}\boldsymbol{\nabla}^2 + V_{\rm s}(\boldsymbol{r})\right]\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r})\,,\qquad(30.3.27)$$

and the density has to be determined via

$$n_{\rm e}(\boldsymbol{r}) = \sum_{i=1}^{N_{\rm e}} |\phi_i(\boldsymbol{r})|^2 ,$$
 (30.3.28)

where the summation goes over the lowest energy occupied states. Thus the one-particle wavefunctions are also unique functionals of the density.

The wavefunction $|\Psi_s\rangle$ of this noninteracting system is a Slater determinant formed from the one-particle wavefunctions. The expectation value of the kinetic energy operator is

$$T_{\rm s}[n_{\rm e}(\boldsymbol{r})] = \langle \Psi_{\rm s}|T|\Psi_{\rm s}\rangle = \sum_{i=1}^{N_{\rm e}} \int \phi_i^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m_{\rm e}}\boldsymbol{\nabla}^2\right) \phi_i(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$
(30.3.29)

It is important to note that it is not equal to the total kinetic energy,

$$T_{\rm s}[n_{\rm e}(\boldsymbol{r})] \neq T[n_{\rm e}(\boldsymbol{r})],$$
 (30.3.30)

since the expectation value of T is not taken with the correct wavefunction. The difference can be incorporated into the correlation energy. Adding to it the contribution of the potential $V_{\rm s}$, the total energy functional is

$$E[n_{\rm e}(\mathbf{r})] = T_{\rm s}[n_{\rm e}(\mathbf{r})] + \int V_{\rm s}(\mathbf{r})n_{\rm e}(\mathbf{r})\,\mathrm{d}\mathbf{r}\,.$$
(30.3.31)

Naturally the principle of energy minimum holds for this system as well, i.e., this functional has its minimum at the true ground-state density and the value of the energy minimum is the ground-state energy.

The as yet unknown potential has to be determined self-consistently from the requirement that the energy functional of this fictitious noninteracting system be as close as possible to the true energy functional. Its minimum will then give a good approximation for the ground-state energy and density. Thus, all the difficulty is reduced to finding a good potential $V_{\rm s}$. In order to be able to say something about it, we subtract three terms from $E[n_{\rm e}(\mathbf{r})]$: the term $T_{\rm s}$, the contribution of the external potential

$$E_{\text{ext}}[n_{\text{e}}(\boldsymbol{r})] = \int V_{\text{ext}}(\boldsymbol{r}) n_{\text{e}}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,, \qquad (30.3.32)$$

and the Hartree approximation to the electron-electron interaction,

$$U_{\rm H}[n_{\rm e}(\boldsymbol{r})] = \frac{\tilde{e}^2}{2} \iint \frac{n_{\rm e}(\boldsymbol{r})n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' \,\mathrm{d}\boldsymbol{r} \,. \tag{30.3.33}$$

The remaining term $E_{\rm xc}[n_{\rm e}(\boldsymbol{r})]$ defined by

$$E[n_{e}(\boldsymbol{r})] = \langle \Psi_{s} | T | \Psi_{s} \rangle + \int V_{ext}(\boldsymbol{r}) n_{e}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} + \frac{\tilde{e}^{2}}{2} \iint \frac{n_{e}(\boldsymbol{r}) n_{e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}\boldsymbol{r}' \, \mathrm{d}\boldsymbol{r} + E_{xc}[n_{e}(\boldsymbol{r})]$$
(30.3.34)

is called the exchange–correlation energy. It contains all corrections beyond the Hartree approximation, including the correlation correction to the kinetic energy:

$$E_{\rm xc}[n_{\rm e}(\boldsymbol{r})] = T[n_{\rm e}(\boldsymbol{r})] - T_{\rm s}[n_{\rm e}(\boldsymbol{r})] + U[n_{\rm e}(\boldsymbol{r})] - U_{\rm H}[n_{\rm e}(\boldsymbol{r})].$$
(30.3.35)

Note that the exchange–correlation energy has a simple interpretation if the relationship derived previously between the energy and the density– density correlation function is used. It can be written in the form

$$E_{\rm xc}[n_{\rm e}(\boldsymbol{r})] = \frac{\tilde{e}^2}{2} \iint \frac{n_{\rm e}(\boldsymbol{r})n_{\rm xc}(\boldsymbol{r},\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' \,\mathrm{d}\boldsymbol{r} \,, \qquad (30.3.36)$$

where

$$n_{\rm xc}(\boldsymbol{r}, \boldsymbol{r}') = n_{\rm e}(\boldsymbol{r}) \big[\tilde{g}(\boldsymbol{r}, \boldsymbol{r}') - 1 \big]$$
(30.3.37)

and $\tilde{g}(\mathbf{r}, \mathbf{r}')$ is a mean of the pair distribution function over the coupling strength. We have seen in Chapter 28 that both quantum mechanical exchange

and Coulomb repulsion lead to a decrease of the pair distribution function at short distances. Electrons create Fermi and Coulomb holes around themselves. Since $n_{\rm xc}(\mathbf{r}, \mathbf{r}')$ is related to the hole density at \mathbf{r}' created by an electron at \mathbf{r} , $E_{\rm xc}[n_{\rm e}(\mathbf{r})]$ can be viewed as the interaction of electrons with their exchange–correlation holes.

Substituting (30.3.34) into (30.3.24) which expresses the minimum condition for the ground-state energy, we find

$$\frac{\delta T_{\rm s}[n_{\rm e}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})} + V_{\rm ext}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' + V_{\rm xc}[n_{\rm e}(\boldsymbol{r})] = \mu , \qquad (30.3.38)$$

where

$$V_{\rm xc}[n_{\rm e}(\boldsymbol{r})] = \frac{\delta E_{\rm xc}[n_{\rm e}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})}$$
(30.3.39)

is the exchange–correlation potential. On the other hand, when noninteracting particles moving in a potential $V_{\rm s}(\mathbf{r})$ are considered, the minimum condition of functional (30.3.31) leads to

$$\frac{\delta T_{\rm s}[n_{\rm e}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})} + V_{\rm s}(\boldsymbol{r}) = \mu. \qquad (30.3.40)$$

Comparison of (30.3.38) with (30.3.40) gives

$$V_{\rm s}(\boldsymbol{r}) = V_{\rm ext}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' + V_{\rm xc}[n_{\rm e}(\boldsymbol{r})]. \qquad (30.3.41)$$

This effective one-particle potential is known as the Kohn–Sham potential and the Schrödinger equations using this potential,

$$\left[-\frac{\hbar^2}{2m_{\rm e}}\boldsymbol{\nabla}^2 + V_{\rm ext}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\boldsymbol{r}' + V_{\rm xc}[n_{\rm e}(\boldsymbol{r})]\right] \phi_i(\boldsymbol{r}) = \varepsilon_i \phi_i(\boldsymbol{r}) \,, \tag{30.3.42}$$

are the Kohn–Sham equations. It follows from our earlier considerations that the density determined via (30.3.28) from the solutions of these equations is equal to the true ground-state density of the many-body system.

Finally, knowing the density and using (30.3.34), the total ground-state energy can be calculated from

$$E[n_{\rm e}(\boldsymbol{r})] = \sum_{i=1}^{N_{\rm e}} \int \phi_i^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 \right) \phi_i(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} + \int V_{\rm ext}(\boldsymbol{r}) n_{\rm e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} + \frac{\tilde{e}^2}{2} \iint \frac{n_{\rm e}(\boldsymbol{r}) n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \,\mathrm{d}\boldsymbol{r}' \,\mathrm{d}\boldsymbol{r} + E_{\rm xc}[n_{\rm e}(\boldsymbol{r})] \,.$$
(30.3.43)

It can be seen using (30.3.27) that

$$T_{\rm s}[n_{\rm e}(\boldsymbol{r})] = \sum_{i=1}^{N_{\rm e}} \int \phi_i^*(\boldsymbol{r}) [\varepsilon_i - V_{\rm s}(\boldsymbol{r})] \phi_i(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r}$$

$$= \sum_{i=1}^{N_{\rm e}} \varepsilon_i - \int V_{\rm s}(\boldsymbol{r}) n_{\rm e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r}, \qquad (30.3.44)$$

which leads to a more convenient expression for the total energy:

$$E[n_{e}(\boldsymbol{r})] = \sum_{i=1}^{N_{e}} \varepsilon_{i} - \int V_{s}(\boldsymbol{r})n_{e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} + \int V_{ext}(\boldsymbol{r})n_{e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} + \frac{\tilde{e}^{2}}{2} \iint \frac{n_{e}(\boldsymbol{r})n_{e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \,\mathrm{d}\boldsymbol{r}' \,\mathrm{d}\boldsymbol{r} + E_{xc}[n_{e}(\boldsymbol{r})] = \sum_{i=1}^{N_{e}} \varepsilon_{i} - \frac{\tilde{e}^{2}}{2} \iint \frac{n_{e}(\boldsymbol{r})n_{e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \,\mathrm{d}\boldsymbol{r}' \,\mathrm{d}\boldsymbol{r} + E_{xc}[n_{e}(\boldsymbol{r})] - \int n_{e}(\boldsymbol{r})V_{xc}[n_{e}(\boldsymbol{r})] \,\mathrm{d}\boldsymbol{r} \,.$$
(30.3.45)

Provided we know the potential $V_{\text{ext}}(\mathbf{r})$ and the exchange-correlation energy functional $E_{\text{xc}}[n_{\text{e}}(\mathbf{r})]$, or the exchange-correlation potential $V_{\text{xc}}[n_{\text{e}}(\mathbf{r})]$, the density and the ground-state energy can be calculated self-consistently. The coordinates \mathbf{R}_n of the atoms and their charge Z_n are input parameters together with the total number of electrons. Taking an initial form for the density $n_{\text{e}}(\mathbf{r})$ first the potential $V_{\text{s}}(\mathbf{r})$ is calculated using (30.3.41). Then the solution of the Kohn–Sham equations in (30.3.42) leads to a new set of wavefunctions from which a new density is obtained via (30.3.28). This iterative procedure is repeated until self-consistency is established.

30.3.3 Local-Density Approximation

The procedure explained above is in principle exact. However, we do not have an explicit expression for $E_{\rm xc}[n_{\rm e}(\mathbf{r})]$ or its functional derivative, $V_{\rm xc}[n_{\rm e}(\mathbf{r})]$. An approximate form can be obtained if we assume that for systems where $n_{\rm e}(\mathbf{r})$ varies slowly on the scale of the Fermi wavelength the exchange–correlation potential is a function of the local density. In this *local-density approximation* (LDA) the exchange–correlation energy is chosen in the form

$$E_{\rm xc}^{\rm LDA}[n_{\rm e}(\boldsymbol{r})] = \int n_{\rm e}(\boldsymbol{r}) \varepsilon_{\rm xc}^{\rm hom}[n_{\rm e}(\boldsymbol{r})] \,\mathrm{d}\boldsymbol{r} \,, \qquad (30.3.46)$$

where $\varepsilon_{\rm xc}^{\rm hom}[n_{\rm e}]$ is the exchange–correlation energy per particle in the homogeneous electron gas of density $n_{\rm e}$. The exchange–correlation potential is then

$$V_{\rm xc}^{\rm LDA}(\boldsymbol{r}) = \frac{\delta E_{\rm xc}^{\rm LDA}[n_{\rm e}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})} = \frac{\mathrm{d}n_{\rm e}\varepsilon_{\rm xc}^{\rm hom}[n_{\rm e}])}{\mathrm{d}n_{\rm e}}\Big|_{n_{\rm e}=n_{\rm e}(\boldsymbol{r})]}$$
$$= \varepsilon_{\rm xc}^{\rm hom}[n_{\rm e}(\boldsymbol{r})] + n_{\rm e}(\boldsymbol{r})\frac{\mathrm{d}\varepsilon_{\rm xc}^{\rm hom}(n_{\rm e})}{\mathrm{d}n_{\rm e}}\Big|_{n_{\rm e}=n_{\rm e}(\boldsymbol{r})]}.$$
(30.3.47)

If the dimensionless radius $r_{\rm s}$ is used to characterize the density,

$$V_{\rm xc}^{\rm LDA} = \left(1 - \frac{r_{\rm s}}{3} \frac{\rm d}{{\rm d}r_{\rm s}}\right) \varepsilon_{\rm xc}^{\rm hom}(r_{\rm s}), \qquad (30.3.48)$$

where we used the relationship between $r_{\rm s}$ and $n_{\rm e}$ valid in a homogeneous electron gas.

It follows from (30.1.11) derived for the exchange correction to the energy of the homogeneous electron gas that

$$\varepsilon_{\rm x}^{\rm hom} = -\frac{3}{4\pi} \tilde{e}^2 k_{\rm F} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \tilde{e}^2 n_{\rm e}^{1/3} ,$$
 (30.3.49)

or in terms of the parameter $r_{\rm s}$

$$\varepsilon_{\rm x}^{\rm hom}(r_{\rm s}) = -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{\tilde{e}^2}{r_{\rm s}a_0} = -\frac{0.458}{r_{\rm s}} \frac{\tilde{e}^2}{a_0} \,. \tag{30.3.50}$$

The exchange energy in the local-density approximation is then

$$E_{\rm x}^{\rm LDA} = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \tilde{e}^2 \int n_{\rm e}^{4/3}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r}$$
(30.3.51)

and the exchange potential, the functional derivative of the exchange energy, is

$$V_{\rm x}^{\rm LDA}(\boldsymbol{r}) = -\left(\frac{3}{\pi}\right)^{1/3} \tilde{e}^2 n_{\rm e}^{1/3}(\boldsymbol{r}) \,. \tag{30.3.52}$$

This form corresponds to taking $\alpha = 2/3$ in the Slater exchange potential [see (30.1.24)].

For the correlation energy, one can use one of the parametrized analytical forms given in the previous section. In most calculations the Vosko–Wilk–Nusair, the Perdew–Zunger, or the Perdew–Wang parametrizations given in (30.2.24), (30.2.25), and (30.2.26), or (30.2.27), respectively, are used nowa-days.

30.3.4 Spin-Polarized Systems

We assumed until now that the system is unpolarized and the density of spin-up and spin-down electrons is the same. That is why the system could be characterized by a single function, the density of electrons. This is not possible any more in the presence of an external magnetic field or when the system is spontaneously polarized, and the densities are different for the two spin orientations, $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$. Besides the coupling of the number-density operator $n(\mathbf{r})$ to the external potential, another term appears in V, which describes the coupling of the operator of the magnetization density $\mathbf{m}(\mathbf{r})$ to the magnetic induction:

$$V = \int \left[V_{\text{ext}}(\boldsymbol{r}) n(\boldsymbol{r}) - \boldsymbol{B}(\boldsymbol{r}) \cdot \boldsymbol{m}(\boldsymbol{r}) \right] d\boldsymbol{r} , \qquad (30.3.53)$$

where

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$$n(\mathbf{r}) = \sum_{i} \delta(\mathbf{r} - \mathbf{r}_{i})$$
(30.3.54)

and

$$\boldsymbol{m}(\boldsymbol{r}) = g_{\rm e}\mu_{\rm B}\sum_{i}\boldsymbol{s}\delta(\boldsymbol{r}-\boldsymbol{r}_{i}) = \frac{1}{2}g_{\rm e}\mu_{\rm B}\sum_{i}\boldsymbol{\sigma}\delta(\boldsymbol{r}-\boldsymbol{r}_{i})$$
(30.3.55)

with σ the Pauli operator.

Quite similar to the procedure applied above for unpolarized systems, it can now be shown that different wavefunctions cannot give identical particle density and magnetization density,

$$n_{\rm e}(\boldsymbol{r}) = \langle \Psi | n(\boldsymbol{r}) | \Psi \rangle, \qquad \boldsymbol{M}(\boldsymbol{r}) = \langle \Psi | \boldsymbol{m}(\boldsymbol{r}) | \Psi \rangle.$$
 (30.3.56)

To prove this, the same inequalities are used except that the two problems that we compare have potential $V_{\text{ext}}(\mathbf{r})$ and induction $\mathbf{B}(\mathbf{r})$ on the one hand and potential $V'_{\text{ext}}(\mathbf{r})$ and induction $\mathbf{B}'(\mathbf{r})$ on the other hand. As a consequence (30.3.15) is replaced with

$$\langle \Psi | V - V' | \Psi \rangle = \int n_{\rm e}(\mathbf{r}) \left[V_{\rm ext}(\mathbf{r}) - V'_{\rm ext}(\mathbf{r}) \right] d\mathbf{r} - \int \mathbf{M}(\mathbf{r}) \cdot \left[\mathbf{B}(\mathbf{r}) - \mathbf{B}'(\mathbf{r}) \right] d\mathbf{r} .$$
(30.3.57)

It follows from the generalization of the first Hohenberg–Kohn theorem that every observable quantity is a unique functional of $n_{\rm e}(\mathbf{r})$ and $\mathbf{M}(\mathbf{r})$. This theory is called *spin-density-functional theory*. The energy functional is obtained by adding the contribution of the magnetic field to (30.3.21):

$$E[n_{e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})] = F[n_{e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})] + \int V_{ext}(\boldsymbol{r})n_{e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} - \int \boldsymbol{B}(\boldsymbol{r}) \cdot \boldsymbol{M}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$
(30.3.58)

For a fixed external potential $V_{\text{ext}}(\mathbf{r})$ and induction $\mathbf{B}(\mathbf{r})$, this functional takes its minimum at the physical particle density $n_{\text{e}}(\mathbf{r})$ and magnetization density $\mathbf{M}(\mathbf{r})$ which have to be calculated self-consistently from the ground-state wavefunction. If the constraint for the particle number is taken into account by a Lagrange multiplier we find

$$\frac{\delta E[n_{\rm e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})} \equiv \frac{\delta F[n_{\rm e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})} + V_{\rm ext}(\boldsymbol{r}) = \mu,$$

$$\frac{\delta E[n_{\rm e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta \boldsymbol{M}(\boldsymbol{r})} \equiv \frac{\delta F[n_{\rm e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta \boldsymbol{M}(\boldsymbol{r})} - \boldsymbol{B}(\boldsymbol{r}) = 0.$$
(30.3.59)

The Kohn–Sham equations can also be generalized for spin-polarized systems by introducing an effective magnetic induction in addition to the effective one-particle potential $V_{\rm s}(\mathbf{r})$:

$$\sum_{\sigma'} \left\{ \left[-\frac{\hbar^2}{2m_{\rm e}} \boldsymbol{\nabla}^2 + V_{\rm s}(\boldsymbol{r}) \right] \delta_{\sigma\sigma'} - \frac{1}{2} g_{\rm e} \mu_{\rm B} \boldsymbol{\sigma}_{\sigma\sigma'} \cdot \boldsymbol{B}_{\rm s}(\boldsymbol{r}) \right\} \phi_{i\sigma'}(\boldsymbol{r}) = \varepsilon_{i\sigma} \phi_{i\sigma}(\boldsymbol{r}) \,.$$
(30.3.60)

Just as for unpolarized systems, the origin of this effective field is best understood if we subtract out the kinetic energy of the noninteracting system, the contribution of the external potential and of the magnetic field as well as the Hartree term (which depends solely on the density) from the total energy functional. The remaining term is the exchange–correlation energy:

$$E[n_{e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})] = T_{s}[n_{e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})] + \int V_{ext}(\boldsymbol{r})n_{e}(\boldsymbol{r}) \,d\boldsymbol{r}$$
$$-\int \boldsymbol{B}(\boldsymbol{r}) \cdot \boldsymbol{M}(\boldsymbol{r}) \,d\boldsymbol{r} + \frac{\tilde{e}^{2}}{2} \iint \frac{n_{e}(\boldsymbol{r})n_{e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \,d\boldsymbol{r}' \,d\boldsymbol{r}$$
$$+ E_{xc}[n_{e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})].$$
(30.3.61)

This yields

$$V_{\rm s}(\boldsymbol{r}) = V_{\rm ext}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + \frac{\delta E_{\rm xc}[n_{\rm e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta n_{\rm e}(\boldsymbol{r})},$$

$$\boldsymbol{B}_{\rm s}(\boldsymbol{r}) = \boldsymbol{B}(\boldsymbol{r}) - \frac{\delta E_{\rm xc}[n_{\rm e}(\boldsymbol{r}), \boldsymbol{M}(\boldsymbol{r})]}{\delta \boldsymbol{M}(\boldsymbol{r})}$$
(30.3.62)

for the effective potential and effective induction.

In a uniform magnetic field or when the magnetic moments are collinear, the particle densities of electrons with the two spin orientations may be used instead of the total particle density and magnetization density. The Kohn–Sham equations from which the one-particle states with spin σ have to be calculated,

$$\left[-\frac{\hbar^2}{2m_{\rm e}}\boldsymbol{\nabla}^2 + V_{\rm s\sigma}(\boldsymbol{r})\right]\phi_{i\sigma}(\boldsymbol{r}) = \varepsilon_{i\sigma}\phi_{i\sigma}(\boldsymbol{r}),\qquad(30.3.63)$$

contain a spin-dependent effective potential

$$V_{s\sigma}(\boldsymbol{r}) = V_{ext}(\boldsymbol{r}) + \tilde{e}^2 \int \frac{n_e(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + V_{xc\sigma}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] - \frac{1}{2}g_e\mu_B\sigma B, \qquad (30.3.64)$$

where

$$V_{\mathrm{xc}\sigma}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] = \frac{\delta E_{\mathrm{xc}}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})]}{\delta n_{\sigma}(\boldsymbol{r})}$$
(30.3.65)

is the spin-dependent exchange–correlation potential. The procedure is selfconsistent if the density of electrons with spin σ satisfies the equation

$$n_{\sigma}(\mathbf{r}) = \sum_{i=1}^{N_{\sigma}} |\phi_{i\sigma}(\mathbf{r})|^2, \qquad (30.3.66)$$

where the summation goes over the lowest energy occupied states and the total density is $n_{\rm e}(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$.

Similar to (30.3.45), the total energy is obtained from

$$E[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \varepsilon_{i\sigma} - \frac{\tilde{e}^2}{2} \iint \frac{n_{\rm e}(\boldsymbol{r})n_{\rm e}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' d\boldsymbol{r}$$
(30.3.67)
+
$$E_{\rm xc}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] - \sum_{\sigma} \int n_{\sigma}(\boldsymbol{r}) V_{\rm xc\sigma}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] d\boldsymbol{r}.$$

The local-density approximation can be used to get an approximate expression for the spin-dependent exchange–correlation energy, too. It then has the name *local-spin-density approximation* (LSDA). We assume that instead of (30.3.46) the exchange–correlation energy can be written in the form

$$E_{\rm xc}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] = \int \varepsilon_{\rm xc}[n_{\uparrow}(\boldsymbol{r}), n_{\downarrow}(\boldsymbol{r})] n_{\rm e}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,. \tag{30.3.68}$$

The exchange contribution can relatively simply be expressed in terms of the exchange energy of the unpolarized electron gas. Since there is no exchange between particles of opposite spin, the contributions of electrons of the two spin orientations are additive:

$$E_{\mathbf{x}}[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2} \left(E_{\mathbf{x}}[2n_{\uparrow}] + E_{\mathbf{x}}[2n_{\downarrow}] \right).$$
(30.3.69)

With the known form for the exchange energy of the unpolarized electron gas we have

$$E_{\rm x}^{\rm LSDA}[n_{\uparrow},n_{\downarrow}] = -2^{1/3} \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \tilde{e}^2 \int \left[n_{\uparrow}^{4/3}(\boldsymbol{r}) + n_{\downarrow}^{4/3}(\boldsymbol{r})\right] d\boldsymbol{r}.$$
 (30.3.70)

Instead of $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$ it is customary to use the total density $n_{\rm e}(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$ and the parameter

$$\zeta(\mathbf{r}) = \frac{n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})}{n_{\rm e}(\mathbf{r})}$$
(30.3.71)

characterizing the relative polarization. We have

$$E_{\mathbf{x}}^{\mathrm{LSDA}}[n_{\mathrm{e}},\zeta] = \int \varepsilon_{\mathbf{x}} \big[n_{\mathrm{e}}(\boldsymbol{r}), \zeta(\boldsymbol{r}) \big] n_{\mathrm{e}}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r}$$
(30.3.72)

with

$$\varepsilon_{\mathbf{x}}[n_{\mathbf{e}},\zeta] = -\frac{1}{2} \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \tilde{e}^2 n_{\mathbf{e}}^{1/3}(\mathbf{r}) \left\{ \left[1+\zeta(\mathbf{r})\right]^{4/3} + \left[1-\zeta(\mathbf{r})\right]^{4/3} \right\}.$$
(30.3.73)

Using $r_{\rm s}$ instead of $n_{\rm e}$, it is customarily rewritten in the form

$$\varepsilon_{\mathbf{x}}^{\mathrm{LSDA}}(r_{\mathrm{s}},\zeta) = \varepsilon_{\mathbf{x}}(r_{\mathrm{s}},\zeta=0) + \left[\varepsilon_{\mathbf{x}}(r_{\mathrm{s}},\zeta=1) - \varepsilon_{\mathbf{x}}(r_{\mathrm{s}},\zeta=0)\right] f(\zeta) , \qquad (30.3.74)$$

where

$$\begin{split} \varepsilon_{\rm x}(r_{\rm s},\zeta=0) &= -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_{\rm s}} \frac{\tilde{e}^2}{a_0} \,, \\ \varepsilon_{\rm x}(r_{\rm s},\zeta=1) &= 2^{1/3} \varepsilon_{\rm x}(r_{\rm s},\zeta=0) \,, \end{split}$$
(30.3.75)

and

$$f(\zeta) = \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2(2^{1/3} - 1)}.$$
 (30.3.76)

The additivity of the contributions coming from electrons of the two spin orientations is not valid for the spin-dependent correlation energy. Nevertheless, it is often assumed that a form analogous to (30.3.74) holds for the correlation energy of partially polarized systems, that is

$$\varepsilon_{\rm c}(r_{\rm s},\zeta) = \varepsilon_{\rm c}(r_{\rm s},\zeta=0) + \left[\varepsilon_{\rm c}(r_{\rm s},\zeta=1) - \varepsilon_{\rm c}(r_{\rm s},\zeta=0)\right] f(\zeta) \,.$$
(30.3.77)

Using the Perdew–Zunger parametrization of the correlation energy, the expressions given in (30.2.25) and (30.2.26) are used in the unpolarized, $\zeta = 0$ case. When $0 \le r_{\rm s} \le 1$,

$$\varepsilon_{\rm c}^{\rm PZ}(r_{\rm s},\zeta=0) = [0.0311\ln r_{\rm s} - 0.048 + 0.0020r_{\rm s}\ln r_{\rm s} - 0.0116r_{\rm s}]\,\tilde{e}^2/a_0\,,$$
(30.3.78)

while for $r_{\rm s} \ge 1$

$$\varepsilon_{\rm c}^{\rm PZ}(r_{\rm s},\zeta=0) = -\frac{0.1423}{1+1.0529\sqrt{r_{\rm s}}+0.3334r_{\rm s}}\frac{\tilde{e}^2}{a_0}\,.$$
 (30.3.79)

Similar expressions are valid in the fully polarized state but with different coefficients. In the range $0 \le r_s \le 1$,

$$\varepsilon_{\rm c}^{\rm PZ}(r_{\rm s},\zeta=1) = [0.01555\ln r_{\rm s} - 0.0269 + 0.0007r_{\rm s}\ln r_{\rm s} - 0.0048r_{\rm s}]\,\tilde{e}^2/a_0\,,$$
(30.3.80)

while when $r_{\rm s} \ge 1$,

$$\varepsilon_{\rm c}^{\rm PZ}(r_{\rm s},\zeta=1) = -\frac{0.0843}{1+1.3981\sqrt{r_{\rm s}}+0.2611r_{\rm s}}\frac{\tilde{e}^2}{a_0}\,. \tag{30.3.81}$$

VOSKO, WILK, and NUSAIR proposed a form somewhat different from (30.3.77), namely

$$\varepsilon_{\rm c}(r_{\rm s},\zeta) = \varepsilon_{\rm c}(r_{\rm s},\zeta=0) + \alpha_{\rm c}(r_{\rm s})\frac{f(\zeta)}{f''(0)}(1-\zeta^4) + \left[\varepsilon_{\rm c}(r_{\rm s},\zeta=1) - \varepsilon_{\rm c}(r_{\rm s},\zeta=0)\right]f(\zeta)\zeta^4$$
(30.3.82)

with

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$$\begin{aligned} \alpha_{\rm c}(r_{\rm s}) &= -0.0169 \left\{ \ln \left(\frac{r_{\rm s}}{r_{\rm s} + 1.1311 \sqrt{r_{\rm s}} + 13.0045} \right) \\ &+ 0.3177 \arctan \left(\frac{7.1231}{2\sqrt{r_{\rm s}} + 1.1311} \right) \\ &+ 0.0004 \ln \left[\frac{(\sqrt{r_{\rm s}} + 0.0048)^2}{r_{\rm s} + 1.1311 \sqrt{r_{\rm s}} + 13.0045} \right] \right\} \frac{\tilde{e}^2}{a_0} \,, \end{aligned}$$

to interpolate between the unpolarized and fully polarized systems. The expression given earlier as the Vosko–Wilk–Nusair parametrization of the correlation energy is used for the unpolarized system,

$$\begin{split} \varepsilon_{\rm c}^{\rm VWN}(r_{\rm s},\zeta=0) &= 0.0311 \left\{ \ln \left(\frac{r_{\rm s}}{r_{\rm s}+3.7274\sqrt{r_{\rm s}}+12.9352} \right) \\ &+ 1.2474 \arctan \left(\frac{6.1520}{2\sqrt{r_{\rm s}}+3.7274} \right) \qquad (30.3.84) \\ &+ 0.0312 \ln \left[\frac{(\sqrt{r_{\rm s}}+0.1050)^2}{r_{\rm s}+3.7274\sqrt{r_{\rm s}}+12.9352} \right] \right\} \frac{\tilde{e}^2}{a_0} \,, \end{split}$$

while the expression for the fully polarized system has a similar form with different parameters,

$$\begin{split} \varepsilon_{\rm c}^{\rm VWN}(r_{\rm s},\zeta=1) &= 0.01555 \left\{ \ln \left(\frac{r_{\rm s}}{r_{\rm s}+7.0604\sqrt{r_{\rm s}}+18.0578} \right) \right. \\ &+ 3.3767 \arctan \left(\frac{4.7309}{2\sqrt{r_{\rm s}}+7.0604} \right) \qquad (30.3.85) \right. \\ &+ 0.1446 \ln \left[\frac{(\sqrt{r_{\rm s}}+0.3250)^2}{r_{\rm s}+7.0604\sqrt{r_{\rm s}}+18.0578} \right] \right\} \frac{\tilde{e}^2}{a_0} \,. \end{split}$$

The energy expression (30.3.82) is used in the Perdew–Wang parametrization as well with $\alpha_c(r_s)$ and $\varepsilon_c(r_s, \zeta = 1)$ given in a form similar to (30.2.27), albeit with different coefficients.

The LDA and the LSDA are commonly used for calculating the exchange– correlation energy. Several attempts have been made to go beyond these approximations, e.g., by taking into account gradient corrections or to use nonlocal functionals. In the *generalized gradient approximation* (GGA) the exchange–correlation energy is written as the integral of a functional of both the density and the gradient of the density:

$$E_{\rm xc}^{\rm GGA} = \int d\boldsymbol{r} f(n_{\uparrow}, n_{\downarrow}, \boldsymbol{\nabla} n_{\uparrow}, \boldsymbol{\nabla} n_{\downarrow}) \,. \tag{30.3.86}$$

Several GGA exchange functionals have been developed. They would, however, take us too far afield, and we will not go into such detail.

30.3.5 Applications of the Density-Functional Theory

The density-functional theory was introduced with the aim of finding a good approximation to the ground-state energy and other observable quantities that can be determined from the ground-state wavefunction. That is why it is used extensively in quantum chemistry to calculate the binding energy of molecules. Its applications in solid-state physics far exceed the calculation of cohesive energy, although the applicability of the method is based in many cases on experience without rigorous theoretical foundations.

When we determine the ground-state energy $E_0(N_e)$ of a system of N_e electrons, the ionization potential of a semiconductor or insulator can be obtained from

$$I = E_0(N_e - 1) - E_0(N_e), \qquad (30.3.87)$$

while the electron affinity is

$$A = E_0(N_e) - E_0(N_e + 1).$$
(30.3.88)

It can be shown that these quantities can be related to the energy of the fictitious one-particle states obtained from the Kohn–Sham equations:

$$I = -\varepsilon_{N_{\rm e}}^{N_{\rm e}}, \qquad (30.3.89)$$

where $\varepsilon_{N_e}^{N_e}$ is the energy of the highest occupied state of the system with N_e electrons. Similarly

$$A = -\varepsilon_{N_{\rm e}+1}^{N_{\rm e}+1}.$$
 (30.3.90)

In metals, the energy of the highest occupied fictitious level is equal to the chemical potential.

A further exact result that has been assumed tacitly is that the one-particle states obtained from the solution of the Kohn–Sham equations are filled according to Fermi statistics. It can be shown that this is in fact true. One must pay attention, however, that the fictitious particles of the Kohn–Sham equations are not strictly identical to the quasiparticles introduced to describe the excited states of normal Fermi systems. When these excited states are to be described accurately, the application of the methods of the many-body problem cannot be avoided. Nevertheless, experience shows that the one-particle states obtained in the density-functional theory represent a good approximation to the Bloch states forming the electronic bands and the Kohn-Sham eigenvalues can be interpreted as being the band energies. However, if one calculates the band gap of semiconductors by taking the difference between the energy of the lowest unoccupied and the highest occupied Kohn–Sham eigenstates, the experimental value is consistently underestimated by at least a factor of 2. This error is due partially to the local-density approximation and partially to the fact that a continuous exchange-correlation potential is used in the calculations while it must have discontinuities at integer particle numbers.

The methods of band structure calculation have been explained in Chapter 19. A series of methods have been discussed which allow one to determine the energy of Bloch states in the presence of a lattice-periodic one-particle potential $V(\mathbf{r})$. It was mentioned that besides the potential of the ions this potential contains an effective potential due to mobile electrons as well. No discussion was given, however, about how this effective potential can be determined. The density-functional theory provides us with a tool to construct this potential. Therefore, the modern methods of band structure calculation combine the density-functional theory with one of the methods outlined in Chapter 19. These methods are used to solve the Kohn–Sham equations.

Besides the total energy and the band structure, we can calculate a host of other quantities using the density-functional theory. The lattice structure and the atomic coordinates \mathbf{R}_n serve as input parameters in the calculations. By calculating the total energy for a variety of different possible primitive unit cells, one can predict the stable crystalline structure. Once the structure is known and the ground-state energy is determined for different lattice parameters, the minimum yields the equilibrium lattice constants. The bulk modulus can be extracted from the variation of the energy about the minimum. The phonon spectrum can also be determined in the Born–Oppenheimer approximation, i.e., by assuming that the electrons can adjust very quickly to a change in the ionic positions. By varying the position of an atom inside a cluster of other atoms, the elements of the dynamical matrix can be obtained. The phonon energies can be determined directly from a "frozen phonon" calculation by calculating the total energy, compared to the ground-state energy, of a configuration, in which the static deformation of the lattice corresponds to a phonon of a particular branch of a chosen wave vector \boldsymbol{q} and polarization λ.

Further Reading

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Excitations in the Interacting Electron Gas

However interesting it may be to calculate the total energy of the electron system, which is an essential component of the cohesive energy of solids, as precisely as possible, it is even more important to know the energies of the excited states of electrons if we want to study the physical properties of solids. These calculations are made possible by the quasiparticle picture which is valid for the low-lying excitations. Even if the ground-state wavefunction of the interacting many-body system is not known, adding (removing) a few electrons to (from) the ground state can be interpreted as if a few quasiparticles with renormalized energies $\widetilde{\varepsilon}_{k}$ were added (removed) to (from) the system. Therefore as far as the thermal, electric, or magnetic properties are considered, in which the low-lying excited states play a dominant role, normal metals can be viewed as if independent, free electronlike quasiparticles with renormalized energies were propagating in it. That is the reason why the Drude and Sommerfeld models were so successful in describing the properties of simple metals. In this chapter, these quasiparticles will be studied going beyond the Hartree–Fock approximation.

Unlike phonons, the number of electrons is conserved. When no charge carriers are introduced from an external source, the only excitations to exist are those in which one or more electrons are taken from their initial states into new, so far unoccupied states, leaving holes behind. The basic excitations are thus electron-hole pair excitations. In metals, these excitations form a broad continuum with no energy gap, similar to what has been found in the free-electron gas. In addition a new type of excitation, spontaneous spatial and temporal oscillations, may appear in the electronic charge density due to the Coulomb interaction. This can easily be understood if the results obtained in Chapter 16 for the high-frequency properties of the classical electron gas are recalled. We learnt there that collective longitudinal oscillations, plasma oscillations, can propagate in the system of interacting electrons. The wavelength and frequency of these oscillations are determined by those values of q and ω where the dielectric function vanishes. Here a more accurate, quantum mechanical treatment of these collective oscillations will be given.

J. Sólyom, Fundamentals of the Physics of Solids, DOI 10.1007/978-3-642-04518-9 4, © Springer-Verlag Berlin Heidelberg 2010 The situation is different in semiconductors and ionic crystals. On the one hand, finite energy is needed to create an electron-hole pair due to the finite band gap. On the other hand, screening is weak or missing, and for this reason the Coulomb interaction between the electron and the hole becomes important. The excitation spectrum is therefore drastically different from the spectrum in metals. The continuum of the electron-hole pair excitations starts at a finite value, there are no low-energy pairs, and bound states may appear inside the gap.

In magnetically polarized systems, oscillations similar to the plasma oscillations may appear in the magnetic-moment density. We will consider the most important properties of these excitations at the end of this chapter.

31.1 One-Particle and Electron–Hole Pair Excitations

The bare, unscreened Coulomb interaction was used in the Hartree–Fock approximation to calculate the quasiparticle energy. This led to the result that the effective mass of the quasiparticles vanishes at the Fermi energy. If that were true, the thermodynamic behavior of the interacting electron system would be completely different from that of the noninteracting electron gas. We know from experiments that this is not so. Simple metals can be described relatively well in terms of a free electron model. The failure of the Hartree–Fock approximation is due to the complete neglect of screening. One can ask the question, what is the spectrum of quasiparticles if a better approximation is used, e.g., the RPA.

31.1.1 One-Particle Elementary Excitations

To find the one-particle excitations we look first at the problem of adding an extra particle to the ground state of the interacting system. According to the formalism sketched in Appendix H, the field operator $\hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}', t')$ creates an electron of spin σ at position \mathbf{r}' at time t'. Thus the new state containing the extra electron can be written in the form

$$|\Psi\rangle = \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}', t')|\Psi_0\rangle, \qquad (31.1.1)$$

where $|\Psi_0\rangle$ is the ground-state wavefunction. The probability of finding this electron with the same spin at r at a later time t is the absolute square of the probability amplitude

$$\left\langle \Psi_{0} \middle| \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \middle| \Psi_{0} \right\rangle.$$
(31.1.2)

Provided that $|\Psi\rangle$ is an eigenstate of the total Hamiltonian with energy E, the time dependence of this quantity is given by

$$\langle \Psi_0 | \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') | \Psi_0 \rangle = \mathrm{e}^{-\mathrm{i}(E-E_0)(t-t')/\hbar} \langle \Psi_0 | \hat{\psi}_{\sigma}(\boldsymbol{r}) | \Psi \rangle \langle \Psi | \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}') | \Psi_0 \rangle,$$
(31.1.3)

that is the probability of finding the particle does not decay in time. If, on the other hand, $\hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}')$ does not create an exact eigenstate, but a linear combination of states in a range of width Γ around an energy E, the probability of finding the particle at a later time decays exponentially. When the width Γ is small compared to $E - E_0$, the excited state $|\Psi\rangle$ has a simple interpretation: an elementary excitation of energy $E - E_0$ and lifetime $\tau \sim 1/\Gamma$ are added to the ground state.

To calculate the energy and lifetime of elementary excitations, the Green functions of the many-body problem will be used. Their definition and most important properties are given in Appendix K. A consistent perturbative calculation can be done only for the causal Green function. When the successive terms in perturbation theory are represented by Feynman diagrams, the processes taken into account can be represented pictorially. One can either try to sum the contributions of all processes up to a given order, if the coupling constant is a small parameter, or one may use physical considerations to try to find the most important classes of processes and to sum their contributions up to infinity. In these cases the region of validity and the accuracy of the approximation can also be estimated.

A much simpler procedure is provided by the equation-of-motion method. Although it has the disadvantage that its accuracy is less controllable, we will use this method for its simplicity in studying the elementary excitations.

The retarded Green function describing the propagation of a particle is

$$G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},t,\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\Big\langle \big[\hat{\psi}_{\sigma}(\boldsymbol{r},t),\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}',t')\big]_{+}\Big\rangle, \qquad (31.1.4)$$

where $[\ldots,\ldots]_+$ denotes the anticommutator of operators. The equation of motion is obtained by taking the derivative with respect to time t':

$$\frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t'} G^{\mathrm{R}}_{\sigma}(\boldsymbol{r}, t, \boldsymbol{r}', t') = \delta(t - t') \left\langle \left[\hat{\psi}_{\sigma}(\boldsymbol{r}, t), \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}', t') \right]_{+} \right\rangle \\
-\theta(t - t') \left\langle \left[\hat{\psi}_{\sigma}(\boldsymbol{r}, t), \frac{\mathrm{d}\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}', t')}{\mathrm{d}t'} \right]_{+} \right\rangle \qquad (31.1.5)$$

$$= \delta(t - t') \delta(\boldsymbol{r} - \boldsymbol{r}') - \theta(t - t') \left\langle \left[\hat{\psi}_{\sigma}(\boldsymbol{r}, t), \frac{\mathrm{d}\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}', t')}{\mathrm{d}t'} \right]_{+} \right\rangle,$$

where we made use of the equal-time anticommutator of the field operators.

The time derivative of $\hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}', t')$ in the second term of the right-hand side can be expressed using the equation

$$\frac{\mathrm{d}\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}',t')}{\mathrm{d}t'} = \frac{\mathrm{i}}{\hbar} \left[\mathcal{H}, \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}',t') \right]_{-}.$$
(31.1.6)

With the Hamiltonian given in (28.1.20) we find

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$$\frac{\hbar}{i} \frac{\mathrm{d}\hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}',t')}{\mathrm{d}t'} = \left[-\frac{\hbar^2}{2m_{\rm e}} \nabla_{\mathbf{r}'}^2 + V_{\rm ion}(\mathbf{r}') \right] \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}',t')$$

$$+ \frac{1}{2} \sum_{\sigma'} \int \mathrm{d}\mathbf{r}'' \, \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}',t') \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}'',t') U(\mathbf{r}'-\mathbf{r}'') \hat{\psi}_{\sigma'}(\mathbf{r}'',t')$$

$$- \frac{1}{2} \sum_{\sigma'} \int \mathrm{d}\mathbf{r}'' \, \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}'',t') \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}',t') U(\mathbf{r}''-\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}'',t') .$$
(31.1.7)

Since the last two terms give identical contributions, we have

$$\begin{bmatrix} \frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t'} + \frac{\hbar^2}{2m_{\mathrm{e}}} \nabla_{\mathbf{r}'}^2 - V_{\mathrm{ion}}(\mathbf{r}') \end{bmatrix} \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}', t') \qquad (31.1.8)$$
$$= \sum_{\sigma'} \int \mathrm{d}\mathbf{r}'' \, \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}', t') \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}'', t') U(\mathbf{r}' - \mathbf{r}'') \hat{\psi}_{\sigma'}(\mathbf{r}'', t') \,.$$

Substitution into (31.1.5) leads to the following equation of motion for the Green function:

$$\begin{bmatrix}
\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'} + \frac{\hbar^2}{2m_{\mathrm{e}}}\boldsymbol{\nabla}_{\boldsymbol{r}'}^2 - V_{\mathrm{ion}}(\boldsymbol{r}')
\end{bmatrix} G_{\sigma}^{\mathrm{R}}(\boldsymbol{r},t,\boldsymbol{r}',t') = \delta(t-t')\delta(\boldsymbol{r}-\boldsymbol{r}') \\
- \frac{\mathrm{i}}{\hbar}\theta(t-t')\sum_{\sigma'}\int \mathrm{d}\boldsymbol{r}''\,U(\boldsymbol{r}'-\boldsymbol{r}'') \\
\times \left\langle \left[\hat{\psi}_{\sigma}(\boldsymbol{r},t),\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t')\hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}'',t')\hat{\psi}_{\sigma'}(\boldsymbol{r}'',t')\right]_{+}\right\rangle.$$
(31.1.9)

Before trying to solve this equation, we consider the Green function of noninteracting electrons. If we neglect the potential of the ions, the Green function of free electrons is defined via

$$\left[\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'} + \frac{\hbar^2}{2m_{\mathrm{e}}}\boldsymbol{\nabla}_{\boldsymbol{r}'}^2\right]G^{(0)}_{\sigma}(\boldsymbol{r},t,\boldsymbol{r}',t') = \delta(t-t')\delta(\boldsymbol{r}-\boldsymbol{r}')\,.$$
(31.1.10)

If the Green function is written as a Fourier integral in the form

$$G_{\sigma}^{(0)}(\boldsymbol{r},t,\boldsymbol{r}',t') = \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3} \frac{\mathrm{d}\omega}{2\pi} G_{\sigma}^{(0)}(\boldsymbol{k},\omega) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')-\mathrm{i}\omega(t-t')},\qquad(31.1.11)$$

the equation of motion for the Fourier transform simplifies to an algebraic equation:

$$\left(\hbar\omega - \frac{\hbar^2 \boldsymbol{k}^2}{2m_{\rm e}}\right) G_{\sigma}^{(0)}(\boldsymbol{k},\omega) = 1.$$
(31.1.12)

Its solution is

$$G_{\sigma}^{(0)}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \varepsilon_{\boldsymbol{k}}^{(0)}} + a\delta(\hbar\omega - \varepsilon_{\boldsymbol{k}}^{(0)}), \qquad (31.1.13)$$

where $\varepsilon_{\mathbf{k}}^{(0)} = \hbar^2 \mathbf{k}^2 / 2m_{\rm e}$. The constant *a* is not determined by the equation itself, since the same equation would have been obtained for the advanced or

causal Green functions as well. Its value is fixed by the analytic properties of the Green function. The retarded function has to be analytic in the upper half-plane and may have poles in the lower half-plane. This is satisfied if $a = -i\pi$, that is

$$G_{\sigma}^{(0)\mathrm{R}}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \varepsilon_{\boldsymbol{k}}^{(0)} + \mathrm{i}\delta}, \qquad (31.1.14)$$

where δ is a positive infinitesimal. The pole of the free electron Green function is exactly at the energy $\hbar \omega = \hbar^2 k^2 / 2m_e$ of one-particle excitations.

In the presence of a lattice-periodic potential, but still neglecting the electron–electron interaction,

$$\left[\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'} + \frac{\hbar^2}{2m_{\mathrm{e}}}\boldsymbol{\nabla}_{\boldsymbol{r}'}^2 - V(\boldsymbol{r}')\right]G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},t,\boldsymbol{r}',t') = \delta(t-t')\delta(\boldsymbol{r}-\boldsymbol{r}'). \quad (31.1.15)$$

The field operators appearing in the definition of the Green function can be expanded in terms of the creation and annihilation operators of Bloch states:

$$G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},t,\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\sum_{n\boldsymbol{k}n'\boldsymbol{k}'} \left\langle \left[c_{n\boldsymbol{k}\sigma}(t),c^{\dagger}_{n'\boldsymbol{k}'\sigma}(t')\right]_{+} \right\rangle \psi_{n\boldsymbol{k}\sigma}(\boldsymbol{r})\psi^{*}_{n'\boldsymbol{k}'\sigma}(\boldsymbol{r}') \,.$$
(31.1.16)

Using the time dependence of the operators in the Heisenberg picture as well as the anticommutator of the fermion operators, we get

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{r},t,\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\sum_{\boldsymbol{nk}}\mathrm{e}^{-\mathrm{i}\varepsilon_{\boldsymbol{nk}}(t-t')/\hbar}\psi_{\boldsymbol{nk}\sigma}(\boldsymbol{r})\psi_{\boldsymbol{nk}\sigma}^{*}(\boldsymbol{r}')\,,\quad(31.1.17)$$

where ε_{nk} is the energy of the Bloch state. Taking the Fourier transform with respect to time the integral is made to converge with the help of the adiabatic factor $\exp[-\delta(t-t')]$ with an infinitesimal δ .¹ The retarded Green function is

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{n\boldsymbol{k}} \frac{\psi_{n\boldsymbol{k}\sigma}(\boldsymbol{r})\psi_{n\boldsymbol{k}\sigma}^{*}(\boldsymbol{r}')}{\hbar\omega - \varepsilon_{n\boldsymbol{k}} + \mathrm{i}\delta}, \qquad (31.1.18)$$

and the corresponding Green operator has the form

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',\varepsilon) = \sum_{\boldsymbol{n}\boldsymbol{k}} \frac{\left|\psi_{\boldsymbol{n}\boldsymbol{k}\sigma}(\boldsymbol{r})\right\rangle \langle \psi_{\boldsymbol{n}\boldsymbol{k}\sigma}(\boldsymbol{r}')\right|}{\varepsilon - \varepsilon_{\boldsymbol{n}\boldsymbol{k}} + \mathrm{i}\delta} \,. \tag{31.1.19}$$

The spatial variables can be transformed out if, instead of taking the Fourier transform, the quantity

$$G_{nn'\sigma}^{\rm R}(\boldsymbol{k},\boldsymbol{k}',\omega) = \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}' \psi_{n\boldsymbol{k}\sigma}^{*}(\boldsymbol{r}) G_{\sigma}^{\rm R}(\boldsymbol{r},\boldsymbol{r}',\omega) \psi_{n'\boldsymbol{k}'\sigma}(\boldsymbol{r}') \qquad (31.1.20)$$

is defined in terms of the Bloch functions. Inverting the transformation using the completeness of the Bloch functions we have

¹ Note that the same δ ensures the correct analytic properties of the Green function.

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$$G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{n\boldsymbol{k}n'\boldsymbol{k}'} \psi_{n\boldsymbol{k}\sigma}(\boldsymbol{r}) G^{\mathrm{R}}_{nn'\sigma}(\boldsymbol{k},\boldsymbol{k}',\omega) \psi^{*}_{n'\boldsymbol{k}'\sigma}(\boldsymbol{r}') \,. \tag{31.1.21}$$

The orthonormality of the Bloch functions leads to

$$G_{nn'\sigma}^{\rm R}(\boldsymbol{k},\boldsymbol{k}',\omega) = \delta_{nn'}\delta_{\boldsymbol{k}\boldsymbol{k}'}\frac{1}{\hbar\omega - \varepsilon_{n\boldsymbol{k}} + \mathrm{i}\delta}.$$
 (31.1.22)

Thus, similar to the Green function of free electrons, the Green function of noninteracting Bloch electrons has a simple pole on the lower half-plane, exactly at ε_{nk} , at the energy of Bloch electrons.

We return now to (31.1.9) from which the Green function of interacting electrons has to be determined, assuming for the sake of simplicity a uniform background. A two-particle Green function appears in the equation of motion owing to the electron–electron interactions. This higher order Green function contains four operators and describes the propagation of two particles. When the equation of motion is written down for this Green function, in general a term containing even more operators will appear. Continuing along this line yields an infinite hierarchy of higher order Green functions. An approximate solution can be obtained if, similar to the decoupling procedure used for the response functions, the hierarchy is truncated somewhere, i.e., the higher order Green functions are expressed as products of lower order ones. As the simplest example we show how the two-particle Green function can be decoupled.

The correlated motion of two particles can be studied by considering the quantity

$$\left\langle \hat{\psi}_{\sigma_1}(\boldsymbol{r}_1,t_1)\hat{\psi}_{\sigma_2}(\boldsymbol{r}_2,t_2)\hat{\psi}^{\dagger}_{\sigma_3}(\boldsymbol{r}_3,t_3)\hat{\psi}^{\dagger}_{\sigma_4}(\boldsymbol{r}_4,t_4)\right\rangle,$$

which is the probability amplitude of finding the particles at the space-time positions \mathbf{r}_1, t_1 and \mathbf{r}_2, t_2 with spins σ_1 and σ_2 , if they were added to the system at \mathbf{r}_3 at time t_3 and at \mathbf{r}_4 at time t_4 with spins σ_3 and σ_4 , respectively. In the simplest approximation the propagation of the two particles can be thought to be independent, i.e., the two-particle propagator can be approximated by the product of two one-particle propagators. Note that the term appearing on the right-hand side of (31.1.9) describes a process in which only one of the particles propagates truly, the other is added and removed immediately at the same moment and at the same position. It therefore seems natural to choose the decoupling in the form

$$\left\langle \begin{bmatrix} \hat{\psi}_{\sigma}(\boldsymbol{r},t), \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}'',t') \hat{\psi}_{\sigma'}(\boldsymbol{r}'',t') \end{bmatrix}_{+} \right\rangle$$

$$\approx \left\langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}'',t') \hat{\psi}_{\sigma'}(\boldsymbol{r}'',t') \right\rangle \left\langle \begin{bmatrix} \hat{\psi}_{\sigma}(\boldsymbol{r},t), \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \end{bmatrix}_{+} \right\rangle.$$

$$(31.1.23)$$

This decoupling corresponds to replacing the operator of the electron density by its expectation value and gives exactly the result of the Hartree approximation. A better approximation can be achieved by the decoupling

$$\left\langle \begin{bmatrix} \hat{\psi}_{\sigma}(\boldsymbol{r},t), \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}'',t') \hat{\psi}_{\sigma'}(\boldsymbol{r}'',t') \end{bmatrix}_{+} \right\rangle$$

$$\approx \left\langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}'',t') \hat{\psi}_{\sigma'}(\boldsymbol{r}'',t') \right\rangle \left\langle \begin{bmatrix} \hat{\psi}_{\sigma}(\boldsymbol{r},t), \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \end{bmatrix}_{+} \right\rangle$$

$$- \left\langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \hat{\psi}_{\sigma'}(\boldsymbol{r}'',t') \right\rangle \left\langle \begin{bmatrix} \hat{\psi}_{\sigma}(\boldsymbol{r},t), \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}'',t') \end{bmatrix}_{+} \right\rangle$$

$$(31.1.24)$$

that takes into account the indistinguishability of electrons The minus sign in front of the second term comes from changing the order of two fermion operators. As we will see, this antisymmetrized decoupling is equivalent to the Hartree–Fock approximation.

Indeed, inserting this into (31.1.9) we get

$$\left[\frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t'} + \frac{\hbar^2}{2m_{\mathrm{e}}} \nabla_{\mathbf{r}'}^2 - V_0 \right] G_{\sigma}^{\mathrm{R}}(\mathbf{r}, t, \mathbf{r}', t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}')$$

$$+ \sum_{\sigma'} \int \mathrm{d}\mathbf{r}'' \, U(\mathbf{r}' - \mathbf{r}'') \left\langle \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}'', t') \hat{\psi}_{\sigma'}(\mathbf{r}'', t') \right\rangle G_{\sigma}^{\mathrm{R}}(\mathbf{r}, t, \mathbf{r}', t')$$

$$- \sum_{\sigma'} \int \mathrm{d}\mathbf{r}'' \, U(\mathbf{r}' - \mathbf{r}'') \left\langle \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}', t') \hat{\psi}_{\sigma}(\mathbf{r}'', t') \right\rangle G_{\sigma}^{\mathrm{R}}(\mathbf{r}, t, \mathbf{r}', t')$$

for the homogeneous electron gas, where $V_{\text{ion}}(\mathbf{r})$ takes a spatially uniform value V_0 . The Fourier transform of the Green function satisfies the equation

$$\begin{bmatrix} \hbar\omega - \frac{\hbar^2 k^2}{2m_{\rm e}} - V_0 \end{bmatrix} G^{\rm R}_{\sigma}(\boldsymbol{k},\omega) = 1 + U(\boldsymbol{q}=0) \sum_{\sigma'} \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3} \langle n_{\boldsymbol{k}'\sigma'} \rangle G^{\rm R}_{\sigma}(\boldsymbol{k},\omega)$$

$$- \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3} U(\boldsymbol{k}-\boldsymbol{k}') \langle n_{\boldsymbol{k}'\sigma} \rangle G^{\rm R}_{\sigma}(\boldsymbol{k},\omega) \,.$$
(31.1.26)

Rearrangement of the terms gives

$$\begin{bmatrix} \hbar\omega - \frac{\hbar^2 k^2}{2m_{\rm e}} - V_0 - U(\boldsymbol{q} = 0) \sum_{\sigma'} \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3} \langle n_{\boldsymbol{k}'\sigma'} \rangle \\ + \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3} U(\boldsymbol{k} - \boldsymbol{k}') \langle n_{\boldsymbol{k}'\sigma} \rangle \end{bmatrix} G^{\rm R}_{\sigma}(\boldsymbol{k}, \omega) = 1.$$
(31.1.27)

The potential of the uniform background is exactly compensated by the Hartree term proportional to $U(\mathbf{q} = 0)$. Requiring the correct analytic property for the retarded Green function, the solution is

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}\sigma} + \mathrm{i}\delta}, \qquad (31.1.28)$$

where

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$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \frac{\hbar^2 k^2}{2m_{\rm e}} - \int \frac{\mathrm{d}\boldsymbol{k}'}{(2\pi)^3} U(\boldsymbol{k} - \boldsymbol{k}') \langle n_{\boldsymbol{k}'\sigma} \rangle \tag{31.1.29}$$

is the quasiparticle energy in the Hartree–Fock approximation. Thus even if the interaction is treated in the Hartree–Fock approximation, the Green function has a pole at the energy of quasiparticles. Similar results are obtained for Bloch electrons in the Hartree–Fock approximation. We find

$$G_{nn'\sigma}^{\rm R}(\boldsymbol{k},\boldsymbol{k}',\omega) = \delta_{nn'}\delta_{\boldsymbol{k}\boldsymbol{k}'}\frac{1}{\hbar\omega - \widetilde{\varepsilon}_{n\boldsymbol{k}} + \mathrm{i}\delta},\qquad(31.1.30)$$

where $\tilde{\varepsilon}_{nk}$ is the renormalized energy of Bloch electrons.

The simplest way to go beyond Hartree–Fock is to take the screening of the Coulomb interaction into account.² Then, from the pole of the Green function, we get

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \frac{\hbar^2 k^2}{2m_{\rm e}} - \frac{1}{V} \sum_{\boldsymbol{k}'} \frac{U(\boldsymbol{k} - \boldsymbol{k}')}{\epsilon_{\rm r}(\boldsymbol{k} - \boldsymbol{k}')} \langle n_{\boldsymbol{k}'\sigma} \rangle \tag{31.1.31}$$

for the quasiparticle energy. When the Thomas–Fermi form of the dielectric function is used,

$$\widetilde{\varepsilon}_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m_{\rm e}} - \frac{1}{V} \sum_{\boldsymbol{k}'} \frac{4\pi \widetilde{e}^2}{|\boldsymbol{k} - \boldsymbol{k}'|^2 + q_{\rm TF}^2} \langle n_{\boldsymbol{k}'\sigma} \rangle \qquad (31.1.32)$$

for an unpolarized electron gas, where the excitation energies are spin independent. It is sometimes more convenient to write it in the form

$$\widetilde{\varepsilon}_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m_{\rm e}} - \frac{1}{V} \sum_{\boldsymbol{q}} \frac{4\pi \widetilde{e}^2}{q^2 + q_{\rm TF}^2} \langle n_{\boldsymbol{k}+\boldsymbol{q}} \rangle \,. \tag{31.1.33}$$

31.1.2 Effective Mass of Quasiparticles

The effective mass of quasiparticles near the Fermi surface can be obtained from (28.3.96) or, in the isotropic case, from the equivalent expression

$$\frac{1}{m^*} = \frac{1}{\hbar^2 k_{\rm F}} \hat{\boldsymbol{k}} \cdot \frac{\partial \tilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}}}{\partial \boldsymbol{k}} \big|_{|\boldsymbol{k}|=k_{\rm F}}, \qquad (31.1.34)$$

where \mathbf{k} is the unit vector in the direction of \mathbf{k} . We have seen in Chapter 28 that the Hartree–Fock approximation leads to an unphysical result for the effective mass of quasiparticles. If $\tilde{\varepsilon}_{\mathbf{k}}$ is expanded about the Fermi energy to linear order, the effective mass defined by

² We will see in Appendix K that the corrections appearing in the equation of motion of the Green function can be visualized as scattering processes occurring in the course of propagation. When these processes are described by diagrams, it is easy to identify which processes the screening corresponds to.

$$\widetilde{\varepsilon}_k = \varepsilon_{\rm F} + \frac{\hbar^2 k_{\rm F}}{m^*} (k - k_{\rm F}) \tag{31.1.35}$$

vanishes. To go beyond the Hartree–Fock approximation we take (31.1.33) for the quasiparticle energy and make use of the fact that $\langle n_{\mathbf{k}+\mathbf{q}} \rangle$ is a step function $\theta(k_{\rm F} - |\mathbf{k} + \mathbf{q}|)$ at zero temperature. Hence

$$\frac{\partial \langle n_{\boldsymbol{k}+\boldsymbol{q}} \rangle}{\partial \boldsymbol{k}} = \frac{\partial \theta(k_{\rm F} - |\boldsymbol{k}+\boldsymbol{q}|)}{\partial \boldsymbol{k}} = -\delta(k_{\rm F} - |\boldsymbol{k}+\boldsymbol{q}|)\frac{\boldsymbol{k}+\boldsymbol{q}}{|\boldsymbol{k}+\boldsymbol{q}|}.$$
 (31.1.36)

With the change of variables $\boldsymbol{q}
ightarrow \boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{q}$ we get

$$\frac{1}{m^*} = \frac{1}{m_{\rm e}} + \frac{1}{\hbar^2 k_{\rm F}} \frac{1}{V} \sum_{\mathbf{k}'} \frac{4\pi \tilde{e}^2}{|\mathbf{k} - \mathbf{k}'|^2 + q_{\rm TF}^2} \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'} \,\delta(k_{\rm F} - |\mathbf{k}'|)
= \frac{1}{m_{\rm e}} + \frac{1}{\hbar^2 k_{\rm F}} \int \frac{\mathrm{d}\mathbf{k}'}{(2\pi)^3} \frac{4\pi \tilde{e}^2}{|\mathbf{k} - \mathbf{k}'|^2 + q_{\rm TF}^2} \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'} \,\delta(k_{\rm F} - |\mathbf{k}'|),$$
(31.1.37)

where k has to be taken at the Fermi surface. We integrate first over the length of k'. Denoting the angle between k and k' by θ we find

$$\frac{1}{m^*} = \frac{1}{m_{\rm e}} + \frac{k_{\rm F}}{4\pi^2\hbar^2} \int_0^{\pi} \sin\theta \,\mathrm{d}\theta \frac{4\pi\tilde{e}^2}{2k_{\rm F}^2(1-\cos\theta) + q_{\rm TF}^2} \cos\theta \,. \tag{31.1.38}$$

This expression shows that the correction to the effective mass is a weighted average of the potential acting between electrons. We will give a more general derivation later. The quantity $q_{\rm TF}^2$ defined in (29.2.13) can be rewritten as

$$q_{\rm TF}^2 = \frac{4}{\pi} \frac{k_{\rm F}}{a_0} \,, \tag{31.1.39}$$

and the Fermi momentum can be expressed in terms of $r_{\rm s}$ via $k_{\rm F}a_0 = 1/\alpha r_{\rm s}$ with $\alpha = (4/9\pi)^{1/3} = 0.521$. We then obtain

$$\frac{m_{\rm e}}{m^*} = 1 + \frac{1}{4} \int_0^{\pi} \sin\theta \,\mathrm{d}\theta \frac{\alpha r_{\rm s}/\pi}{\frac{1}{2}(1 - \cos\theta) + \alpha r_{\rm s}/\pi} \cos\theta \,. \tag{31.1.40}$$

Integration over the angular variable gives

$$\frac{m_{\rm e}}{m^*} = 1 + \frac{\alpha r_{\rm s}}{\pi} \left(\frac{1}{2} + \frac{\alpha r_{\rm s}}{\pi}\right) \ln \frac{\pi + \alpha r_{\rm s}}{\alpha r_{\rm s}} - \frac{\alpha r_{\rm s}}{\pi} \tag{31.1.41}$$

with $\alpha r_{\rm s}/\pi = 0.166 r_{\rm s}$. For both high- and low-density electron gases, in the limits $r_{\rm s} \rightarrow 0$ and $r_{\rm s} \rightarrow \infty$, the effective mass becomes equal to the electron mass. For densities characteristic of metals $m_{\rm e}/m^*$ varies between 1.04 and 1.05. That is, the effective mass of quasiparticles due to the screened Coulomb repulsion is only slightly smaller than the electron mass.

Had we used the Lindhard function for the dielectric function, the energy of quasiparticles near the Fermi momentum would have been

$$\widetilde{\varepsilon}_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_{\rm e}} - \frac{\alpha r_{\rm s}}{\pi} \left(1 + \frac{1}{2} \ln \frac{\alpha r_{\rm s}}{\pi} + \cdots \right) \frac{\hbar^2 k_{\rm F} k}{m_{\rm e}} = \frac{\hbar^2 k^2}{2m_{\rm e}} - 0.083 r_{\rm s} (\ln r_{\rm s} + 0.203) \frac{\hbar^2 k_{\rm F} k}{m_{\rm e}} + \cdots$$
(31.1.42)

in a dense electron gas, where an expansion in powers of $r_{\rm s}$ can be used. Thus in the RPA, the leading terms in the expansion in $r_{\rm s}$ give

$$\frac{m_{\rm e}}{m^*} = 1 - 0.083 \, r_{\rm s} \big(\ln r_{\rm s} + 0.203 \big) + \cdots \tag{31.1.43}$$

for the effective mass. These are precisely the leading terms if the results obtained in the Thomas–Fermi approximation are expanded. This again shows that in a homogeneous electron gas the effective mass of quasiparticles on the Fermi surface is very close to that of free electrons.

31.1.3 Lifetime of Electron States

A further consequence of the electron–electron interaction is that the oneparticle states are no longer eigenstates of the full Hamiltonian and their lifetime becomes finite. The quasiparticle picture can be used reasonably only if the lifetime is relatively long. Since the energy uncertainty of the state is proportional to the inverse of the lifetime, the condition

$$\hbar/\tau_{\boldsymbol{k}} \ll |\varepsilon_{\boldsymbol{k}} - \varepsilon_{\mathrm{F}}| \tag{31.1.44}$$

has to be satisfied. We show that in normal fermion systems this condition is satisfied for states near the Fermi energy.

Consider a state with energy $\varepsilon_{\mathbf{k}} > \varepsilon_{\mathrm{F}}$ and try to estimate its lifetime due to two-particle scattering processes. At T = 0, this particle can be scattered only by those electrons inside the Fermi sphere whose wave vector \mathbf{k}' lies in a narrow range of width $\varepsilon_{\mathbf{k}} - \varepsilon_{\mathrm{F}}$ below the Fermi energy satisfying

$$\varepsilon_{\rm F} - \varepsilon_{\mathbf{k}'} < \varepsilon_{\mathbf{k}} - \varepsilon_{\rm F}$$
. (31.1.45)

Otherwise the total energy of the two particles is not high enough, and the electrons cannot be scattered into empty states outside the Fermi sphere. The energy of only one of the scattered particles can be chosen freely, and the energy of the other is fixed by energy conservation, but even this energy cannot be bigger than $\varepsilon_{\mathbf{k}}$. If the inverse of the lifetime is calculated from the transition probability of the scattering processes and the limitations on the energy of the particles are taken into account,

$$\frac{1}{\tau_{\boldsymbol{k}}} \propto \left(\varepsilon_{\boldsymbol{k}} - \varepsilon_{\mathrm{F}}\right)^2. \tag{31.1.46}$$

A more quantitative expression can be obtained if the transition probability is calculated using Fermi's golden rule. The inverse lifetime is

$$\frac{1}{\tau_{\boldsymbol{k}\sigma}} = \frac{2\pi}{\hbar} \frac{1}{V^2} \sum_{\boldsymbol{k}'\boldsymbol{q}\sigma'} |U(\boldsymbol{q})|^2 f_0(\varepsilon_{\boldsymbol{k}'\sigma'}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma})\right] \left[1 - f_0(\varepsilon_{\boldsymbol{k}'-\boldsymbol{q}\sigma'})\right] \\ \times \delta\left(\varepsilon_{\boldsymbol{k}\sigma} + \varepsilon_{\boldsymbol{k}'\sigma'} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}\right), \qquad (31.1.47)$$

where the Fermi functions ensure that the state with wave vector \mathbf{k}' on which the electron is scattered is filled initially, while the states into which the electrons are scattered are empty. The potential is the screened Coulomb potential at frequency and momentum corresponding to the energy and momentum transfer during the scattering process,

$$U(\boldsymbol{q}) = \frac{4\pi\tilde{e}^2}{q^2\epsilon_{\rm r}(-\boldsymbol{q}, -\omega_{\boldsymbol{k}\boldsymbol{q}})},\qquad(31.1.48)$$

and $\hbar\omega_{kq} = \varepsilon_{k+q} - \varepsilon_k$. It follows from the energy conservation and the restrictions imposed by the Fermi functions that the scattered particle has to lose energy, $\varepsilon_{\rm F} < \varepsilon_{k+q} < \varepsilon_k$, and therefore the dielectric function is taken at positive frequencies in this formula.

We can recognize the imaginary part of the dielectric function in the expression for the lifetime, since (29.2.49) could be written in the form

$$\epsilon_2(\boldsymbol{q},\omega) = \frac{4\pi^2 \tilde{e}^2}{q^2} \frac{1}{V} \sum_{\boldsymbol{k}'\sigma} f_0(\varepsilon_{\boldsymbol{k}'\sigma}) \left[1 - f_0(\varepsilon_{\boldsymbol{k}'+\boldsymbol{q}\sigma})\right] \delta(\hbar\omega - \varepsilon_{\boldsymbol{k}'+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}'\sigma}) \,.$$
(31.1.49)

Thus

$$\frac{1}{\tau_{\boldsymbol{k}\sigma}} = \frac{2\pi}{\hbar} \frac{1}{V} \sum_{\boldsymbol{q}} \frac{1}{\pi} \frac{4\pi\tilde{e}^2}{q^2} \frac{\epsilon_2(-\boldsymbol{q}, -\omega_{\boldsymbol{k}\boldsymbol{q}})}{|\epsilon_r(-\boldsymbol{q}, -\omega_{\boldsymbol{k}\boldsymbol{q}})|^2} \left[1 - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma})\right].$$
(31.1.50)

Note that this result could have been derived from a calculation of the quasiparticle energy for a screened interaction. The imaginary part of the frequencydependent dielectric function leads to an imaginary part of the self-energy correction, and the Green function acquires the form

$$G_{\sigma}^{\rm R}(\boldsymbol{k},\omega) = \frac{Z_{\boldsymbol{k}}}{\hbar\omega - \tilde{\varepsilon}_{\boldsymbol{k}\sigma} + \mathrm{i}\Gamma_{\boldsymbol{k}\sigma}}.$$
(31.1.51)

Transformed back to time, the imaginary part of the self-energy gives rise to a decay of the probability of finding the particle at a later time, hence $\Gamma_{k\sigma}$ is the inverse of the lifetime, $\Gamma_{k\sigma} = \hbar/2\tau_{k\sigma}$, while Z_k is the quasiparticle weight. Condition (31.1.44) for the applicability of the quasiparticle concept means that the imaginary part has to be much smaller than the real part.

The summation over q in (31.1.50) can be carried out if

$$\epsilon_2(\boldsymbol{q},\omega) = \frac{\pi}{2} \frac{\hbar\omega}{\hbar v_{\rm F} q} \frac{q_{\rm TF}^2}{q^2}, \qquad (31.1.52)$$

which was derived in (29.2.56) in the RPA for low frequencies, that is for small energies, is used for the dielectric function, and we find

$$\frac{1}{\tau_{\boldsymbol{k}}} = \frac{\pi^2 \sqrt{3}}{128} \omega_{\rm p} \left(\frac{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\rm F}}{\varepsilon_{\rm F}}\right)^2 \,. \tag{31.1.53}$$

At finite temperatures, particles sitting on the Fermi surface can also participate in scattering processes owing to the smearing of the Fermi distribution function, but the partners in the scattering process have to be in a range of width $k_{\rm B}T$, and the contribution of these processes to the scattering probability is proportional to $(k_{\rm B}T)^2$. The coefficient of this T^2 term can be estimated if the Coulomb interaction is replaced with the screened potential

$$U(\mathbf{q}) = \frac{4\pi\tilde{e}^2}{q^2 + q_{\rm TF}^2} \qquad \text{with} \qquad q_{\rm TF}^2 = 4\pi\tilde{e}^2\rho(\varepsilon_{\rm F})\,. \tag{31.1.54}$$

If the matrix element is approximated by its value at q = 0, we find

$$|U(\boldsymbol{q})|^2 \approx \left(\frac{1}{\rho(\varepsilon_{\rm F})}\right)^2.$$
 (31.1.55)

The summation over momenta is restricted to an energy range of width $k_{\rm B}T$. Taking account of energy conservation

$$\frac{\hbar}{\tau} \sim \left(\frac{1}{\rho(\varepsilon_{\rm F})}\right)^2 \rho^2(\varepsilon_{\rm F}) \frac{(k_{\rm B}T)^2}{\varepsilon_{\rm F}} = \frac{(k_{\rm B}T)^2}{\varepsilon_{\rm F}} \,. \tag{31.1.56}$$

Combining these results, in the general case we have

$$\frac{\hbar}{\tau_{\boldsymbol{k}}} \approx \frac{1}{\varepsilon_{\rm F}} \left[a \left(\varepsilon_{\boldsymbol{k}} - \varepsilon_{\rm F} \right)^2 + b \left(k_{\rm B} T \right)^2 \right], \qquad (31.1.57)$$

where a and b are constants of order unity. Note that the lifetime of particles is infinitely long on the Fermi surface at T = 0 and becomes finite at finite temperatures or as we move away from the Fermi energy. Nevertheless, (31.1.44) is still satisfied at low temperatures for states in the neighborhood of the Fermi surface.

31.1.4 Electron–Hole Pair Excitations

If the number of particles is conserved, the excited states of the free electron gas can be generated by exciting successively electron-hole pairs. The operator that creates an electron-hole pair from the ground state is

$$\alpha^{\dagger}_{\boldsymbol{k}\boldsymbol{q}\sigma} = c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma}c_{\boldsymbol{k}\sigma}\,,\qquad(31.1.58)$$

where $|\mathbf{k}| \leq k_{\rm F}$ and $|\mathbf{k} + \mathbf{q}| \geq k_{\rm F}$. In what follows this restriction will be understood tacitly even when it is not written out explicitly. As shown in Fig. 28.9 the energies

$$\hbar\omega_{kq\sigma} = \varepsilon_{k+q\sigma} - \varepsilon_{k\sigma} \tag{31.1.59}$$

form a broad continuum.

The situation is similar when the Hamiltonian of the interacting electron system is treated in the Hartree–Fock approximation. The low-lying excitations are pairs of a quasielectron and a quasihole, and it follows from Koopmans' theorem that the excitation energy is simply the sum of the energies of the quasielectron and of the quasihole:

$$\hbar\omega_{\boldsymbol{k}\boldsymbol{q}\sigma} = \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\sigma} - \widetilde{\varepsilon}_{\boldsymbol{k}\sigma} \,. \tag{31.1.60}$$

The pairs do not interact and, therefore, have an infinite lifetime.

When the electron–electron interaction is treated more accurately, the operator $\alpha^{\dagger}_{kq\sigma}$ acting on the ground-state wavefunction $|\Psi_0\rangle$ of the interacting electron system no longer creates an exact eigenstate of the system. The electron–hole pair can be scattered into another pair state where k is different but the total momentum q of the pair is conserved. The excited state should contain all possible electron–hole pairs that can be mixed by the interaction. The wavefunction of the excited state could be looked for as the linear combination

$$|\Psi_{\boldsymbol{q}}\rangle = \sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c_{\boldsymbol{k}\sigma} |\Psi_{0}\rangle, \qquad (31.1.61)$$

and the operator

$$\alpha_{\boldsymbol{q}\sigma}^{\dagger} = \sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}\boldsymbol{q}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma}$$
(31.1.62)

that generates the excited state $|\Psi_q\rangle$ from the ground state could be considered as the creation operator of the excitation. In general, states with several electron-hole pairs should also be mixed in, but these configurations will be neglected in this approximation and the so far undetermined coefficients $\phi_{kq\sigma}$ will be determined from the requirement that the state created by this operator be as close to an eigenstate as possible.

If $|\Psi_{q}\rangle$ were an eigenstate of the Hamiltonian with an excitation energy $\hbar\omega_{q\sigma}$ above the ground-state energy E_{0} ,

$$\mathcal{H}|\Psi_{\boldsymbol{q}}\rangle = \mathcal{H}\alpha_{\boldsymbol{q}\sigma}^{\dagger}|\Psi_{0}\rangle = \left[E_{0} + \hbar\omega_{\sigma}(\boldsymbol{q})\right]\alpha_{\boldsymbol{q}\sigma}^{\dagger}|\Psi_{0}\rangle \tag{31.1.63}$$

would hold. $|\Psi_0\rangle$ is an eigenstate of \mathcal{H} with energy E_0 , and thus

$$\mathcal{H}\alpha^{\dagger}_{\boldsymbol{q}\sigma}|\Psi_{0}\rangle = \alpha^{\dagger}_{\boldsymbol{q}\sigma}\mathcal{H}|\Psi_{0}\rangle + \hbar\omega_{\boldsymbol{q}\sigma}\alpha^{\dagger}_{\boldsymbol{q}\sigma}|\Psi_{0}\rangle, \qquad (31.1.64)$$

from which it follows that

$$\left[\mathcal{H}, \alpha_{\boldsymbol{q}\sigma}^{\dagger}\right]_{-} |\Psi_{0}\rangle = \hbar\omega_{\boldsymbol{q}\sigma}\alpha_{\boldsymbol{q}\sigma}^{\dagger}|\Psi_{0}\rangle. \qquad (31.1.65)$$

Thus, when acting on the ground state,

$$\left[\mathcal{H}, \alpha_{\boldsymbol{q}\sigma}^{\dagger}\right]_{-} = \hbar \omega_{\boldsymbol{q}\sigma} \alpha_{\boldsymbol{q}\sigma}^{\dagger} \,. \tag{31.1.66}$$

Moreover if $|\Psi_q\rangle$ is properly normalized, $\alpha^{\dagger}_{q\sigma}$ and its Hermitian adjoint satisfy the commutation relation

$$\left[\alpha_{\boldsymbol{q}\sigma}, \alpha^{\dagger}_{\boldsymbol{q}'\sigma'}\right]_{-} = \delta_{\boldsymbol{q}\boldsymbol{q}'}\delta_{\sigma\sigma'}, \qquad (31.1.67)$$

but again only when both sides act on the ground state.

Let us assume that these relations hold quite generally, that is (31.1.66) is an identity and the operators $\alpha^{\dagger}_{q\sigma}$ and $\alpha_{q\sigma}$ are bosonic creation and annihilation operators. Then the Hamiltonian can be written in terms of these operators in the form

$$\mathcal{H} = \sum_{\boldsymbol{q}\sigma} \hbar \omega_{\boldsymbol{q}\sigma} \alpha^{\dagger}_{\boldsymbol{q}\sigma} \alpha_{\boldsymbol{q}\sigma} \,. \tag{31.1.68}$$

The interacting electron system could then be mapped onto a noninteracting gas of bosons. All excited states of the system could be obtained by applying successively the creation operators $\alpha^{\dagger}_{q\sigma}$ of the elementary excitations.

Unfortunately, the coefficients $\phi_{kq\sigma}$ appearing in $\alpha^{\dagger}_{q\sigma}$ cannot in general be chosen in such a way that (31.1.66) be satisfied exactly. When it is satisfied at least approximately, $\alpha^{\dagger}_{q\sigma}$ could still be considered as the creation operator of an elementary excitation, and the system could be viewed as a noninteracting gas of fictitious particles. Therefore we will try to fix $\phi_{kq\sigma}$ from the requirement that this relationship be valid at least approximately. As will be seen, the self-consistency requirement of the procedure will lead to an equation that gives immediately the quantity we are interested in: the energy of excitation.

To calculate the commutator we make use of

$$\left[\mathcal{H}, c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}c_{\boldsymbol{k}\sigma}\right]_{-} = \left[\mathcal{H}, c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}\right]_{-}c_{\boldsymbol{k}\sigma} + c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}\left[\mathcal{H}, c_{\boldsymbol{k}\sigma}\right]_{-}$$
(31.1.69)

and

$$\begin{aligned} \left[\mathcal{H}, c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}\right]_{-} &= \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger} + \frac{1}{V} \sum_{\boldsymbol{k}'\boldsymbol{q}'\sigma'} U(\boldsymbol{q}') c_{\boldsymbol{k}+\boldsymbol{q}-\boldsymbol{q}'\sigma}^{\dagger} c_{\boldsymbol{k}'+\boldsymbol{q}'\sigma'}^{\dagger} c_{\boldsymbol{k}'\sigma'}, \\ \left[\mathcal{H}, c_{\boldsymbol{k}\sigma}\right]_{-} &= -\varepsilon_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} - \frac{1}{V} \sum_{\boldsymbol{k}'\boldsymbol{q}'\sigma'} U(\boldsymbol{q}') c_{\boldsymbol{k}'+\boldsymbol{q}'\sigma'}^{\dagger} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}+\boldsymbol{q}'\sigma}. \end{aligned}$$
(31.1.70)

Thus we get

$$\begin{aligned} \left[\mathcal{H}, c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \right]_{-} &= \left(\varepsilon_{\mathbf{k}+\mathbf{q}\sigma} - \varepsilon_{\mathbf{k}\sigma} \right) c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \\ &+ \frac{1}{V} \sum_{\mathbf{k}' \mathbf{q}' \sigma'} U(\mathbf{q}') c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}^{\dagger} c_{\mathbf{k}'+\mathbf{q}'\sigma'}^{\dagger} c_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} \\ &- \frac{1}{V} \sum_{\mathbf{k}' \mathbf{q}'\sigma'} U(\mathbf{q}') c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}'+\mathbf{q}'\sigma'}^{\dagger} c_{\mathbf{k}'\sigma'} c_{\mathbf{k}+\mathbf{q}'\sigma} . \end{aligned}$$
(31.1.71)

We will apply the procedure already used repeatedly in mean-field approaches, namely the terms with four operators will be approximated by replacing two of them with their expectation values. The choice 31.1 One-Particle and Electron–Hole Pair Excitations 189

$$c^{\dagger}_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}c^{\dagger}_{\mathbf{k}'+\mathbf{q}'\sigma'}c_{\mathbf{k}'\sigma'}c_{\mathbf{k}\sigma} \approx \langle c^{\dagger}_{\mathbf{k}'+\mathbf{q}'\sigma'}c_{\mathbf{k}'\sigma'} \rangle c^{\dagger}_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}c_{\mathbf{k}\sigma} + \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}c_{\mathbf{k}\sigma} \rangle c^{\dagger}_{\mathbf{k}'+\mathbf{q}'\sigma'}c_{\mathbf{k}'\sigma'}$$
(31.1.72)

seems to be natural in the second term on the right-hand side. As long as the system does not undergo a phase transition to a new broken-symmetry phase, the only nonvanishing expectation value is

$$\langle c^{\dagger}_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}'\sigma'}\rangle = f_0(\varepsilon_{\boldsymbol{k}})\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\sigma\sigma'}.$$
 (31.1.73)

Since the q' = 0 component of the interaction U(q') vanishes in the homogeneous electron gas, the first term of (31.1.72) gives no contribution and thus

$$c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}-\boldsymbol{q}'\sigma}c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}'\sigma'}c_{\boldsymbol{k}'\sigma'}c_{\boldsymbol{k}\sigma} \approx \delta_{\boldsymbol{q}\boldsymbol{q}'}f_0(\varepsilon_{\boldsymbol{k}\sigma})c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'}c_{\boldsymbol{k}'\sigma'}.$$
(31.1.74)

If a similar decoupling procedure is used in the third term on the righthand side of (31.1.71), we find

$$\begin{bmatrix} \mathcal{H}, c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}\sigma} \end{bmatrix}_{-} = (\varepsilon_{\mathbf{k}+\mathbf{q}\sigma} - \varepsilon_{\mathbf{k}\sigma}) c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}\sigma}$$

$$+ \frac{1}{V} \sum_{\mathbf{k}'\sigma'} U(\mathbf{q}) [f_0(\varepsilon_{\mathbf{k}\sigma}) - f_0(\varepsilon_{\mathbf{k}+\mathbf{q}\sigma})] c^{\dagger}_{\mathbf{k}'+\mathbf{q}\sigma'}c_{\mathbf{k}'\sigma'}.$$

$$(31.1.75)$$

Multiplying this equation by $\phi_{kq\sigma}$, summing it over k and σ , and then inserting the expression into (31.1.66) gives

$$\sum_{\boldsymbol{k}\sigma} \left[\hbar \omega_{\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma} \right] \phi_{\boldsymbol{k}\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c_{\boldsymbol{k}\sigma}
= \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} U(\boldsymbol{q}) \left[f_0(\varepsilon_{\boldsymbol{k}\sigma}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma}) \right] \phi_{\boldsymbol{k}\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} .$$
(31.1.76)

Interchanging the summation indices, $\mathbf{k} \leftrightarrow \mathbf{k}'$ and $\sigma \leftrightarrow \sigma'$, on the right-hand side we may require that the identity

$$\left[\hbar\omega_{\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma}\right]\phi_{\boldsymbol{k}\boldsymbol{q}\sigma} = \frac{1}{V}\sum_{\boldsymbol{k}'\sigma'}U(\boldsymbol{q})\left[f_0(\varepsilon_{\boldsymbol{k}'\sigma'}) - f_0(\varepsilon_{\boldsymbol{k}'+\boldsymbol{q}\sigma'})\right]\phi_{\boldsymbol{k}'\boldsymbol{q}\sigma'}$$
(31.1.77)

hold for each operator $c^{\dagger}_{\mathbf{k}+q\sigma}c_{\mathbf{k}\sigma}$ separately. Since the right-hand side of this equation is independent of \mathbf{k} and σ , the solution is sought in the form

$$\phi_{\boldsymbol{k}\boldsymbol{q}\sigma} = \frac{\phi(\boldsymbol{q})}{\hbar\omega_{\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma}} \,. \tag{31.1.78}$$

Insertion into the previous equation yields a self-consistency condition:

$$1 = U(\boldsymbol{q}) \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{f_0(\varepsilon_{\boldsymbol{k}\sigma}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma})}{\hbar\omega_{\boldsymbol{q}\sigma} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \varepsilon_{\boldsymbol{k}\sigma}}.$$
 (31.1.79)

The solutions of this equation give the possible energies $\hbar \omega_{q\sigma}$ of electron-hole pair excitations in an interacting electron system, where U(q) is the strength of the two-particle interaction. Looking at (29.2.42) we immediately see that the excitation energies are obtained from the zeros of the dielectric function, that is those ω, q pairs have to be found for which

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 0. \tag{31.1.80}$$

Before trying to find the solutions of this equation it is appropriate to make a few remarks about the approximations that led to this equation. In a more careful decoupling procedure of the four-operator terms one should choose the operators, which are replaced with their expectation values, in all possible ways. In doing so we would recognize terms that correspond to the self-energy corrections in the Hartree–Fock approximation. Incorporating these corrections into the one-particle energy we get

$$\begin{aligned} \left[\mathcal{H}, c_{\mathbf{k}+q\sigma}^{\dagger} c_{\mathbf{k}\sigma}\right]_{-} &= \left(\widetilde{\varepsilon}_{\mathbf{k}+q\sigma} - \widetilde{\varepsilon}_{\mathbf{k}\sigma}\right) c_{\mathbf{k}+q\sigma}^{\dagger} c_{\mathbf{k}\sigma} \end{aligned} \tag{31.1.81} \\ &+ \frac{1}{V} \sum_{\mathbf{k}'\sigma'} \left[U(\mathbf{q}) - U(\mathbf{k} - \mathbf{k}') \delta_{\sigma\sigma'} \right] \left\langle c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \right\rangle c_{\mathbf{k}'+q\sigma'}^{\dagger} c_{\mathbf{k}'\sigma'} \\ &- \frac{1}{V} \sum_{\mathbf{k}'\sigma'} \left[U(\mathbf{q}) - U(\mathbf{k} - \mathbf{k}') \delta_{\sigma\sigma'} \right] \left\langle c_{\mathbf{k}+q\sigma}^{\dagger} c_{\mathbf{k}+q\sigma'} c_{\mathbf{k}'\sigma'} \right. \end{aligned}$$

instead of (31.1.75). Following the procedure proposed by Hubbard for the dielectric function as explained in Appendix J and writing the thermal averages in terms of the Fermi distribution function, we find

$$\begin{bmatrix} \mathcal{H}, c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \end{bmatrix}_{-} = \left(\widetilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\sigma} - \widetilde{\varepsilon}_{\mathbf{k}\sigma} \right) c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} c_{\mathbf{k}\sigma}$$

$$+ \frac{1}{V} \sum_{\mathbf{k}'\sigma'} U(\mathbf{q}) \left[1 - G(\mathbf{q}) \right] \left[f_0(\widetilde{\varepsilon}_{\mathbf{k}\sigma'}) - f_0(\widetilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\sigma'}) \right] c_{\mathbf{k}'+\mathbf{q}\sigma'}^{\dagger} c_{\mathbf{k}'\sigma'} ,$$

$$(31.1.82)$$

where

$$G(\boldsymbol{q}) = \frac{1}{2} \frac{q^2}{q^2 + k_{\rm F}^2} \,. \tag{31.1.83}$$

From here we can proceed as before to arrive at the self-consistency requirement

$$1 = U(\boldsymbol{q}) \left[1 - G(\boldsymbol{q}) \right] \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{f_0(\tilde{\varepsilon}_{\boldsymbol{k}\sigma}) - f_0(\tilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\sigma})}{\hbar\omega_{\boldsymbol{q}\sigma} - \tilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\sigma} + \tilde{\varepsilon}_{\boldsymbol{k}\sigma}}$$
(31.1.84)

that determines the eigenvalues. Comparison with (31.1.79) shows that the structure of the equations is identical: the Lindhard function appears in both cases, but the one-particle energies are renormalized in (31.1.84) by the Hartree–Fock self-energy correction and the interaction $U(\mathbf{q})$ is multiplied by the Hubbard factor. Note that here again the solution of this equation is equivalent to finding the zeros of the dielectric function if (J.2.96) derived in the Hubbard approximation is used.

The solutions of the self-consistency equation can be found graphically by the trick we applied earlier in Chapter 11 (see Fig. 11.14) to find the vibration spectrum of a lattice containing impurities. When the right-hand side of (31.1.79) or (31.1.84) is considered as a function of $\hbar\omega_{q\sigma}$, this function has a discontinuity at all possible energies of electron-hole pairs and varies wildly from $+\infty$ to $-\infty$ between the singular points. There is necessarily a solution of (31.1.79) or (31.1.84) with $\hbar\omega$ lying between two successive energies of the free electron-hole pairs. These excitation energies form a quasicontinuum, although the density of states in the continuum may be different from that of the free system. We will return to this question later.

31.2 Collective Excitations

We have seen that a dense set of zeros of the real part of the dielectric function exists in the quasicontinuum of electron-hole pair excitations. The true excitation energies are in fact defined by the position of the zeros. The imaginary part of the dielectric function is finite in this energy range. But another kind of solution of (31.1.80) also exists. The real part of the dielectric function vanishes, at least for small values of q, at an energy which lies well above the continuum, where the imaginary part of the dielectric function vanishes as well. These solutions correspond to stable collective density oscillations of the electron system, in agreement with what has been mentioned already in the introduction of this chapter: spontaneous density oscillations are expected to appear with such wave vectors q and frequencies ω for which $\epsilon_r(q, \omega) = 0$. The physical reasoning underlying this statement is that according to (29.1.19) even an infinitesimally weak external perturbation can create such density fluctuations with finite amplitude.

An estimate of the frequency of this oscillation can already be obtained from the classical treatment of the electron system. As known from Chapter 16, the longitudinal dielectric function has the form

$$\epsilon_{\rm r}(\omega) = 1 - \frac{\omega_{\rm p}^2}{\omega^2} \tag{31.2.1}$$

at high frequencies [see (16.1.71)] with

$$\omega_{\rm p}^2 = \frac{4\pi n_{\rm e} \tilde{e}^2}{m_{\rm e}} \tag{31.2.2}$$

introduced in (16.1.69). Thus the oscillation frequency of the interacting electron gas is the classical plasma frequency $\omega_{\rm p}$. Because of this analogy to the classical plasma oscillations, the collective density oscillations of the electron system are called *plasmons*. In what follows, the dispersion relation of these oscillations will be calculated more precisely using the quantum mechanical expression derived above for the dielectric function.

31.2.1 Dispersion Relation of Plasmons

Starting from (29.2.46) derived in the RPA, we will consider the real part of the dielectric function at frequencies that correspond to much higher energies than the typical energies of electron-hole pairs. Since the imaginary part vanishes at these energies,

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{q^2} \frac{2}{V} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}}) \\ \times \left[\frac{1}{\hbar\omega - \hbar^2 \boldsymbol{k} \cdot \boldsymbol{q}/m_{\rm e} - \varepsilon_q} - \frac{1}{\hbar\omega + \hbar^2 \boldsymbol{k} \cdot \boldsymbol{q}/m_{\rm e} + \varepsilon_q} \right].$$
(31.2.3)

After a change of variables $k \to -k$ in the second term we have

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - 4\pi \tilde{e}^2 \frac{\hbar^2}{m_{\rm e}} \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}})}{(\hbar\omega - \hbar^2 \boldsymbol{k} \cdot \boldsymbol{q}/m_{\rm e})^2 - (\varepsilon_q)^2} \,. \tag{31.2.4}$$

The energy of plasmons can be calculated analytically for small q. Expanding the last factor for large ω and keeping the terms up to order q^2 we find

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi\tilde{e}^2}{m_{\rm e}\omega^2} \frac{2}{V} \sum_{\boldsymbol{k}} f_0(\varepsilon_{\boldsymbol{k}}) \left[1 + 2\frac{\hbar}{m_{\rm e}\omega} \boldsymbol{k} \cdot \boldsymbol{q} + 3\left(\frac{\hbar}{m_{\rm e}\omega}\right)^2 (\boldsymbol{k} \cdot \boldsymbol{q})^2 \right].$$
(31.2.5)

Taking first only the leading term, the summation over k gives the number of occupied k states, i.e., $N_{\rm e}/2$, which is half of the number of electrons. In this approximation we recover the known result:

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{\omega_{\rm p}^2}{\omega^2}. \qquad (31.2.6)$$

Thus the frequency of collective plasmon oscillations is $\omega = \omega_p$ even in the quantum mechanical treatment.

To get an estimate of the energy of plasmons we express the density of the electron gas via r_0 using (16.2.29) and then via the dimensionless r_s :

$$(\hbar\omega_{\rm p})^2 = \hbar^2 \frac{3}{4\pi r_0^3} \frac{4\pi \tilde{e}^2}{m_{\rm e}} = 12 \left(\frac{a_0}{r_0}\right)^3 \frac{\hbar^2}{2m_{\rm e}a_0^2} \frac{\tilde{e}^2}{2a_0} \,. \tag{31.2.7}$$

Recognizing that $\hbar^2/(2m_{\rm e}a_0^2)$ is equal to the Rydberg unit of energy, $\tilde{e}^2/2a_0$,

$$\hbar\omega_{\rm p} = \frac{\sqrt{12}}{r_{\rm s}^{3/2}} \,\text{Ry}\,. \tag{31.2.8}$$

Thus the plasmon energy is on the order of a rydberg. Since this is much larger than the Fermi energy of most metals, which are on the order of a few electron volts, this justifies a posteriori the large- ω expansion that led to

Element	$\hbar \omega_{\rm p}^{\rm theo}$ (Ry)	$\hbar \omega_{\rm p}^{\rm theo}$ (eV)	$\hbar \omega_{\rm p}^{\rm exp}$ (eV)
Li	0.59	8.02	7.1
Na	0.44	5.95	5.7
Κ	0.32	4.29	3.7
Al	1.16	15.83	14.9
Be	1.35	18.43	18.7
Mg	0.80	10.86	10.3
\mathbf{Sb}	1.11	15.06	15.3

Table 31.1. Calculated and measured plasmon energies of a few metals

(31.2.5). Table 31.1 gives the calculated and measured values of the plasmon energy for a few metals.

The values were calculated using the parameters of the free electron model, relying, e.g., on the electron density or $r_{\rm s}$ given in Table 16.6. Had we used the effective mass m^* instead of the electron mass, the agreement between theory and experiment would be better. An even better agreement could be achieved by taking into account that the polarizability of core electrons gives an extra contribution to the dielectric function.

A wave number-dependent correction is obtained to the plasmon energy if we keep the terms proportional to q^2 in (31.2.5). The term proportional to qgives no contribution when the integration over the Fermi sphere is performed and we find

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{4\pi n_{\rm e}\tilde{e}^2}{m_{\rm e}\omega^2} \left[1 + \frac{3}{5} \left(\frac{\hbar k_{\rm F}q}{m_{\rm e}\omega} \right)^2 + \cdots \right].$$
(31.2.9)

The solution of $\epsilon_{\rm r}(\boldsymbol{q},\omega) = 0$ leads to

$$\omega^2 = \omega_{\rm p}^2 + \frac{3}{5}q^2v_{\rm F}^2 + \cdots, \qquad (31.2.10)$$

from which we get

$$\omega = \omega_{\rm p} \left[1 + \frac{3}{10} \left(\frac{q v_{\rm F}}{\omega_{\rm p}} \right)^2 + \dots \right] = \omega_{\rm p} \left[1 + \frac{9}{10} \left(\frac{q}{q_{\rm TF}} \right)^2 + \dots \right] \qquad (31.2.11)$$

for the frequency of oscillations. The dispersion curve of plasmons and its position relative to the continuum of electron–hole pair excitations is shown in Fig. 31.1.

The concept of plasmons as collective excitations with a well-defined energy and wave vector is meaningful as long as the corresponding \boldsymbol{q}, ω values are outside the electron-hole continuum, and the imaginary part of the dielectric function vanishes, $\epsilon_2(\boldsymbol{q}, \omega) = 0$. This is the case for small \boldsymbol{q} values. At larger wave numbers, beyond a critical $q_c \approx \omega_p/v_F$, plasmons can decay into


Fig. 31.1. Dispersion curve of plasmons relative to the continuum of electron–hole pair excitations

electron-hole pairs. This is the *Landau damping*.³ The lifetime of plasmons becomes so short that these collective excitations cannot be meaningfully defined and only the electron-hole pair excitations have physical meaning.

It is worth noting that the fact that the long-wavelength plasmons appear in metals at high energies, well above the electron-hole continuum, is a consequence of the Coulomb repulsion between charged electrons. For neutral fermions, such as the ³He liquid, the spectrum of collective excitations has a completely different character. The collective excitations have to be determined from the solutions of (31.1.79), where, however, a short-range potential appears in place of the long-range Coulomb interaction, i.e., the singular Fourier transform $4\pi \tilde{e}^2/q^2$ is replaced with a constant. As a consequence, the energy of the collective density oscillations is proportional to q. Since the propagation of sound (acoustic vibrations) is related to density oscillations, this branch of excitations of neutral fermion systems was called *zero sound* by LANDAU (1957). One has to emphasize that there is an essential physical difference between the hydrodynamic sound wave on the one hand and the zero sound or plasmon on the other. Sound waves can propagate in a gas if scattering events between the gas particles are frequent compared to the period of oscillation of the wave. If τ is the average time between subsequent scattering events of a particle, $\omega \tau \ll 1$ has to be satisfied. This is the so-called hydrodynamic regime. On the contrary, zero-sound and plasmons are well-defined elementary excitations in the collisionless limit, $\omega \tau \gg 1$, i.e., when the lifetime of these excitations is long compared to the period of oscillations.

31.2.2 Study of Plasmons with Inelastic Scattering of Electrons

Owing to their high energy, plasmons are not excited thermally. Nevertheless, their energy can be determined directly by measuring the energy loss of transmitted electrons when a high-energy electron beam is directed onto the surface

³ L. D. LANDAU, 1946.

of a metal. The peaks in the energy-loss spectrum correspond to the generation of one or several plasmons. As has been pointed out in Appendix E, the cross section of inelastic scattering of particles by solids is proportional to the density-density correlation function of that constituent of the solid by which the particles are scattered. More precisely, the cross section is proportional to the Fourier transform of the correlation function, which is the dynamical structure factor $S(\boldsymbol{q}, \omega)$:

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\varepsilon \mathrm{d}\Omega} \propto S(\boldsymbol{K}, \varepsilon/\hbar) \,, \tag{31.2.12}$$

where $\hbar K$ is the change in the momentum of the scattered particle and ε is the energy loss.

We have seen in (29.1.35) and (29.1.36) that the dynamical structure factor can be related to the imaginary part of the density-density response function via the fluctuation-dissipation theorem and also to the imaginary part of the inverse of the dielectric function. Although the imaginary part of the dielectric function vanishes at energies corresponding to the energy of plasmons, the Kramers-Kronig relations (29.2.58) and (29.2.59) can be satisfied only if the imaginary part of the inverse of the dielectric function is nonvanishing at the plasmon energy.

Expanding the dielectric function about the plasma frequency $\omega_{\rm p}$, from (31.2.6) we find

$$\epsilon_{\rm r}(\omega) \approx \frac{2}{\omega_{\rm p}} (\omega - \omega_{\rm p}),$$
 (31.2.13)

and thus

$$\operatorname{Re} \frac{1}{\epsilon_{\mathrm{r}}} \approx \frac{\omega_{\mathrm{p}}}{2} \frac{1}{\omega - \omega_{\mathrm{p}}}.$$
 (31.2.14)

The Kramers–Kronig relations can be satisfied only with a singular imaginary part

$$\operatorname{Im} \frac{1}{\epsilon_{\rm r}} \approx -\frac{\pi}{2} \omega_{\rm p} \delta(\omega - \omega_{\rm p}) , \qquad (31.2.15)$$

which means that the correct expression for the inverse of the dielectric function near ω_p is

$$\frac{1}{\epsilon_{\rm r}} \approx \frac{\omega_{\rm p}}{2} \frac{1}{\omega - \omega_{\rm p} + \mathrm{i}\delta} \,. \tag{31.2.16}$$

The Dirac delta in the imaginary part of $1/\epsilon_{\rm r}$ gives rise to a sharp peak in the structure factor and thus in the inelastic cross section at the plasmon energy. The experimental energy-loss spectra of electrons scattered from aluminum and magnesium are shown in Fig. 31.2. A series of more or less sharp peaks are seen, since electrons can create more than one plasmon as they traverse the sample. The peaks at integer multiples of $\hbar\omega_{\rm p} = 15.3 \,\mathrm{eV}$ in aluminum and at multiples of $\hbar\omega_{\rm p} = 10.6 \,\mathrm{eV}$ in magnesium are due to plasmons. The extra peaks at $\hbar\omega'_{\rm p} = 10.3$ and 7.1 eV, respectively, are due to surface plasmons.



Fig. 31.2. Energy-loss spectra of high-energy electrons scattered from aluminum and magnesium, respectively [Reprinted with permission from C. J. Powell and J. B. Swan, *Phys. Rev.* 115, 869 (1959) and 116, 81 (1959). © (1959) by the American Physical Society]

The contribution of the electron-hole pair excitations should also show up in the dynamical structure factor and hence in the cross section. This gives, however, a negligible contribution to the scattered intensity at small momentum transfers. The dominant process is the creation of plasmons. This can be shown by using the sum rules for the dynamical structure factor. If (31.2.15) is used for the imaginary part of the inverse dielectric function, the T = 0 limit of (29.1.36) gives

$$S(\boldsymbol{q},\omega) = \frac{\pi\hbar}{n_{\rm e}} \frac{q^2}{4\pi\tilde{e}^2} \omega_{\rm p} \delta(\omega - \omega_{\rm p}) = \pi \frac{\hbar q^2}{m_{\rm e}\omega_{\rm p}} \delta(\omega - \omega_{\rm p})$$
(31.2.17)

for the dynamical structure factor. Although this expression contains the contribution of plasmons only, the sum rules (J.2.20) and (J.2.21) are satisfied. On the other hand we know that (28.4.102), which is due entirely to the continuum of noninteracting electron-hole pairs, satisfies the same sum rules. This indicates that the excitation spectrum of the electron gas is rearranged drastically by the interactions, reducing the weight of the electron-hole continuum. In the frequency range of the continuum we find

$$S_{\text{RPA}}(\boldsymbol{q},\omega) = \frac{S_{\text{HF}}(\boldsymbol{q},\omega)}{|\epsilon_{\text{r}}(\boldsymbol{q},\omega)|^2}$$
(31.2.18)

in the RPA, while the plasmon peak gains a strong weight. Figure 31.3 shows the frequency dependence of the dynamical structure factor for several values of q, without the Dirac delta corresponding to the plasmon peak. Comparing it with the results in Fig. 28.10 we see that the spectral weight of the continuum is in fact much reduced for small values of $q/k_{\rm F}$, where the plasmon is a well-defined excitation.



Fig. 31.3. Frequency dependence of the dynamical structure factor calculated in the RPA for several values of q in an electron gas of density $r_s = 3$

At larger wave numbers, where the plasmon branch merges into the electron-hole continuum, the scattering cross section is finite only within the continuum. When q is close to $k_{\rm F}$, a relatively sharp peak is seen near the upper edge of the continuum which widens and gets smoother with increasing q. At even larger q values the interaction has no effect at all.

31.2.3 Transverse Excitations in the Electron Gas

The plasmon oscillations of the electron density are accompanied by a longitudinal oscillation of the electric field. That is why plasmons can be excited by a longitudinal electric field and by charged particles, but cannot be excited by a transverse electromagnetic field. It is natural to ask what kind of transverse electromagnetic oscillations can propagate in an interacting electron gas.

In a nonmagnetic material in the absence of external current, the first and second Maxwell equations can be written in the form

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$$\operatorname{curl} \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t}, \qquad \operatorname{curl} \boldsymbol{E} = -\mu_0 \frac{\partial \boldsymbol{H}}{\partial t}.$$
 (31.2.19)

Combining these equations we get

$$\operatorname{curl}\operatorname{curl}\boldsymbol{E} = -\mu_0 \frac{\partial^2 \boldsymbol{D}}{\partial t^2}$$
(31.2.20)

or

grad div
$$\boldsymbol{E} - \boldsymbol{\nabla}^2 \boldsymbol{E} = -\mu_0 \frac{\partial^2 \boldsymbol{D}}{\partial t^2}$$
. (31.2.21)

If the fields vary in space and times as $\exp(i\boldsymbol{q}\cdot\boldsymbol{r}-i\omega t)$,

$$-\boldsymbol{q}\cdot(\boldsymbol{q}\cdot\boldsymbol{E}) + q^2\boldsymbol{E} = \mu_0\omega^2\boldsymbol{D}. \qquad (31.2.22)$$

Making use of the tensorial relationship between D and E we find

$$\sum_{\beta} \left[q^2 \delta_{\alpha\beta} - q_{\alpha} q_{\beta} - \mu_0 \omega^2 \epsilon_{\alpha\beta} \right] E_{\beta} = 0.$$
 (31.2.23)

Spontaneous oscillations may arise in the system if this equation has a nontrivial solution for the amplitude of the field. The necessary condition for this is the vanishing of the determinant

$$\det \left| q^2 \delta_{\alpha\beta} - q_{\alpha} q_{\beta} - \mu_0 \omega^2 \epsilon_{\alpha\beta} \right| = 0.$$
 (31.2.24)

Written in an equivalent form

$$\det \left| q^2 \delta_{\alpha\beta} - q_{\alpha} q_{\beta} - \frac{\omega^2}{c^2} \frac{\epsilon_{\alpha\beta}}{\epsilon_0} \right| = 0.$$
 (31.2.25)

This gives back the condition $\epsilon_{\parallel}(\boldsymbol{q},\omega) = 0$ for longitudinal oscillations. For transverse fields we find

$$q^2 = \frac{\omega^2}{c^2} \frac{\epsilon_\perp(\boldsymbol{q},\omega)}{\epsilon_0} \,. \tag{31.2.26}$$

In the long-wavelength limit, where the diamagnetic term gives the leading contribution to the transverse conductivity, and hence

$$\sigma_{\perp}(0,\omega) = i \frac{n_e e^2}{m_e \omega}, \qquad (31.2.27)$$

the transverse dielectric function is

$$\frac{\epsilon_{\perp}(0,\omega)}{\epsilon_0} = 1 + \frac{\mathrm{i}}{\epsilon_0\omega}\sigma_{\perp}(0,\omega) = 1 - \frac{n_\mathrm{e}e^2}{\epsilon_0m_\mathrm{e}\omega^2} = 1 - \frac{\omega_\mathrm{p}^2}{\omega^2}.$$
 (31.2.28)

This then leads to

$$\omega^2 = \omega_{\rm p}^2 + c^2 q^2 \tag{31.2.29}$$

for the frequency of excitations, in agreement with (25.1.55). In the limit $cq \gg \omega_{\rm p}$ we recover $\omega \approx cq$ which shows that the electromagnetic field is

almost completely decoupled from the electrons in the short-wavelength limit. On the other hand, the coupling is strong for $cq \ll \omega_{\rm p}$ and the electromagnetic field propagates in solids with the plasma frequency. Electromagnetic waves with smaller frequencies are not allowed in metals; the dielectric function is negative for $\omega < \omega_{\rm p}$ and the amplitude of such waves decays exponentially fast inside the sample.

One can show using a more accurate expression for the dielectric function that another collective excitation could exist with frequency on the order of $qv_{\rm F}$. This would, however, require an interaction much stronger than what we have in metals.

31.3 Bound Electron–Hole Pairs, Excitons

When looking for electron-hole excitations, it was found that although the interaction shifts somewhat their energies, they form the same continuum as before and the collective excitations appear above the continuum. This picture changes dramatically in two respects in the case of semiconductors or insulators instead of metals. On the one hand, in these materials, the electron– hole pair can be created by taking an electron out of one band (the valence band in semiconductors) and putting it into an empty state of another band (the conduction band in semiconductor) and therefore this excitation requires a finite energy larger than the band gap. The continuum does not extend to zero energy. On the other hand, while the Coulomb repulsion becomes short ranged in metals due to screening, it remains long ranged in semiconductors and insulators, since their dielectric constant is finite in the $q \to 0$ limit and screening is not complete. As a consequence, while electrons and holes interact weakly in metals and can be taken to be independent to a good approximation, the interaction between the oppositely charged electrons and holes remains strong enough in semiconductors and insulators to lead to bound states inside the gap, much like the donor or acceptor states in semiconductors. This bound state of an electron and a hole is called an *exciton*. Unlike the bound states around impurities, excitons are not localized however and propagate in the system.

31.3.1 Electron–Hole Pairs in Semiconductors and Insulators

The creation operator that creates an electron and a hole in the same band near the Fermi energy was defined in (31.1.58). In semiconductors and insulators, the relevant electron-hole pairs consist of a hole in the highest occupied band and an electron in the lowest unoccupied band. They are created by the operators

$$c^{\dagger}_{\mathbf{n}\boldsymbol{k}+\boldsymbol{q}\sigma}c_{\mathbf{p}\boldsymbol{k}\sigma}\,,\qquad\qquad(31.3.1)$$

where $c_{\mathbf{p}\boldsymbol{k}\sigma}$ is the annihilation operator of a Bloch state in the valence band (the creation operator of the hole) and $c^{\dagger}_{\mathbf{n}\boldsymbol{k}\sigma}$ is the creation operator of the electron state in the conduction band. Similar to the case of metals, this state is not an eigenstate of the Hamiltonian of the interacting system, but an approximate eigenstate can be found by taking a linear combination of such states.

It will be convenient sometimes to use the localized Wannier states instead of the extended Bloch states. The creation of an electron-hole pair can then be given by the creation and annihilation operators of the Wannier states as

$$c_{\mathbf{n}\boldsymbol{R}_{i}+\boldsymbol{R}_{j}\sigma}^{\dagger}c_{\mathbf{p}\boldsymbol{R}_{i}\sigma}.$$
(31.3.2)

A propagating pair is obtained if linear combinations are taken with coefficients depending on the lattice vectors \mathbf{R}_i and \mathbf{R}_j . To simplify the calculations, the excitation spectrum will be determined in two limiting cases.

31.3.2 Wannier Excitons

The physical picture introduced above that interprets the bound state as a special propagating electron-hole pair is due to G. H. WANNIER (1937). Since both the electron and the hole move in the periodic potential of the lattice and they interact with each other via a weakened Coulomb interaction due to the finite dielectric constant, the Hamiltonian of the two-particle system is

$$\mathcal{H} = \left[\frac{1}{2m_{\rm e}} \left(\frac{\hbar}{\rm i} \boldsymbol{\nabla}_{\boldsymbol{r}_{\rm n}}\right)^2 + V(\boldsymbol{r}_{\rm n})\right] - \left[\frac{1}{2m_{\rm e}} \left(\frac{\hbar}{\rm i} \boldsymbol{\nabla}_{\boldsymbol{r}_{\rm p}}\right)^2 + V(\boldsymbol{r}_{\rm p})\right] - \frac{\tilde{e}^2}{\epsilon_{\rm r} |\boldsymbol{r}_{\rm n} - \boldsymbol{r}_{\rm p}|},$$
(31.3.3)

where \mathbf{r}_{n} and \mathbf{r}_{p} denote the position of the electron and the hole, respectively. The terms describing the hole appear with negative sign since a hole corresponds to the removal of one particle. The sign of the Coulomb interaction was chosen so as to describe attraction between the electron and the hole. Neglecting first the Coulomb interaction but taking into account the periodic potential, the states of the electron and of the hole can be determined from the Schrödinger equation

$$\left[\frac{1}{2m_{\rm e}}\left(\frac{\hbar}{\rm i}\boldsymbol{\nabla}_{\boldsymbol{r}}\right)^2 + V(\boldsymbol{r})\right]\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon_{n\boldsymbol{k}}\psi_{n\boldsymbol{k}}(\boldsymbol{r}). \qquad (31.3.4)$$

Let us assume that the energies ε_{nk} of the Bloch states are known. Then the Wannier theorem can be applied to eliminate the periodic potential from the one-particle problem. We have seen in Chapter 22 that the operator

$$\varepsilon_n(-i\boldsymbol{\nabla}),$$
 (31.3.5)

which is obtained by replacing the wave vector \boldsymbol{k} in the energy $\varepsilon_{n\boldsymbol{k}}$ of Bloch electrons by $-i\boldsymbol{\nabla}$ plays the role of an effective Hamiltonian and the Schrödinger equation takes the form

$$\varepsilon_n(-i\nabla)\psi_{nk}(\mathbf{r}) = \varepsilon_{nk}\psi_{nk}(\mathbf{r}).$$
 (31.3.6)

If the relevant states of the conduction and valence bands can be characterized by scalar effective masses, m_n^* and m_p^* , respectively, that is

$$\varepsilon_{\mathbf{n}\boldsymbol{k}} = \varepsilon_{\mathbf{c}} + \frac{\hbar^2 \boldsymbol{k}^2}{2m_{\mathbf{n}}^*}, \qquad \varepsilon_{\mathbf{p}\boldsymbol{k}} = \varepsilon_{\mathbf{v}} - \frac{\hbar^2 \boldsymbol{k}^2}{2m_{\mathbf{p}}^*}, \qquad (31.3.7)$$

then the eigenvalue problem of the interacting electron–hole pair is equivalent to solving the two-particle Schrödinger equation

$$\begin{cases} \left[\varepsilon_{\rm c} + \frac{\hbar^2}{2m_{\rm n}^*} \left(-i\boldsymbol{\nabla}_{\boldsymbol{r}_{\rm n}}\right)^2\right] - \left[\varepsilon_{\rm v} - \frac{\hbar^2}{2m_{\rm p}^*} \left(-i\boldsymbol{\nabla}_{\boldsymbol{r}_{\rm p}}\right)^2\right] \\ - \frac{\tilde{e}^2}{\epsilon_{\rm r}|\boldsymbol{r}_{\rm n} - \boldsymbol{r}_{\rm p}|} \end{cases} \psi(\boldsymbol{r}_{\rm n}, \boldsymbol{r}_{\rm p}) = \varepsilon\psi(\boldsymbol{r}_{\rm n}, \boldsymbol{r}_{\rm p}) \,. \tag{31.3.8}$$

Instead of working with the position vectors of the electron and the hole, it is more convenient to use the center-of-mass and relative coordinates:

$$\boldsymbol{R} = \frac{m_{\rm n}^* \boldsymbol{r}_{\rm n} + m_{\rm p}^* \boldsymbol{r}_{\rm p}}{m_{\rm n}^* + m_{\rm p}^*}, \qquad \boldsymbol{r} = \boldsymbol{r}_{\rm n} - \boldsymbol{r}_{\rm p}.$$
(31.3.9)

Then the Schrödinger equation from which the states of the pair has to be determined takes the form

$$\left[-\frac{\hbar^2}{2(m_{\rm n}^*+m_{\rm p}^*)}\boldsymbol{\nabla}_{\boldsymbol{R}}^2 - \frac{\hbar^2}{2m_{\rm r}}\boldsymbol{\nabla}_{\boldsymbol{r}}^2 - \frac{\tilde{\epsilon}^2}{\epsilon_{\rm r}|\boldsymbol{r}|}\right]\psi(\boldsymbol{R},\boldsymbol{r}) = \left[\varepsilon - \varepsilon_{\rm c} + \varepsilon_{\rm v}\right]\psi(\boldsymbol{R},\boldsymbol{r}),$$
(31.3.10)

where $m_{\rm r}$ is the reduced mass,

$$\frac{1}{m_{\rm r}} = \frac{1}{m_{\rm n}^*} + \frac{1}{m_{\rm p}^*} \,. \tag{31.3.11}$$

We assume that the wavefunction is separable in the variables R and r, that is the motion of the center of mass is independent of the relative motion within the pair:

$$\psi(\mathbf{R}, \mathbf{r}) = g(\mathbf{R})f(\mathbf{r}). \qquad (31.3.12)$$

Since the center-of-mass motion contributes to the kinetic energy only and the corresponding Schrödinger equation is identical to the wave equation of a free particle, this motion can be characterized by a wave vector \mathbf{k} ,

$$g(\boldsymbol{R}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}}, \qquad (31.3.13)$$

and the kinetic energy is

$$\frac{\hbar^2 k^2}{2(m_{\rm n}^* + m_{\rm p}^*)}.$$
(31.3.14)

The wavefunction describing the relative motion satisfies

$$\left[-\frac{\hbar^2}{2m_{\rm r}}\boldsymbol{\nabla}_{\boldsymbol{r}}^2 - \frac{\tilde{e}^2}{\epsilon_{\rm r}|\boldsymbol{r}|}\right]f(\boldsymbol{r}) = \left[\varepsilon - \varepsilon_{\rm c} + \varepsilon_{\rm v} - \frac{\hbar^2\boldsymbol{k}^2}{2(m_{\rm n}^* + m_{\rm p}^*)}\right]f(\boldsymbol{r}). \quad (31.3.15)$$

This is nothing else than an effective hydrogen problem, the Schrödinger equation of a particle of charge -e with mass $m_{\rm r}$ in a Coulomb potential that is weakened by the dielectric constant. The energy eigenvalues of the full problem are then

$$\varepsilon = \varepsilon_{\rm c} - \varepsilon_{\rm v} - \frac{m_{\rm r}\tilde{e}^4}{2\hbar^2\epsilon_{\rm r}^2}\frac{1}{n^2} + \frac{\hbar^2k^2}{2(m_{\rm n}^* + m_{\rm p}^*)},\qquad(31.3.16)$$

where n is the principal quantum number of the hydrogenlike state. The energies belonging to the same n form an exciton band.

Compared to the energy levels in a hydrogen atom the binding energies are multiplied by a factor $m_r/m_e\epsilon_r^2$ as is the case for the donor and acceptor levels in doped semiconductors. The measured exciton energies are listed in Table 31.2 for a few semiconductors and ionic crystals.

Semiconductor	$\Delta \varepsilon_{\rm exc} ({\rm meV})$	Ionic crystal	$\Delta \varepsilon_{\rm exc} ({\rm meV})$
Si	14.7	KCl	400
Ge	4.1	KI	480
GaAs	4.2	RbCl	440
GaP	3.5	AgCl	30

Table 31.2. Binding energy of excitons in a few materials

Due to the large value of the dielectric constant and the small effective mass, the binding energy of excitons is on the order of 1–10 meV in semiconductors. The states are in general quite close to the bottom of the conduction band and are practically fully ionized by thermal excitation. They are therefore uninteresting when the properties of semiconductors are studied. The exciton energies are much larger in ionic crystals, where the dielectric constant is usually smaller ($\epsilon_r \approx 5$) and the effective mass is larger than in semiconductors. The energies are on the order of the energy of infrared photons. Thus, excitons play a role in the infrared optical transitions.

The treatment exposed above is in fact valid for semiconductors only, where the typical spatial dimension of excitons is on the order of 100 Å. This estimate comes from multiplying the Bohr radius by $\epsilon_{\rm r} m_{\rm e}/m_{\rm r}$. The assumption that the electrons move in a homogeneous medium characterized by a dielectric constant is questionable in ionic crystals, where the size of the exciton is close to the atomic dimensions. In this case, the excitons have to be treated differently.

31.3.3 Frenkel Excitons

To get a simple picture of the formation of excitons in insulating ionic or molecular crystals, we follow the arguments of J. FRENKEL (1931). For simplicity, we forget about the spin of electrons and assume that the system has one electron per atom ($N_e = N$). Owing to the intra-atomic Coulomb repulsion, one electron sits on each atom in the ground state, and when they are excited, they remain preferentially on the same atom. Jumps to another atom which already has an electron on it require high energy. The state in which the excited electron is localized to one atom is not an eigenstate and the excitation propagates through the crystal due to interatomic interaction processes: the excited electron on site j returns to its ground state, while an electron on a neighboring site is excited.

Such states of the many-electron system can be described in terms of the Wannier functions $\phi_n(\mathbf{r} - \mathbf{R}_j)$. We assume further that the Wannier states can be approximated by atomic wavefunctions satisfying the atomic Schrödinger equation

$$\mathcal{H}(\boldsymbol{r},\boldsymbol{R}_j)\phi_n(\boldsymbol{r}-\boldsymbol{R}_j) = \varepsilon_n\phi_n(\boldsymbol{r}-\boldsymbol{R}_j). \qquad (31.3.17)$$

Although some overlap between the atomic wavefunctions of neighboring atoms is needed for the propagation of the excitations just as in the tightbinding approximation, we can assume that

$$\int \phi_n^*(\boldsymbol{r} - \boldsymbol{R}_j) \phi_{n'}(\boldsymbol{r} - \boldsymbol{R}_{j'}) \,\mathrm{d}\boldsymbol{r} = \delta_{nn'} \delta_{jj'}$$
(31.3.18)

when the wavefunction is normalized.

In the Hartree–Fock approximation, the relevant wavefunctions of the electron system can be given in Slater-determinant form. In the ground state, where all electrons are in their atomic ground state ϕ_0 , the wavefunction is

$$\Psi_{0} = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_{0}(\boldsymbol{r}_{1} - \boldsymbol{R}_{1}) & \phi_{0}(\boldsymbol{r}_{1} - \boldsymbol{R}_{2}) & \dots & \phi_{0}(\boldsymbol{r}_{1} - \boldsymbol{R}_{N}) \\ \phi_{0}(\boldsymbol{r}_{2} - \boldsymbol{R}_{1}) & \phi_{0}(\boldsymbol{r}_{2} - \boldsymbol{R}_{2}) & \dots & \phi_{0}(\boldsymbol{r}_{2} - \boldsymbol{R}_{N}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{0}(\boldsymbol{r}_{N} - \boldsymbol{R}_{1}) & \phi_{0}(\boldsymbol{r}_{N} - \boldsymbol{R}_{2}) & \dots & \phi_{0}(\boldsymbol{r}_{N} - \boldsymbol{R}_{N}) \end{vmatrix} .$$
(31.3.19)

Excited states can be formed by putting one of the electrons into one of the atomic excited states ϕ_n while all other electrons remain in their ground state. If the excited atom is at site \mathbf{R}_j and one of the electrons is in the lowest energy excited state ϕ_1 , the wavefunction is

$$\Psi_{j} = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_{0}(\boldsymbol{r}_{1} - \boldsymbol{R}_{1}) & \phi_{0}(\boldsymbol{r}_{1} - \boldsymbol{R}_{2}) & \dots & \phi_{1}(\boldsymbol{r}_{1} - \boldsymbol{R}_{j}) & \dots & \phi_{0}(\boldsymbol{r}_{1} - \boldsymbol{R}_{N}) \\ \phi_{0}(\boldsymbol{r}_{2} - \boldsymbol{R}_{1}) & \phi_{0}(\boldsymbol{r}_{2} - \boldsymbol{R}_{2}) & \dots & \phi_{1}(\boldsymbol{r}_{2} - \boldsymbol{R}_{j}) & \dots & \phi_{0}(\boldsymbol{r}_{2} - \boldsymbol{R}_{N}) \\ \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\ \phi_{0}(\boldsymbol{r}_{N} - \boldsymbol{R}_{1}) & \phi_{0}(\boldsymbol{r}_{N} - \boldsymbol{R}_{2}) & \dots & \phi_{1}(\boldsymbol{r}_{N} - \boldsymbol{R}_{j}) & \dots & \phi_{0}(\boldsymbol{r}_{N} - \boldsymbol{R}_{N}) \end{vmatrix} .$$
(31.3.20)

An eigenstate with proper translational properties can be obtained by taking linear combinations of such states with appropriate phase factors:

$$\Psi_{\text{exc}} = \frac{1}{\sqrt{N}} \sum_{j} e^{i \mathbf{k} \cdot \mathbf{R}_{j}} \Psi_{j} \,. \tag{31.3.21}$$

If the energy in the atomic ground state ϕ_0 is denoted by ε_0 , and ε_1 is the energy of the excited state, then the energy of the exciton is

$$E_{\text{exc}} = \varepsilon_1 - \varepsilon_0 + \sum_{jj'} e^{i \mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_{j'})} V_{jj'}, \qquad (31.3.22)$$

where $V_{jj'}$ is the matrix element of the interaction between states Ψ_j and $\Psi_{j'}$. Similar to what has been seen in the tight-binding approximation, the dominant matrix elements are the ones between Wannier functions belonging to nearest neighbors. Hence the spectrum of excitons is similar to the band structure in the tight-binding approximation. The dispersion relations start as k^2 for small values of k.

Frenkel excitons behave almost as bosons. Since the electron and the hole are created on the same atom, if index p denotes band states belonging to Wannier state ϕ_0 and index n denotes band states belonging to Wannier state ϕ_1 , the creation operator of an exciton is

$$\alpha_{\boldsymbol{q}}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{j} e^{i\boldsymbol{q}\cdot\boldsymbol{R}_{j}} c_{n\boldsymbol{R}_{j}\sigma}^{\dagger} c_{p\boldsymbol{R}_{j}\sigma}. \qquad (31.3.23)$$

The commutator of creation and annihilation operators is easily calculated:

$$\begin{aligned} \left[\alpha_{\boldsymbol{q}}, \alpha_{\boldsymbol{q}'}^{\dagger}\right]_{-} &= \frac{1}{N} \sum_{jj'} e^{-i(\boldsymbol{q} \cdot \boldsymbol{R}_{j} - \boldsymbol{q}' \cdot \boldsymbol{R}_{j'})} \left[c_{p\boldsymbol{R}_{j}\sigma}^{\dagger} c_{n\boldsymbol{R}_{j}\sigma}, c_{n\boldsymbol{R}_{j'}\sigma}^{\dagger} c_{p\boldsymbol{R}_{j'}\sigma}\right]_{-} \\ &= \frac{1}{N} \sum_{j} e^{-i(\boldsymbol{q} - \boldsymbol{q}') \cdot \boldsymbol{R}_{j}} \left(c_{p\boldsymbol{R}_{j}\sigma}^{\dagger} c_{p\boldsymbol{R}_{j}\sigma} - c_{n\boldsymbol{R}_{j}\sigma}^{\dagger} c_{n\boldsymbol{R}_{j}\sigma}\right) \\ &= \frac{1}{N} \sum_{j} e^{-i(\boldsymbol{q} - \boldsymbol{q}') \cdot \boldsymbol{R}_{j}} \left(1 - 2c_{n\boldsymbol{R}_{j}\sigma}^{\dagger} c_{n\boldsymbol{R}_{j}\sigma}\right) \\ &= \delta_{\boldsymbol{q}\boldsymbol{q}'} - \frac{2}{N} \sum_{j} e^{-i(\boldsymbol{q} - \boldsymbol{q}') \cdot \boldsymbol{R}_{j}} c_{n\boldsymbol{R}_{j}\sigma}^{\dagger} c_{n\boldsymbol{R}_{j}\sigma}, \qquad (31.3.24) \end{aligned}$$

where we have used the fact that there is exactly one electron on each site, either in the ground state or in the excited state. Assuming that the number of excited states is small we recover the commutation relation valid for bosons.

When the binding energy of the exciton is larger than the bandwidth, the picture presented above – exciton states inside the gap – breaks down. The system goes over into a different state, the *excitonic insulator* state, where the ground state is a coherent superposition of electron–hole pairs.

Another state is found when electron-hole pairs are generated in a macroscopic number in a semiconductor by optical pumping, i.e., exposing it to a strong beam of light. In this case, it is no longer energetically favorable for the system to form bound pairs; the electrons and holes condense rather into droplets of finite, macroscopic size. In this *electron-hole liquid* state the semiconductor behaves as a conductor.

31.4 Magnetic Excitations

We have seen, when magnetic correlations were studied, that the Coulomb repulsion gives rise to an increase of magnetic fluctuations. Nevertheless, no magnetic analogue of the plasmon was found. This can easily be understood if we recall that the expressions obtained in the RPA for the magnetic and dielectric responses have a very similar form, but Π_0 and Σ_0 differ in sign. Therefore, since the collective density oscillations appear above the electron-hole continuum, they would have to appear below the continuum in the magnetic case. Such bound states cannot exist if the continuum starts without a gap. When the system is put into a magnetic field, and the continuum of spin-flip excitations starts with a finite gap, well-defined collective excitations may appear inside the gap. A physically more interesting situation may occur when the Stoner enhancement factor is large enough. Then the continuum, which nevertheless have a long enough lifetime to be observable.

31.4.1 Paramagnons in Nearly Ferromagnetic Metals

Assume that the Coulomb repulsion is strong enough so that $U\rho_{\sigma}(\varepsilon_{\rm F})$ in the Stoner enhancement factor is close to unity. This could be the case in 4d and 5d metals, in particular in platinum and palladium, and their compounds. As already mentioned in Chapter 29, these materials are nonmagnetic but are rather close to the threshold where the unpolarized, paramagnetic electron system becomes unstable against transition to a ferromagnetic state. They are therefore called nearly ferromagnetic metals. Although, as will be seen in Chapter 33, a better approximation sets a stronger constraint for the magnetic instability, we will use the RPA, where the threshold is at $[U\rho_{\sigma}(\varepsilon_{\rm F})]_{\rm c} = 1$ and will calculate the dynamical susceptibility for materials where $U\rho_{\sigma}(\varepsilon_{\rm F}) < 1$ but close to the threshold.

Apart from a sign difference which already appeared in (29.8.43) for the dynamical susceptibility, $\Sigma_0(q, \omega)$ has the same form as the Lindhard function determined for the dielectric function. When its real part (29.2.52) is expanded for small values of q and ω assuming that $\omega \ll v_{\rm F}q$, and the imaginary part is taken from (29.2.56), we find

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$$\Sigma_0(\boldsymbol{q},\omega) = \rho_\sigma(\varepsilon_{\rm F}) \left(1 + \mathrm{i} \frac{\pi\omega}{2v_{\rm F}q} - \frac{q^2}{12k_{\rm F}^2} + \cdots \right).$$
(31.4.1)

Inserting this into (29.8.43) we get in the limit $U\rho_{\sigma}(\varepsilon_{\rm F}) \approx 1$

$$\chi(\boldsymbol{q},\omega) \approx \frac{\frac{1}{4}g_{\rm e}^2\mu_{\rm B}^2\mu_0\rho_{\sigma}(\varepsilon_{\rm F})}{1 - U\rho_{\sigma}(\varepsilon_{\rm F}) - \mathrm{i}\frac{\pi\omega}{2v_{\rm F}q} + \frac{q^2}{12k_{\rm F}^2} + \cdots} \,.$$
(31.4.2)

Figure 31.4 shows the imaginary part of the susceptibility compared to the case when the interaction is neglected. While Im χ increases slowly in a free electron gas, the same quantity in the interacting system exhibits a relatively narrow peak at low energies when $U\rho_{\sigma}(\varepsilon_{\rm F})$ is close to the instability threshold.



Fig. 31.4. The peak appearing in the imaginary part of the magnetic susceptibility of the electron gas due to the interaction, for several values of U. The momentum is fixed at $q/k_{\rm F} = 0.1$

At small values of q, for $q \ll k_{\rm F} [1 - U \rho_{\sigma}(\varepsilon_{\rm F})]^{1/2}$, the peak is at

$$\omega = \frac{2}{\pi} v_{\rm F} q \left[1 - U \rho_\sigma(\varepsilon_{\rm F}) \right], \qquad (31.4.3)$$

while for $q \gg k_{\rm F} [1 - U\rho_{\sigma}(\varepsilon_{\rm F})]^{1/2}$ the position of the peak varies as the third power of q. To interpret this narrow peak we recall that the inelastic cross section of scattering of high-energy electrons on a solid is proportional to the dynamical structure factor, which in turn is related to the imaginary part of the dielectric function. Sharp resonances appear in the cross section at energies where elementary excitations can be created or annihilated. Similar considerations lead to the conclusion that the cross section of magnetic scattering of neutrons is proportional to the imaginary part of the magnetic susceptibility, the sharp peaks in the inelastic scattering processes are due to magnetic excitations, and the position of the peak gives their energy. The relatively sharp peak in the imaginary part of the magnetic susceptibility is therefore an indication that, even though the system is in the paramagnetic state, overdamped collective excitations, resembling spin waves (magnons), propagate in the sample. These excitations are called *paramagnons*.

When the Coulomb interaction is strong and the system is close to the ferromagnetic instability, the lifetime of these excitations may be quite long. The thermally excited, long-lived paramagnons modify the thermal properties of paramagnetic metals. At low temperatures they give a contribution proportional to $T^3 \ln T$ in the specific heat. Paramagnons might even play a role in high-temperature superconductors, where the superconducting state appears in the phase diagram next to a magnetically ordered state. If magnetic fluctuations are still strong in the superconducting state, they may contribute to the formation of Cooper pairs and that may explain the unconventional symmetry of the pairs and the unconventional properties of these systems.

31.4.2 Spin Waves in Magnetic Field

Another type of collective magnetic excitations may appear in paramagnetic systems if they are polarized by an external magnetic field. The field shifts the one-particle energies oppositely for the two spin orientations,

$$\varepsilon_{\mathbf{k}\uparrow} = \varepsilon_{\mathbf{k}} - \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}H, \qquad \varepsilon_{\mathbf{k}\downarrow} = \varepsilon_{\mathbf{k}} + \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}H, \qquad (31.4.4)$$

and the lower bound of the continuum of electron–hole pair excitations with opposite spins; the minimum of

$$\hbar\omega_{\boldsymbol{k}\boldsymbol{q}} = \varepsilon_{\boldsymbol{k}+\boldsymbol{q}\uparrow} - \varepsilon_{\boldsymbol{q}\downarrow} \tag{31.4.5}$$

for a fixed q becomes finite. It takes the value

$$\Delta = |g_{\rm e}|\mu_{\rm B}\mu_0 H \tag{31.4.6}$$

at q = 0. The effect of interactions will again be considered in the Hubbard model, where the energy of the one-particle excitations is given in a mean-field approximation by (29.8.3):

$$\widetilde{\varepsilon}_{\boldsymbol{k}\uparrow} = \varepsilon_{\boldsymbol{k}} + U\langle n_{\downarrow}\rangle - \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}H, \quad \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow} = \varepsilon_{\boldsymbol{k}} + U\langle n_{\uparrow}\rangle + \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}H. \quad (31.4.7)$$

When an electron-hole pair is excited with opposite spins, its energy is

$$\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} - \widetilde{\varepsilon}_{\boldsymbol{q}\downarrow} = \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{q}} + U[\langle n_{\downarrow} \rangle - \langle n_{\uparrow} \rangle] - g_{e} \mu_{B} \mu_{0} H.$$
(31.4.8)

The continuum of excitations then starts at

$$\widetilde{\varepsilon}_{\boldsymbol{k}\uparrow} - \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow} = U[\langle n_{\downarrow} \rangle - \langle n_{\uparrow} \rangle] - g_{\rm e} \mu_{\rm B} \mu_0 H \qquad (31.4.9)$$

for q = 0. The difference in the occupation numbers for the two spin directions can be expressed in terms of the magnetization using (29.8.5) and then in terms of the external field using (29.8.10). The splitting between the two subbands with opposite spin orientations becomes 208 31 Excitations in the Interacting Electron Gas

$$\widetilde{\varepsilon}_{\boldsymbol{k}\uparrow} - \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow} = |g_{e}|\mu_{B}\mu_{0}\frac{U\rho_{\sigma}(\varepsilon_{F})}{1 - U\rho_{\sigma}(\varepsilon_{F})}H + |g_{e}|\mu_{B}\mu_{0}H$$

$$= \frac{|g_{e}|\mu_{B}\mu_{0}H}{1 - U\rho_{\sigma}(\varepsilon_{F})} = \frac{\Delta}{1 - U\rho_{\sigma}(\varepsilon_{F})}.$$
(31.4.10)

The electron–electron interaction enhances the splitting caused by the external field in a free electron gas. The continuum of electron–hole pairs with opposite spins for a finite total momentum q of the pair is shown in Fig. 31.5.



Fig. 31.5. Continuum of electron-hole pair excitations with opposite spins and the excitation energy of spin waves

Since the continuum starts at finite energies, collective spin excitations may appear at lower energies inside the gap. Following the procedure applied earlier to get the collective density oscillations, the plasmons, we search for states created by the operator

$$\alpha_{\boldsymbol{q}}^{\dagger} = \sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}\boldsymbol{q}} c_{\boldsymbol{k}+\boldsymbol{q}\uparrow}^{\dagger} c_{\boldsymbol{k}\downarrow} \,. \tag{31.4.11}$$

Not surprisingly we find that magnetic excitations can propagate in the system for wave vectors and frequencies for which the transverse susceptibility defined in (29.8.48) is singularly large. This happens, according to (29.8.54), when

$$1 = U \Sigma_{\perp}^{0}(\boldsymbol{q}, \omega) \,. \tag{31.4.12}$$

If (29.8.52) is used for $\Sigma^0_{\perp}(\boldsymbol{q},\omega)$, the excitation energies are the solutions of

$$1 = U \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_0(\tilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}) - f_0(\tilde{\varepsilon}_{\boldsymbol{k}\downarrow})}{\hbar\omega - \tilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} + \tilde{\varepsilon}_{\boldsymbol{k}\downarrow}} \,. \tag{31.4.13}$$

The summation can be performed in the limit $q \rightarrow 0$ if (31.4.9) is inserted into the denominator. This leads to

$$1 = U \frac{\langle n_{\uparrow} \rangle - \langle n_{\downarrow} \rangle}{\hbar \omega - U [\langle n_{\downarrow} \rangle - \langle n_{\uparrow} \rangle] - |g_{\rm e}| \mu_{\rm B} \mu_0 H}, \qquad (31.4.14)$$

giving

$$\hbar\omega = |g_{\rm e}|\mu_{\rm B}\mu_0 H \tag{31.4.15}$$

for the solution. For finite q values the energy starts from this finite value and has a weak q^2 dependence, just as for plasmons. This dispersion relation is also shown in Fig. 31.5. These collective magnetic excitations are called spin waves, although they appear in paramagnetic systems which are polarized by an external magnetic field. If the Stoner enhancement factor is large enough, the spin waves are well separated from the continuum and can be observed experimentally.

Further Reading

- P. Nozières, Theory of Interacting Fermi Systems, W. A. Benjamin, New York (1964).
- D. Pines, *Elementary Excitations in Solids*, W. A. Benjamin, New York (1963).
- D. Pines and P. Nozières, The Theory of Quantum Liquids, Vol. 1: Normal Fermi Liquids, Addison Wesley, Redwood City (1988).

Fermion Liquids

In the previous chapters, we presented various methods that allow for taking the electron–electron interaction into account and studied some of its effects. One important finding was that a low-order perturbative treatment is not sufficient for a quantitatively correct description of the properties of even the simplest metals since the Coulomb repulsion between electrons is strong and long ranged. The whole panoply of many-body physics is needed. In spite of this, experiments show that – rather surprisingly – simple metals behave in many respects as the noninteracting chargeless fermion gas: the heat capacity varies linearly with T and the Pauli susceptibility is independent of temperature. Similar behavior is observed in the normal liquid phase of ³He, which is a fermionic system, while ⁴He is a Bose liquid. There are of course exceptions. The most notable are superconductors, whose thermal and magnetic properties differ drastically from those of normal metals.

In 1956 L. D. LANDAU pointed out that the almost-free-electron-like behavior is not accidental but is an inherent property of Fermi systems under certain conditions. Systems without long-range order in spite of strong interactions were called *normal Fermi liquids*. In Landau's original formulation the theory was aimed at describing the low-temperature properties of ³He liquid, which does not crystallize at ambient pressure even at very low temperatures owing to quantum fluctuations. The theory also had its greatest success there. Not only did it give a simple description of the low-temperature properties in terms of a few phenomenological parameters which could be fit to experiments, but it was able to explain and predict quantitatively a wide variety of new phenomena.

The quasiparticle picture and the Landau theory is, however, applicable more generally to explain those properties of normal metals in which only the states near the Fermi surface play an important role, although the results are quantitatively much less spectacular than in ³He. This is because other interactions besides the electron–electron interaction, such as the periodic potential of the lattice and the electron–phonon interaction, also play a decisive role. Furthermore, the quasiparticles have to be defined relative to a nonspherical

J. Sólyom, Fundamentals of the Physics of Solids, DOI 10.1007/978-3-642-04518-9_5, © Springer-Verlag Berlin Heidelberg 2010 Fermi surface, which means that the use of a scalar effective mass may not be sufficient and the parametrization of the interaction is more difficult. Its importance lies rather in the fact that the concepts on which this theory is based, namely the adiabatic continuity between the noninteracting and interacting systems, the existence of quasiparticles, and the way the interaction between them is handled, give a general theoretical framework in which the behavior of normal metals can easily be understood.

Fermi-liquid-like behavior is not the only possibility for an interacting electron gas even if no symmetry is broken. The assumptions underlying the Landau theory, for example, the applicability of perturbation theory, which is a prerequisite for the existence of a Fermi surface, are not satisfied in the one-dimensional interacting electron gas. The momentum distribution function cannot be calculated in perturbation theory since logarithmic singularities appear at the Fermi momentum already in low orders of the perturbation. The new type of behavior exhibited by one-dimensional systems will be demonstrated in two models and their common features will lead us to the *Luttinger-liquid* concept. Although the models we study are one dimensional in a mathematical sense, Luttinger-liquid behavior may be observed in physically realistic, strongly anisotropic, *quasi-one-dimensional* systems, in which electrons can propagate with high probability only in one direction.

The case of two-dimensional systems is more delicate. The theory of Luttinger liquids cannot be generalized simply to two dimensions, and the experimental results that indicate deviations from Fermi-liquid behavior in layered materials are not fully understood. We will consider one special case, the pronounced non-Fermi-liquid properties of the two-dimensional electron gas in strong magnetic field. A new type of quantum liquid state, the quantum Hall liquid, is observed there.

After a brief presentation of Landau's phenomenological theory of normal Fermi liquids the Luttinger-liquid behavior of several one-dimensional models is studied at some length in this chapter. Some properties of quantum Hall liquids are discussed at the end.

32.1 Ground State and Excited States of Normal Fermi Systems

It is well known that the low-lying excited states of a vibrating lattice can be identified to good approximation by the states of a free gas of bosonic phonons. Some features of the dispersion curve are determined by the mass of the ions and the interaction between them, but the bosonic character of the collective excitations does not depend on whether the ions have integer or halfodd-integer spins. The acoustic phonons are the soft Goldstone bosons that have to appear owing to the broken translational symmetry in the crystalline state, but the higher lying optical phonons, too, have a bosonic character.

Something similar happens in magnetically ordered systems as well. The interaction between localized spins may give rise to a complicated excitation spectrum in ferromagnets described by the Heisenberg Hamiltonian. The low-lying part of the spectrum corresponding to states in which the number of reversed spins is not too high, i.e., the magnetization is close to saturation, could be considered as a superposition of independent bosonic magnons. Bosonic magnons appear in antiferromagnets, too, irrespective of the value of the spin quantum number S, whether integer or half-integer. The soft magnons are the Goldstone bosons: they are the consequences of breaking the continuous rotational symmetry of the Heisenberg Hamiltonian.

These examples show that if we consider only the low-lying excited states of a strongly interacting system – by low lying we mean energies comparable to or smaller than the thermal energy at room temperature, which is smaller than the typical energy scales in the band structure – these excited states can be described in terms of a system of weakly interacting bosons. These bosons are *collective excitations*. They lose their identity when the interaction between ions is switched off. The excited states of a free atom or of a free spin are very different from phonons or magnons.

The situation is different in the system of electrons. Bosonic collective excitations, such as plasmons, appear in such systems, too, owing to the Coulomb interaction. However, the fermionic one-particle excited states play a dominant role. Their energies have been determined in the previous chapters in the Hartree–Fock approximation. As stated by Koopmans' theorem, if an electron is excited from its initial state to a final state, the excitation energy is the difference between the energies of the corresponding quasiparticle states. This is not true any more when a large number of quasiparticles are excited. Nevertheless at low temperatures, where the number of thermally excited quasiparticles is small, the interacting electron system can be treated in a first approximation as a free gas of quasiparticles. One reason for that is Pauli's exclusion principle, but the weakening of the strong Coulomb repulsion due to screening also plays an important role.

Contrary to the bosonic collective excitations, which are defined only in an interacting system, the fermionic elementary excitations go over to similar excited states of the free system, when the interaction is switched off adiabatically. Reversing this statement we can assume that starting from the ground state of the noninteracting system and switching on the interaction adiabatically, the ground state of the interacting system is obtained. This assumption is very important for the applicability of perturbation theory. Moreover, a similar one-to-one correspondence is assumed between the excited states of the noninteracting and interacting systems. This *adiabatic continuity* is a basic concept in the theory of normal metals.

32.1.1 Ground State of Normal Fermi Systems

The adiabatic continuity does not mean, though, that the momentum distribution function

$$\langle n_{\boldsymbol{k}\sigma} \rangle = \left\langle c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \right\rangle \tag{32.1.1}$$

calculated for the ground state of the interacting system remains a unit step function. As has been seen in Chapter 28, there are empty states below the Fermi energy and the probability of finding electrons above the Fermi energy is nonvanishing. Nevertheless, one can prove that $\langle n_{k\sigma} \rangle$ exhibits a discontinuous jump (see Fig. 28.3) if perturbation theory is applicable, although the value of the jump is less than unity, and the energy of one-particle excitations vanishes at the same points in **k**-space. Systems where this happens are called *normal Fermi systems* and these points define the Fermi surface of the interacting system.

The Luttinger theorem mentioned in Chapter 28 states that the interaction leaves the volume enclosed by the Fermi surface invariant. Thus in an isotropic system, where the Fermi surface is spherical, its radius, the Fermi momentum $k_{\rm F}$, has the same value as in the noninteracting electron gas. In nonisotropic systems the Fermi surface is not spherical and the interaction may distort its shape. Adiabatic switching of the interaction may then not take the ground state of the noninteracting system into that of the interacting system and perturbation theory may fail. This can be corrected by adding an appropriate counter term to the Hamiltonian of the free system – which of course has to be compensated in the interaction part – such that the Fermi surfaces of the free and of the interacting systems coincide. The adiabatic continuity between the ground states of the noninteracting and interacting systems can be established after such a reformulation of the problem and thus the Landau theory of Fermi liquids could be valid for systems with anisotropic Fermi surface as well.

Of course quite often the above-sketched scenario does not apply. The ground state of the interacting system may be very different from that of the free system and cannot be generated by adiabatically switching on the interaction. This is the case, e.g., in superconductors, in magnetically ordered fermion systems, and in density-wave systems. The properties of such systems will be described in subsequent chapters. Throughout this section we will assume that the ground state of the noninteracting system evolves into that of the interacting one after adiabatically switching on the interaction.

32.1.2 Quasiparticles in Normal Fermi Systems

From now on we will consider normal systems only. Let us add an electron with wave vector \mathbf{k} to the ground state and switch on again the interaction adiabatically. The properties of the initially free particle will be modified by the interaction, but the excited state of the interacting system will have the same \mathbf{k} vector, since the momentum is conserved in the interaction processes.

We will look upon this state as if a *quasiparticle* were added to the interacting ground state. Denoting by $|\Psi_{\rm FS}\rangle$ the ground state of the free Fermi gas from which the ground state $|\Psi_0\rangle$ of the Fermi liquid evolves after switching on the interaction adiabatically, the state which evolves from $c_{k\sigma}^{\dagger}|\Psi_{\rm FS}\rangle$ will be denoted as $\alpha_{k\sigma}^{\dagger}|\Psi_0\rangle$. The operator $\alpha_{k\sigma}^{\dagger}$ can then be interpreted as the creation operator of a quasiparticle, if k is outside the Fermi sphere. Similarly, if the state into which the state with one hole (the state $c_{k\sigma}|\Psi_{\rm FS}\rangle$ with k inside the Fermi sphere) evolves is denoted by $\beta_{k\sigma}^{\dagger}|\Psi_0\rangle$; the operator $\beta_{k\sigma}^{\dagger}$ is the creation operator of a quasihole. The quasiparticles defined outside the Fermi surface and the quasiholes defined inside it are the key elements of the Fermi-liquid theory.

As the interaction between the extra particle and the Fermi sea is turned on, its energy and mass are modified. Since the particle repels or attracts the other particles of the system, it drags along a "cloud" formed by these particles as it propagates. In other words we may say that the initially "bare" particle is "dressed" by the interaction. This accounts for the interaction-dependent effective mass of the quasiparticle. A major contribution of the interactions is taken into account by this mass renormalization. The remaining interactions between the dressed particles are weak. That is why quasiparticles could be treated in the one-particle approximation.

Alternatively, one could say that the low-lying excited state $|\Psi_{k\sigma}\rangle$ with one quasiparticle has a finite overlap with the state in which a free particle with momentum k is added to the ground state of the interacting system, that is

$$\langle \Psi_{\boldsymbol{k}\sigma} | c^{\dagger}_{\boldsymbol{k}\sigma} | \Psi_0 \rangle = Z^{1/2}_{\boldsymbol{k}\sigma}, \qquad (32.1.2)$$

where $Z_{k\sigma}$ is of order unity and not of order $1/N_{\rm e}$. This could also be taken as the definition of a state containing one quasiparticle. The factor $Z_{k\sigma}$ is the *quasiparticle weight*. It gives the probability of finding a quasiparticle in the state created by the operator $c_{k\sigma}^{\dagger}$.

In a free electron gas, the energy of particles and holes varies linearly with momentum near the Fermi energy. In normal Fermi liquids, where the quasiparticle energy measured from the chemical potential vanishes at the Fermi surface, a similar behavior should hold. In an unpolarized system

$$\varepsilon_{k\sigma} = \mu + v_{\rm F}^* \hbar (k - k_{\rm F}) = \mu + \frac{\hbar^2 k_{\rm F}}{m^*} (k - k_{\rm F})$$
 (32.1.3)

with some effective Fermi velocity $v_{\rm F}^*$ and effective mass m^* instead of the quantities characterizing the free particles. The effective Fermi velocity and the effective mass are two basic parameters of the theory; they determine the density of states of the quasiparticles at the Fermi energy:

$$\rho(\varepsilon_{\rm F}) = \frac{1}{V} \sum_{k\sigma} \delta(\varepsilon_{k\sigma} - \varepsilon_{\rm F}) = \frac{m^* k_{\rm F}}{\pi^2 \hbar^2} \,. \tag{32.1.4}$$

The excitation spectrum given in (32.1.3) is displayed in Fig. 32.1(a). If there is a finite gap in the excitation spectrum above the ground state, as in Fig. 32.1(b), the system cannot be a normal Fermi liquid.



Fig. 32.1. The spectrum of low-lying excitations in (a) a normal and (b) a not normal Fermi system

The excitation spectrum of quasiparticles was drawn intentionally near the Fermi momentum only. The one-particle states of the free system are not stationary solutions in the interacting system, they decay due to scattering processes, and the electronic states have a finite lifetime. The quasiparticle concept is useful only if the lifetime is long enough, in other words if the uncertainty in the energy, which is on the order of \hbar/τ , is less than the energy itself. Otherwise the state decays before it is really formed in the adiabatic process. As we have seen in the previous chapter, the reciprocal of the lifetime is proportional to the square of the energy measured relative to the Fermi energy. That means that only the states created near the Fermi surface will have a sufficiently long lifetime. There is also a constraint on the temperature range for the existence of quasiparticles. At room temperatures a lifetime of the order $\tau \sim 10^{-11}$ s is obtained from electron-electron interactions. Other scattering mechanisms, like scattering by impurities or by phonons, give a much shorter lifetime of order 10^{-14} s. Owing to the finite lifetime, the quasiparticle concept is useful only at low temperatures and near the Fermi surface. The quasiparticle picture is therefore inadequate to give the total energy of a fermion system, but it may be very appropriate in the study of thermal and transport properties.

32.2 Landau's Theory of Fermi Liquids

The Landau theory describes the behavior of interacting Fermi systems in terms of fermionic quasiparticles. In the foregoing the quasiparticles were defined by considering how the state with an extra electron or an extra hole added to the ground state of a noninteracting system evolves as the interaction is switched on. This concept is useful if the low-lying states of the interacting system can be described as superpositions of quasiparticle excitations. We will assume that when several particles are added to (removed from) the ground state of a noninteracting system and the interaction is turned on adiabatically, the same number of quasiparticles (quasiholes) are generated. The occupation number of any particular \mathbf{k} -state with spin σ may change by ± 1 . A smooth function $\delta n_{\mathbf{k}\sigma}$ can be defined by averaging over a small neighborhood in \mathbf{k} -space or taking the thermal average. Note that the same $\delta n_{\mathbf{k}\sigma}$ characterizes the excited states of the free as well as of the interacting systems. The numbers $\delta n_{\mathbf{k}\sigma}$ are positive for \mathbf{k} vectors lying outside the Fermi sphere and give the number of quasiparticles, they are negative for \mathbf{k} vectors inside the Fermi sphere, and their absolute value gives the number of quasiholes. Although we attribute physical meaning only to $\delta n_{\mathbf{k}\sigma}$, the number of quasiparticles or quasiholes can formally be written as the difference

$$\delta n_{\boldsymbol{k}\sigma} = n_{\boldsymbol{k}\sigma} - n_{\boldsymbol{k}\sigma}^0 \,, \tag{32.2.1}$$

where $n_{k\sigma}$ is the occupation number in the excited state and

$$n_{\boldsymbol{k}\sigma}^{0} = \theta(k_{\rm F} - |\boldsymbol{k}|) \tag{32.2.2}$$

is the occupation number in the ground state of the free Fermi sea. Since this quantity depends on the energy only, it is more convenient to work with the expression

$$n^{0}_{\boldsymbol{k}\sigma} = \theta(\mu - \varepsilon_{\boldsymbol{k}\sigma}), \qquad (32.2.3)$$

where μ is the chemical potential. Although $n_{k\sigma}$ or $n_{k\sigma}^0$ may appear in the intermediate steps of the calculations, the physical quantities are independent of them.

The Landau theory is a phenomenological theory that relies on the assumptions that the number of quasiparticles is small compared to the total number of particles: $\delta n_{k\sigma}$ can then be used as an expansion parameter, and the interaction between the quasiparticles can be described in terms of a few parameters. A more precise theory could be given using the methods of manybody theory. This would allow us to treat the interacting fermion systems microscopically and to lay a foundation for the Landau theory. One could

- 1. determine the range of validity of the theory, the energy and temperature range in which the quasiparticle concept is meaningful;
- 2. determine the relationship between the phenomenological parameters that characterize the interaction of quasiparticles and the electron–electron interaction appearing in the microscopic Hamiltonian; and
- 3. calculate the corrections beyond the phenomenological theory.

This microscopic theory is beyond the scope of this book. We will consider the phenomenological description only.

32.2.1 Energy of Quasiparticles and Their Interaction

As the quasiparticle is formed out of the free particle as the interaction is switched on, it acquires a renormalized energy $\varepsilon_{k\sigma}$. The velocity of quasiparticles can be determined using the well-known relationship

$$\boldsymbol{v}_{\boldsymbol{k}\sigma} = \frac{1}{\hbar} \frac{\partial \varepsilon_{\boldsymbol{k}\sigma}}{\partial \boldsymbol{k}} \,. \tag{32.2.4}$$

In an unpolarized isotropic system

$$\boldsymbol{v}_{\boldsymbol{k}\sigma} = \frac{\boldsymbol{k}}{|\boldsymbol{k}|} \boldsymbol{v}_{\mathrm{F}}^* \tag{32.2.5}$$

for states near the Fermi surface, where $v_{\rm F}^*$ is the effective Fermi velocity. Assuming the form given in (32.1.3) for $\varepsilon_{k\sigma}$, the relationship between the effective Fermi velocity and the effective mass is given by

$$v_{\rm F}^* = \frac{\hbar k_{\rm F}}{m^*} \,.$$
 (32.2.6)

Neglecting for the moment the interaction between quasiparticles, the total energy of the system can be obtained by adding the one-particle energies. Thus we have

$$E = E_0 + \sum_{k\sigma} \varepsilon_{k\sigma} \,\delta n_{k\sigma} \,. \tag{32.2.7}$$

If the number of particles is not conserved, a grand canonical ensemble has to be used and the quantity $E - \mu N_{\rm e}$ has to be considered instead of the energy. At finite temperatures this will then be replaced with the free energy, and we have

$$F = F_0 + \sum_{k\sigma} \left(\varepsilon_{k\sigma} - \mu \right) \, \delta n_{k\sigma} \,. \tag{32.2.8}$$

The corrections to the ground-state energy are always positive since creation of a hole corresponds to removing a particle; thus, $\delta n_{k\sigma} = -1$ if a state with $\varepsilon_{k\sigma} < \mu$ is excited.

When stopping at this point, the description would be identical to that of a free system, and the properties of the Fermi liquid would also be identical with the only exception that the electron mass, wherever it appears, should be replaced with the effective mass m^* of the quasiparticles. The important new element of the Landau theory is that instead of this expression, which is linear in $\delta n_{k\sigma}$, LANDAU proposed taking into account the remaining weak interaction between quasiparticles by a term which is higher order in $\delta n_{k\sigma}$.

As a simple example let us consider the electron gas in the Hartree–Fock approximation. The total energy of the system is given by

$$E_{\rm HF} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} n_{\boldsymbol{k}\sigma} - \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma} U(\boldsymbol{k}' - \boldsymbol{k}) n_{\boldsymbol{k}\sigma} n_{\boldsymbol{k}'\sigma} \,. \tag{32.2.9}$$

Separating out the ground-state energy and using $\delta n_{k\sigma}$, the physically relevant number of quasiparticles excited above the ground state, this expression can be written in the form

$$E_{\rm HF} = E_{\rm HF}^0 + \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma}^{\rm HF} \delta n_{\boldsymbol{k}\sigma} - \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma} U(\boldsymbol{k}' - \boldsymbol{k}) \delta n_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}'\sigma} , \qquad (32.2.10)$$

where $E_{\rm HF}^0$ is the ground-state energy in the Hartree–Fock approximation and $\varepsilon_{k\sigma}^{\rm HF}$ is the excitation energy of one-particle states obtained in the same approximation:

$$\varepsilon_{\boldsymbol{k}\sigma}^{\rm HF} = \varepsilon_{\boldsymbol{k}\sigma} - \frac{1}{V} \sum_{\boldsymbol{k}'} U(\boldsymbol{k}' - \boldsymbol{k}) n_{\boldsymbol{k}'\sigma}^0 \,. \tag{32.2.11}$$

This contains the interaction with all the particles filling the Fermi sea.

The last term in (32.2.10) describes the interaction between the quasiparticles. A similar expression could be obtained for the free energy. LANDAU's idea can be viewed as the generalization of this expression. He assumed that the free energy is a functional of the quasiparticle distribution $\delta n_{k\sigma}$, and at temperatures low compared to the Fermi temperature, where only a relatively small number of quasiparticles are excited, it is sufficient to go to second order in the expansion of the free energy in powers of $\delta n_{k\sigma}$:

$$F = F_0 + \sum_{\boldsymbol{k}\sigma} (\varepsilon_{\boldsymbol{k}\sigma} - \mu) \delta n_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}'\sigma'}, \quad (32.2.12)$$

where the coefficients $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}')$, which characterize the interaction between quasiparticles, are known as the *Fermi-liquid parameters* or *Landau parameters*. Note that in the Hartree–Fock approximation, where the quasiparticles have infinitely long lifetime, there is no limitation on the summation in \mathbf{k} space. More generally, however, since the quasiparticles are defined only in the neighborhood of the Fermi surface, the summations over \mathbf{k} and \mathbf{k}' are restricted to the neighborhood of the Fermi surface.

Note also that although formally we have the first- and second-order terms of the expansion of the free energy with respect to the small parameters $\delta n_{k\sigma}$, the contributions of the two terms are in fact of the same order of magnitude. This is because the quasiparticles are excited in a narrow range around the Fermi surface, that is $\delta n_{k\sigma}$ differs from zero in that range only, and the excitation energies themselves, $\varepsilon_{k\sigma} - \mu$, are also small in this region. Thus a consistent treatment of quasiparticles requires taking both terms into account on an equal footing.

The quantity $\varepsilon_{k\sigma}$ is the energy of an independent quasiparticle when it is alone in the system. The energy needed to add a quasiparticle to a system in which other quasiparticles are already present is different owing to its interaction with them. The renormalized energy is equal to the change in the free energy,

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} - \mu = \frac{\delta F}{\delta n_{\boldsymbol{k}\sigma}} = \varepsilon_{\boldsymbol{k}\sigma} - \mu + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'}.$$
(32.2.13)

Thus the Landau parameter $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}')$ divided by the volume gives the change in the energy of the quasiparticle with quantum numbers \mathbf{k} and σ owing to its interaction with another quasiparticle of quantum numbers \mathbf{k}' and σ' :

$$\frac{1}{V}f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}') = \frac{\delta\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}}{\delta n_{\boldsymbol{k}'\sigma'}}.$$
(32.2.14)

The Landau parameters depend only on the relative orientation of the spins in an unpolarized system. To see that we should recognize that $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}')$ is the second derivative of the free energy,

$$\frac{1}{V}f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}') = \frac{\delta^2 F}{\delta n_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}'\sigma'}}; \qquad (32.2.15)$$

it is therefore symmetric in its arguments:

$$f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') = f_{\sigma'\sigma}(\boldsymbol{k}', \boldsymbol{k}). \qquad (32.2.16)$$

Time-reversal symmetry should hold if no magnetic field is applied, hence

$$f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}') = f_{-\sigma,-\sigma'}(-\boldsymbol{k},-\boldsymbol{k}'). \qquad (32.2.17)$$

If the system has inversion symmetry, the Landau parameters are invariant under the transformation $k \rightarrow -k$. Together with the time-reversal symmetry this leads to the identity

$$f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}') = f_{-\sigma,-\sigma'}(\boldsymbol{k},\boldsymbol{k}'). \qquad (32.2.18)$$

It is therefore sufficient to use the parameters $f_{\uparrow\uparrow} = f_{\downarrow\downarrow}$ and $f_{\uparrow\downarrow} = f_{\downarrow\uparrow}$, or, more conveniently, the symmetric and antisymmetric combinations:

$$f^{\mathrm{s}}(\boldsymbol{k},\boldsymbol{k}') = \frac{1}{2} \left[f_{\uparrow\uparrow}(\boldsymbol{k},\boldsymbol{k}') + f_{\uparrow\downarrow}(\boldsymbol{k},\boldsymbol{k}') \right],$$

$$f^{\mathrm{a}}(\boldsymbol{k},\boldsymbol{k}') = \frac{1}{2} \left[f_{\uparrow\uparrow}(\boldsymbol{k},\boldsymbol{k}') - f_{\uparrow\downarrow}(\boldsymbol{k},\boldsymbol{k}') \right].$$
(32.2.19)

Expressing the original parameters in terms of the new ones we have

$$f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') = f^{s}(\boldsymbol{k}, \boldsymbol{k}') + f^{a}(\boldsymbol{k}, \boldsymbol{k}') [2\delta_{\sigma\sigma'} - 1]$$

= $f^{s}(\boldsymbol{k}, \boldsymbol{k}') + \sigma \sigma' f^{a}(\boldsymbol{k}, \boldsymbol{k}').$ (32.2.20)

When the weak dependence on the lengths of \mathbf{k} and \mathbf{k}' near $k_{\rm F}$ is neglected, $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}')$ depends only on the angle ξ between \mathbf{k} and \mathbf{k}' in the isotropic case. More precisely it depends on $\cos \xi = \mathbf{k} \cdot \mathbf{k}' / k_{\rm F}^2$. The Fermi-liquid parameters can then be expanded in Legendre polynomials in the form

$$f^{s(a)}(\boldsymbol{k}, \boldsymbol{k}') = \sum_{l=0}^{\infty} f_l^{s(a)} P_l(\cos \xi) \,.$$
(32.2.21)

The inverse relations can be derived with the aid of the orthogonality relationship

$$\int_{-1}^{+1} P_l(x) P_{l'}(x) \, \mathrm{d}x = \delta_{l,l'} \frac{2}{2l+1}$$
(32.2.22)

of the Legendre polynomials. We find

$$f_l^{s(a)} = \frac{2l+1}{2} \int_0^{\pi} f^{s(a)}(\boldsymbol{k}, \boldsymbol{k}') P_l(\cos\xi) \sin\xi \,d\xi \,.$$
(32.2.23)

The interacting Fermi system can thus be characterized by the set of parameters $f_l^{s(a)}$. In what follows it will be convenient to use dimensionless parameters defined by

$$F_l^{s(a)} = \rho(\varepsilon_F) f_l^{s(a)} = \frac{m^* k_F}{\pi^2 \hbar^2} f_l^{s(a)} . \qquad (32.2.24)$$

Although an infinite set of parameters appear in the expansion of the free energy, only a few of them are relevant for the interesting physical quantities. Almost the full behavior of a Fermi liquid can be described in terms of just a few parameters.

32.2.2 Distribution Function of Quasiparticles

When the system is in thermal equilibrium at a finite temperature, the occupation numbers $n_{k\sigma}$ are different from what they are in the ground state. The distribution function of quasiparticles can be determined by the methods of statistical mechanics. Since the excited states of the interacting system are in a one-to-one correspondence with the possible states of the free fermion system, the same $\delta n_{k\sigma}$ characterizes the excited states of the noninteracting system and the distribution of quasiparticles of the interacting system. Owing to the same counting of the states the entropy can be written in the form

$$S = -k_{\rm B} \sum_{\boldsymbol{k}\sigma} \left[n_{\boldsymbol{k}\sigma} \ln n_{\boldsymbol{k}\sigma} + (1 - n_{\boldsymbol{k}\sigma}) \ln(1 - n_{\boldsymbol{k}\sigma}) \right]$$
(32.2.25)

known for a free Fermi gas. When quasiparticles are added to the system and the distribution function is changed by $\delta n_{k\sigma}$, the change in the entropy is

$$\delta S = -k_{\rm B} \sum_{k\sigma} \delta n_{k\sigma} \ln \frac{n_{k\sigma}}{1 - n_{k\sigma}} , \qquad (32.2.26)$$

and the change in the number of particles is

$$\delta N = \sum_{k\sigma} \delta n_{k\sigma} \,. \tag{32.2.27}$$

The variation in the total energy can be written in terms of the quasiparticle energies as

$$\delta E = \sum_{k\sigma} \tilde{\varepsilon}_{k\sigma} \delta n_{k\sigma} , \qquad (32.2.28)$$

where of course the renormalized quasiparticle energies appear that contain contributions from the interaction with the other quasiparticles. Using the relation

$$\delta E = T\delta S + \mu\delta N \tag{32.2.29}$$

well known from thermodynamics we have

$$\sum_{k\sigma} \widetilde{\varepsilon}_{k\sigma} \delta n_{k\sigma} = \sum_{k\sigma} \left(-k_{\rm B} T \ln \frac{n_{k\sigma}}{1 - n_{k\sigma}} + \mu \right) \delta n_{k\sigma} \,. \tag{32.2.30}$$

This can be satisfied if

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = -k_{\rm B}T\ln\frac{n_{\boldsymbol{k}\sigma}}{1-n_{\boldsymbol{k}\sigma}} + \mu \qquad (32.2.31)$$

holds for each k and σ separately, from which the usual Fermi–Dirac distribution function is recovered:

$$n_{\boldsymbol{k}\sigma} = \frac{1}{\mathrm{e}^{(\tilde{\varepsilon}_{\boldsymbol{k}\sigma}-\mu)/k_{\mathrm{B}}T}+1} \,. \tag{32.2.32}$$

Since f_0 is used conventionally in the Fermi-liquid theory to denote an interaction parameter, the notation

$$n_0(\tilde{\varepsilon}_{k\sigma}, T) = \frac{1}{\mathrm{e}^{(\tilde{\varepsilon}_{k\sigma} - \mu)/k_\mathrm{B}T} + 1}$$
(32.2.33)

will be used for the distribution function in thermal equilibrium. It is important to emphasize once more that this result was obtained using (32.2.28); therefore, the $\tilde{\varepsilon}_{k\sigma}$ appearing here depend on the distribution function itself. Whenever the number of quasiparticles is used in the subsequent calculations, this self-consistency condition should be taken into account.

32.2.3 Thermodynamic Properties of Fermi Liquids

The thermodynamic properties are obtained by summing the contributions of all quasiparticles. Since the density of states of the quasiparticles [see (32.1.4)] is different from that of the noninteracting Fermi gas, it is expected that the density of states entering thermodynamic quantities is the quasiparticle density of states. As a first example we consider the heat capacity.

The difference between the distribution function $n_0(\tilde{\epsilon}_{k\sigma}, T)$ and the step function,

$$\delta n_{\boldsymbol{k}\sigma} = n_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}, T) - \theta(\mu - \varepsilon_{\boldsymbol{k}\sigma}), \qquad (32.2.34)$$

can be interpreted as the number of thermally excited quasiparticles when the Fermi liquid is in thermal equilibrium at a finite temperature. The renormalized energy $\tilde{\varepsilon}_{\boldsymbol{k}\sigma}$ appearing here has to be determined self-consistently by combining this equation with (32.2.13):

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}\sigma} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \left[n_0(\widetilde{\varepsilon}_{\boldsymbol{k}'\sigma'}, T) - \theta(\mu - \varepsilon_{\boldsymbol{k}'\sigma'}) \right].$$
(32.2.35)

The free energy of the thermally excited Fermi liquid is obtained by substituting the self-consistent solution for $\delta n_{k\sigma}$ in

$$F = F_0 + \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}\sigma} + \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}'\sigma'}.$$
(32.2.36)

First, we demonstrate that the number of thermally excited quasiparticles is proportional to T^2 , and the leading correction to the energy of quasiparticles is also of order T^2 . Assuming that this is true, $\tilde{\varepsilon}_{\mathbf{k}'\sigma'}$ may be replaced with $\varepsilon_{\mathbf{k}'\sigma'}$ in $n_0(\tilde{\varepsilon}_{\mathbf{k}'\sigma'}, T)$ on the right-hand side of (32.2.35). The sum over \mathbf{k}' can be replaced by an angular average and an integral over the length of \mathbf{k}' or over energy using the density of states:

$$\frac{1}{V} \sum_{\mathbf{k}'\sigma'} g(\varepsilon_{\mathbf{k}'}) h(\cos\xi) \to \sum_{\sigma'} \int \mathrm{d}\varepsilon \rho_{\sigma'}(\varepsilon) g(\varepsilon) \iint \frac{\sin\theta' \,\mathrm{d}\theta' \,\mathrm{d}\varphi'}{4\pi} h(\cos\xi) \,, \tag{32.2.37}$$

where $\rho_{\sigma'}(\varepsilon)$ is the density of states of quasiparticles for one spin orientation. We apply this transformation in (32.2.35) by choosing the z-axis of the coordinate system in the direction of \mathbf{k} . The angle ξ between \mathbf{k} and $\mathbf{k'}$ is then equal to the polar angle θ' of $\mathbf{k'}$. This angular variable appears in the Landau parameters only, and the integration over θ' can be carried out if the Landau parameters are expanded in Legendre polynomials. Only the symmetric l = 0component gives a nonvanishing contribution:

$$\frac{1}{2}\sum_{\sigma'} \iint f_{\sigma\sigma'}(\cos\theta') \frac{\sin\theta'\,\mathrm{d}\theta'\,\mathrm{d}\varphi'}{4\pi} = f_0^{\mathrm{s}}.$$
(32.2.38)

The change in the quasiparticle energy can be expressed as

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} - \varepsilon_{\boldsymbol{k}\sigma} \approx f_0^{\rm s} \int \rho(\varepsilon) \left[\frac{1}{\mathrm{e}^{\beta(\varepsilon-\mu)} + 1} - \theta(\mu - \varepsilon) \right] \mathrm{d}\varepsilon \,. \tag{32.2.39}$$

The integral can be evaluated using the Sommerfeld expansion and we find

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} - \varepsilon_{\boldsymbol{k}\sigma} \approx f_0^{\mathrm{s}} \frac{\pi^2}{6} (k_{\mathrm{B}}T)^2 \left. \frac{\mathrm{d}\rho(\varepsilon)}{\mathrm{d}\varepsilon} \right|_{\varepsilon=\mu}.$$
(32.2.40)

The correction to the quasiparticle energy is in fact of order T^2 . It then follows immediately that also the number of thermally excited quasiparticles is proportional to the square of the temperature,

$$\sum_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}\sigma} \sim (k_{\rm B}T)^2 \,, \qquad (32.2.41)$$

provided the Fermi-liquid parameters are temperature independent.

The correction to the free energy owing to the interaction of quasiparticles is of order T^4 and can be neglected compared to the leading term of order $(k_{\rm B}T)^2$. The free energy is then

$$F = F_0 + \sum_{k\sigma} \varepsilon_{k\sigma} \left[\frac{1}{e^{\beta(\varepsilon_{k\sigma} - \mu)} + 1} - \theta(k_{\rm F} - |\mathbf{k}|) \right]$$

= $F_0 + V \int \varepsilon \,\rho(\varepsilon) \left[\frac{1}{e^{\beta(\varepsilon - \mu)} + 1} - \theta(\mu - \varepsilon) \right] d\varepsilon.$ (32.2.42)

Application of the Sommerfeld expansion gives

$$F = F_0 + V \frac{\pi^2}{6} (k_{\rm B}T)^2 \rho(\varepsilon_{\rm F}) \,. \tag{32.2.43}$$

The heat capacity can be calculated to leading order from the expressions

$$C_V(T) = \left(\frac{\partial E}{\partial T}\right)_N \approx \left(\frac{\partial F}{\partial T}\right)_\mu.$$
 (32.2.44)

Clearly the heat capacity per unit volume of the Fermi liquid has the same form as that of the free Fermi gas given in (16.2.91),

$$c_V(T) = \frac{\pi^2}{3} \rho(\varepsilon_{\rm F}) k_{\rm B}^2 T$$
, (32.2.45)

but here $\rho(\varepsilon_{\rm F})$ is the density of states of quasiparticles, which is proportional to the effective mass. This enables us to determine m^* from experiments.

32.2.4 Creation of Quasiparticles by External Perturbation

We consider now the situation when an external perturbation drives the system out of equilibrium. The number of quasiparticles in the perturbed state is

$$\delta n_{\boldsymbol{k}\sigma} = n_{\boldsymbol{k}\sigma} - n_{\boldsymbol{k}\sigma}^0 \,, \qquad (32.2.46)$$

and their energy is given by

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}\sigma} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'}. \qquad (32.2.47)$$

If the quasiparticles were in thermal equilibrium, their number would be

$$\delta n_{\boldsymbol{k}\sigma}^{\text{therm}} = n_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}, T) - n_{\boldsymbol{k}\sigma}^0 \,. \tag{32.2.48}$$

We will show in the following sections that some properties of the Fermi liquid can be written in a simpler form if the number of extra quasiparticles excited in addition to those present in thermal equilibrium,

$$\delta \bar{n}_{\boldsymbol{k}\sigma} = \delta n_{\boldsymbol{k}\sigma} - \delta n_{\boldsymbol{k}\sigma}^{\text{therm}} = n_{\boldsymbol{k}\sigma} - n_0(\tilde{\varepsilon}_{\boldsymbol{k}\sigma}, T), \qquad (32.2.49)$$

is used instead of the actual number of quasiparticles. For that we first demonstrate that a simple relationship exists between $\delta \bar{n}_{k\sigma}$ and $\delta n_{k\sigma}$ at T = 0 in an isotropic system.

Expansion of $n_0(\tilde{\varepsilon}_{k\sigma}, T=0)$ about the unrenormalized energy gives

$$\delta \bar{n}_{\boldsymbol{k}\sigma} = n_{\boldsymbol{k}\sigma} - n_0(\varepsilon_{\boldsymbol{k}\sigma}, T=0) - \frac{\partial n_0(\varepsilon_{\boldsymbol{k}\sigma}, T=0)}{\partial \varepsilon_{\boldsymbol{k}\sigma}} \left(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} - \varepsilon_{\boldsymbol{k}\sigma} \right)$$

$$= \delta n_{\boldsymbol{k}\sigma} - \frac{\partial n_{\boldsymbol{k}\sigma}^0}{\partial \varepsilon_{\boldsymbol{k}\sigma}} \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'} \,.$$
(32.2.50)

The symmetric and antisymmetric combinations of the quasiparticle distributions are defined via

$$\delta n_{\boldsymbol{k}\uparrow} = \delta n_{\boldsymbol{k}}^{\rm s} + \delta n_{\boldsymbol{k}}^{\rm a} , \qquad \delta n_{\boldsymbol{k}\downarrow} = \delta n_{\boldsymbol{k}}^{\rm s} - \delta n_{\boldsymbol{k}}^{\rm a} , \qquad (32.2.51)$$

and similarly

$$\delta \bar{n}_{\boldsymbol{k}\uparrow} = \delta \bar{n}^{\rm s}_{\boldsymbol{k}} + \delta \bar{n}^{\rm a}_{\boldsymbol{k}}, \qquad \delta \bar{n}_{\boldsymbol{k}\downarrow} = \delta \bar{n}^{\rm s}_{\boldsymbol{k}} - \delta \bar{n}^{\rm a}_{\boldsymbol{k}}. \tag{32.2.52}$$

Equation (32.2.50) can be rewritten for these combinations with the result

$$\delta \bar{n}_{\boldsymbol{k}}^{s} = \delta n_{\boldsymbol{k}}^{s} - \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \frac{2}{V} \sum_{\boldsymbol{k}'} f^{s}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{s},$$

$$\delta \bar{n}_{\boldsymbol{k}}^{a} = \delta n_{\boldsymbol{k}}^{a} - \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \frac{2}{V} \sum_{\boldsymbol{k}'} f^{a}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{a}.$$
(32.2.53)

Since the quasiparticles are defined near the Fermi energy only, the dependence on the length of the wave vector is uninteresting, only the dependence on the polar and azimuthal angles θ and φ of k is relevant, and the quasiparticle distribution can be expanded in spherical harmonics in the form

$$\delta n_{\boldsymbol{k}}^{\mathrm{s(a)}} = -\frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \sum_{lm} \delta n_{lm}^{\mathrm{s(a)}} Y_{l}^{m}(\theta,\varphi) ,$$

$$\delta \bar{n}_{\boldsymbol{k}}^{\mathrm{s(a)}} = -\frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \sum_{lm} \delta \bar{n}_{lm}^{\mathrm{s(a)}} Y_{l}^{m}(\theta,\varphi) .$$
(32.2.54)

Inserting these expansions into (32.2.53) and using the orthogonality relationship [see (C.4.27)]

$$\int_{0}^{2\pi} \mathrm{d}\varphi \int_{0}^{\pi} \sin\theta \,\mathrm{d}\theta \,Y_{l}^{m*}(\theta,\varphi)Y_{l'}^{m'}(\theta,\varphi) = \delta_{ll'}\delta_{mm'}$$
(32.2.55)

of the spherical harmonics we get

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$$\delta \bar{n}_{lm}^{\mathrm{s(a)}} = \delta n_{lm}^{\mathrm{s(a)}} + \frac{2}{V} \sum_{\mathbf{k}'} \sum_{l'm'} \iint \sin \theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \qquad (32.2.56)$$
$$\times \left(-\frac{\partial n_{\mathbf{k}'}^0}{\partial \varepsilon_{\mathbf{k}'}} \right) Y_l^{m*}(\theta, \varphi) f^{\mathrm{s(a)}}(\cos \xi) \, \delta n_{l'm'}^{\mathrm{s(a)}} Y_{l'}^{m'}(\theta', \varphi') \,,$$

where ξ is the angle between \mathbf{k} and \mathbf{k}' , i.e., between the directions given by the angles θ, φ and θ', φ' . Using the step function for the ground-state distribution we have

$$\frac{\partial n^0_{\mathbf{k}'\sigma'}}{\partial \varepsilon_{\mathbf{k}'}} = -\delta(\varepsilon_{\mathbf{k}'} - \mu). \qquad (32.2.57)$$

Replacing the sum over k' by an integral over the angular variables and over the energy using the density of states for one spin orientation we find

$$\delta \bar{n}_{lm}^{\mathrm{s(a)}} = \delta n_{lm}^{\mathrm{s(a)}} + \frac{2}{V} \sum_{l'm'} \frac{1}{4\pi} \iint \sin \theta' \, \mathrm{d}\theta' \, \mathrm{d}\varphi' \iint \sin \theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \qquad (32.2.58)$$
$$\times \rho_{\sigma}(\varepsilon_{\mathrm{F}}) Y_{l}^{m*}(\theta,\varphi) f^{\mathrm{s(a)}}(\cos \xi) \, \delta n_{l'm'}^{\mathrm{s(a)}} Y_{l'}^{m'}(\theta',\varphi') \, .$$

The Legendre polynomials in the expansion of the Fermi-liquid parameters can be expressed in terms of the spherical harmonics associated with the angles θ, φ and θ', φ' using

$$P_{l}(\cos \xi) = P_{l}(\cos \theta)P_{l}(\cos \theta')$$

$$+2\sum_{m=1}^{l} \frac{(l-m)!}{(l+m)!}P_{l}^{m}(\cos \theta)P_{l}^{m}(\cos \theta')\cos m(\varphi - \varphi')$$

$$= \frac{4\pi}{2l+1}\sum_{m=-l}^{+l}Y_{l}^{m*}(\theta,\varphi)Y_{l}^{m}(\theta',\varphi'). \qquad (32.2.59)$$

The orthogonality relationship of the spherical harmonics then leads to

$$\delta \bar{n}_{lm}^{s(a)} = \delta n_{lm}^{s(a)} \left(1 + \frac{F_l^{s(a)}}{2l+1} \right).$$
(32.2.60)

32.2.5 Susceptibility of Fermi Liquids

Next we consider the magnetic susceptibility. Neglecting the diamagnetic contribution coming from the orbital motion we will consider the interaction of the spin of the quasiparticles with an external magnetic field of strength H. If the field is applied in the z-direction and the quantization axis is the z-axis, the one-particle energies are shifted to

$$\varepsilon_{\boldsymbol{k}\sigma}(H) = \varepsilon_{\boldsymbol{k}} - \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\sigma H. \qquad (32.2.61)$$

The states have to be filled up to the same chemical potential for the two spin orientations and therefore $k_{\rm F}$ becomes spin dependent in the presence of the



Fig. 32.2. (a) Expanded and contracted Fermi spheres for particles with \uparrow and \downarrow spins in a magnetically polarized Fermi liquid. (b) Quasielectron and quasihole excitations of opposite spins created by a magnetic field

field. As seen in Fig. 32.2, the radius of the Fermi sphere for spin-up ($\sigma = +1$) particles shrinks and for spin-down ($\sigma = -1$) particles expands.

The polarized state contains an equal number of spin-down quasiparticles and spin-up quasiholes with renormalized energy

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}(H) = \varepsilon_{\boldsymbol{k}} - \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_{0}\sigma H + \frac{1}{V}\sum_{\boldsymbol{k}'\sigma'}f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}')\delta n_{\boldsymbol{k}'\sigma'}.$$
(32.2.62)

For a given strength of the magnetic field the actual number of quasiparticles has to be determined self-consistently from the condition that the one-particle states are filled up to the same Fermi energy for both spin orientations. Using the Fermi–Dirac distribution function for the occupation number we have

$$n_{\boldsymbol{k}\sigma}(H) = n_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}) = n_0(\widetilde{\varepsilon}_{\boldsymbol{k}} - \frac{1}{2}g_{\rm e}\mu_{\rm B}\mu_0\sigma H), \qquad (32.2.63)$$

where of course $\tilde{\epsilon}_k$ is the renormalized quasiparticle energy, and the number of quasiparticles and quasiholes is obtained from the difference

$$\delta n_{\boldsymbol{k}\sigma} = n_{\boldsymbol{k}\sigma}(H) - n_{\boldsymbol{k}\sigma}(H=0)$$

= $n_0(\widetilde{\varepsilon}_{\boldsymbol{k}} - \frac{1}{2}g_{\mathrm{e}}\mu_{\mathrm{B}}\mu_0\sigma H, T) - n_{\boldsymbol{k}\sigma}^0$. (32.2.64)

Expanding the right-hand side to linear order in the deviation of the renormalized quasiparticle energy from the energy of a lone quasiparticle and neglecting the thermal corrections we have

$$\delta n_{\boldsymbol{k}\sigma} = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} (\widetilde{\varepsilon}_{\boldsymbol{k}} - \frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} \sigma H - \varepsilon_{\boldsymbol{k}}) = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \bigg[-\frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} \sigma H + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'} \bigg].$$
(32.2.65)

Writing them separately for the two spin orientations

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$$\delta n_{\boldsymbol{k}\uparrow} = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \bigg\{ -\frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} H + \frac{1}{V} \sum_{\boldsymbol{k}'} \bigg[f_{\uparrow\uparrow\uparrow}(\boldsymbol{k},\boldsymbol{k}') \delta n_{\boldsymbol{k}'\uparrow} + f_{\uparrow\downarrow}(\boldsymbol{k},\boldsymbol{k}') \delta n_{\boldsymbol{k}'\downarrow} \bigg] \bigg\},$$

$$(32.2.66)$$

$$\delta n_{\boldsymbol{k}\downarrow} = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \bigg\{ \frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} H + \frac{1}{V} \sum_{\boldsymbol{k}'} \bigg[f_{\downarrow\uparrow}(\boldsymbol{k},\boldsymbol{k}') \delta n_{\boldsymbol{k}'\uparrow} + f_{\downarrow\downarrow}(\boldsymbol{k},\boldsymbol{k}') \delta n_{\boldsymbol{k}'\downarrow} \bigg] \bigg\}.$$

When the symmetric and antisymmetric combinations introduced in (32.2.51) are used, we have

$$\delta n_{\boldsymbol{k}}^{s} + \delta n_{\boldsymbol{k}}^{a} = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \bigg\{ -\frac{1}{2} g_{e} \mu_{B} \mu_{0} H + \frac{2}{V} \sum_{\boldsymbol{k}'} \bigg[f^{s}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{s} + f^{a}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{a} \bigg] \bigg\},$$

$$(32.2.67)$$

$$\delta n_{\boldsymbol{k}}^{s} - \delta n_{\boldsymbol{k}}^{a} = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \bigg\{ \frac{1}{2} g_{e} \mu_{B} \mu_{0} H + \frac{2}{V} \sum_{\boldsymbol{k}'} \bigg[f^{s}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{s} - f^{a}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{a} \bigg] \bigg\},$$

from which

$$\delta n_{\boldsymbol{k}}^{s} = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \frac{2}{V} \sum_{\boldsymbol{k}'} f^{s}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{s},$$

$$\delta n_{\boldsymbol{k}}^{a} = \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \left[-\frac{1}{2} g_{e} \mu_{B} \mu_{0} H + \frac{2}{V} \sum_{\boldsymbol{k}'} f^{a}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'}^{a} \right].$$
(32.2.68)

Comparing this expression with (32.2.53) we get

$$\delta \bar{n}_{\boldsymbol{k}}^{\mathrm{s}} = 0, \qquad \delta \bar{n}_{\boldsymbol{k}}^{\mathrm{a}} = -\frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}}} \frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \mu_{0} H. \qquad (32.2.69)$$

The quasiparticle distribution is independent of the polar angles in a uniform magnetic field. It follows from (32.2.54) that only the component l = 0, m = 0 is nonvanishing, that is

$$\delta \bar{n}_{00}^{a} = \frac{1}{2} g_{e} \mu_{B} \mu_{0} H. \qquad (32.2.70)$$

It is easily seen that the same component appears in the magnetization. It can be obtained from the occupation numbers corresponding to the two spin orientations via

$$M = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{1}{2} g_{\mathrm{e}} \mu_{\mathrm{B}} \sigma \,\delta n_{\boldsymbol{k}\sigma} = \frac{1}{V} \sum_{\boldsymbol{k}} g_{\mathrm{e}} \mu_{\mathrm{B}} \,\delta n_{\boldsymbol{k}}^{\mathrm{a}} \,. \tag{32.2.71}$$

If δn_k^a is expanded according to (32.2.54), the term l = 0, m = 0 alone survives after integration over the angular variables and we get

$$M = g_{\rm e} \mu_{\rm B} \rho_{\sigma}(\varepsilon_{\rm F}) \,\delta n_{00}^{\rm a} \,. \tag{32.2.72}$$

Using (32.2.60) that gives the relationship between $\delta \bar{n}_{00}^{a}$ and δn_{00}^{a} ,

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$$M = g_{\rm e} \mu_{\rm B} \rho_{\sigma}(\varepsilon_{\rm F}) \frac{\delta \bar{n}_{00}^{\rm a}}{1 + F_0^{\rm a}} \,. \tag{32.2.73}$$

Combining this expression with (32.2.70) we find

$$M = \frac{1}{2} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \rho_\sigma(\varepsilon_{\rm F}) \frac{1}{1 + F_0^{\rm a}} H, \qquad (32.2.74)$$

and the susceptibility is

$$\chi = \frac{1}{2} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \rho_\sigma(\varepsilon_{\rm F}) \frac{1}{1 + F_0^{\rm a}} \,. \tag{32.2.75}$$

The same form is obtained as for the Pauli susceptibility of a free electron gas, apart from the factor $1/(1 + F_0^{\rm a})$, but with the density of states of the quasiparticles which contains the effective mass. The factor $1 + F_0^{\rm a}$ in the denominator appears owing to the interaction between the quasiparticles. The Landau parameter $F_0^{\rm a}$ is negative for repulsive interaction between quasiparticles of opposite spin, resulting in an enhancement of the susceptibility. The factor $1/(1 + F_0^{\rm a})$ can be considered as the generalization of the Stoner enhancement factor. The paramagnetic state is stable as long as $1 + F_0^{\rm a} > 0$. Otherwise the interaction between fermions of opposite spins can give rise to magnetic ordering.

32.2.6 Effective Mass of Quasiparticles

The self-consistency of Landau's Fermi-liquid theory implies that the effective mass of quasiparticles can be expressed in terms of the Landau parameters, since the mass enhancement is caused by the same interactions which are incorporated into these parameters. In order to find this relationship we calculate and equate the current carried by the particles in the noninteracting and in the interacting systems.

In a noninteracting system, a particle of momentum $\hbar k$ carries a particlecurrent density

$$\boldsymbol{j}_{n\boldsymbol{k}} = \frac{1}{V} \boldsymbol{v}_{\boldsymbol{k}}^{(0)} = \frac{1}{V} \frac{\hbar \boldsymbol{k}}{m_{\rm e}},$$
 (32.2.76)

where of course the bare mass $m_{\rm e}$ appears. When the state with wave vector \boldsymbol{k} and spin σ is occupied with probability $n_{\boldsymbol{k}\sigma}$, the total particle-current density is given by

$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{\hbar \boldsymbol{k}}{m_{\rm e}} n_{\boldsymbol{k}\sigma} \,. \tag{32.2.77}$$

Since no net current flows in the ground state, the current is due to the extra electrons outside the Fermi sphere and the holes inside the Fermi sphere, that is

$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{\hbar \boldsymbol{k}}{m_{\rm e}} \delta n_{\boldsymbol{k}\sigma} \,. \tag{32.2.78}$$

The total momentum and hence the total current is a conserved quantity in a translation-invariant system. As the interaction is switched on adiabatically, the total momentum is unchanged (the current operator commutes with the two-particle potential) and the current is still given by (32.2.78). In order to express this current in terms of the quantities characterizing the quasiparticles one has to take into account that the interaction between the extra particle and the Fermi sea will modify the energies and thereby the velocities of the particles inside the Fermi sea. Therefore, a distribution $\delta n_{k\sigma}$ of quasiparticles gives rise to a total current density which can be written to linear order in δn as the sum of two terms,

$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \boldsymbol{v}_{\boldsymbol{k}} \delta n_{\boldsymbol{k}\sigma} + \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \delta \boldsymbol{v}_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma}^{0} , \qquad (32.2.79)$$

where the summation in the second term goes formally over the whole Fermi sea. As will be seen, in reality only the quasiparticles near the Fermi surface contribute to this term, too.

The change in the velocity of a particle can be obtained from (32.2.4) using the renormalized energy:

$$\boldsymbol{v}_{\boldsymbol{k}} + \delta \boldsymbol{v}_{\boldsymbol{k}} = \frac{1}{\hbar} \frac{\partial \widetilde{\varepsilon}_{\boldsymbol{k}}}{\partial \boldsymbol{k}} \,.$$
 (32.2.80)

Inserting (32.2.13) for the renormalized energy we have

$$\delta \boldsymbol{v}_{\boldsymbol{k}} = \frac{1}{\hbar} \frac{\partial}{\partial \boldsymbol{k}} \frac{1}{V} \sum_{\boldsymbol{k}' \sigma'} f_{\sigma \sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}' \sigma'} \,. \tag{32.2.81}$$

Thus

$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \boldsymbol{v}_{\boldsymbol{k}} \delta n_{\boldsymbol{k}\sigma} + \frac{1}{V^{2}} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} \left[\frac{1}{\hbar} \frac{\partial}{\partial \boldsymbol{k}} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'} \right] n_{\boldsymbol{k}\sigma}^{0} . \quad (32.2.82)$$

Replacing the sum over k by an integral, integration by parts gives

$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \boldsymbol{v}_{\boldsymbol{k}} \delta n_{\boldsymbol{k}\sigma} - \frac{1}{V^{2}} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} \frac{1}{\hbar} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'} \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \boldsymbol{k}} .$$
(32.2.83)

Since $n_{\boldsymbol{k}\sigma}^0$ depends on \boldsymbol{k} via the energy only, indirect differentiation gives

$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \boldsymbol{v}_{\boldsymbol{k}} \delta n_{\boldsymbol{k}\sigma} - \frac{1}{V^{2}} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'} \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}\sigma}} \boldsymbol{v}_{\boldsymbol{k}}$$
$$= \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \left[\delta n_{\boldsymbol{k}\sigma} - \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}\sigma}} \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'} \right] \boldsymbol{v}_{\boldsymbol{k}}.$$
(32.2.84)

This expression could be rewritten according to (32.2.50) as
$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \delta \bar{n}_{\boldsymbol{k}\sigma} \boldsymbol{v}_{\boldsymbol{k}} \,. \tag{32.2.85}$$

The current depends in fact on how much the distribution of quasiparticles differs from the equilibrium distribution.

With the change of variables $\mathbf{k} \leftrightarrow \mathbf{k}'$ and $\sigma \leftrightarrow \sigma'$ in the second term of (32.2.84) we have

$$\boldsymbol{j}_{n} = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \left[\boldsymbol{v}_{\boldsymbol{k}} - \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma'\sigma}(\boldsymbol{k}', \boldsymbol{k}) \frac{\partial n_{\boldsymbol{k}'\sigma'}^{0}}{\partial \varepsilon_{\boldsymbol{k}'\sigma'}} \boldsymbol{v}_{\boldsymbol{k}'} \right] \delta n_{\boldsymbol{k}\sigma} \,. \tag{32.2.86}$$

From this one can read off the current carried by the quasiparticle of wave vector k:

$$\boldsymbol{j}_{n\boldsymbol{k}} = \frac{1}{V} \left[\boldsymbol{v}_{\boldsymbol{k}} - \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma'\sigma}(\boldsymbol{k}', \boldsymbol{k}) \frac{\partial n_{\boldsymbol{k}'\sigma'}^0}{\partial \varepsilon_{\boldsymbol{k}'\sigma'}} \boldsymbol{v}_{\boldsymbol{k}'} \right].$$
(32.2.87)

As the propagating quasiparticle interacts with the rest of the system, the other quasiparticles generate an extra contribution to the current. This "back-flow" is described by the second term. Using (32.2.57) one sees immediately that only quasiparticles near the Fermi surface contribute.

Although this result is very suggestive, it involves in the intermediate steps a summation over all particles and the variation of their velocity due to the interaction with the quasiparticles. To be consistent with the philosophy of the Landau theory we present another derivation where only the contribution of the quasiparticles is taken into account in the intermediate steps as well. For this we recall that the current density is the expectation value of the current operator:

$$\boldsymbol{j}_{n} = \frac{1}{V} \left\langle \sum_{i} \frac{\boldsymbol{p}_{i}}{m_{e}} \right\rangle.$$
(32.2.88)

Let us consider what happens when the wave number of all particles is shifted in the ground state by the same q. This is equivalent to studying the system in a new frame which moves with a uniform velocity $-\hbar q/m_{\rm e}$.

According to the Galilean transformation between the laboratory and the moving frames, the total energy and the total momentum of a state in the frame moving with velocity v are given by

$$E' = E - \mathbf{P} \cdot \mathbf{v} + \frac{1}{2}Mv^2,$$

$$\mathbf{P}' = \mathbf{P} - M\mathbf{v},$$
(32.2.89)

where M is the total mass of the system. These expressions can be derived by boosting the momentum of each particle by the same amount in the kinetic energy and taking into account that the interaction part is unchanged under a Galilean transformation. The transformed Hamiltonian is then 232 32 Fermion Liquids

$$\mathcal{H}' = \sum_{i} \frac{(\boldsymbol{p}_{i} + \hbar \boldsymbol{q})^{2}}{2m_{\mathrm{e}}} + \mathcal{H}_{\mathrm{int}} = \mathcal{H} + \hbar \boldsymbol{q} \cdot \sum_{i} \frac{\boldsymbol{p}_{i}}{m_{\mathrm{e}}} + N_{\mathrm{e}} \frac{(\hbar \boldsymbol{q})^{2}}{2m_{\mathrm{e}}} \,. \tag{32.2.90}$$

The current carried by a quasiparticle of wave vector \mathbf{k} and spin σ can thus be calculated by adding a quasiparticle to the boosted system and taking the derivative of its energy with respect to \mathbf{q} :

$$\boldsymbol{j}_{n\boldsymbol{k}\sigma} = \frac{1}{\hbar V} \frac{\partial \widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}+\boldsymbol{q}\sigma}}{\partial \boldsymbol{q}}$$
(32.2.91)

The energy of the quasiparticle in the moving frame is different from that in the laboratory frame not only due to the boost but also due to the quasielectrons and quasiholes created on opposite sides of the Fermi surface in the moving system (see Fig. 32.3). We have

$$\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\sigma} = \varepsilon_{\boldsymbol{k}\sigma} + \hbar \boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'}. \qquad (32.2.92)$$



Fig. 32.3. Displaced Fermi sphere with quasiparticles and quasiholes when the wave vectors of all particles are shifted by the same q

For a displacement of the Fermi surface by $\delta k_{\rm F}(\theta, \varphi)$ in the direction characterized by the polar angles θ and φ , we have

$$\delta n_{\boldsymbol{k}\sigma} = -\frac{\partial n_{\boldsymbol{k}\sigma}^0}{\partial \varepsilon_{\boldsymbol{k}\sigma}} v_{\mathrm{F}}^* \delta k_{\mathrm{F}}(\theta,\varphi) \,. \tag{32.2.93}$$

In the present case, when the Fermi surface is displaced uniformly by the same q,

$$\delta n_{\boldsymbol{k}\sigma} = -\boldsymbol{q} \cdot \frac{\partial n_{\boldsymbol{k}\sigma}^0}{\partial \boldsymbol{k}} = -\hbar \boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}\sigma}^0}{\partial \varepsilon_{\boldsymbol{k}\sigma}}, \qquad (32.2.94)$$

and the current carried by the quasiparticle is

$$\boldsymbol{j}_{n\boldsymbol{k}} = \frac{1}{V} \left[\boldsymbol{v}_{\boldsymbol{k}} - \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \frac{\partial n_{\boldsymbol{k}'\sigma'}^0}{\partial \varepsilon_{\boldsymbol{k}'\sigma'}} \boldsymbol{v}_{\boldsymbol{k}'} \right].$$
(32.2.95)

This expression is identical to the result obtained in (32.2.87).

Equating this expression with (32.2.76) and writing the velocity of quasiparticles in terms of the effective mass as

$$\boldsymbol{v}_{\boldsymbol{k}} = \frac{\hbar \boldsymbol{k}}{m^*} \,, \tag{32.2.96}$$

we get

$$\frac{\boldsymbol{k}}{m_{\rm e}} = \frac{\boldsymbol{k}}{m^*} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta(\varepsilon_{\boldsymbol{k}'} - \mu) \frac{\boldsymbol{k}'}{m^*} \,. \tag{32.2.97}$$

Multiplication of this equation by \mathbf{k} gives a scalar equation. Since only the wave vectors near the Fermi surface are relevant, the lengths of \mathbf{k} and \mathbf{k}' are equal in the isotropic case and $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}')$ depends only on the angle ξ between the vectors. We then have

$$\frac{1}{m_{\rm e}} = \frac{1}{m^*} + \frac{1}{V} \sum_{k'\sigma'} f_{\sigma\sigma'}(\cos\xi) \delta(\varepsilon_{k'} - \mu) \frac{\cos\xi}{m^*} \,. \tag{32.2.98}$$

Replacing the sum over k' by an integral and carrying out the integration over the length of k' as an integration over the energy, the equation determining the effective mass is

$$\frac{1}{m_{\rm e}} = \frac{1}{m^*} + \frac{1}{4\pi} \sum_{\sigma'} \int \mathrm{d}\varepsilon \,\rho_{\sigma'}(\varepsilon) \delta(\varepsilon - \mu) \iint f_{\sigma'\sigma}(\cos\xi) \frac{\cos\xi}{m^*} \sin\theta' \,\mathrm{d}\theta' \,\mathrm{d}\varphi'.$$
(32.2.99)

Only the spin-symmetric combination f^s gives a contribution after summation over the spin variable. Choosing again the z-axis of the coordinate system in the direction of k and expanding the Fermi-liquid parameters according to (32.2.21) in terms of the Legendre polynomials, the only nonvanishing contribution to the integral over the angular variables comes from the term l = 1owing to the extra factor $\cos \xi$ in the integrand. We find

$$\frac{m^*}{m_{\rm e}} = 1 + \frac{1}{3}F_1^{\rm s}. \tag{32.2.100}$$

The condition of stability requires that the mass be positive, i.e., $F_1^{\rm s} > -3$ has to be satisfied.

32.2.7 Stability Condition of Fermi Liquids

When studying the susceptibility and the effective mass it was shown that the Fermi-liquid state is stable only if conditions $F_0^a > -1$ and $F_1^s > -3$ are simultaneously satisfied. A similar condition is obtained when the compressibility or the sound velocity, that is the velocity of acoustic waves propagating in the Fermi liquid, are studied. For the compressibility one finds

$$\frac{1}{\kappa} = N_{\rm e}\rho \frac{\partial \mu}{\partial N_{\rm e}} = N_{\rm e}\rho \frac{1}{\rho(\varepsilon_{\rm F})} (1+F_0^{\rm s}), \qquad (32.2.101)$$

and the sound velocity is obtained from

$$c^{2} = \frac{N_{\rm e}}{m_{\rm e}} \frac{\partial \mu}{\partial N_{\rm e}} = \frac{N_{\rm e}}{m_{\rm e}} \frac{1}{\rho(\varepsilon_{\rm F})} (1 + F_{0}^{\rm s}).$$
 (32.2.102)

The compressibility diverges and the sound velocity vanishes if $1 + F_0^s = 0$. The Fermi-liquid state is stable only if F_0^s is larger than -1. We will show now quite generally that the condition

$$F_l^{\rm s(a)} > -(2l+1)$$
 (32.2.103)

has to be satisfied for each l.

The spherical Fermi surface with the same $k_{\rm F}$ in all directions is deformed in such a way that the states with spin σ are filled up to $k_{\rm F} + u_{\sigma}(\theta, \varphi)$ in the direction characterized by the angles θ and φ . That is we add quasiparticles to the system with distribution $\delta n_{k\sigma} = 1$ for $k_{\rm F} < k < k_{\rm F} + u_{\sigma}(\theta, \varphi)$. When $u_{\sigma}(\theta, \varphi)$ is negative, quasiholes are created in the system $\delta n_{k\sigma} = -1$ in the range $k_{\rm F} + u_{\sigma}(\theta, \varphi) < k < k_{\rm F}$. The Fermi-liquid state is unstable if such deformations of the Fermi surface can result in lowering the free energy.

To calculate the variation of the free energy owing to such deformations, we write the vectors \mathbf{k} and \mathbf{k}' in the free energy (32.2.12) in polar coordinates:

$$\delta F = \frac{V}{(2\pi)^3} \sum_{\sigma} \iint \sin \theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \, \int_{k_{\mathrm{F}}}^{k_{\mathrm{F}}+u_{\sigma}} (\varepsilon_{\boldsymbol{k}\sigma} - \mu) k^2 \, \mathrm{d}k \\ + \frac{1}{2} \frac{V}{(2\pi)^6} \sum_{\sigma\sigma'} \iint \sin \theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \, \iint \sin \theta' \, \mathrm{d}\theta' \, \mathrm{d}\varphi' \\ \times \int_{k_{\mathrm{F}}}^{k_{\mathrm{F}}+u_{\sigma}} k^2 \, \mathrm{d}k \, \int_{k_{\mathrm{F}}}^{k_{\mathrm{F}}+u'_{\sigma'}} k'^2 \, \mathrm{d}k' f_{\sigma\sigma'}(\cos \xi) \,, \qquad (32.2.104)$$

where ξ denotes the angle between k and k'. Integration over the lengths of the vectors can be carried out using the expansion

$$\int_{a}^{a+x} f(y) \, \mathrm{d}y = f(a)x + \frac{1}{2}f'(a)x^2 + \cdots$$
 (32.2.105)

The first term in (32.2.104) gives no contribution to first order in u since the integrand vanishes at the Fermi surface; thus, both terms are proportional to u^2 . We have

$$\delta F = \frac{V}{(2\pi)^3} \sum_{\sigma} \iint \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\varphi \,u_{\sigma}^2(\theta,\varphi) k_{\mathrm{F}}^2 \left. \frac{1}{2} \frac{\partial \varepsilon_{\mathbf{k}}}{\partial k} \right|_{k=k_{\mathrm{F}}} \\ + \frac{1}{2} \frac{V}{(2\pi)^6} \sum_{\sigma\sigma'} \iint \sin\theta \,\mathrm{d}\theta \,\mathrm{d}\varphi \iint \sin\theta' \,\mathrm{d}\theta' \,\mathrm{d}\varphi' \\ \times u_{\sigma}(\theta,\varphi) u_{\sigma'}(\theta',\varphi') k_{\mathrm{F}}^4 f_{\sigma\sigma'}(\cos\xi) \,.$$
(32.2.106)

Using

$$\frac{\partial \varepsilon_{\boldsymbol{k}}}{\partial k} = \frac{\hbar^2 k}{m^*} \tag{32.2.107}$$

in the first term and the dimensionless Landau parameters $F_{\sigma\sigma'}$ in the second term we find

$$\delta F = \frac{1}{2} \frac{V}{(2\pi)^3} \frac{\hbar^2 k_{\rm F}^3}{m^*} \left[\sum_{\sigma} \iint \sin \theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \, u_{\sigma}^2(\theta, \varphi) + \frac{1}{8\pi} \sum_{\sigma\sigma'} \iint \sin \theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \iint \sin \theta' \, \mathrm{d}\theta' \, \mathrm{d}\varphi' \right] \\ \times u_{\sigma}(\theta, \varphi) u_{\sigma'}(\theta', \varphi') F_{\sigma\sigma'}(\cos \xi) \left].$$
(32.2.108)

We introduce the spin-symmetric and spin-antisymmetric combinations with the definition

$$u_{\uparrow}(\theta,\varphi) = u^{s}(\theta,\varphi) + u^{a}(\theta,\varphi),$$

$$u_{\downarrow}(\theta,\varphi) = u^{s}(\theta,\varphi) - u^{a}(\theta,\varphi),$$
(32.2.109)

and expand them in spherical harmonics in the form

$$u^{\mathrm{s(a)}}(\theta,\varphi) = \sum_{lm} u_{lm}^{\mathrm{s(a)}} Y_l^m(\theta,\varphi) \,. \tag{32.2.110}$$

Then, using the properties of the spherical harmonics, we find

$$\delta F = \frac{V}{(2\pi)^3} \frac{k_{\rm F}^3}{m^*} \sum_{lm} \left[|u_{lm}^{\rm s}|^2 \left(1 + \frac{F^{\rm s}}{2l+1} \right) + |u_{lm}^{\rm a}|^2 \left(1 + \frac{F^{\rm a}}{2l+1} \right) \right]. \tag{32.2.111}$$

The system is stable, i.e., the free energy is increased by small deformations of the Fermi surface, if indeed (32.2.103) is satisfied for each l. The physical meaning of these conditions has already been discussed in special cases. When the conditions fail for any l, the Fermi-liquid state breaks down. This is the Pomeranchuk instability.¹

32.2.8 ³He as a Normal Fermi Liquid

Landau's Fermi-liquid theory applies naturally to describing the properties of ³He. Assuming that the ³He atoms are almost free, the degeneracy temperature $T_{\rm F}$, below which quantum effects are important, can be estimated from (16.2.28) replacing the electron mass by the mass of the ³He atoms and the density of electrons by the density in the fluid phase of helium. This degeneracy temperature is about 5 K. The non-Fermi-liquid superfluid phases of

¹ Ya. I. Pomeranchuk, 1958.

 ${}^{3}\text{He}$ – in which spin-triplet pairs are formed – appear much below this temperature. The Fermi-liquid theory is applicable in the normal phase, above the transition temperature to the superfluid phases, but well below the degeneracy temperature, below about 0.1 K, where quantum effects are dominant.

The Landau parameters $F_0^{\rm s}$, $F_0^{\rm a}$, and $F_1^{\rm s}$ can be determined from the measurement of compressibility, susceptibility, and heat capacity. The parameters measured on ³He for several values of the pressure are shown in Table 32.1. It can be seen that the interaction is not weak, the enhancement of both the mass and the susceptibility is quite significant, nevertheless ³He is a stable Fermi liquid at the available pressures.

Pressure (bar)	F_0^{s}	$F_0^{\mathbf{a}}$	F_1^s	m^*/m
0	9.28	-0.70	5.39	2.80
6	22.49	-0.73	7.45	3.48
12	35.42	-0.75	9.09	4.03
18	48.46	-0.76	10.60	4.53
24	62.16	-0.76	12.07	5.02
30	77.02	-0.75	13.50	5.50

Table 32.1. Measured values of the effective mass and the Landau parameters of 3 He at six different pressures

In the form presented until now the Landau theory gives a simple framework to parametrize the equilibrium properties of the homogeneous liquid phase of ³He. It becomes a predictive theory when generalized to the case where the distribution of quasiparticles becomes inhomogeneous due to external perturbations. When the spatial variations of the perturbation occur on a length scale larger than the inverse of Δk , where $\Delta k = k_{\rm B}T/\hbar v_{\rm F}^*$ is the scale on which the distribution function varies in reciprocal space, the distribution of quasiparticles can be characterized by a semiclassical function depending on \mathbf{k} and \mathbf{r} . Denoting by $\delta n_{\mathbf{k}\sigma}(\mathbf{r})$ the density of quasiparticles of wave vector \mathbf{k} and spin σ at the position \mathbf{r} , the free energy is assumed to have the form

$$F = F_0 + \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \int d\boldsymbol{r} \left(\varepsilon_{\boldsymbol{k}\sigma} - \mu\right) \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r})$$

$$+ \frac{1}{2V^2} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} \iint d\boldsymbol{r} d\boldsymbol{r}' f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{r}, \boldsymbol{k}', \boldsymbol{r}') \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r}) \delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{r}'),$$
(32.2.112)

which is a natural generalization of (32.2.12) with the interaction parameters $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{r}, \mathbf{k}', \mathbf{r}')$ depending only on the difference between \mathbf{r} and \mathbf{r}' . The renormalized quasiparticle energy is then position dependent and is given by

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}(\boldsymbol{r}) = \varepsilon_{\boldsymbol{k}\sigma} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} \int \mathrm{d}\boldsymbol{r}' f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{r}, \boldsymbol{k}', \boldsymbol{r}') \delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{r}') \,.$$
(32.2.113)

If the range of the interaction is shorter than the characteristic scale of inhomogeneities, we find

$$F = F_0 + \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \int d\boldsymbol{r} \left(\varepsilon_{\boldsymbol{k}\sigma} - \mu\right) \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r}) + \frac{1}{2V^2} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} \int d\boldsymbol{r} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r}) \delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{r}), \qquad (32.2.114)$$

where

$$f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}') = \int \mathrm{d}\boldsymbol{r}' f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{r},\boldsymbol{k}',\boldsymbol{r}') \qquad (32.2.115)$$

and

~

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}(\boldsymbol{r}) = \varepsilon_{\boldsymbol{k}\sigma} + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{r}) \,.$$
(32.2.116)

The behavior of the inhomogeneous Fermi liquid is then determined by the same Landau parameters as in equilibrium.

When the distribution of quasiparticles varies in time, possibly in the presence of external space- and time-dependent forces, the free energy, too, varies in time. Assuming that the interaction between quasiparticles is short ranged and instantaneous, we have

$$F(t) = F_0 + \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \int d\boldsymbol{r} \left(\varepsilon_{\boldsymbol{k}\sigma} - \mu\right) \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r}, t)$$

$$+ \frac{1}{2V^2} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} \int d\boldsymbol{r} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r}, t) \delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{r}, t) .$$
(32.2.117)

The space and time dependence of the distribution function is determined by a kinetic equation, which is analogous to the Boltzmann equation studied in Chapter 24 for the transport of electrons. Following the procedure used there we consider how the number of quasiparticles varies in a phase space volume element $d\mathbf{k} d\mathbf{r}$ as the quasiparticles drift in phase space and undergo collisions during which their momenta change suddenly. We find

$$\frac{\partial n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)}{\partial t} + \boldsymbol{v}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) + \boldsymbol{F}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) = I[\delta n_{\boldsymbol{k}\sigma}].$$
(32.2.118)

The term on the right-hand side originates from the quasiparticle collisions.

The basic assumption of the kinetic theory is that the velocity of quasiparticles is obtained from the derivative of the position-dependent quasiparticle energy $\tilde{\varepsilon}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)$ with respect to \boldsymbol{k} , and the force acting on the quasiparticles is equal to the negative gradient of the energy:

$$\boldsymbol{v}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) = \frac{1}{\hbar} \boldsymbol{\nabla}_{\boldsymbol{k}} \widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t), \qquad \boldsymbol{F}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) = -\boldsymbol{\nabla}_{\boldsymbol{r}} \widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t). \quad (32.2.119)$$

This leads to the Landau kinetic equation:

$$\frac{\partial n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)}{\partial t} + \frac{1}{\hbar} \boldsymbol{\nabla}_{\boldsymbol{k}} \widetilde{\varepsilon}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)
- \frac{1}{\hbar} \boldsymbol{\nabla}_{\boldsymbol{r}} \widetilde{\varepsilon}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) = I[\delta n_{\boldsymbol{k}\sigma}].$$
(32.2.120)

Although it is formally a usual Boltzmann equation, an important difference appears through the term containing

$$\boldsymbol{\nabla}_{\boldsymbol{r}} \widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}\sigma}(\boldsymbol{r}) = \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}') \boldsymbol{\nabla}_{\boldsymbol{r}} \delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{r}), \qquad (32.2.121)$$

namely an effective force acts on the quasiparticles even in the absence of external forces owing to the inhomogeneous distribution of the other quasiparticles around them. This term is responsible for many interesting features of nonequilibrium phenomena in Fermi liquids.

Note that summation of both sides of (32.2.120) over \boldsymbol{k} and σ leads to the continuity equation

$$\frac{\partial n(\boldsymbol{r},t)}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_n(\boldsymbol{r},t) = 0, \qquad (32.2.122)$$

where

$$n(\mathbf{r},t) = \frac{1}{V} \sum_{\mathbf{k}\sigma} n_{\mathbf{k}\sigma}(\mathbf{r},t) \qquad (32.2.123)$$

and

$$\boldsymbol{j}_{n}(\boldsymbol{r},t) = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{1}{\hbar} \big[\boldsymbol{\nabla}_{\boldsymbol{k}} \widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) \big] n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) \,. \tag{32.2.124}$$

The sum over k of the collision integral vanishes owing to the conservation of the number of quasiparticles in collisions. When only the terms linear in the number of quasiparticles are kept we have

$$\boldsymbol{j}_{n}(\boldsymbol{r},t) = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \left[\frac{1}{\hbar} \left(\boldsymbol{\nabla}_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}\sigma} \right) \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) + n_{\boldsymbol{k}\sigma}^{0} \frac{1}{\hbar} \boldsymbol{\nabla}_{\boldsymbol{k}} \delta \widetilde{\varepsilon}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) \right]$$

$$= \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \boldsymbol{v}_{\boldsymbol{k}\sigma} \delta \bar{n}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) .$$
(32.2.125)

For a homogeneous system we recover the current density derived earlier.

The transition probabilities in the collision term can be expressed by the known Landau parameters; no new parameters appear in the transport equation. Hence the kinetic coefficients, such as the heat conduction, the spin diffusion, or the viscosity, can be expressed in terms of the Fermi-liquid parameters, and their values can be estimated quantitatively in ³He. The agreement with the experimental data gives a self-consistency check of the theory.

Returning to (32.2.120) we rewrite it keeping only the terms linear in the quasiparticle distribution $\delta n_{k\sigma}(\mathbf{r}, t)$. We have

$$\frac{\partial \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)}{\partial t} + \boldsymbol{v}_{\boldsymbol{k}} \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) - \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}\sigma}} \boldsymbol{v}_{\boldsymbol{k}} \cdot \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}') \boldsymbol{\nabla}_{\boldsymbol{r}} \delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{r},t) + \frac{1}{\hbar} \boldsymbol{F} \cdot \boldsymbol{\nabla}_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) = I[\delta n_{\boldsymbol{k}\sigma}], \quad (32.2.126)$$

where \boldsymbol{F} is the external force acting on the quasiparticles. When such forces are present, the number of excited quasiparticles is proportional to them and $n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)$ in the last term on the left-hand side can be approximated by $n_{\boldsymbol{k}\sigma}^0$. Using relation (32.2.50) we find

$$\frac{\partial \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)}{\partial t} + \boldsymbol{v}_{\boldsymbol{k}} \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} \delta \bar{n}_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) + \boldsymbol{F} \cdot \boldsymbol{v}_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}\sigma}} = I[\delta n_{\boldsymbol{k}\sigma}]. \quad (32.2.127)$$

In the collisionless limit, when $\omega \tau \gg 1$, new collective oscillations may appear in the quasiparticle distribution. Their frequencies and dispersion relations can be obtained from the kinetic equation. For plane-wave-like spatial and temporal variations of $\delta n_{k\sigma}(\mathbf{r}, t)$ in the form

$$\delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) = \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{q},\omega) \mathrm{e}^{\mathrm{i}(\boldsymbol{q}\cdot\boldsymbol{r}-\omega t)}$$
(32.2.128)

we have

$$(\boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} - \omega)\delta n_{\boldsymbol{k}\sigma}(\boldsymbol{q}, \omega) - \boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}\sigma}} \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{k}')\delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{q}, \omega) = 0$$
(32.2.129)

in the absence of external forces. One possible solution of this equation is a density oscillation with linear dispersion relation. This is the *zero sound* observed experimentally after being predicted by the theory. It propagates with a velocity c_0 which is different from the velocity c of ordinary (first) sound. This latter exists in the hydrodynamic ($\omega \tau < 1$) regime.

32.2.9 Charged Fermi Liquid in Metals

The Landau theory as exposed in the foregoing is well suited for neutral Fermi liquids where the interaction is of short range. The situation is more complicated in metals where the long-range Coulomb interaction between the charged electrons has to be taken into account. Looking at the expression derived for the quasiparticle energy in the Hartree–Fock approximation, we see that the Landau parameters are the Fourier components of the Coulomb interaction. In the Hartree–Fock theory this interaction originates from exchange and acts between particles of identical spins only:

$$f_{\uparrow\uparrow}(\mathbf{k},\mathbf{k}') = -\frac{4\pi\tilde{e}^2}{|\mathbf{k}-\mathbf{k}'|^2}, \qquad f_{\uparrow\downarrow}(\mathbf{k},\mathbf{k}') = 0.$$
(32.2.130)

The use of a singular Fermi-liquid parameter would be in contradiction with the spirit of the Landau theory. A way out of this discrepancy is found if the screening of the long-range Coulomb interaction, which is missing in the Hartree–Fock theory, is taken into account. Assuming that the Landau parameters are related to the screened, short-ranged interaction between quasiparticles, the Landau theory is expected to be applicable to the charged electron system as well. The Fermi-liquid parameters of the homogeneous electron gas can be estimated from the results of Monte Carlo calculations. The values for F_0^s and F_0^a are given in Table 32.2 for different values of the density. They are obtained with the assumption that the mass enhancement is so small that F_1^s is practically zero. Otherwise the values given here refer to $F_0^s/(1+F_1^s/3)$ and $F_0^a/(1+F_1^s/3)$.

 Table 32.2.
 Landau parameters for the homogeneous electron gas as derived from

 Monte Carlo calculations at different densities

$r_{\rm s}$	F_0^{s}	$F_0^{\mathbf{a}}$
1	-0.17	-0.13
2	-0.36	-0.23
3	-0.55	-0.32
4	-0.74	-0.38
5	-0.95	-0.44

The charge of electrons and the electric polarization cannot be neglected in an inhomogeneous system, when transport or oscillation phenomena are studied. The interaction between charged quasiparticles can then be partitioned into a regular part $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}')$ and a singular part given by the Fourier transform of the Coulomb interaction. This latter can be treated as a polarization term $\mathbf{E}_{\rm p}(\mathbf{r},t)$ in the electric field, which is generated by the quasiparticle distribution $\delta n_{\mathbf{k}\sigma}(\mathbf{r},t)$ varying in space and time. Their relationship is given by the Poisson equation

div
$$\epsilon_0 \boldsymbol{E}_{\rm p}(\boldsymbol{r},t) = -e \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)$$
. (32.2.131)

Even if no external electromagnetic field is present, the polarization term has to appear in the kinetic equation:

$$\frac{\partial \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t)}{\partial t} + \boldsymbol{v}_{\boldsymbol{k}} \cdot \boldsymbol{\nabla}_{\boldsymbol{r}} \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) - \boldsymbol{v}_{\boldsymbol{k}} \cdot \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}\sigma}} \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}') \boldsymbol{\nabla}_{\boldsymbol{r}} \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{r},t) + \left(\boldsymbol{F} - e\boldsymbol{E}_{\mathrm{p}}\right) \cdot \boldsymbol{v}_{\boldsymbol{k}} \frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial \varepsilon_{\boldsymbol{k}\sigma}} = I[\delta n_{\boldsymbol{k}\sigma}].$$
(32.2.132)

This is known as the Landau–Silin equation,² and the Fermi-liquid theory for charged fermions is referred to as the Landau–Silin theory.

For periodically varying quasiparticle distribution

$$\boldsymbol{E}_{\mathrm{p}}(\boldsymbol{q},\omega) = \mathrm{i}\boldsymbol{q}\frac{e}{\epsilon_0 q^2} \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{q},\omega) \,. \tag{32.2.133}$$

In the absence of external forces in the collisionless regime we find

$$(\boldsymbol{q} \cdot \boldsymbol{v}_{\boldsymbol{k}} - \omega) \delta n_{\boldsymbol{k}\sigma}(\boldsymbol{q}, \omega) \tag{32.2.134}$$

$$-\boldsymbol{q}\cdot\boldsymbol{v}_{\boldsymbol{k}}\frac{\partial n_{\boldsymbol{k}\sigma}^{0}}{\partial\varepsilon_{\boldsymbol{k}\sigma}}\frac{1}{V}\sum_{\boldsymbol{k}'\sigma'}\left[f_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{k}')+\frac{4\pi\tilde{e}^{2}}{q^{2}}\right]\delta n_{\boldsymbol{k}'\sigma'}(\boldsymbol{q},\omega)=0$$

instead of (32.2.129). The collective excitations of a charged Fermi liquid, the plasmons, are not sound-wave-like excitations with linear dispersion relation, as in neutral Fermi systems, owing to the singular Coulomb term. They have a finite excitation energy $\hbar\omega_{\rm p}$.

The effects of interaction between electrons appear in two places in the Landau theory. On the one hand, it is due to this interaction that the effective Fermi velocity and the effective mass are different from the free electron values. On the other hand, the same interaction gives rise to the interaction between quasiparticles. A detailed account of the Landau theory would allow us to demonstrate that some physical properties of the Fermi system do not depend on the interaction between quasiparticles. That is, they can be accounted for in the one-particle picture provided the correct effective mass is used. This is the case, for example, for the cyclotron resonance, the Azbel–Kaner resonance, or the de Haas–van Alphen effect. These are precisely the methods that are best suited for measuring the parameters of the Fermi surface. We can thus state that, in spite of the interaction between electrons, the evaluation of these measurements in the one-particle picture gives correct information about the Fermi surface.

A further difficulty for the Landau theory of metals is that the Fermi surface is inherently nonspherical owing to the periodic potential of the ions, and the strength $f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}')$ of the interaction between the quasiparticles depends on \mathbf{k} and \mathbf{k}' separately, not only on the angle between them. Even if this dependence can be neglected, the effective mass determined from the heat capacity measurements contains not only the contribution of the electron– electron interaction, but the mass enhancement due to the periodic potential is also incorporated in it. The measured effective mass is in fact

$$m^* = m_{\rm c} \left(1 + \frac{1}{3} F_1^{\rm s} \right),$$
 (32.2.135)

where m_c is the band mass due to the periodic potential. This is enhanced according to (32.2.100) by the interaction between quasiparticles. Similarly, the enhancement of the Pauli susceptibility is given by

² V. P. Silin, 1957.

$$\frac{\chi}{\chi_{\rm p}^{(0)}} = \frac{m^*}{m_{\rm e}} \frac{1}{1 + F_0^{\rm a}} = \frac{m_{\rm c}}{m_{\rm e}} \frac{1 + \frac{1}{3}F_1^{\rm s}}{1 + F_0^{\rm a}} \,. \tag{32.2.136}$$

The first factor is due to the periodic potential and the second is due to the interaction between the quasiparticles. It is a difficult task to separate the two contributions in the analysis of the experimental data. As a conclusion we can say that although the Landau theory is much less quantitative for metals than for ³He it is extremely important conceptually. The physical picture underlying the theory, namely that the complex many-body system of interacting electrons can be regarded as a gas of weakly interacting quasiparticles, provides us with a qualitative explanation of why the properties of most metals can be described reasonably well in the free electron model.

32.3 Tomonaga–Luttinger Model

In the foregoing it seemed natural to assume that the fermions propagate in all three directions of space with practically the same probability. Indeed in the isotropic liquid ³He the three directions are equivalent. Although crystalline materials are anisotropic, a weak anisotropy is irrelevant in the sense that it does not destroy the Fermi-liquid behavior of normal metals. More and more new materials were synthesized in the last decades, which are quasi-one dimensional at least concerning their electronic properties. It is reasonable to ask the question when can Landau's Fermi-liquid theory be used to describe the electronic properties of such systems and if a different behavior is observed, what its main features should be.

With this aim we study first a model due to S. TOMONAGA³ (1950) and J. M. LUTTINGER (1963). TOMONAGA was the first to realize that the lowenergy excitations of the one-dimensional electron gas, which are electronhole pairs in the noninteracting system, are phononlike bosonic elementary excitations with linear dispersion relation for a specially chosen long-range (small-momentum transfer) electron–electron interaction.⁴ A modified version of the Tomonaga model known as the Luttinger model was shown to be exactly solvable with rather unusual properties: there are no low-energy fermionic quasiparticle in the system, the usual definition of the Fermi surface fails, and the correlation functions decay asymptotically at large distances and long times with nonuniversal exponents. This model is presented in this section. We show in the subsequent sections that the one-dimensional Hubbard model and the one-dimensional XXZ model behave similarly. It will be pointed

³ SIN-ITIRO TOMONAGA (1906–1979) shared the Nobel Prize with J. SCHWINGER and R. P. FEYNMAN in 1965 "for their fundamental work in quantum electrodynamics, with deep-ploughing consequences for the physics of elementary particles".

⁴ That the electron-hole excitations in the one-dimensional noninteracting electron gas can be described as sound waves was discovered by F. BLOCH already in 1934.

out that this is not an accident. The non-Fermi-liquid behavior is a generic property of one-dimensional Fermi systems. The models mentioned above are special realizations of *Luttinger liquids* also known as *Tomonaga–Luttinger liquids*.

32.3.1 Linearized Dispersion Relation

To understand the basic features of quasi-one-dimensional materials a very simple electronic band structure is chosen with a single band near the Fermi energy. The dispersion relation can be assumed to be parabolic when the periodic potential is weak, while it is proportional to $\cos ka$ (a is the lattice constant) in the opposite limit, in the tight-binding approximation, when the overlap is negligible beyond nearest neighbors. The corresponding dispersion curves are displayed in Fig. 32.4.



Fig. 32.4. Dispersion curves of the one-dimensional fermion gas: (a) in the freeelectron model and (b) in the tight-binding approximation

The "Fermi surface" consists of two points, $\pm k_{\rm F}$, in one dimension. The most interesting physical properties are determined by single-particle and electron-hole pair excitations where the excited particles are situated in the neighborhood of the Fermi points, in a range of width $k_{\rm B}T$. The states well below this range are practically always completely filled, and the states well above this range are always empty. For this reason it is sufficient to consider states within a finite bandwidth 2D about the Fermi energy neglecting the states that are outside this range.

The physically interesting portion of the dispersion curve can be approximated by two straight lines both in the free electron and in the tight-binding models, except for nearly filled or nearly empty bands. The finer details of the band structure are relevant at higher energies only. Accordingly we will assume in all our further calculations that the band energy measured from the chemical potential, $\xi_k = \varepsilon_k - \mu$, can be written in the form

$$\xi_k = \begin{cases} \hbar v_{\rm F}(k - k_{\rm F}) & k_{\rm F} - k_{\rm c} < k < k_{\rm F} + k_{\rm c} ,\\ -\hbar v_{\rm F}(k + k_{\rm F}) & -k_{\rm F} - k_{\rm c} < k < -k_{\rm F} + k_{\rm c} , \end{cases}$$
(32.3.1)

where k_c is a momentum cutoff. The bandwidth cutoff D and the momentum cutoff k_c are related via $D = \hbar v_F k_c$. Our results should not depend qualitatively either on their choice or on the position of the allowed momenta in the Brillouin zone $(-\pi/a, \pi/a)$. The linearized dispersion curve is shown in Fig. 32.5.



Fig. 32.5. Linearized dispersion of the one-dimensional electron gas with a finite bandwidth

Not only are there good physical arguments for this choice of the dispersion curve, but it is also very convenient in some of the calculations. In his original work S. TOMONAGA assumed that the linear dispersion relation holds for any momentum except for a break point at k = 0:

$$\xi_k = \begin{cases} \hbar v_{\rm F}(k - k_{\rm F}) & k > 0, \\ -\hbar v_{\rm F}(k + k_{\rm F}) & k < 0. \end{cases}$$
(32.3.2)

This dispersion curve is shown in Fig. 32.6(a).



Fig. 32.6. Linearized dispersion curve of one-dimensional fermions: (a) in the Tomonaga model and (b) in the Luttinger model

It is convenient to use different notations for the right- and left-moving fermions. In what follows, $c_{k\sigma}^{\dagger}(c_{k\sigma})$ denotes the creation (annihilation) operators of right-moving fermions with velocity $v_{\rm F}$. The operators for left-moving fermions with velocity $-v_{\rm F}$ are denoted by $d_{k\sigma}^{\dagger}(d_{k\sigma})$. The Hamiltonian of noninteracting fermions in the Tomonaga model is then

$$\mathcal{H}_0 = \sum_{k>0,\sigma} \hbar v_{\rm F} (k-k_{\rm F}) c_{k\sigma}^{\dagger} c_{k\sigma} - \sum_{k<0,\sigma} \hbar v_{\rm F} (k+k_{\rm F}) d_{k\sigma}^{\dagger} d_{k\sigma}.$$
(32.3.3)

The Tomonaga model can be solved mathematically more rigorously if the two branches with velocities $\pm v_{\rm F}$ do not terminate at k = 0, but continue to infinity on both sides as proposed by LUTTINGER and shown in Fig. 32.6(b):

$$\xi_k = \begin{cases} \hbar v_{\rm F}(k - k_{\rm F}) & -\infty < k < \infty, \\ -\hbar v_{\rm F}(k + k_{\rm F}) & -\infty < k < \infty. \end{cases}$$
(32.3.4)

Thus in contrast to (32.3.3), the summation over momentum runs over the region $-\infty < k < \infty$ in both terms in the Luttinger model. The ground state of the model is not uniquely defined owing to the infinitely many negative energy states. To cope with this problem, to eliminate this divergent contribution, we assume that all negative energy states are filled in the ground states and the creation and annihilation operators are normal ordered in the Hamiltonian. Normal ordering of the particle-number operators is defined via

$$:c_{k\sigma}^{\dagger}c_{k\sigma}:=c_{k\sigma}^{\dagger}c_{k\sigma}-\left\langle c_{k\sigma}^{\dagger}c_{k\sigma}\right\rangle _{0},$$

$$:d_{k\sigma}^{\dagger}d_{k\sigma}:=d_{k\sigma}^{\dagger}d_{k\sigma}-\left\langle d_{k\sigma}^{\dagger}d_{k\sigma}\right\rangle _{0},$$

$$(32.3.5)$$

where $\langle \cdots \rangle_0$ denotes the ground-state expectation value,

$$\langle c_{k\sigma}^{\dagger} c_{k\sigma} \rangle_0 = \theta(k_{\rm F} - k), \qquad \langle d_{k\sigma}^{\dagger} d_{k\sigma} \rangle_0 = \theta(k + k_{\rm F}).$$
(32.3.6)

By using the anticommutation rules of fermions the normal-ordered operators can be written equivalently in the form

$$:c_{k\sigma}^{\dagger}c_{k\sigma}:=\begin{cases}c_{k\sigma}^{\dagger}c_{k\sigma} & k > k_{\rm F},\\ -c_{k\sigma}c_{k\sigma}^{\dagger} & k < k_{\rm F},\\ :d_{k\sigma}^{\dagger}d_{k\sigma}:=\begin{cases}d_{k\sigma}^{\dagger}d_{k\sigma} & k < -k_{\rm F},\\ -d_{k\sigma}d_{k\sigma}^{\dagger} & k > -k_{\rm F}.\end{cases}$$

$$(32.3.7)$$

The noninteracting Hamiltonian of the Luttinger model then takes the form

$$\mathcal{H}_0 = \sum_{k\sigma} \hbar v_{\rm F}(k-k_{\rm F}) : c_{k\sigma}^{\dagger} c_{k\sigma} : -\sum_{k\sigma} \hbar v_{\rm F}(k+k_{\rm F}) : d_{k\sigma}^{\dagger} d_{k\sigma} : .$$
(32.3.8)

The ground-state energy is $E_0 = 0$. The positive energy excitations are particles outside the Fermi "sphere" and holes inside.

The filled negative energy states far below the Fermi energy are eliminated by this trick. Although there are very high energy excitations above the Fermi energy both in the Tomonaga and in the Luttinger models, they cannot be excited thermally and are therefore physically irrelevant. Thus the model with finite bandwidth describes the same physics as either the Tomonaga or the Luttinger model, and this model will be treated in most of the remaining part of this section. The field theory of the Luttinger model is presented in Appendix L. When the momenta are measured from the corresponding Fermi points, the Hamiltonian of the noninteracting model takes the form

$$\mathcal{H}_{0} = \sum_{k\sigma} \hbar v_{\mathrm{F}} k \left(c_{k_{\mathrm{F}}+k,\sigma}^{\dagger} c_{k_{\mathrm{F}}+k,\sigma} - d_{-k_{\mathrm{F}}+k,\sigma}^{\dagger} d_{-k_{\mathrm{F}}+k,\sigma} \right), \qquad (32.3.9)$$

where the creation and annihilation operators are defined only in the region $-k_{\rm c} < k < k_{\rm c}$ and the summation over k is restricted to this range.

32.3.2 Bosonic Electron–Hole Excitations

As has already been discussed in Chapter 15 in connection with the onedimensional XY model, which is equivalent to a model of noninteracting spinless fermions, low-energy particle-hole pairs can be created in four different ways in a one-dimensional Fermi system owing to the two Fermi points. They are displayed schematically in Fig. 32.7.



Fig. 32.7. Four types of low-energy particle–hole excitations in the one-dimensional Fermi gas

When both the particle and the hole are in the neighborhood of $+k_{\rm F}$ or both of them are in the neighborhood of $-k_{\rm F}$, the total wave number qof the pair is small compared to $k_{\rm F}$. When a particle is excited across the Fermi sea, from one Fermi point to the other, leaving a hole behind, the wave number of the pair is large; it is on the order of $\pm 2k_{\rm F}$. Low-energy particle–hole excitations exist only near q = 0 and $q = \pm 2k_{\rm F}$. This is in contrast with the known properties of the three-dimensional electron gas where the continuum of electron–hole pair excitations starts at zero in the whole range $0 \le q \le 2k_{\rm F}$ as was shown in Fig. 28.9. The spectrum for a one-dimensional tight-binding model is shown in Fig. 32.8(a).⁵ When the excitation of several particle-hole pairs is also allowed for, low-energy excitations appear at integral multiples of $\pm 2k_{\rm F}$ as shown in Fig. 32.8(b).



Fig. 32.8. Continuum of particle-hole pair excitations in the one-dimensional tightbinding model: (a) for a single electron-hole pair and (b) for several electron-hole pairs

If the dispersion curve is approximated by two straight lines near the Fermi points, the excitation energy of the small-momentum electron-hole pairs is $\pm \hbar v_{\rm F} q$ independently of the position of the hole. The continuum shrinks to two lines near q = 0 and to two V-shaped continua near $\pm 2k_{\rm F}$. When several electron-hole pairs are excited, such V-shaped continua appear at any integral multiple of $2k_{\rm F}$, even at q = 0. The energy vs. wave number for these cases is shown in Fig. 32.9.



Fig. 32.9. Continuum of electron-hole pair excitation for a model with linear dispersion curve: (a) for a single electron-hole pair and (b) for several electron-hole pairs

If only the physically relevant low-energy excitations are considered, the same energies are obtained with the linearized dispersion curve as for the tightbinding model. This energy spectrum is highly degenerate since the energy of

⁵ The continuum of particle-hole excitations is similar to the spectrum shown in Fig. 15.13 except that the soft modes are shifted from $\pm \pi/a$ to $\pm 2k_{\rm F}$.

the state created by the operator $c_{k_{\rm F}+k+q,\sigma}^{\dagger}c_{k_{\rm F}+k,\sigma}$ is $\hbar v_{\rm F}q$ independently of the value of k. We can therefore describe this spectrum equivalently by taking the linear combinations

$$n_{+,\sigma}(q) = \sum_{k} c^{\dagger}_{k_{\rm F}+k,\sigma} c_{k_{\rm F}+k+q,\sigma},$$

$$n_{-,\sigma}(q) = \sum_{k} d^{\dagger}_{-k_{\rm F}+k,\sigma} d_{-k_{\rm F}+k+q,\sigma}.$$
(32.3.10)

Both the electron and the hole have to be created within the band in the model with finite bandwidth. Accordingly the summation over k has to be carried out for $-k_c < k < k_c - q$ when q > 0, while k is restricted to the range $-k_c - q < k < k_c$ if q < 0. The expressions are well defined at q = 0 as well. In the Luttinger model, on the other hand, we would have an infinite number of particles for q = 0. This infinity can be eliminated if the pair-creation operators are normal ordered:

$$n_{+,\sigma}(q) = \sum_{k} c^{\dagger}_{k_{\mathrm{F}}+k,\sigma} c_{k_{\mathrm{F}}+k+q,\sigma} - \delta_{q,0} \sum_{k} \left\langle c^{\dagger}_{k_{\mathrm{F}}+k,\sigma} c_{k_{\mathrm{F}}+k+q,\sigma} \right\rangle_{0},$$

$$n_{-,\sigma}(q) = \sum_{k} d^{\dagger}_{-k_{\mathrm{F}}+k,\sigma} d_{-k_{\mathrm{F}}+k+q,\sigma} - \delta_{q,0} \sum_{k} \left\langle d^{\dagger}_{-k_{\mathrm{F}}+k,\sigma} d_{-k_{\mathrm{F}}+k+q,\sigma} \right\rangle_{0}.$$
(32.3.11)

In what follows the q = 0 component will be treated separately.

The density operators n(q) commute with each other in three dimensions. The same is true for the Fourier components of the full density in one dimension. When we treat the densities of right- and left-moving fermions separately, their Fourier transform obey the Kac–Moody commutation relations. We prove it below for right-moving fermions.

Using the anticommutation rules for fermions we find

$$[n_{+,\sigma}(q), n_{+,\sigma'}(q')]_{-} = \sum_{kk'} \left[c^{\dagger}_{k_{\rm F}+k,\sigma} c_{k_{\rm F}+k+q,\sigma}, c^{\dagger}_{k_{\rm F}+k',\sigma'} c_{k_{\rm F}+k'+q',\sigma'} \right]_{-} (32.3.12)$$

= $\delta_{\sigma\sigma'} \sum_{k} \left(c^{\dagger}_{k_{\rm F}+k,\sigma} c_{k_{\rm F}+k+q+q',\sigma} - c^{\dagger}_{k_{\rm F}+k-q',\sigma} c_{k_{\rm F}+k+q,\sigma} \right).$

When $q \neq -q'$, the commutator might have nonvanishing matrix elements only between states that differ by a particle-hole pair, but in fact the contribution of the two terms cancel each other exactly when q and q' are small compared to k_c . This cancellation can be shown formally by shifting the summation index in the second term from k to k + q' whereby the two terms become equal. The same cancellation does not hold when q = -q'. In that case the commutator

$$\left[n_{+,\sigma}(q), n_{+,\sigma'}(-q)\right]_{-} = \delta_{\sigma\sigma'} \sum_{k} \left(c_{k_{\mathrm{F}}+k,\sigma}^{\dagger} c_{k_{\mathrm{F}}+k,\sigma} - c_{k_{\mathrm{F}}+k+q,\sigma}^{\dagger} c_{k_{\mathrm{F}}+k+q,\sigma}\right)$$
(32.3.13)

has only diagonal matrix elements and behaves as a *c*-number. We evaluate it first for the spectrum proposed by TOMONAGA. Since the sum over k for right-moving fermions is restricted to the range $k_{\rm F} + k \ge 0$ if q > 0, the second term can compensate only the contribution of the region $k \ge -k_{\rm F} + q$ and thus

$$[n_{+,\sigma}(q), n_{+,\sigma}(-q)]_{-} = \sum_{-k_{\rm F} < k < -k_{\rm F} + q} c^{\dagger}_{k_{\rm F} + k,\sigma} c_{k_{\rm F} + k,\sigma} \quad \text{for } q > 0. \quad (32.3.14)$$

A similar expression is obtained for negative q but with opposite sign since then the summation goes over the region $-k_{\rm F} + k + q \ge 0$ and only the contribution of the region $-k_{\rm F} < k < -k_{\rm F} - q$ survives:

$$[n_{+,\sigma}(q), n_{+,\sigma}(-q)]_{-} = -\sum_{-k_{\rm F} < k < -k_{\rm F} - q} c^{\dagger}_{k_{\rm F} + k,\sigma} c_{k_{\rm F} + k,\sigma} \quad \text{for } q < 0.$$
(32.3.15)

These states are far below the Fermi energy and are practically always completely filled. The possible k values are quantized in units of $2\pi/L$ in a sample of length L; hence, the number of states in a range of width q is $qL/2\pi$. This gives

$$\left[n_{+,\sigma}(q), n_{+,\sigma'}(q')\right]_{-} = \delta_{\sigma\sigma'}\delta_{q,-q'}\frac{qL}{2\pi}.$$
(32.3.16)

One can show similarly that

$$\left[n_{-,\sigma}(q), n_{-,\sigma'}(q')\right]_{-} = -\delta_{\sigma\sigma'}\delta_{q,-q'}\frac{qL}{2\pi}$$
(32.3.17)

and

$$\left[n_{+,\sigma}(q), n_{-,\sigma'}(q')\right]_{-} = 0.$$
 (32.3.18)

It is shown in Appendix L that the same commutators are obtained if the dispersion curves proposed by LUTTINGER are used. While the commutators were approximately evaluated in the previous calculations with the assumption that states far below the Fermi energy are practically always filled, relations (32.3.16), (32.3.17), and (32.3.18) are exact in the Luttinger model.

Consider now the model with finite bandwidth. The wave numbers should lie in a range of width $2k_c$. When q > 0, the sum over k is restricted to the range $-k_c < k < k_c - q$. Shifting the summation index by q in the second term we have

$$\left[n_{+,\sigma}(q), n_{+,\sigma}(-q)\right]_{-} = \sum_{-k_{c} < k < k_{c} - q} c^{\dagger}_{k_{F}+k,\sigma} c_{k_{F}+k,\sigma} - \sum_{-k_{c}+q < k < k_{c}} c^{\dagger}_{k_{F}+k,\sigma} c_{k_{F}+k,\sigma} .$$
(32.3.19)

The contributions of the two terms cancel each other in the region between $-k_c + q$ and $k_c - q$ and we are left with

$$\left[n_{+,\sigma}(q), n_{+,\sigma}(-q)\right]_{-} = \sum_{-k_c < k < -k_c + q} c^{\dagger}_{k_{\rm F}+k,\sigma} c_{k_{\rm F}+k,\sigma} - \sum_{k_c - q < k < k_c} c^{\dagger}_{k_{\rm F}+k,\sigma} c_{k_{\rm F}+k,\sigma}$$
(32.3.20)

The states at the bottom of the band, with $-k_c < k < -k_c + q$, are all filled and the states at the top, in the range $k_c - q < k < k_c$, are empty if q is small compared to the momentum cutoff k_c . The model with bandwidth cutoff thus gives the same commutator for the long-wavelength density fluctuations as the Tomonaga or Luttinger models. While the commutators are exact in the Luttinger model, they are only valid for long-wavelength fluctuations in the model with finite bandwidth. This restriction should be taken into account in calculating the physical quantities by a cutoff in the summation over q.

It follows from the definition of $n_{\pm,\sigma}(q)$ that

$$n_{\pm,\sigma}(-q) = n_{\pm,\sigma}^{\dagger}(q),$$
 (32.3.21)

and the commutation relations can be written in the concise form

$$\left[n_{\lambda,\sigma}(q), n^{\dagger}_{\lambda',\sigma'}(q')\right]_{-} = \delta_{\lambda\lambda'} \delta_{\sigma\sigma'} \delta_{qq'} \lambda \frac{qL}{2\pi}, \qquad (32.3.22)$$

where $\lambda = +1$ for right-moving particles and $\lambda = -1$ for left movers. If we use $n_{\pm,\sigma}(q)$ and its adjoint, it suffices to define these operators either for q > 0 or for q < 0 only. We will use a different convention. The density operators and their adjoints with index $\lambda = +1$ will be defined for q > 0, and those with index $\lambda = -1$ are defined for q < 0.6 Introducing the operators

$$b_{q\sigma} = \begin{cases} \sum_{k} \left(\frac{2\pi}{Lq}\right)^{1/2} c^{\dagger}_{k_{\rm F}+k,\sigma} c_{k_{\rm F}+k+q,\sigma} & q > 0 ,\\ \sum_{k} \left(\frac{2\pi}{L|q|}\right)^{1/2} d^{\dagger}_{-k_{\rm F}+k,\sigma} d_{-k_{\rm F}+k+q,\sigma} & q < 0 , \end{cases}$$
(32.3.23-a)
$$b^{\dagger}_{q\sigma} = \begin{cases} \sum_{k} \left(\frac{2\pi}{Lq}\right)^{1/2} c^{\dagger}_{k_{\rm F}+k+q,\sigma} c_{k_{\rm F}+k,\sigma} & q > 0 ,\\ \sum_{k} \left(\frac{2\pi}{L|q|}\right)^{1/2} d^{\dagger}_{-k_{\rm F}+k+q,\sigma} d_{-k_{\rm F}+k,\sigma} & q < 0 , \end{cases}$$
(32.3.23-b)

they satisfy the usual bosonic commutation relations:

$$\left[b_{q\sigma}, b_{q'\sigma'}^{\dagger}\right]_{-} = \delta_{\sigma\sigma'} \delta_{qq'} \,. \tag{32.3.24}$$

 $b_{q\sigma}^{\dagger}$ $(b_{q\sigma})$ is the creation (annihilation) operator of a collective excitation involving the coherent superposition of a large number of electron-hole pairs. It follows from the definition that the operator $b_{q\sigma}$ gives zero when acting on the ground state of the noninteracting Fermi sea,

$$b_{q\sigma}|\Psi_{\rm FS}\rangle = 0\,,\qquad(32.3.25)$$

that is the ground state of the Fermi gas is the vacuum of these bosons.

⁶ Note that another convention is also quite common in the literature. The bosons with negative q formed from left-moving particle-hole pairs are replaced by another boson branch with positive q defined via $\tilde{b}_{q\sigma} = b_{-q\sigma}$ and $\tilde{b}_{q\sigma}^{\dagger} = b_{-q\sigma}^{\dagger}$.

32.3.3 Bosonic Form of the Noninteracting Hamiltonian

It follows from the linear dispersion curve that the energy of the electronhole pair created by the operator $c^{\dagger}_{k_{\rm F}+k+q,\sigma}c_{k_{\rm F}+k,\sigma}$ is $\hbar v_{\rm F}q$, irrespective of the value of k, if q > 0. The pair created around $-k_{\rm F}$ by the operator $d^{\dagger}_{-k_{\rm F}+k+q,\sigma}d_{-k_{\rm F}+k,\sigma}$ has the same excitation energy, $\hbar v_{\rm F}|q|$, if q < 0. Thus $b^{\dagger}_{q\sigma}$ creates an excitation with this energy for both q > 0 and q < 0, and $b_{q\sigma}$ annihilates such an excitation. We therefore expect that the kinetic energy of the one-dimensional noninteracting electron gas can be written in the form

$$\mathcal{H}_0 = \sum_{q\sigma} \hbar v_{\rm F} |q| b_{q\sigma}^{\dagger} b_{q\sigma} \,. \tag{32.3.26}$$

To prove that, consider the commutator of the fermionic form of the noninteracting Hamiltonian (32.3.9) with $b_{q\sigma}$ and $b_{q\sigma}^{\dagger}$, respectively. Simple algebraic manipulations lead to the result

$$\left[\mathcal{H}_{0}, b_{q\sigma}\right]_{-} = -\hbar v_{\mathrm{F}} |q| b_{q\sigma} , \qquad \left[\mathcal{H}_{0}, b_{q\sigma}^{\dagger}\right]_{-} = +\hbar v_{\mathrm{F}} |q| b_{q\sigma}^{\dagger} . \qquad (32.3.27)$$

The same commutation relations are obtained if (32.3.26) is used for the noninteracting Hamiltonian. Thus in the low-energy sector of the Hilbert space, where the excitations are small-momentum particle-hole pairs, the one-dimensional free electron gas is equivalent to a noninteracting boson gas.

The particle and the hole are created with the same spin and the same chirality⁷ in the small-momentum excitations. There are, however, other types of low-energy excitations, too. The electron and the hole may be created with opposite chirality, in which case the wave number of the pair is close to $\pm 2k_{\rm F}$. When the creation of the pair is accompanied by a spin flip, the particle and the hole have opposite spins. The generation of these excitations can be decomposed into two subsequent steps. Starting from the ground state, where there is an equal number of fermions in each branch, we first change the number of fermions by $\delta N_{\lambda\sigma}$ in the branch of chirality λ and spin σ filling the lowest energy states in agreement with the Pauli exclusion principle. Electronhole pairs are then created in a second step within the branches. The excited states are thus characterized by the numbers $\delta N_{\lambda\sigma}$ in addition to the numbers of the excited bosons with quantum number q and σ .

All four branches $(\lambda = \pm 1, \sigma = \uparrow, \downarrow)$ are filled up to the same $k_{\rm F}$ in the ground state. When the number of particles on branch with quantum numbers λ and σ is changed by $\delta N_{\lambda\sigma}$, the Fermi wave number is shifted by

$$\delta k_{\mathrm{F}\lambda\sigma} = \lambda \frac{2\pi}{L} \delta N_{\lambda\sigma} \,. \tag{32.3.28}$$

The average value of the kinetic energy of the added particles with velocity $\pm v_{\rm F}$ is $\pm \hbar v_{\rm F} \, \delta k_{\rm F\lambda\sigma}/2$. Hence the change of the total kinetic energy is

⁷ The chirality of the particle tells whether it is right or left moving, that is whether its wave number is close to $+k_{\rm F}$ or $-k_{\rm F}$.

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$$\delta E_{\lambda\sigma} = \frac{1}{2} \lambda \hbar v_{\rm F} \, \delta k_{\rm F\lambda\sigma} \, \delta N_{\lambda\sigma} = \frac{\pi \hbar v_{\rm F}}{L} (\delta N_{\lambda\sigma})^2. \tag{32.3.29}$$

When bosons are created within the branches in the second step, their energies should appear in the total Hamiltonian together with this energy correction and we have

$$\mathcal{H}_0 = \sum_{q \neq 0,\sigma} \hbar v_{\rm F} |q| b_{q\sigma}^{\dagger} b_{q\sigma} + \frac{\pi \hbar v_{\rm F}}{L} \sum_{\lambda \sigma} (\delta N_{\lambda \sigma})^2 \,. \tag{32.3.30}$$

The term q = 0 is excluded from the summation over q in the first term. The contribution of the q = 0 component of the density appears in the second term.

The construction of the collective bosonic excitations was made possible by the high degeneracy of the particle-hole pair excitations. It is natural to ask whether this degeneracy is correctly reproduced in the bosonic description. In order to show that the two representations are faithful in this respect, too, we calculate the thermal energy and the heat capacity in both the fermionic and the bosonic representations. Starting from (32.3.9) where the kinetic energy is given in terms of the fermion operators we find

$$\Delta E = \langle \mathcal{H}_0 \rangle - \langle \mathcal{H}_0 \rangle_{T=0}$$

$$= \sum_{\sigma} \sum_{k=-k_c}^{k_c} \left[\frac{\hbar v_{\mathrm{F}} k}{\mathrm{e}^{\beta \hbar v_{\mathrm{F}} k} + 1} - \hbar v_{\mathrm{F}} k \, \theta(-k) \right]$$

$$+ \sum_{\sigma} \sum_{k=-k_c}^{k_c} \left[\frac{-\hbar v_{\mathrm{F}} k}{\mathrm{e}^{-\beta \hbar v_{\mathrm{F}} k} + 1} + \hbar v_{\mathrm{F}} k \, \theta(k) \right].$$
(32.3.31)

With the change of variables $k \to -k$ in the region k < 0 we have

$$\Delta E = 4 \sum_{\sigma} \sum_{k=0}^{k_{\rm c}} \frac{\hbar v_{\rm F} k}{\mathrm{e}^{\beta \hbar v_{\rm F} k} + 1} \,. \tag{32.3.32}$$

Replacing the sum by an integral and extending the region of integration to infinity, which is a good approximation at low temperatures, by making use of (C.2.17) we find

$$\Delta E = 8 \frac{L}{2\pi} \int_{0}^{\infty} \frac{\hbar v_{\rm F} k}{\mathrm{e}^{\beta \hbar v_{\rm F} k} + 1} \mathrm{d}k = 8 \frac{L}{2\pi} \frac{(k_{\rm B} T)^2}{\hbar v_{\rm F}} \frac{\pi^2}{12} \,. \tag{32.3.33}$$

The heat capacity per unit length is

$$c_V = \frac{2\pi}{3} k_{\rm B} \frac{k_{\rm B} T}{\hbar v_{\rm F}} \,. \tag{32.3.34}$$

This expression is in agreement with the known result [see (16.2.91)] for the heat capacity per unit volume of the free electron gas,

$$c_V = \frac{\pi^2}{3} k_{\rm B}^2 T \rho(\varepsilon_{\rm F}),$$
 (32.3.35)

if the correct expression

$$\rho(\varepsilon_{\rm F}) = \frac{2}{\pi \hbar v_{\rm F}} \tag{32.3.36}$$

is substituted for the density of states of the one-dimensional electron gas at the Fermi energy.

In the boson representation, we may use (32.3.26) for the Hamiltonian, since the contributions of the particles added to or removed from the branches vanish in the thermodynamic limit. We then have

$$\Delta E = \sum_{\sigma} \sum_{q} \frac{\hbar v_{\rm F} |q|}{\mathrm{e}^{\beta \hbar v_{\rm F} |q|} - 1} = 2 \sum_{\sigma} \sum_{q>0} \frac{\hbar v_{\rm F} q}{\mathrm{e}^{\beta \hbar v_{\rm F} q} - 1} \,. \tag{32.3.37}$$

Replacing again the sum by an integral and carrying out the integration to infinity with the aid of (C.2.8) we find

$$\Delta E = 4 \frac{L}{2\pi} \frac{(k_{\rm B}T)^2}{\hbar v_{\rm F}} \frac{\pi^2}{6} \,. \tag{32.3.38}$$

This yields precisely the same expression for the Debye heat capacity of the boson gas as the heat capacity (32.3.35) derived in the fermion representation. This shows that the low-energy excitations of the one-dimensional Fermi system are faithfully represented by the bosonic density fluctuations.

The Pauli susceptibility, too, is recovered exactly. The particles are rearranged in an external magnetic field, some of them are transferred from the \uparrow spin to the \downarrow spin branches:

$$\delta N_{\lambda\uparrow} = -\delta N_{\lambda\downarrow} \,, \tag{32.3.39}$$

with the natural expectation that the left–right symmetry is preserved. In the lowest energy state, where no bosons are excited, the energy in the presence of the external field is

$$E = E_{0} + \frac{\pi \hbar v_{\rm F}}{L} \left[(\delta N_{+,\uparrow})^{2} + (\delta N_{+,\downarrow})^{2} + (\delta N_{-,\uparrow})^{2} + (\delta N_{-,\downarrow})^{2} \right] - \frac{1}{2} g_{\rm e} \mu_{\rm B} \mu_{0} \left(\delta N_{+,\uparrow} - \delta N_{+,\downarrow} + \delta N_{-,\uparrow} - \delta N_{-,\downarrow} \right) H.$$
(32.3.40)

The number of particles transferred to (from) the branches is obtained by minimizing this expression. We find

$$\delta N_{\lambda\uparrow} = L \frac{g_{\rm e}\mu_{\rm B}\mu_0}{4\pi\hbar v_{\rm F}} H, \qquad (32.3.41)$$

yielding a magnetic-moment density

$$M = \frac{1}{2L} g_{\rm e} \mu_{\rm B} \left(\delta N_{+,\uparrow} - \delta N_{+,\downarrow} + \delta N_{-,\uparrow} - \delta N_{-,\downarrow} \right)$$

$$= \frac{1}{2} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \frac{1}{\pi \hbar v_{\rm F}} H$$
 (32.3.42)

and a susceptibility

$$\chi = \frac{1}{4} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \frac{2}{\pi \hbar v_{\rm F}} , \qquad (32.3.43)$$

which agrees precisely with the usual expression for the Pauli susceptibility

$$\chi_{\rm P} = \frac{1}{4} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \rho(\varepsilon_{\rm F}) \,, \qquad (32.3.44)$$

if the density of states of the one-dimensional electron gas is used.

32.3.4 Spin–Charge Separation

In what follows it will be convenient to use the spin-symmetric and spin-antisymmetric combinations of the chiral densities. The quantities

$$n_{\lambda c}(q) = \frac{1}{\sqrt{2}} \left[n_{\lambda \uparrow}(q) + n_{\lambda \downarrow}(q) \right]$$
(32.3.45)

and

$$n_{\lambda s}(q) = \frac{1}{\sqrt{2}} \left[n_{\lambda \uparrow}(q) - n_{\lambda \downarrow}(q) \right]$$
(32.3.46)

are related to the particle density and the spin density, respectively, of the right- and left-moving particles. The indices c and s refer to charge and spin, respectively.⁸ These operators satisfy the commutation rules

$$\left[n_{\lambda c}(q), n_{\lambda' c}(q')\right]_{-} = \left[n_{\lambda s}(q), n_{\lambda' s}(q')\right]_{-} = \delta_{\lambda \lambda'} \delta_{q, -q'} \lambda \frac{qL}{2\pi}, \qquad (32.3.47)$$

and the commutator of operators with different indices vanishes. Bosonic commutation relations are obeyed if a proper normalization factor is chosen, or equivalently if the combinations

$$b_{qc} = \frac{1}{\sqrt{2}} (b_{q\uparrow} + b_{q\downarrow}), \qquad b_{qs} = \frac{1}{\sqrt{2}} (b_{q\uparrow} - b_{q\downarrow}),$$

$$b_{qc}^{\dagger} = \frac{1}{\sqrt{2}} (b_{q\uparrow}^{\dagger} + b_{q\downarrow}^{\dagger}), \qquad b_{qs}^{\dagger} = \frac{1}{\sqrt{2}} (b_{q\uparrow}^{\dagger} - b_{q\downarrow}^{\dagger})$$
(32.3.48)

are used. The spin and charge bosons appear separately in the Hamiltonian:

$$\mathcal{H}_{0} = \sum_{q \neq 0} \hbar v_{\rm F} |q| b_{qc}^{\dagger} b_{qc} + \sum_{q \neq 0} \hbar v_{\rm F} |q| b_{qs}^{\dagger} b_{qs} \,. \tag{32.3.49}$$

The separation of the spin and charge degrees of freedom holds for the topological excitations as well. Introduce the combinations

$$\delta N_{c} = \delta N_{+,\uparrow} + \delta N_{+,\downarrow} + \delta N_{-,\uparrow} + \delta N_{-,\downarrow} ,$$

$$N_{s} = \delta N_{+,\uparrow} - \delta N_{+,\downarrow} + \delta N_{-,\uparrow} - \delta N_{-,\downarrow} ,$$

$$J_{c} = \delta N_{+,\uparrow} + \delta N_{+,\downarrow} - \delta N_{-,\uparrow} - \delta N_{-,\downarrow} ,$$

$$J_{s} = \delta N_{+,\uparrow} - \delta N_{+,\downarrow} - \delta N_{-,\uparrow} + \delta N_{-,\downarrow} ,$$
(32.3.50)

⁸ The notations ρ and σ are also common.

which give the change in the total number of particles, the total spin, as well as the charge and spin currents; the total Hamiltonian is the sum of two terms:

$$\mathcal{H}_0 = \mathcal{H}_{0c} + \mathcal{H}_{0s} \,, \tag{32.3.51}$$

with

$$\mathcal{H}_{0c} = \sum_{q} \hbar v_{\rm F} |q| b_{qc}^{\dagger} b_{qc} + \frac{\pi \hbar v_{\rm F}}{4L} \left[\left(\delta N_{\rm c} \right)^2 + J_{\rm c}^2 \right],$$

$$\mathcal{H}_{0s} = \sum_{q} \hbar v_{\rm F} |q| b_{qs}^{\dagger} b_{qs} + \frac{\pi \hbar v_{\rm F}}{4L} \left[N_{\rm s}^2 + J_{\rm s}^2 \right].$$
(32.3.52)

The term with $(\delta N_c)^2$ is the energy of the topological charge excitations. It is the energy needed to add particles symmetrically to the lowest energy available states, $\delta N_c/4$ particles to each of the four branches. The term proportional to J_c^2 is the energy of a topological charge-current excitation: $J_c/4$ particles from the highest occupied states of each left-moving branch are transferred to the lowest unoccupied right-moving states with the same spin. The terms with N_s^2 and $J_s^2/4$ correspond to the analogous topological excitations in the spin sector.

The total momentum of the excited state can also be determined easily. The momentum of the density fluctuations with wave number q is $\hbar q$. Hence the momentum of the bosonic excitations is

$$\mathcal{P} = \sum_{q\sigma} \hbar q b_{q\sigma}^{\dagger} b_{q\sigma} \,, \qquad (32.3.53)$$

or when written in terms of the charge and spin bosons,

$$\mathcal{P} = \sum_{q} \hbar q b_{qc}^{\dagger} b_{qc} + \sum_{q} \hbar q b_{qs}^{\dagger} b_{qs} \,. \tag{32.3.54}$$

The momentum is changed when particles are added to the branches. Since the Fermi momentum changes from $k_{\rm F}$ to $k_{\rm F} + (2\pi/L)\delta N_{+,\sigma}$ when the number of right-moving particles changes by $\delta N_{+,\sigma}$ [similarly the Fermi momentum changes from $-k_{\rm F}$ to $-k_{\rm F} - (2\pi/L)\delta N_{-,\sigma}$ when the number of left-moving particles changes by $\delta N_{-,\sigma}$], the change in the momentum is

$$\Delta P = \hbar \sum_{\lambda \sigma} \lambda \left[k_{\rm F} + (\pi/L) \delta N_{\lambda \sigma} \right] \delta N_{\lambda \sigma} \,. \tag{32.3.55}$$

Using the spin-symmetric and spin-antisymmetric combinations we have

$$\Delta P = \hbar k_{\rm F} J_{\rm c} + \hbar \frac{\pi}{2L} \left(\delta N_{\rm c} J_{\rm c} + N_{\rm s} J_{\rm s} \right). \qquad (32.3.56)$$

In the ground state, where the N_c^0 particles are distributed equally among the four branches, k_F is given by

$$k_{\rm F} = \frac{1}{4} N_{\rm c}^0 \frac{2\pi}{L} \,, \tag{32.3.57}$$

and hence

$$\Delta P = \hbar \frac{\pi}{2L} \left(N_{\rm c}^0 + \delta N_{\rm c} \right) J_{\rm c} + \hbar \frac{\pi}{2L} N_{\rm s} J_{\rm s}$$
$$= \hbar \frac{\pi}{2L} N_{\rm c} J_{\rm c} + \hbar \frac{\pi}{2L} N_{\rm s} J_{\rm s}$$
(32.3.58)

with N_c the total number of particles. The total momentum is the sum of the contributions of the bosonic excitations and of the particles added to the system:

$$\mathcal{P} = \sum_{q} \hbar q b_{qc}^{\dagger} b_{qc} + \hbar \frac{\pi}{2L} N_{c} J_{c} + \sum_{q} \hbar q b_{qs}^{\dagger} b_{qs} + \hbar \frac{\pi}{2L} N_{s} J_{s} . \qquad (32.3.59)$$

When particle-hole excitations are considered, the total number of particles is conserved ($\delta N_c = 0$) and the charge current J_c is an even number. Since the wave number q is quantized in units of $2\pi/L$ in a finite chain of length L, the eigenvalues of the total Hamiltonian \mathcal{H}_0 given in (32.3.51) and (32.3.52) are

$$E = E_0 + \hbar v_{\rm F} \frac{2\pi}{L} \left(n_{\rm c,+} + n_{\rm c,-} + \Delta_{\rm c,+} + \Delta_{\rm c,-} \right) + \hbar v_{\rm F} \frac{2\pi}{L} \left(n_{\rm s,+} + n_{\rm s,-} + \Delta_{\rm s,+} + \Delta_{\rm s,-} \right) , \qquad (32.3.60)$$

and the eigenvalues of the total momentum are

$$P = \hbar k_{\rm F} J_{\rm c} + \hbar \frac{2\pi}{L} \left(n_{\rm c,+} - n_{\rm c,-} + \Delta_{\rm c,+} - \Delta_{\rm c,-} \right) + \hbar \frac{2\pi}{L} \left(n_{\rm s,+} - n_{\rm s,-} + \Delta_{\rm s,+} - \Delta_{\rm s,-} \right) , \qquad (32.3.61)$$

where $n_{c,\pm}$ and $n_{s,\pm}$ are integers, and

$$\Delta_{c,\pm} = \frac{1}{16} \left(\delta N_c \pm J_c \right)^2, \Delta_{s,\pm} = \frac{1}{16} \left(N_s \pm J_s \right)^2.$$
(32.3.62)

For $J_c = 0$, when the same number of particles move to the right and to the left, the energies of the spin-symmetric and spin-antisymmetric excitations form overlapping V-shaped "towers" with their tips at q = 0. When more particles move to the right or to the left, similar "towers" appear at integer multiples of $2k_{\rm F}$, and the V-shaped quasicontinua start at a small finite energy, above a parabola with coefficient of order 1/N. This is important when correlation functions are calculated. This excitation spectrum is shown in Fig. 32.10. The continuum of excitations displayed in Fig. 32.9 is recovered for an infinitely long chain.



Fig. 32.10. Spectrum of particle-hole excitations in a discrete chain

32.3.5 Interactions in the Tomonaga–Luttinger Model

The electron–electron interaction is given in the most general form in (28.1.34). Since the momenta of the particles both before and after the scattering process have to be in a range of width $2k_c$ about the Fermi points $\pm k_F$, the momentum transfer is either small or of the order of $\pm 2k_F$ if k_c is smaller than the Fermi wave number. Taking a screened interaction with slowly varying q dependence, the scattering processes can be classified according to the momentum transfer as well as the chirality and the spin orientation of the scattered particles. Neglecting for the moment the spin dependence, four distinct scattering processes are allowed by momentum conservation. Their strength is characterized by momentum-independent coupling constants. The four processes are displayed in Fig. 32.11.



Fig. 32.11. Scattering processes in the one-dimensional Fermi gas. Right-moving fermions are denoted by solid lines and left-moving fermions by dashed lines

When two oppositely moving particles collide and the right-moving particle transfers a momentum of the order of $2k_{\rm F}$ to the other particle, the right mover becomes a left mover and the left mover is scattered into a right-moving state by acquiring this momentum. This is a backward-scattering process. Its coupling constant is g_1 in the conventional notation of the "g-ology" model. When the momentum transfer is small between a right- and a left-moving particle, they remain in the same branch after scattering. The coupling constant

of this forward-scattering process is denoted by g_2 . Forward scattering is possible also between particles moving in the same direction. This is a g_4 process. Finally, when two particles moving in the same direction are scattered into the neighborhood of the opposite Fermi point, we are dealing with an umklapp process. Its coupling constant is denoted by g_3 . Umklapp processes become important in a half-filled band where $k_{\rm F} = \pi/2a$ since the conservation of crystal momentum can be satisfied in low-energy processes with total momentum transfer $\pm 4k_{\rm F} = \pm 2\pi/a$ which are reciprocal-lattice vectors of the one-dimensional model.

Allowing for the spin dependence of the coupling constants the explicit expression of the interaction Hamiltonian is

$$\begin{aligned} \mathcal{H}_{\text{int}} &= \frac{1}{2L} \sum_{kk'q\sigma\sigma'} g_{1\sigma\sigma'} \left[c^{\dagger}_{k_{\text{F}}+k+q,\sigma} d^{\dagger}_{-k_{\text{F}}+k'-q,\sigma'} c_{k_{\text{F}}+k',\sigma'} d_{-k_{\text{F}}+k,\sigma} \right. \\ &\quad \left. + d^{\dagger}_{-k_{\text{F}}+k+q,\sigma} c^{\dagger}_{k_{\text{F}}+k'-q,\sigma'} d_{-k_{\text{F}}+k',\sigma'} c_{k_{\text{F}}+k,\sigma} \right] \\ &\quad \left. + \frac{1}{2L} \sum_{kk'q\sigma\sigma'} g_{2\sigma\sigma'} \left[c^{\dagger}_{k_{\text{F}}+k+q,\sigma} d^{\dagger}_{-k_{\text{F}}+k'-q,\sigma'} d_{-k_{\text{F}}+k',\sigma'} c_{k_{\text{F}}+k,\sigma} \right. \\ &\quad \left. + d^{\dagger}_{-k_{\text{F}}+k+q,\sigma} c^{\dagger}_{k_{\text{F}}+k'-q,\sigma'} c_{k_{\text{F}}+k',\sigma'} d_{-k_{\text{F}}+k,\sigma} \right] \\ &\quad \left. + \frac{1}{2L} \sum_{kk'q\sigma\sigma'} g_{3\sigma\sigma'} \left[c^{\dagger}_{k_{\text{F}}+k+q,\sigma} c^{\dagger}_{k_{\text{F}}+k'-q,\sigma'} d_{-k_{\text{F}}+k',\sigma'} d_{-k_{\text{F}}+k,\sigma} \right. \\ &\quad \left. + d^{\dagger}_{-k_{\text{F}}+k+q,\sigma} d^{\dagger}_{-k_{\text{F}}+k'-q,\sigma'} c_{k_{\text{F}}+k',\sigma'} c_{k_{\text{F}}+k,\sigma} \right] \\ &\quad \left. + \frac{1}{2L} \sum_{kk'q\sigma\sigma'} g_{4\sigma\sigma'} \left[c^{\dagger}_{k_{\text{F}}+k+q,\sigma} c^{\dagger}_{k_{\text{F}}+k'-q,\sigma'} c_{k_{\text{F}}+k',\sigma'} c_{k_{\text{F}}+k,\sigma} \right] \\ &\quad \left. + d^{\dagger}_{-k_{\text{F}}+k+q,\sigma} d^{\dagger}_{-k_{\text{F}}+k'-q,\sigma'} d_{-k_{\text{F}}+k',\sigma'} d_{-k_{\text{F}}+k,\sigma} \right], \quad (32.3.63)
\end{aligned}$$

if left–right symmetry is assumed.

Although the g_1 processes were termed as backscattering, they cannot be distinguished from the g_2 -type forward scattering when $\sigma = \sigma'$. If a right-moving electron collides with a left-moving electron, both having the same spin, and a right- and a left-moving electron emerge after scattering, there is no way to tell – owing to the indistinguishability of the particles in quantum mechanics – whether the right-moving particle was scattered with small momentum transfer to a right-moving state or the left-moving particle acquired a large momentum to become right mover. True backward scattering is found only when $\sigma \neq \sigma'$. The electrons can be distinguished by their spins, and one can tell whether the electron with a given spin transferred small or large momentum to the electron with opposite spin. TOMONAGA and LUTTINGER considered the special case when the large-momentum-transfer processes are neglected and showed that the model can be solved in a very good approximation or even exactly depending on the choice of the linearized spectrum. We will use the name *Tomonaga–Luttinger model* (TL model in short) for the model when only forward-scattering processes are allowed even if the band has a finite bandwidth. Note that if the energy spectrum proposed by LUTTINGER is used, the operators in the interaction should be normal ordered.

The forward-scattering terms can be written in terms of the long-wavelength density components defined in (32.3.10) in the form

$$\mathcal{H}_{\text{int}} = \frac{1}{2L} \sum_{q\sigma\sigma'} g_{2\sigma\sigma'} \Big[n_{+,\sigma}(-q) n_{-,\sigma'}(q) + n_{-,\sigma}(-q) n_{+,\sigma'}(q) \Big] + \frac{1}{2L} \sum_{q\sigma\sigma'} g_{4\sigma\sigma'} \Big[n_{+,\sigma}(-q) n_{+,\sigma'}(q) + n_{-,\sigma}(-q) n_{-,\sigma'}(q) \Big].$$
(32.3.64)

If the boson operators $b_{q\sigma}$ and $b_{q\sigma}^{\dagger}$ are used instead of the densities we have

$$\mathcal{H}_{\text{int}} = \sum_{q\sigma\sigma'} \frac{|q|}{4\pi} g_{2\sigma\sigma'} \left(b^{\dagger}_{q\sigma} b^{\dagger}_{-q\sigma'} + b_{-q\sigma} b_{q\sigma'} \right) + \sum_{q\sigma\sigma'} \frac{|q|}{4\pi} g_{4\sigma\sigma'} \left(b^{\dagger}_{q\sigma} b_{q\sigma'} + b_{-q\sigma} b^{\dagger}_{-q\sigma'} \right).$$
(32.3.65)

The q = 0 term is excluded in the summation. The interaction between the extra particles added to the branches, that is between the q = 0 components of the chiral densities, gives rise to an extra term

$$\mathcal{H}' = \frac{1}{2L} \sum_{\sigma\sigma'} g_{2\sigma\sigma'} \left(\delta N_{+,\sigma} \delta N_{-,\sigma'} + \delta N_{-,\sigma} \delta N_{+,\sigma'} \right) + \frac{1}{2L} \sum_{\sigma\sigma'} g_{4\sigma\sigma'} \left(\delta N_{+,\sigma} \delta N_{+,\sigma'} + \delta N_{-,\sigma} \delta N_{-,\sigma'} \right)$$
(32.3.66)

in the Hamiltonian. The essential feature of the TL model that makes it solvable is the fact that the number of particles of chirality λ and spin σ is conserved separately in each branch, which implies that the particle-number operator $\mathcal{N}_{\lambda\sigma}$ commutes with the total Hamiltonian,

$$\left[\mathcal{N}_{\lambda\sigma},\mathcal{H}\right]_{-} = 0. \qquad (32.3.67)$$

In what follows we will assume that the system is unpolarized, that is, it is invariant under time reversal. The interaction then depends only on the relative orientation of the spins: $g_{i\uparrow\uparrow} = g_{i\downarrow\downarrow}$ and $g_{i\uparrow\downarrow} = g_{i\downarrow\uparrow}$. We will use the notation

$$g_{i\parallel} = g_{i\uparrow\uparrow} = g_{i\downarrow\downarrow}, \qquad g_{i\perp} = g_{i\uparrow\downarrow} = g_{i\downarrow\uparrow} \qquad (32.3.68)$$

for them. The term with $g_{1\parallel}$, which is indistinguishable from forward scattering, could be included by a redefinition of the coupling constants; $g_{2\parallel} - g_{1\parallel}$ would appear instead of $g_{2\parallel}$ in all subsequent formulas.

32.3.6 Excitations in the Interacting Model

The total Hamiltonian of the Tomonaga–Luttinger model is the sum of (32.3.30), (32.3.65), and (32.3.66). The kinetic energy was given in (32.3.51) and (32.3.52) in terms of the charge and spin bosons, the change in the total number of particles, the total spin, as well as the charge and spin currents. When the interaction Hamiltonian is written in terms of the same quantities we have

$$\mathcal{H}_{\text{int}} = \sum_{q} \frac{|q|}{4\pi} g_{2c} \left(b_{qc}^{\dagger} b_{-qc}^{\dagger} + b_{-qc} b_{qc} \right) + \sum_{q} \frac{|q|}{4\pi} g_{2s} \left(b_{qs}^{\dagger} b_{-qs}^{\dagger} + b_{-qs} b_{qs} \right)$$

$$(32.3.69)$$

$$+ \sum_{q} \frac{|q|}{4\pi} g_{4c} \left(b_{qc}^{\dagger} b_{qc} + b_{-qc} b_{-qc}^{\dagger} \right) + \sum_{q} \frac{|q|}{4\pi} g_{4s} \left(b_{qs}^{\dagger} b_{qs} + b_{-qs} b_{-qs}^{\dagger} \right)$$

and

$$\mathcal{H}' = \frac{1}{8L} g_{2c} \left[(\delta N_c)^2 - J_c^2 \right] + \frac{1}{8L} g_{2s} \left[N_s^2 - J_s^2 \right] + \frac{1}{8L} g_{4c} \left[(\delta N_c)^2 + J_c^2 \right] + \frac{1}{8L} g_{4s} \left[N_s^2 + J_s^2 \right], \qquad (32.3.70)$$

where g_{ic} and g_{is} are the spin-symmetric and spin-antisymmetric combinations for the coupling constants defined by

$$g_{2c} = g_{2\parallel} + g_{2\perp}, \qquad g_{2s} = g_{2\parallel} - g_{2\perp}, g_{4c} = g_{4\parallel} + g_{4\perp}, \qquad g_{4s} = g_{4\parallel} - g_{4\perp}.$$
(32.3.71)

The terms with coupling g_{4c} and g_{4s} give rise to a renormalization of the velocity of the charge- and spin-density oscillations, respectively. They can be incorporated in the kinetic energy (32.3.52). The interesting part of the interaction Hamiltonian is the term with coupling constant g_2 .

Even after collecting all the terms, spin-charge separation still holds, that is the full Hamiltonian can be separated into two terms:

$$\mathcal{H} = \mathcal{H}_{\rm c} + \mathcal{H}_{\rm s} \,, \tag{32.3.72}$$

where the first term contains only the charge degrees of freedom,

$$\mathcal{H}_{c} = \sum_{q} \hbar v_{F} (1 + \tilde{g}_{4c}) |q| b_{qc}^{\dagger} b_{qc} + \frac{1}{2} \hbar v_{F} |q| \sum_{q} \tilde{g}_{2c} \left(b_{qc}^{\dagger} b_{-qc}^{\dagger} + b_{-qc} b_{qc} \right) + \frac{\pi \hbar v_{F}}{4L} \left[(1 + \tilde{g}_{4c} + \tilde{g}_{2c}) \left(\delta N_{c} \right)^{2} + (1 + \tilde{g}_{4c} - \tilde{g}_{2c}) J_{c}^{2} \right], \qquad (32.3.73)$$

and the other only the spin degrees of freedom,

$$\mathcal{H}_{s} = \sum_{q} \hbar v_{F} (1 + \tilde{g}_{4s}) |q| b_{qs}^{\dagger} b_{qs} + \frac{1}{2} \hbar v_{F} |q| \sum_{q} \tilde{g}_{2s} (b_{qs}^{\dagger} b_{-qs}^{\dagger} + b_{-qs} b_{qs}) + \frac{\pi \hbar v_{F}}{4L} \left[(1 + \tilde{g}_{4s} + \tilde{g}_{2s}) N_{s}^{2} + (1 + \tilde{g}_{4s} - \tilde{g}_{2s}) J_{s}^{2} \right].$$
(32.3.74)

The shorthand notation

$$\widetilde{g} = \frac{g}{2\pi\hbar v_{\rm F}} \tag{32.3.75}$$

has been used for the dimensionless coupling constants.

The nondiagonal terms appear because the g_2 processes couple the density fluctuations of right- and left-moving electrons. The operators with different chirality quantum numbers are mixed. Both \mathcal{H}_c and \mathcal{H}_s can be diagonalized by a Bogoliubov transformation as shown in Appendix I. Doing it first for the charge part we introduce the operators

$$\beta_{qc} = u_{cq}b_{qc} + v_{cq}b_{-qc}^{\dagger}, \qquad \beta_{qc}^{\dagger} = u_{cq}b_{qc}^{\dagger} + v_{cq}b_{-qc}. \qquad (32.3.76)$$

They obey bosonic commutation rules if

$$u_{cq}^2 - v_{cq}^2 = 1, \qquad (32.3.77)$$

which means that an angle θ_{cq} can be defined via

$$u_{cq} = \cosh \theta_{cq}, \qquad v_{cq} = \sinh \theta_{cq}.$$
 (32.3.78)

The inverse transformation is then

$$b_{qc}^{\dagger} = \beta_{qc}^{\dagger} \cosh \theta_{cq} - \beta_{-qc} \sinh \theta_{cq} , b_{-qc} = \beta_{-qc} \cosh \theta_{cq} - \beta_{qc}^{\dagger} \sinh \theta_{cq} .$$
(32.3.79)

Inserting these expressions in the Hamiltonian the nondiagonal terms vanish if

$$-\left(1+\widetilde{g}_{4c}\right)\cosh\theta_{cq}\sinh\theta_{cq}+\frac{1}{2}\widetilde{g}_{2c}\left(\cosh^{2}\theta_{cq}+\sinh^{2}\theta_{cq}\right)=0.$$
 (32.3.80)

The solution of this equation is

$$\tanh 2\theta_{cq} = \frac{\widetilde{g}_{2c}}{1 + \widetilde{g}_{4c}}.$$
(32.3.81)

The diagonal terms of the charge part of the Hamiltonian give

$$\mathcal{H}_{\rm c} = \sum_{q} \hbar u_{\rm c} |q| \beta_{qc}^{\dagger} \beta_{qc} + \frac{\pi \hbar}{4L} \left[v_{N_{\rm c}} \left(\delta N_{\rm c} \right)^2 + v_{J_{\rm c}} J_{\rm c}^2 \right]$$
(32.3.82)

with

$$u_{\rm c} = v_{\rm F} \sqrt{\left(1 + \tilde{g}_{\rm 4c}\right)^2 - \left(\tilde{g}_{\rm 2c}\right)^2}$$
(32.3.83)

and

$$v_{N_{\rm c}} = v_{\rm F} \left(1 + \tilde{g}_{4{\rm c}} + \tilde{g}_{2{\rm c}} \right), \qquad v_{J_{\rm c}} = v_{\rm F} \left(1 + \tilde{g}_{4{\rm c}} - \tilde{g}_{2{\rm c}} \right).$$
(32.3.84)

Note that the three velocities are not independent, the relationship

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$$u_{\rm c}^2 = v_{N_{\rm c}} \, v_{J_{\rm c}} \tag{32.3.85}$$

has to be satisfied. Introducing the notation

$$K_{\rm c} = \frac{u_{\rm c}}{v_{N_{\rm c}}} = \frac{v_{J_{\rm c}}}{u_{\rm c}} = \sqrt{\frac{1 + \tilde{g}_{4\rm c} - \tilde{g}_{2\rm c}}{1 + \tilde{g}_{4\rm c} + \tilde{g}_{2\rm c}}}$$
(32.3.86)

the Hamiltonian takes the form

$$\mathcal{H}_{\rm c} = \sum_{q} \hbar u_{\rm c} |q| \beta_{qc}^{\dagger} \beta_{qc} + \frac{\pi \hbar}{4L} \left[\frac{u_{\rm c}}{K_{\rm c}} \left(\delta N_{\rm c} \right)^2 + u_{\rm c} K_{\rm c} J_{\rm c}^2 \right].$$
(32.3.87)

In a completely analogous fashion the spin part can be written as

$$\mathcal{H}_{\rm s} = \sum_{q} \hbar u_{\rm s} |q| \beta_{q{\rm s}}^{\dagger} \beta_{q{\rm s}} + \frac{\pi \hbar}{4L} \left(v_{N_{\rm s}} N_{\rm s}^2 + v_{J_{\rm s}} J_{\rm s}^2 \right), \qquad (32.3.88)$$

where

$$u_{\rm s} = v_{\rm F} \sqrt{\left(1 + \tilde{g}_{4\rm s}\right)^2 - \left(\tilde{g}_{2\rm s}\right)^2}$$
 (32.3.89)

and

$$v_{N_{\rm s}} = v_{\rm F} \left(1 + \tilde{g}_{4{\rm s}} + \tilde{g}_{2{\rm s}} \right), \qquad v_{J_{\rm s}} = v_{\rm F} \left(1 + \tilde{g}_{4{\rm s}} - \tilde{g}_{2{\rm s}} \right).$$
(32.3.90)

The relationship between the velocities is now

$$u_{\rm s}^2 = v_{N_{\rm s}} \, v_{J_{\rm s}} \,. \tag{32.3.91}$$

Introducing the quantity

$$K_{\rm s} = \frac{u_{\rm s}}{v_{N_{\rm s}}} = \frac{v_{J_{\rm s}}}{u_{\rm s}} = \sqrt{\frac{1 + \tilde{g}_{4\rm s} - \tilde{g}_{2\rm s}}{1 + \tilde{g}_{4\rm s} + \tilde{g}_{2\rm s}}},\qquad(32.3.92)$$

we have

$$\mathcal{H}_{\rm s} = \sum_{q} \hbar u_{\rm s} |q| \beta_{q{\rm s}}^{\dagger} \beta_{q{\rm s}} + \frac{\pi \hbar}{4L} \left(\frac{u_{\rm s}}{K_{\rm s}} N_{\rm s}^2 + u_{\rm s} K_{\rm s} J_{\rm s}^2 \right).$$
(32.3.93)

The Hamiltonian of the interacting TL model is identical to that of a twocomponent noninteracting boson gas. One component corresponds to charge excitations, the other to spin excitations of the Fermi system. Thus spincharge separation holds even in the interacting TL model. There are three kinds of excitations in both sectors. The bosonic charge-density and spindensity fluctuations propagate with velocities u_c and u_s , respectively. The other excitations are topological in nature; they correspond to adding δN_c particles or generating a conserved current J_c in the charge sector and to creating an imbalance N_s in the number of spin-up and spin-down particles or generating a spin current J_s in the spin sector. The velocities of these excitations, v_{N_c} and v_{J_c} in the charge sector, v_{N_s} and v_{J_s} in the spin sector, are not independent. They satisfy relations (32.3.85) and (32.3.91).

The separation of charge and spin degrees of freedom taken together with the fact that charge and spin fluctuations propagate with different velocities has interesting consequences. For example, if a particle is added to the system at the origin and the expectation value of the charge density is measured at a later time, the propagation is determined entirely by the charge bosons. The wavefunction of the state with an extra right-moving particle at the origin at t = 0 can be given in terms of the field operator $\hat{\psi}^{\dagger}_{+,\sigma}(0,0)$ defined in (L.2.98) as $\hat{\psi}^{\dagger}_{+,\sigma}(0,0)|\Psi_{\rm FS}\rangle$. The operator of the particle density is

$$n(x,t) = \sum_{\sigma} \hat{\psi}^{\dagger}_{\sigma}(x,t) \hat{\psi}_{\sigma}(x,t)$$

=
$$\sum_{\sigma} \left[\hat{\psi}^{\dagger}_{+,\sigma}(x,t) \hat{\psi}_{+,\sigma}(x,t) + \hat{\psi}^{\dagger}_{-,\sigma}(x,t) \hat{\psi}_{-,\sigma}(x,t) \right].$$
 (32.3.94)

A straightforward calculation using the techniques developed in Appendix L yields

$$\left\langle \Psi_{\rm FS} | \hat{\psi}_{+,\sigma}(0,0) n(x,t) \hat{\psi}_{+,\sigma}^{\dagger}(0,0) | \Psi_{\rm FS} \right\rangle \propto \delta(x-u_{\rm c}t) \,. \tag{32.3.95}$$

We would get $\delta(x + u_c t)$ if a left-moving particle is added to the system at the origin. Similar calculation for the expectation value of the spin density

$$\sigma(x,t) = \hat{\psi}^{\dagger}_{+,\uparrow}(x,t)\hat{\psi}_{+,\uparrow}(x,t) - \hat{\psi}^{\dagger}_{+,\downarrow}(x,t)\hat{\psi}_{+,\downarrow}(x,t) + \hat{\psi}^{\dagger}_{-,\uparrow}(x,t)\hat{\psi}_{-,\uparrow}(x,t) - \hat{\psi}^{\dagger}_{-,\downarrow}(x,t)\hat{\psi}_{-,\downarrow}(x,t)$$
(32.3.96)

gives

$$\left\langle \Psi_{\rm FS} | \hat{\psi}_{+,\sigma}(0,0)\sigma(x,t)\hat{\psi}_{+,\sigma}^{\dagger}(0,0) | \Psi_{\rm FS} \right\rangle \propto \delta(x-u_{\rm s}t) \,. \tag{32.3.97}$$

Later we will see more generally that only the bosons with velocity u_c contribute to those quantities that depend on long-wavelength charge fluctuations. Similarly the bosons propagating with velocity u_s contribute to those properties that are related to long-wavelength spin fluctuations.

In a finite system of length L, where q is quantized in units of $2\pi/L$, the energy eigenvalues are given by

$$E = L\varepsilon_{0} + \hbar u_{c} \frac{2\pi}{L} \left(n_{c,+} + n_{c,-} + \Delta_{c,+} + \Delta_{c,-} \right) + \hbar u_{s} \frac{2\pi}{L} \left(n_{s,+} + n_{s,-} + \Delta_{s,+} + \Delta_{s,-} \right), \qquad (32.3.98)$$

where ε_0 is the ground-state energy per site in an infinite system, $n_{\rm c,\pm}$ and $n_{\rm s,\pm}$ are integers, and

$$\begin{aligned} \Delta_{\mathrm{c},\pm} &= \frac{1}{16} \left(\frac{1}{\sqrt{K_{\mathrm{c}}}} \delta N_{\mathrm{c}} \pm \sqrt{K_{\mathrm{c}}} J_{\mathrm{c}} \right)^2, \\ \Delta_{\mathrm{s},\pm} &= \frac{1}{16} \left(\frac{1}{\sqrt{K_{\mathrm{s}}}} N_{\mathrm{s}} \pm \sqrt{K_{\mathrm{s}}} J_{\mathrm{s}} \right)^2. \end{aligned}$$
(32.3.99)

The momentum of the state can be written, using (32.3.59), with the same parameters in the form

$$P = \hbar k_{\rm F} J_{\rm c} + \hbar \frac{2\pi}{L} \left(n_{\rm c,+} - n_{\rm c,-} + \Delta_{\rm c,+} - \Delta_{\rm c,-} \right) + \hbar \frac{2\pi}{L} \left(n_{\rm s,+} - n_{\rm s,-} + \Delta_{\rm s,+} - \Delta_{\rm s,-} \right).$$
(32.3.100)

The excitation spectrum of the TL model exhibits a similar tower structure as in the noninteracting case. The role of the interaction is to renormalize the values of the parameters K_c , K_s , u_c , and u_s . The parameters u_c and u_s modify the opening angle of the towers, while K_c and K_s shift the positions of the tips of the towers. As we will see, the latter determine the critical exponents of the correlation functions which have power-law behavior even in the interacting model, though the exponents are not universal; they depend on the coupling strengths via K_c and K_s .

Note that although the noninteracting eigenstates of the one-dimensional model are particlelike, the low-energy excitations of the interacting system are collective bosonic density fluctuations. The one-to-one correspondence between the interacting and noninteracting eigenstates is destroyed, so that the system described by the TL model is not a normal Fermi liquid. Nevertheless, the new features do not show up in the thermodynamic behavior. They can be seen, however, in the correlation functions.

32.3.7 Thermodynamic Properties and Correlation Functions

The low-temperature properties of the Tomonaga–Luttinger model are best calculated in the boson representation. The heat capacity is linear in temperature owing to the gapless linear dispersion relation. It follows from (32.3.38) that the heat capacity per unit length of a two-component boson gas propagating with velocity u is

$$c_V = \frac{2\pi}{3} \frac{k_{\rm B}^2 T}{\hbar u} \,. \tag{32.3.101}$$

Since the two components propagate with different velocities in the interacting model, the heat capacity per unit length of the TL model is

$$c_V = \frac{\pi}{3} \frac{k_{\rm B}^2 T}{\hbar u_{\rm c}} + \frac{\pi}{3} \frac{k_{\rm B}^2 T}{\hbar u_{\rm s}} \,. \tag{32.3.102}$$

Writing it as $c_V(T) = \gamma T$ we have

$$\gamma/\gamma_0 = \frac{1}{2} \left(\frac{v_{\rm F}}{u_{\rm c}} + \frac{v_{\rm F}}{u_{\rm s}} \right), \qquad (32.3.103)$$

where

$$\gamma_0 = \frac{\pi^2}{3} k_{\rm B}^2 \rho(\varepsilon_{\rm F}) = \frac{2\pi}{3} \frac{k_{\rm B}^2}{\hbar v_{\rm F}} \,. \tag{32.3.104}$$

A static external magnetic field disturbs only the spin sector. It couples to $N_{\rm s}$ creating an imbalance in the number of spin-up and spin-down particles. At T = 0, where no bosons are excited, the energy in the presence of the field is

$$E = \frac{\pi\hbar}{4L} v_{N_{\rm s}} N_{\rm s}^2 - \frac{1}{2} g_{\rm e} \mu_{\rm B} \mu_0 N_{\rm s} H. \qquad (32.3.105)$$

The value of $N_{\rm s}$ is obtained from the minimum of this expression. Inserting the minimum value into the expression for the magnetic moment per unit length,

$$M = \frac{1}{2L} g_{\rm e} \mu_{\rm B} N_{\rm s} = \left(\frac{1}{2} g_{\rm e} \mu_{\rm B}\right)^2 \mu_0 \frac{2}{\pi \hbar v_{N_{\rm s}}} H, \qquad (32.3.106)$$

from which we get

$$\chi = \frac{1}{4} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \frac{2}{\pi \hbar v_{N_{\rm s}}}$$
(32.3.107)

for the susceptibility. The response to a static field is similar to that of a normal Fermi liquid: the susceptibility is multiplied by a factor depending on the interactions. Compared to the noninteracting model

$$\frac{\chi}{\chi_0} = \frac{v_{\rm F}}{v_{N_{\rm s}}} = \frac{v_{\rm F}}{u_{\rm s}} K_{\rm s} \,. \tag{32.3.108}$$

The Wilson ratio in the TL model is then

$$R_{\rm W} = \frac{\chi}{\gamma} \frac{\gamma_0}{\chi_0} = \frac{2u_{\rm c}}{u_{\rm c} + u_{\rm s}} K_{\rm s} \,. \tag{32.3.109}$$

The dynamical response and the corresponding correlation functions behave drastically differently from normal Fermi liquids. In order to show that, we consider the variations of the particle (charge) density due to an external scalar potential, which can be given according to linear response theory by the density–density response function defined in (29.1.29). In the one-dimensional case we have

$$\Pi(q,\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{L} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \left\langle \left[n(q,t), n(-q,0) \right]_{-} \right\rangle, \qquad (32.3.110)$$

where

$$n(q) = \sum_{k} \left(c_{k\uparrow}^{\dagger} c_{k+q\uparrow} + c_{k\downarrow}^{\dagger} c_{k+q\downarrow} \right).$$
(32.3.111)

Similarly, the variations of the spin density due to an external magnetic field can be given by the longitudinal response function $\Sigma_{\parallel}(q,\omega)$ defined in (29.8.19). The corresponding quantity in the one-dimensional model is

$$\Sigma(q,\omega) = \frac{\mathrm{i}}{\hbar} \frac{1}{L} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \left\langle \left[\sigma(q,t), \sigma(-q,0) \right]_{-} \right\rangle, \qquad (32.3.112)$$

where

$$\sigma(q) = \sum_{k} \left(c_{k\uparrow}^{\dagger} c_{k+q\uparrow} - c_{k\downarrow}^{\dagger} c_{k+q\downarrow} \right)$$
(32.3.113)

is the Fourier transform of the difference between the densities of particles with \uparrow and \downarrow spins.

In these expressions the operators $c_{k\sigma}$ and $c_{k\sigma}^{\dagger}$ refer to both the rightand left-moving particles. To calculate the response functions in the longwavelength limit, for small q values, it is convenient to consider separately the chiral densities of the right- and the left-moving particles and to define the quantities

$$\Pi_{\lambda\sigma\lambda'\sigma'}(q,t) = -\frac{\mathrm{i}}{\hbar} \frac{1}{L} \theta(t) \left\langle \left[n_{\lambda\sigma}(q,t), n_{\lambda'\sigma'}(-q,0) \right]_{-} \right\rangle.$$
(32.3.114)

They will be calculated using the equation-of-motion method. The Hamiltonian of the TL model can be written in a simple form in terms of the chiral densities and the commutator of the densities with the Hamiltonian gives

$$\begin{bmatrix} \mathcal{H}, n_{\lambda\sigma}(q, t) \end{bmatrix}_{-} = -\lambda \hbar v_{\mathrm{F}} q n_{\lambda\sigma}(q, t) - \lambda \sum_{\sigma'} \frac{g_{2\sigma\sigma'}}{2\pi} q n_{-\lambda\sigma'}(q, t) - \lambda \sum_{\sigma'} \frac{g_{4\sigma\sigma'}}{2\pi} q n_{\lambda\sigma'}(q, t) .$$
(32.3.115)

Using this in the equation of motion for the frequency Fourier transform of $\Pi_{\lambda\sigma\lambda'\sigma'}(q,t)$ we have

$$(\hbar\omega - \lambda\hbar v_{\rm F}q) \Pi_{\lambda\sigma\lambda'\sigma'}(q,\omega) = \frac{\lambda q}{2\pi} \delta_{\lambda\lambda'} \,\delta_{\sigma\sigma'} + \lambda \sum_{\sigma''} \frac{g_{2\sigma\sigma''}}{2\pi} q \Pi_{-\lambda\sigma''\lambda'\sigma'}(q,\omega) + \lambda \sum_{\sigma''} \frac{g_{4\sigma\sigma''}}{2\pi} q \Pi_{\lambda\sigma''\lambda'\sigma'}(q,\omega) \,. \tag{32.3.116}$$

Taking the spin-symmetric and spin-antisymmetric combinations corresponding to the charge and spin densities defined in (32.3.45) and (32.3.46), respectively, the charge-density and spin-density response functions are separated. We give here the result for the charge-density response:

$$(\hbar\omega - \lambda\hbar v_{\rm F}q) \Pi_{\lambda c\lambda' c}(q,\omega) = \frac{\lambda q}{2\pi} \delta_{\lambda\lambda'} + \lambda \frac{g_{2c}}{2\pi} q \Pi_{-\lambda c\lambda' c}(q,\omega) + \lambda \frac{g_{4c}}{2\pi} q \Pi_{\lambda c\lambda' c}(q,\omega) .$$
(32.3.117)
The solution is

$$\begin{split} \Pi_{+,c,+,c}(q,\omega) &= \frac{1}{2\pi} \frac{q [\hbar \omega + (\hbar v_{\rm F} + g_{4c}/2\pi)q]}{(\hbar \omega)^2 - (\hbar u_c q)^2} ,\\ \Pi_{+,c,-,c}(q,\omega) &= -\frac{1}{2\pi} \frac{(g_{2c}/\pi)q^2}{(\hbar \omega)^2 - (\hbar u_c q)^2} ,\\ \Pi_{-,c,-,c}(q,\omega) &= -\frac{1}{2\pi} \frac{q [\hbar \omega - (\hbar v_{\rm F} + g_{4c}/2\pi)q]}{(\hbar \omega)^2 - (\hbar u_c q)^2} ,\\ \Pi_{-,c,+,c}(q,\omega) &= -\frac{1}{2\pi} \frac{(g_{2c}/\pi)q^2}{(\hbar \omega)^2 - (\hbar u_c q)^2} , \end{split}$$
(32.3.118)

and the total density-density response is given by

$$\Pi(q,\omega) = \frac{2}{\pi\hbar} \frac{v_{J_c} q^2}{\omega^2 - u_c^2 q^2}.$$
(32.3.119)

This response function, which is related to the dielectric function, is entirely determined by the spin-symmetric excitations, the charge bosons, propagating with velocity u_c .

Similar calculation for the spin-antisymmetric combinations gives

$$\Sigma(q,\omega) = -\frac{2}{\pi\hbar} \frac{v_{J_{\rm s}} q^2}{\omega^2 - u_{\rm s}^2 q^2}$$
(32.3.120)

for the spin density–spin density response function. Only the spin bosons propagating with velocity u_s contribute to this quantity. Its relation to the longitudinal dynamical susceptibility is given by

$$\chi_{\parallel}(q,\omega) = \frac{1}{4}g_{\rm e}^2\mu_{\rm B}^2\mu_0\Sigma(q,\omega)\,. \tag{32.3.121}$$

In the static limit $\omega \to 0$ we find

$$\chi_{\parallel} = \frac{1}{4} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \frac{2v_{J_{\rm s}}}{\pi \hbar u_{\rm s}^2} = \frac{1}{4} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \frac{2}{\pi \hbar v_{N_{\rm s}}} = \frac{1}{4} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0 \frac{2}{\pi \hbar u_{\rm s}} K_{\rm s} \qquad (32.3.122)$$

reproducing (32.3.107).

We have seen in Chapter 29 that the $q = 2k_{\rm F}$ component of the polarization bubble $\Pi_0(q, \omega)$ exhibits a logarithmic singularity in one dimension. This quantity describes the propagation of an electron-hole pair where the particle moves to the right and the hole to the left or vice versa. A few low-order diagrams illustrating the propagation of such a pair are depicted in Fig. 32.12.

Unlike in the RPA, all diagrams are irreducible since large-momentumtransfer processes are absent in the model. The polarization bubble for large-momentum-transfer can therefore be given in terms of the renormalized propagators of the left- and right-moving particles, and the renormalized large-momentum-transfer vertex as shown in Fig. 32.13.



Fig. 32.12. Diagrams illustrating the propagation of an electron-hole pair with total momentum $2k_{\rm F}$. Right-moving fermions are denoted by solid lines and left-moving fermions by dashed lines



Fig. 32.13. Large-momentum-transfer polarization bubble. The heavy lines denote renormalized propagators with self-energy corrections

This vertex satisfies an exact Ward identity⁹ relating it to the Green functions; thus, the response functions of the TL model can be calculated exactly in real-space and time representation. The equation-of-motion method can also be used to calculate the propagator of such electron-hole pairs, or more generally the time evolution of a state where particles are added to or removed from the various branches. Without going into the details of this rather tedious calculation we only list the result. When a right-moving electron and a left-moving hole are added to the system at the origin at time t = 0 and we let them propagate to position x till time t, the asymptotic form of the propagator is

$$N(x,t) \propto \frac{1}{(x^2 - u_{\rm c}^2 t^2)^{K_{\rm c}/2} (x^2 - u_{\rm s}^2 t^2)^{K_{\rm s}/2}}.$$
 (32.3.123)

When the right-moving particle and the left-moving hole have different spin orientations, their propagator is

$$\chi(x,t) \propto \frac{\cos(2k_{\rm F}x)}{(x^2 - u_{\rm c}^2 t^2)^{K_{\rm c}/2} (x^2 - u_{\rm s}^2 t^2)^{1/(2K_{\rm s})}} \,. \tag{32.3.124}$$

⁹ J. C. WARD, 1950.

These are special cases of a more general expression that can be derived by using the conformal invariance of the Luttinger model that shows up in the tower structure of the excitation spectrum or by using the field-theoretic formulation of Luttinger liquids discussed in Appendix L. Taking an operator \mathcal{O} that changes the number of particles with chirality $\lambda = \pm 1$ and spin σ by $\delta N_{\pm,\sigma}$ at the origin at time t = 0 and studying the propagation of these particles to space-time position x, t we find

$$\left\langle \mathcal{O}(x,t)\mathcal{O}^{\dagger}(0,0)\right\rangle \sim \frac{\mathrm{e}^{-\mathrm{i}k_{\mathrm{F}}J_{\mathrm{c}}x}}{(x-u_{\mathrm{c}}t)^{2\Delta_{\mathrm{c},+}}(x+u_{\mathrm{c}}t)^{2\Delta_{\mathrm{c},-}}(x-u_{\mathrm{s}}t)^{2\Delta_{\mathrm{s},+}}(x+u_{\mathrm{s}}t)^{2\Delta_{\mathrm{s},-}}}(32.3.125)$$

where $\Delta_{c,\pm}$ and $\Delta_{s,\pm}$ are the scaling dimensions introduced in (32.3.99). In the special case when a right-moving particle and a left-moving hole is added to the system with the same spin, $\delta N_c = N_s = 0$, $J_c = 2$, and $J_s = \pm 2$ depending on the orientation of the spins. This gives precisely the exponents in (32.3.123). When the particle and the hole have opposite spins, $\delta N_c = J_s = 0$, $J_c = 2$, and $N_s = \pm 2$, and we recover the expression given in (32.3.124) for the susceptibility.

32.3.8 Absence of the Fermi Edge

As a special example we study the propagation of an extra particle added to the TL model. This propagation is best described by the causal Green functions

$$G_{+,\sigma}(k,t-t') = -\frac{\mathrm{i}}{\hbar} \left\langle T\left\{c_{k_{\mathrm{F}}+k,\sigma}(t)c_{k_{\mathrm{F}}+k,\sigma}^{\dagger}(t')\right\}\right\rangle$$
(32.3.126)

or

$$G_{-,\sigma}(k,t-t') = -\frac{i}{\hbar} \Big\langle T \Big\{ d_{-k_{\rm F}+k,\sigma}(t) d^{\dagger}_{-k_{\rm F}+k,\sigma}(t') \Big\} \Big\rangle,$$
(32.3.127)

where T is the time-ordering operator. When taking the time derivative of the Green function, the commutator with the Hamiltonian of the TL model leads to a higher order Green function

$$F_{+,\sigma,\lambda',\sigma'}(k,q,t-t',t'') = -\frac{\mathrm{i}}{\hbar} \Big\langle T \big\{ c_{k_{\mathrm{F}}+k+q\sigma}(t) n_{\lambda'\sigma'}(q,t'') c^{\dagger}_{k_{\mathrm{F}}+k\sigma}(t') \big\} \Big\rangle.$$
(32.3.128)

When the equation of motion is written for this new Green function by taking the derivative with respect to t'', no further higher order Green functions appear owing to the special choice of the interactions in the TL model. The system of equations closes and can be solved in space-time representation. We get

$$G_{\pm}(x,t) \sim \frac{\mathrm{e}^{\pm \mathrm{i}k_{\mathrm{F}}x}}{\sqrt{(x \mp u_{\mathrm{c}}t)(x \mp u_{\mathrm{s}}t)}} \left(x^{2} - u_{\mathrm{c}}^{2}t^{2}\right)^{-2\Delta_{\mathrm{c}}} \left(x^{2} - u_{\mathrm{s}}^{2}t^{2}\right)^{-2\Delta_{\mathrm{s}}},$$
(32.3.129)

where

$$\Delta_{\rm c} = \frac{1}{16} \left(\frac{1}{\sqrt{K_{\rm c}}} - \sqrt{K_{\rm c}} \right)^2 = \frac{(K_{\rm c} - 1)^2}{16K_{\rm c}},$$

$$\Delta_{\rm s} = \frac{1}{16} \left(\frac{1}{\sqrt{K_{\rm s}}} - \sqrt{K_{\rm s}} \right)^2 = \frac{(K_{\rm s} - 1)^2}{16K_{\rm s}}.$$
(32.3.130)

Precisely the same expression would be obtained by applying the general expression (32.3.125) to the present case, that is when the field operator of fermions is substituted for $\mathcal{O}(x,t)$. When a right-moving fermion is added to the system, either $\delta N_{+,\uparrow} = +1$ or $\delta N_{+,\downarrow} = +1$, and consequently

$$\delta N_{\rm c} = J_{\rm c} = N_{\rm s} = J_{\rm s} = +1 \tag{32.3.131}$$

or

$$\delta N_{\rm c} = J_{\rm c} = -N_{\rm s} = -J_{\rm s} = +1.$$
 (32.3.132)

In both cases

$$\Delta_{c,+} = \Delta_{c} + \frac{1}{4} , \qquad \Delta_{c,-} = \Delta_{c} , \Delta_{s,+} = \Delta_{s} + \frac{1}{4} , \qquad \Delta_{s,-} = \Delta_{s} .$$
 (32.3.133)

On the other hand, when a left-moving fermion is added to the system, either $\delta N_{-,\uparrow} = +1$ or $\delta N_{-,\downarrow} = +1$, and therefore

$$\delta N_{\rm c} = -J_{\rm c} = N_{\rm s} = -J_{\rm s} = +1 \tag{32.3.134}$$

or

$$\delta N_{\rm c} = -J_{\rm c} = -N_{\rm s} = J_{\rm s} = +1.$$
 (32.3.135)

Thus we have

$$\Delta_{c,+} = \Delta_{c}, \qquad \Delta_{c,-} = \Delta_{c} + \frac{1}{4},
\Delta_{s,+} = \Delta_{s}, \qquad \Delta_{s,-} = \Delta_{s} + \frac{1}{4}.$$
(32.3.136)

Substituting these expressions for the exponents in (32.3.125) we in fact recover (32.3.129).

The result that the Green function has a cut and not a pole is a clear indication that the system described by the TL model is not a normal Fermi liquid. The absence of poles implies the absence of fermionic quasiparticles; the bosonic fluctuations describe the full low-energy spectrum. The spectral function $A(k, \omega)$ defined in (K.1.39), which is proportional to the imaginary part of the Green function, has a Lorentzian peak in normal Fermi liquids becoming an infinitely sharp Dirac delta for particles at the Fermi surface. The energy and the lifetime of the quasiparticles are obtained from the position and the width of this peak. Instead of that the spectral function of the TL model exhibits power-law singularities. At the Fermi momentum, as a function of ω we have

$$A_{\sigma}(k_{\rm F},\omega) \propto |\omega|^{4(\Delta_{\rm c}+\Delta_{\rm s})-1}, \qquad (32.3.137)$$

while for wave numbers different from $k_{\rm F}$, singularities may appear at $\omega = \pm u_{\rm c}k$ and $\omega = \pm u_{\rm s}k$. For example when $u_{\rm c} > u_{\rm s}$ we find

$$A_{\sigma}(k,\omega) \propto \begin{cases} |\omega - u_{\rm c}k|^{2\Delta_{\rm c} + 4\Delta_{\rm s} - 1/2} & \text{for } \omega \approx u_{\rm c}k \,, \\ \theta(\omega - u_{\rm s}k) (\omega - u_{\rm s}k)^{4\Delta_{\rm c} + 2\Delta_{\rm s} - 1/2} & \text{for } \omega \approx u_{\rm s}k \,, \\ \theta(-\omega - u_{\rm c}k) (-\omega - u_{\rm c}k)^{2\Delta_{\rm c} + 4\Delta_{\rm s}} & \text{for } -\omega \approx u_{\rm s}k \,. \end{cases}$$

$$(32.3.138)$$

Typical spectral functions of the Green function $G_{+,\sigma}(k,\omega)$ are shown in Fig. 32.14. The largest weight to the spectral function comes from the range between $\omega = u_{\rm s}k$ and $\omega = u_{\rm c}k$.



Fig. 32.14. Spectral function for right-moving fermions in the TL model as a function of ω for (a) k = 0 and (b) k > 0

Knowing the Green function we can calculate the momentum distribution function

$$\langle n_{k\sigma} \rangle = \langle \Psi_0 | c_{k\sigma}^{\dagger} c_{k\sigma} | \Psi_0 \rangle , \qquad (32.3.139)$$

which exhibits a discontinuous jump at $k_{\rm F}$ in normal Fermi liquids, as seen in Fig. 28.3. Instead of that a power-law-like behavior is found in the neighborhood of $k_{\rm F}$ in the TL model:

$$\langle n_{k\sigma} \rangle \sim \frac{1}{2} - C |k - k_{\rm F}|^{4(\Delta_{\rm c} + \Delta_{\rm s})} {\rm sgn}(k - k_{\rm F}) \,.$$
 (32.3.140)

This is shown in Fig. 32.15. The vanishing of the Fermi edge implies that no Fermi surface can be defined in the TL model. The single-particle density of states, which is related to the momentum integral of the imaginary part of the Green function, can also be evaluated. It vanishes at the chemical potential and varies as a power law,

$$\rho(\varepsilon) \propto |\varepsilon - \varepsilon_{\rm F}|^{4(\Delta_{\rm c} + \Delta_{\rm s})}. \tag{32.3.141}$$



Fig. 32.15. Momentum distribution function in the TL model

32.4 The Hubbard Model in One Dimension

The Hubbard model, as one of the simplest models of interacting electrons, plays an important role in the study of correlated systems. The onedimensional model has the additional feature that it is the physically most interesting example of Luttinger-liquid behavior. Assuming that the electrons can hop only to nearest-neighbor sites, it is written conventionally¹⁰ in the form

$$\mathcal{H} = -t \sum_{i\sigma} (c_{i,\sigma}^{\dagger} c_{i+1,\sigma} + c_{i+1,\sigma}^{\dagger} c_{i,\sigma}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} .$$
(32.4.1)

When the Coulomb interaction is omitted, the single-particle spectrum is

$$\varepsilon(k_j) = -2t \cos k_j a \,, \tag{32.4.2}$$

where k_j can take the values $(2\pi/L)n_j$ in a chain of length L = Na with integer n_j . The many-body state of the system of N_e electrons can be characterized by giving the k_j quantum numbers of the occupied one-particle states. The unperturbed energy is

$$E = \sum_{j=1}^{N_{\rm e}} \varepsilon(k_j) = -2t \sum_{j=1}^{N_{\rm e}} \cos k_j a , \qquad (32.4.3)$$

where the summation goes over the occupied states. In the ground state, where the electrons fill the states with both spin orientations equally, the region $-k_{\rm F} < k < k_{\rm F}$ is filled in reciprocal space with

$$k_{\rm F} = \frac{2\pi}{L} \frac{N_{\rm e}}{4} = \frac{\pi}{2a} n_{\rm e} \,.$$
 (32.4.4)

The Fermi velocity is readily obtained from this expression:

$$\hbar v_{\rm F} = 2ta \sin k_{\rm F} a = 2ta \sin \left(\frac{1}{2}\pi n_{\rm e}\right)$$
 (32.4.5)

In what follows, for the sake of simplicity, the lattice constant will be taken to be unity. The length L and the number of sites N will be used interchangeably.

¹⁰ Unlike in (28.1.42), the notation U is used in this chapter instead of $U_{\rm H}$ for the on-site Coulomb repulsion.

32.4.1 Bethe-Ansatz Solution

Just as for the spin-1/2 Heisenberg model, the energy spectrum of the Hubbard model can be solved exactly by the Bethe ansatz in one dimension. We can follow the procedure outlined in Chapter 15 with the additional difficulty that besides the number of particles with spin \downarrow , N_{\downarrow} , the total number of electrons, $N_{\rm e} = N_{\downarrow} + N_{\uparrow}$, can be arbitrary and an extra quantum number appears. We will assume that the number of electrons is less than or equal to the number of lattice sites, the system is at most half filled, $N_{\rm e} \leq N$, and at most half of the electrons have their spins oriented down, $N_{\downarrow} \leq N_{\uparrow}$. The opposite cases can be treated by considering holes instead of electrons or reversing all spins.

The total wavefunction can be written in second quantization as the linear combination of terms like

$$c_{l_{1}\downarrow}^{\dagger}c_{l_{2}\downarrow}^{\dagger}\ldots c_{l_{N_{\downarrow}\downarrow}}^{\dagger}c_{l_{N_{\downarrow}+1}\uparrow}^{\dagger}c_{l_{N_{\downarrow}+2}\uparrow}^{\dagger}\ldots c_{l_{N_{e}\uparrow}}^{\dagger}|0\rangle, \qquad (32.4.6)$$

where $1 \leq l_1 < l_2 < \cdots < l_{N_{\downarrow}} \leq N$ and $1 \leq l_{N_{\downarrow}+1} < l_{N_{\downarrow}+2} < \cdots < l_{N_e} \leq N$, that is the sites occupied by particles with \downarrow and \uparrow spins are ordered separately in increasing order of the site index. The coefficients f that appear in the wavefunction

$$\Psi = \sum_{l_1} \sum_{l_2} \cdots \sum_{l_{N_e}} f(l_1, l_2, \dots l_{N_e}) c^{\dagger}_{l_1 \downarrow} c^{\dagger}_{l_2 \downarrow} \dots c^{\dagger}_{l_{N_{\downarrow}} \downarrow}$$

$$\times c^{\dagger}_{l_{N_{\downarrow}+1}\uparrow} c^{\dagger}_{l_{N_{\downarrow}+2}\uparrow} \dots c^{\dagger}_{l_{N_e}\uparrow} |0\rangle$$
(32.4.7)

are determined from the requirement that this wavefunction be an eigenfunction of the Hubbard Hamiltonian. Operating with the Hamiltonian on this function a coupled system of equations is obtained:

$$-t \sum_{i=1}^{N_{\rm e}} \left[f(l_1, \dots, l_i + 1, \dots, l_{N_{\rm e}}) + f(l_1, \dots, l_i - 1, \dots, l_{N_{\rm e}}) \right] + U \left[\sum_{i < j} \delta_{l_i, l_j} \right] f(l_1, \dots, l_{N_{\rm e}}) = E f(l_1, \dots, l_{N_{\rm e}}) .$$
(32.4.8)

This has to be solved with a periodic boundary condition and subject to the constraint that the total wavefunction has to be antisymmetric under the exchange of any two particles. For this the amplitude $f(l_1, l_2, \ldots, l_{N_e})$ which originally was defined in the segment satisfying $1 \leq l_1 < l_2 < \cdots < l_{N_{\perp}} \leq N$ and $1 \leq l_{N_{\perp}+1} < l_{N_{\perp}+2} < \cdots < l_{N_e} \leq N$ has to be extended to all possible configurations of the occupied lattice sites.

Consider first a dilute electron system where the spins of all electrons have the same \uparrow orientation. None of the sites is doubly occupied and we assume that the singly occupied sites are surrounded by empty sites. Electrons can

then freely hop and the coefficient f can be written as a linear combination of the product of plane waves,

$$f(l_1, \dots, l_{N_e}) = \sum_P A(P) \exp\left[i(k_{P1}l_1 + \dots + k_{PN_e}l_{N_e})\right], \qquad (32.4.9)$$

where $P = \{P1, P2, \ldots, PN_e\}$ is a permutation of the numbers $\{1, 2, \ldots, N_e\}$. The state of the system is characterized by $N_e = N_{\uparrow}$ wave numbers and the summation goes over all possible permutations of the wave numbers. The energy takes the same form,

$$E = -2t \sum_{j=1}^{N_{\rm e}} \cos k_j \,, \qquad (32.4.10)$$

as that of the noninteracting system, though the values of the wave numbers, just as in the Bethe-ansatz solution of the Heisenberg model, may be shifted from their values in the noninteracting system.

When particles with \downarrow spin are also present, the amplitude A(P) of the plane-wave factors depends not only on the permutation of the $N_{\rm e}$ wave numbers, on the way they are assigned to the $N_{\rm e}$ electrons, but also on the positions $l_1, l_2, \ldots, l_{N_{\downarrow}}$ of the spin-down electrons relative to the positions $l_{N_{\downarrow}+1}, l_{N_{\downarrow}+2}, \ldots, l_{N_{\rm e}}$ of the spin-up electrons. That can be characterized by the permutation $\{Q1, Q2, \ldots, QN_{\rm e}\}$ of the numbers $\{1, 2, \ldots, N_{\rm e}\}$ that orders the occupied lattice sites in increasing order irrespective of the spin of the electrons:

$$1 \le l_{Q1} \le l_{Q2} \le \dots \le l_{QN_e} \le N$$
. (32.4.11)

The coefficient f depends on both permutations, P and Q:

$$f(l_1, \dots, l_{N_e}) = \sum_P A[Q, P] \exp\left[i(k_{P1}l_{Q1} + \dots + k_{PN_e}l_{QN_e})\right].$$
 (32.4.12)

The state is characterized by the $N_{\rm e}$ wave numbers k_j and by N_{\downarrow} other quantum numbers, called rapidities and denoted by λ_{α} . They are related to the state of the spins. When the system is dilute and there are no doubly occupied sites, the energy of this state is still given by (32.4.10).

There exist, however, configurations in which there are doubly occupied sites. The Bethe ansatz is the hypothesis that the wavefunction and the energy eigenvalues can still be written in the form given above. When two electrons with wave numbers k_1 and k_2 interact on a doubly occupied site, they continue to propagate after the interaction with the same wave numbers; the interaction only causes a phase shift and a possible exchange of the spins. Moreover, this phase shift depends only on k_1 and k_2 and does not depend on the state of the other particles. Formulated in the language of scattering theory, the scattering matrix is factorizable. This hypothesis does not work for most models studied in solid-state physics. The one-dimensional Hubbard model, together with some other models like the spin-1/2 Heisenberg chain, is an exception owing to the particular choice of the interaction. The amplitudes A[Q, P] are fixed by the uniqueness of the wavefunction when two particles occupy the same site irrespective of which of the two Q permutations satisfying (32.4.11) is chosen. Further conditions are given by the requirement that the energy take the form given in (32.4.10) even if double occupancy occurs.¹¹ Moreover, the periodic boundary condition is used to fix the values of the wave numbers. One finds after a rather lengthy calculation that the $N_{\rm e}$ wave numbers and the N_{\perp} rapidities satisfy the *Lieb–Wu equations*:¹²

$$e^{ik_j L} = \prod_{\alpha=1}^{N_{\perp}} \frac{\lambda_{\alpha} - \sin k_j - iu}{\lambda_{\alpha} - \sin k_j + iu},$$

$$\prod_{j=1}^{N_e} \frac{\lambda_{\alpha} - \sin k_j - iu}{\lambda_{\alpha} - \sin k_j + iu} = \prod_{\substack{\beta=1\\\beta \neq \alpha}}^{N_{\perp}} \frac{\lambda_{\alpha} - \lambda_{\beta} - 2iu}{\lambda_{\alpha} - \lambda_{\beta} + 2iu},$$
(32.4.13)

where u = U/4t is the dimensionless strength of the interaction. Once these equations are solved, the energy and momentum of the state can be calculated. Both are given solely in terms of the wave numbers and the expressions have the same form as for a free system,

$$E = -2t \sum_{j=1}^{N_{\rm e}} \cos k_j , \qquad P = \sum_{j=1}^{N_{\rm e}} k_j , \qquad (32.4.14)$$

but the wave numbers are shifted from their values in the noninteracting case and the energy is renormalized accordingly.

Taking the logarithm of both sides of the equations determining the quantum numbers we find

$$k_j L = 2\pi I_j + 2\sum_{\alpha=1}^{N_{\downarrow}} \arctan\left[(\lambda_{\alpha} - \sin k_j)/u\right], \qquad (32.4.15)$$
$$2\sum_{j=1}^{N_e} \arctan\left[(\lambda_{\alpha} - \sin k_j)/u\right] = 2\pi J_{\alpha} + 2\sum_{\beta=1}^{N_{\downarrow}} \arctan\left[(\lambda_{\alpha} - \lambda_{\beta})/2u\right],$$

where the quantum numbers I_j and J_{α} are integers or half-integers depending on the parity of N_{\downarrow} and $N_{e} - N_{\downarrow}$:

¹¹ In the spin-1/2 Heisenberg chain, where spins on neighboring sites interact, the Bethe ansatz leads to an extra condition on the wavefunction when spins are reversed on neighboring sites. In the Hubbard model with on-site interaction, the Bethe ansatz provides a constraint for the case when two electrons sit on the same site.

¹² E. H. LIEB and F. Y. WU, 1968.

$$2I_{j} = \begin{cases} \text{even for } N_{\downarrow} \text{ even }, \\ \text{odd for } N_{\downarrow} \text{ odd} \end{cases}$$

$$2J_{\alpha} = \begin{cases} \text{even for } N_{\uparrow} = N_{e} - N_{\downarrow} \text{ odd }, \\ \text{odd for } N_{\uparrow} = N_{e} - N_{\downarrow} \text{ even }. \end{cases}$$

$$(32.4.16)$$

These quantum numbers can be used equivalently instead of the wave numbers and rapidities to characterize the state. It follows from (32.4.15) that the momentum of a state is given by

$$P = \frac{2\pi}{L} \left(\sum_{j=1}^{N_{\rm e}} I_j + \sum_{\alpha=1}^{N_{\downarrow}} J_{\alpha} \right).$$
 (32.4.17)

The wave numbers k_j and rapidities λ_{α} should be different and can be real or complex like the rapidities in the antiferromagnetic Heisenberg chain. When these quantum numbers are real, the I_j and J_{α} numbers are all different in the macroscopically relevant states and J_{α} should be in the interval

$$-\frac{1}{2}(N_{\rm e} - N_{\downarrow}) + \frac{1}{2} \le J_{\alpha} \le \frac{1}{2}(N_{\rm e} - N_{\downarrow}) - \frac{1}{2}.$$
(32.4.18)

Note that in the half-filled case in the limit $u \gg 1$, the Lieb–Wu equations for the variable $\Lambda_{\alpha} = \lambda_{\alpha}/2u$ reduce to

$$2N_{\rm e} \arctan 2\Lambda_{\alpha} = 2\pi J_{\alpha} + 2\sum_{\beta=1}^{N_{\perp}} \arctan(\Lambda_{\alpha} - \Lambda_{\beta}). \qquad (32.4.19)$$

The same equations are satisfied by the rapidities in the spin-1/2 Heisenberg model. This can be checked by taking the logarithm of (15.5.105) and using the relation

$$\arctan z = \frac{1}{2i} \ln \frac{1+iz}{1-iz} = \frac{\pi}{2} + \frac{1}{2i} \ln \frac{z-i}{z+i}.$$
 (32.4.20)

This is not surprising. There are practically no doubly occupied sites in the half-filled Hubbard model in the large U limit. Each site is occupied by one electron, but their spin orientations can vary in two-step exchange processes through high-energy virtual intermediate states. The model is equivalent with an antiferromagnetic Heisenberg model with exchange coupling $J = -2t^2/U$.

32.4.2 Ground State of the Hubbard Chain

We assume for the sake of simplicity that the number of electrons is even but not a multiple of 4, $N_e = 4\nu + 2$ with integer ν , since the unpolarized ground state with $N_{\downarrow} = N_e/2$ is then a nondegenerate singlet. The quantum numbers I_j are half-odd-integers while the quantum numbers J_{α} are integers. They take consecutive values in the ground state, symmetrically about zero, between $\pm (N_e - 1)/2$ and $\pm (N_e/2 - 1)/2$, respectively:

$$\{I_j\} = -(N_{\rm e} - 1)/2, \dots, -1/2, 1/2, \dots, (N_{\rm e} - 1)/2, \{J_{\alpha}\} = -(N_{\rm e}/2 - 1)/2, \dots, -1, 0, 1, \dots, (N_{\rm e}/2 - 1)/2.$$
(32.4.21)

A special example is shown in Fig. 32.16.



Fig. 32.16. Positions of the I_j and J_{α} parameters of the Lieb–Wu equations in the ground state of the Hubbard model for $N_e = 18$ and $N_{\downarrow} = 9$

The wave numbers and the rapidities obtained from the solution of the Lieb–Wu equations fill an interval in the Brillouin zone and on the real axis, respectively, densely but nonuniformly for a long enough chain. In the limit $L \to \infty$, when the distance between subsequent roots is on the order of 1/L, the ground-state distributions of k_j and λ_{α} can be characterized by the root-density functions

$$\rho(k) = \lim_{L \to \infty} \frac{1}{L} \frac{1}{k_{j+1} - k_j}$$
(32.4.22)

and

$$\sigma(\lambda) = \lim_{L \to \infty} \frac{1}{L} \frac{1}{\lambda_{\alpha+1} - \lambda_{\alpha}}, \qquad (32.4.23)$$

and the Lieb–Wu equations can be transformed into integral equations for these functions:

$$\rho(k) = \frac{1}{2\pi} + \cos k \int_{-\lambda_0}^{\lambda_0} \frac{\mathrm{d}\lambda}{2\pi} K_1(\sin k - \lambda) \sigma(\lambda) ,$$

$$\sigma(\lambda) = \int_{-k_0}^{k_0} \frac{\mathrm{d}k}{2\pi} K_1(\lambda - \sin k) \rho(k) - \int_{-\lambda_0}^{\lambda_0} \frac{\mathrm{d}\lambda'}{2\pi} K_2(\lambda - \lambda') \sigma(\lambda')$$
(32.4.24)

with

$$K_n(x) = \frac{2nu}{(nu)^2 + x^2} \,. \tag{32.4.25}$$

The values of k_0 and λ_0 are fixed by the constraints that the integrated densities yield the total number of electrons per site and the number of spin-down electrons per site, respectively:

$$\int_{-k_0}^{k_0} \rho(k) \,\mathrm{d}k = \frac{N_\mathrm{e}}{N} \,, \qquad \int_{-\lambda_0}^{\lambda_0} \sigma(\lambda) \,\mathrm{d}\lambda = \frac{N_\downarrow}{N} \,. \tag{32.4.26}$$

In the absence of magnetic field, when $N_{\downarrow} = N_{\rm e}/2$, the integration over λ extends to the entire real axis and the integral equations for the distribution of the wave numbers and rapidities can be simplified to yield

$$\rho(k) = \frac{1}{2\pi} + \cos k \int_{-k_0}^{k_0} dk' R(\sin k' - \sin k) \rho(k'),$$

$$\sigma(\lambda) = \int_{-k_0}^{k_0} dk \frac{1}{4u \cosh[\pi(\lambda - \sin k)/2u]} \rho(k)$$
(32.4.27)

with the kernel

$$R(x) = \int_{-\infty}^{\infty} \frac{d\xi}{2\pi} \frac{e^{i\xi x}}{1 + e^{2u|\xi|}} = \int_{0}^{\infty} \frac{d\xi}{2\pi} \frac{e^{-\xi u}}{\cosh(\xi u)} \cos(\xi x) \,. \tag{32.4.28}$$

Once the root-density functions are known, the ground-state energy can be calculated via

$$E_0 = -2tN \int_{-k_0}^{k_0} \rho(k) \cos k \, \mathrm{d}k \,. \tag{32.4.29}$$

32.4.3 Low-Energy Excitations

Excited states can be generated in various ways. When the total number of electrons and the total number of spin-down particles are conserved, electron–hole pairs can be created. Charged excitations are obtained by adding (removing) particles with \uparrow or \downarrow spin to (from) the unpolarized ground state. Finally, spin excitations are created when the spin of an electron is reversed. We only treat excitations in less than half-filled bands and consider first spin excitations. The particularities of the excitation spectrum of the Hubbard model at half filling will be discussed later.

Spin Excitations, Spinons

A spin-triplet excitation is obtained when the spin of a particle is reversed while keeping the number of particles fixed. $N_{\uparrow} = N_{\rm e}/2 + 1$ particles have their spin pointing up and $N_{\downarrow} = N_{\rm e}/2 - 1$ particles have their spin pointing down. Both sets of quantum numbers I_j and J_{α} change parity compared to the ground state; I_j s take integer and J_{α} s half-integer values. It follows from the second equation of (32.4.15) that finite, real momenta and rapidities can be obtained only if $|J_{\alpha}| \leq (N_{\rm e} - N_{\downarrow} - 1)/2$, that is J_{α} can take values in the range $[-N_{\rm e}/4, N_{\rm e}/4]$. There are

$$N_{\rm e}/2 + 1 = N_{\perp} + 2 \tag{32.4.30}$$

half-integers in this interval, but only N_{\downarrow} of them are needed, hence two holes are left in the ground-state distribution. Two possible choices of the parameters of an excited state, starting from the ground state sets shown in Fig. 32.16, are displayed in Fig. 32.17.



Fig. 32.17. Possible distributions of the parameters I_j and J_{α} in a spin-triplet excited state for $N_e = 18$ and $N_{\downarrow} = 8$

As seen in the figure, the I_j s cannot be chosen symmetrically. They are consecutive integers for the low-energy excitations, from $-N_e/2 + 1$ to $N_e/2$ or from $-N_e/2$ to $N_e/2 - 1$. Because of the asymmetry, the parameters I_j contribute to the momentum of the state by

$$P = \frac{2\pi}{L} \left(\pm \frac{N_{\rm e}}{2} \right) = \pm \pi n_{\rm e} = \pm 2k_{\rm F} \,. \tag{32.4.31}$$

This momentum shift has to be taken into account when the excitation spectrum is calculated. Since the excited states can be characterized by two parameters, the two missing J_{α} values, they form again a continuum shown in Fig. 32.18. Soft modes occur at $k = 0, \pm 2k_{\rm F}$, and $\pm 4k_{\rm F} \mod 2\pi$.



Fig. 32.18. Typical continuum of the $S_z = 1$ excitations in the low-energy spectrum of the Hubbard model for a moderately strong U for an electron density $n_e = 0.6$ (a) in the extended zone and (b) reduced to the Brillouin zone

This spin-reversed state is the $S_z = 1$ component of a triplet excitation. The $S_z = 0$ and $S_z = -1$ components of the triplet, which have to have the same energy, can be generated by the application of the spin-lowering operator on the $S_z = 1$ state. The $S_z = 0$ state corresponds to an excitation without spin reversal compared to the ground state with an unchanged number of particles. It can be obtained by a particular choice of the parameters I_j and J_{α} which now have the same parity as in the ground state.¹³ The I_j s are consecutive half-integers between $-(N_e - 1)/2$ and $(N_e - 1)/2$ while the J_{α} s take integer values in the range $[-(N_e/2 + 1)/2, (N_e/2 + 1)/2]$ with two holes in the sequence. A special example is displayed in Fig. 32.19.



Fig. 32.19. Possible distribution of the parameters I_j and J_{α} for the $S_z = 0$ component of the spin-triplet excited state for $N_e = 18$ and $N_{\downarrow} = 9$

All rapidities cannot be finite now. The second equation of (32.4.15) is satisfied for $J_{N_e/2} = (N_e/2 + 1)/2$ with finite rapidities except for $\lambda_{N_e/2}$ which takes infinite value. Separating out this rapidity and the corresponding $J_{N_e/2}$, the remaining ones satisfy the Lieb–Wu equations with shifted values of the parameters, $I_j \rightarrow I_j + 1/2$, $J_\alpha \rightarrow J_\alpha + 1/2$ for $\alpha = 1, 2, \ldots, N_e/2 - 1$. Alternatively, we can separate out the parameter $J_1 = -(N_e/2 + 1)/2$ and the corresponding rapidity λ_1 which is now $-\infty$. The remaining parameters are effectively shifted to $I_j - 1/2$ and $J_\alpha - 1/2$ for $\alpha = 2, 3, \ldots, N_e/2$. We thus recover the parameter sets characterizing the $S_z = 1$ component of the triplet and thus the same excitation energy is obtained.

Besides this $S_z = 0$ component of the triplet, it is possible to construct spin-singlet excitations in the same subspace. To get these states, two real rapidities are replaced by a complex conjugate pair. In terms of the parameters J_{α} this corresponds to leaving two holes in the ground-state set and the singlet excitations form a two-parameter continuum. One can show that the singlet and triplet continua coincide in the thermodynamic limit. Similar to the situation found in Chapter 15 for the spin-1/2 antiferromagnetic Heisenberg chain, the degenerate triplet and singlet excitations can be interpreted as spin-triplet and spin-singlet pairs of fictitious spin-1/2 "elementary" excitations called *spinons* with energy $\varepsilon_s(q)$ defined in the interval $-k_F \leq q \leq k_F$. The continuum of composite excitations is obtained by the rule

$$\varepsilon(k) = \varepsilon_{\rm s}(q_1) + \varepsilon_{\rm s}(q_2) \quad \text{with} \quad k = q_1 + q_2 \,.$$
 (32.4.32)

To calculate the dispersion of spinons we first establish that if a J_s is missing from the symmetric ground-state set, the momentum of the state is

¹³ The $S_z = -1$ state, where more than half of the particles have their spins oriented down, can be described by a Bethe-ansatz wavefunction by reversing the role of up- and down-spin electrons. The motion of up-spin particles is considered through the background of down-spin particles.

$$q = -\frac{2\pi}{L} J_{\rm s} \,. \tag{32.4.33}$$

This momentum can vary between $-\pi n_{\rm e}/2$ and $\pi n_{\rm e}/2$, that is between $-k_{\rm F}$ and $k_{\rm F}$. A rapidity $\lambda_{\rm s}(q)$ can be associated with the missing $J_{\rm s}$, that is with q, through the implicit equation

$$q = -\int_{-k_0}^{k_0} 2 \arctan\left(\frac{\lambda_{\rm s}(q) - \sin k}{u}\right) \rho(k) \,\mathrm{d}k + \int_{-\lambda_0}^{\lambda_0} 2 \arctan\left(\frac{\lambda_{\rm s}(q) - \lambda'}{2u}\right) \sigma(\lambda') \,\mathrm{d}\lambda' \,.$$
(32.4.34)

Then one has to solve the closed system of equations

$$\varepsilon_{\rm h}(k) = 2t\cos k + \mu + \int_{-\lambda_0}^{\lambda_0} \frac{\mathrm{d}\lambda}{2\pi} K_1(\sin k - \lambda)\varepsilon_{\rm s}(\lambda) ,$$

$$\varepsilon_{\rm s}(\lambda) = \int_{-k_0}^{k_0} \frac{\mathrm{d}k}{2\pi} K_1(\lambda - \sin k)\cos k\,\varepsilon_{\rm h}(k) - \int_{-\lambda_0}^{\lambda_0} \frac{\mathrm{d}\lambda'}{2\pi} K_2(\lambda - \lambda')\varepsilon_{\rm s}(\lambda')$$
(32.4.35)

for the functions $\varepsilon_{\rm h}(k)$ and $\varepsilon_{\rm s}(\lambda)$, where μ is determined from the condition $\varepsilon_{\rm h}(k_0) = 0$. When the ground state is unpolarized, the integration over λ extends to the whole real axis $(\lambda_0 \to \infty)$ and Fourier transformation leads to

$$\varepsilon_{\rm h}(k) = 2t\cos k + \mu + \int_{-k_0}^{k_0} \mathrm{d}k' R(\sin k' - \sin k)\cos k' \varepsilon_{\rm h}(k'), \qquad (32.4.36)$$
$$\varepsilon_{\rm s}(\lambda) = \int_{-k_0}^{k_0} \mathrm{d}k \frac{\cos k}{4u\cosh[\pi(\lambda - \sin k)/2u]} \varepsilon_{\rm h}(k).$$

The solution $\varepsilon_{\rm s}(\lambda)$ of this system of equations at $\lambda = \lambda_{\rm s}(q)$ gives the spinon energy belonging to momentum q, i.e., the dispersion relation of spinons. A typical dispersion curve is shown in Fig. 32.20.



Fig. 32.20. Typical dispersion curve of spinons for an electron density $n_{\rm e} = 0.6$

Analytic expressions can be obtained for small and large values of U:

$$\varepsilon_{\rm s}(q) = \begin{cases} 2t \left(\cos q - \cos k_{\rm F}\right) & \text{for } U \ll t \,, \\ \frac{1}{2}\pi J_{\rm eff} \cos(q/n_{\rm e}) & \text{for } U \gg t \,, \end{cases}$$
(32.4.37)

where

$$J_{\rm eff} = \frac{4t^2}{U} n_{\rm e} \left[1 - \frac{\sin(2\pi n_{\rm e})}{2\pi n_{\rm e}} \right].$$
(32.4.38)

Linearization of the dispersion curve in the neighborhood of $k_{\rm F}$ yields the velocity $u_{\rm s}$ of spinons. For small values of U we have

$$\hbar u_{\rm s} \approx 2t \sin(\pi n_{\rm e}/2) - \frac{U}{2\pi}$$
 for $U \ll t$, (32.4.39)

while in the large-U limit

$$\hbar u_{\rm s} = \frac{2\pi t^2}{U} \left[1 - \frac{\sin(2\pi n_{\rm e})}{2\pi n_{\rm e}} \right] = \frac{\pi}{2} \frac{J_{\rm eff}}{n_{\rm e}} \,. \tag{32.4.40}$$

In the half-filled case ($n_e = 1$), where the large-U limit of the Hubbard model is equivalent to the spin-1/2 Heisenberg chain, the results derived in Chapter 15 are recovered. The numerically determined spinon velocities are displayed in Fig. 32.21 as a function of the band filling for several values of U/t.



Fig. 32.21. Spinon velocity $u_{\rm s}$ as a function of $n_{\rm e}$ for different values of U/t

Charged Excitations, Holons, and Antiholons

Next we consider excited states obtained by adding or removing a particle. Owing to the restrictions mentioned above we treat the cases when a spin-up particle is added or a spin-down particle is removed. We consider first the latter case. The allowed values of J_{α} are unchanged, but one less is needed to characterize the positions of spin-down particles and there will be a hole J_s in their distribution. The I_j s now have to be integers. The simplest choice is to take them symmetrically with respect to the origin, as seen in Fig. 32.22(a). This choice of the parameters yields the lowest energy excited states at a given momentum. Higher lying excited states are obtained by creating a hole $I_{\rm h}$ in the distribution of I_j choosing instead the smallest unoccupied I_j , as shown in Fig. 32.22(b).



Fig. 32.22. Possible distributions of the parameters I_j and J_{α} of the Lieb–Wu equations when a spin-down particle is removed from the ground state of the Hubbard model with $N_{\rm e} = 18$ and $N_{\downarrow} = 9$

The low-lying excited states form a two-parameter continuum shown schematically in Fig. 32.23, where the states are characterized by the missing $J_{\rm s}$ and the missing $I_{\rm h}$. Soft modes occur at $\pm k_{\rm F}$ and $\pm 3k_{\rm F}$ mod 2π . Further low-energy modes occur at momenta differing by $\pm 2k_{\rm F}$ if more holes are created in the ground-state distribution of I_i .



Fig. 32.23. Excitation spectrum of the Hubbard model when a spin-down particle is removed from the ground state for band filling $n_{\rm e} = 0.6$ in the extended- and in the reduced-zone schemes. The lower edge of the continuum drawn with a solid line coincides with the spinon dispersion curve and the dashed line is the dispersion curve of holons

The excitations in the continuum can again be interpreted as arising from a pair of "elementary" excitations, a spinon, owing to J_s , and a *holon*, owing to the missing I_h . Since I_h is missing from the interval given in (32.4.21), the corresponding momentum

$$q = -\frac{2\pi}{L}I_{\rm h} \tag{32.4.41}$$

is in the interval between $-\pi n_{\rm e}$ and $\pi n_{\rm e}$, that is holons are defined between $-2k_{\rm F}$ and $2k_{\rm F}$. To get their dispersion relation a wave number $k_{\rm h}(q)$ is associated with the momentum of the holon which has to be calculated from the implicit equation

$$q = -k_{\rm h}(q) - \int_{-\infty}^{\infty} 2 \arctan\left(\frac{\sin k_{\rm h}(q) - \lambda}{u}\right) \sigma(\lambda) \,\mathrm{d}\lambda\,,\qquad(32.4.42)$$

and the energy of the holon with momentum q is equal to $\varepsilon_{\rm h}(k)$, calculated from (32.4.36), at $k = k_{\rm h}(q)$. The analytic expressions in the weak- and strong-coupling limits are given by

$$\varepsilon_{\rm h}(q) = \begin{cases} 4t \big(\cos q/2 - \cos k_{\rm F}\big) & \text{for } U \ll t \,, \\ 2t \big(\cos q - \cos 2k_{\rm F}\big) & \text{for } U \gg t \,. \end{cases}$$
(32.4.43)

The energy measured from the chemical potential vanishes at $q = \pm 2k_{\rm F}$. The dispersion curve of holons is illustrated in Fig. 32.24.



Fig. 32.24. Dispersion curve of holons (h) and antiholons (\overline{h}) for an electron density $n_e = 0.6$ in the weak-coupling (dashed line) and strong-coupling (solid line) limits

Linearizing the dispersion curve in the neighborhood of $\pm 2k_{\rm F}$ yields the velocity $u_{\rm c}$ of holons. For small U values we have

$$\hbar u_{\rm c} \approx 2t \sin(\pi n_{\rm e}/2) + \frac{U}{2\pi}, \qquad U \ll t,$$
 (32.4.44)

that is we recover the Fermi velocity $v_{\rm F}$ given in (32.4.5) in the limit $U \to 0$. For large values of U we have

$$\hbar u_{\rm c} = 2t \sin(\pi n_{\rm e}) = 2t \sin 2k_{\rm F} \,. \tag{32.4.45}$$

The factor 2 in the argument, $k_{\rm F}$ for small U and $2k_{\rm F}$ for large U, can be understood if we take into account that doubly occupied sites are not allowed in the large-U limit. The electrons fill the states as if they all had the same spin. The numerically determined holon velocities are displayed in Fig. 32.25 as a function of the band filling for several values of U/t.



Fig. 32.25. Holon velocity u_c as a function of n_e for different values of U/t

We can proceed similarly when a spin-up particle is added to the system. The simplest excited state corresponds to adding a new half-odd integer $I_{\rm h}$ to the ground-state set. Since the parity of the spin-up particles has changed, the quantum numbers J_{α} should take half-odd integer values. There are $N_{\rm e}/2 + 1$ half-odd integers in the interval given in (32.4.18), but only $N_{\downarrow} = N_{\rm e}/2$ of them are needed to characterize the distribution of \downarrow spins in the excited state. If the J_{α} parameters are all different, which is the case for low-lying states, there is a hole at say $J_{\rm s}$ in the distribution of these parameters compared to the ground state. A possible distribution of the half-odd integers is given in Fig. 32.26.



Fig. 32.26. A possible choice of the parameters I_j and J_{α} of the Lieb–Wu equations when a spin-up particle is added to the ground state of the Hubbard model with $N_{\rm e} = 18$ and $N_{\downarrow} = 9$

The continuum of excitations is shown in Fig. 32.27 in the extended-zone scheme. Soft modes occur at $\pm k_{\rm F}$ and $\pm 3k_{\rm F} \mod 2\pi$. Higher lying excitations are obtained if some half-odd integer values are left out of the ground-state interval $[-(N_{\rm e}-1)/2, (N_{\rm e}-1)/2]$ for the parameters I_j and are replaced by half-odd integers outside this interval. Soft modes with $\pm 5k_{\rm F}, \pm 7k_{\rm F}$, etc., can be generated in this way.

This two-parameter continuum, too, where the states are characterized by the extra $I_{\bar{h}}$ and the missing J_s , can be interpreted as arising from combinations of two "elementary" excitations. The missing J_s is equivalent to a spinon, and the extra $I_{\bar{h}}$ corresponds to creating an *antiholon*. Since $I_{\bar{h}}$ has to be outside the interval given in (32.4.21), the corresponding momentum



Fig. 32.27. Excitation spectrum of the Hubbard model when a spin-up particle is added to the ground state for a band filling $n_e = 0.6$. The lower edge of the continuum drawn with a solid line coincides with the spinon dispersion curve and the dashed line is the dispersion curve of antiholons

$$q = \frac{2\pi}{L} I_{\bar{h}} \tag{32.4.46}$$

has to be smaller than $-\pi n_{\rm e}$ $(-2k_{\rm F})$ or larger than $\pi n_{\rm e}$ $(2k_{\rm F})$. Antiholons are defined in a restricted range of the Brillouin zone, in the intervals $[-\pi, -2k_{\rm F}]$ and $[2k_{\rm F}, \pi]$, which is complementary to the region where holons were defined. A wave number $k_{\rm h}(q)$ is associated with the momentum q through the equation

$$q = k_{\bar{h}}(q) + \int_{-\infty}^{\infty} 2 \arctan\left(\frac{\sin k_{\bar{h}}(q) - \lambda}{u}\right) \sigma(\lambda) \,\mathrm{d}\lambda\,, \qquad (32.4.47)$$

and the energy of the antiholon is the negative of $\varepsilon_{\rm h}(k)$ calculated from (32.4.36) at $k = k_{\rm \bar{h}}(q)$,

$$\varepsilon_{\bar{\mathbf{h}}}(q) = -\varepsilon_{\mathbf{h}}(k_{\bar{\mathbf{h}}}(q)). \qquad (32.4.48)$$

The analytic expressions are analogous to the ones obtained for holons,

$$\varepsilon_{\bar{\mathbf{h}}}(q) = \begin{cases} 4t \big(\cos k_{\mathrm{F}} - \cos q/2 \big) & \text{for } U \ll t \,, \\ 2t \big(\cos 2k_{\mathrm{F}} - \cos q \big) & \text{for } U \gg t \,. \end{cases}$$
(32.4.49)

The dispersion curve of antiholons is illustrated in Fig. 32.24 in the weak- and strong-coupling limits.

Thus, adding a particle to the Hubbard chains is equivalent to creating a deconfined spinon–antiholon pair, while removing a particle is equivalent to creating a spinon–holon pair, where the spinon carries the spin and the holon (antiholon) carries the charge:

$$\begin{aligned} \varepsilon_{e^-}(k) &= \varepsilon_{\rm s}(q_1) + \varepsilon_{\bar{\rm h}}(q_2) \qquad \text{with} \quad k = q_1 + q_2 \,, \\ \varepsilon_{e^+}(k) &= \varepsilon_{\rm s}(q_1) + \varepsilon_{\rm h}(q_2) \qquad \text{with} \quad k = q_1 + q_2 \,. \end{aligned} \tag{32.4.50}$$

Note that our previous treatment of the Hubbard chain is valid for less than half-filled bands. When the band is more than half-filled by particles, $N_{\rm e} > N$, the Bethe-ansatz solution can be found by studying the motion of the $2N - N_{\rm e}$

holes. The elementary excitations are again spinons, holons, and antiholons, but adding a particle to the system, i.e., removing a hole, corresponds to creating a deconfined spinon-holon pair, while removing a particle, i.e., adding an extra hole, corresponds to creating a spinon-antiholon pair.

In this context deconfinement means that spinons and holons (antiholons), the constituents of the physical excitations, propagate independently with different velocities. A simple physical picture can be given in the large-U limit, when doubly occupied sites are absent. The effective antiferromagnetic exchange tends to align the neighboring spins antiferromagnetically, even though they cannot be ordered. Figure 32.28 shows such an environment and the processes occurring when a spin-down particle is removed.



Fig. 32.28. Independent propagation of a holon (empty site) and a spinon (domain wall) when a particle is removed from a large-U Hubbard chain, where the spins are locally antiferromagnetically arranged

The inserted hole may propagate by hopping of electrons. On the other hand, the spins of neighboring electrons can be exchanged in a two-step process. Thus the spin configurations found after a few steps contain a hole, around which the spin alternation along the chain is not interrupted, and a domain wall separating two antiferromagnetically ordered regions, in which the spins alternate in opposite phase. The hole – which carries charge but no spin, since the spin arrangement is not modified around it – can be identified with the holon and the domain wall can be interpreted as a spinon. The holon propagation is determined solely by the hopping t, while the propagation of spinons is related to the effective exchange J_{eff} .

Particle–Hole Excitations

We mentioned earlier that spin-singlet excitations, where both the total number of particles and the number of spin-down particles remain unchanged, cannot be described by real rapidities. A pair of complex conjugate rapidities is needed. There is another class of low-energy excitations with conserved $N_{\rm e}$ and N_{\downarrow} , which can be described by real parameters. These are particle–hole excitations, also called $4k_{\rm F}$ excitations, because they are soft at k = 0 and $k = 4k_{\rm F} \mod 2\pi$ but not at $2k_{\rm F}$. Starting from the ground state and keeping the number of I_j and J_{α} parameters unchanged, one of the half-integer I_j s lying in the interval $[-(N_{\rm e} - 1)/2, (N_{\rm e} - 1)/2]$, say $I_{\rm h}$, is left out and an $I_{\rm p}$ is chosen outside this interval, as shown in Fig. 32.29.



Fig. 32.29. Possible choice of the parameters I_j and J_{α} of the Lieb–Wu equations in a particle–hole excitation of the Hubbard model with $N_e = 18$ and $N_{\perp} = 9$

The hole $I_{\rm h}$ and the extra $I_{\rm p}$ give again a two-parameter set and the corresponding excitation energies shown in Fig. 32.30 form a continuum in the thermodynamic limit.



Fig. 32.30. Continuum of particle-hole (holon-antiholon) excitations in the lowenergy spectrum of the Hubbard model for a band filling $n_{\rm e} = 0.6$. The lower edge of the continuum drawn with a solid line coincides with the dispersion curve of antiholons. The dashed line is the dispersion curve of holons

We know from our earlier considerations that a missing $I_{\rm h}$ corresponds to creating a holon and an extra $I_{\rm p}$ corresponds to creating an antiholon. Comparing the boundaries of this continuum with the dispersion curves of holons and antiholons shown in Fig. 32.24 it is readily seen that these particlehole excitations correspond to holon-antiholon pairs:

$$\varepsilon_{\text{p-h}}(k) = \varepsilon_{\text{h}}(q_1) + \varepsilon_{\bar{\text{h}}}(q_2) \quad \text{with} \quad k = q_1 + q_2.$$
 (32.4.51)

Thus holons, antiholons, and spinons are the true elementary excitations of the one-dimensional Hubbard model. These excitations, which have gapless linear dispersion when the system is not half filled, always occur in pairs.

32.4.4 Correlation Functions in a Hubbard Chain

The Lieb–Wu equations were originally derived for finite Hubbard chains, but the spinon and holon excitations were analyzed in the continuum limit, for infinitely long chains. When the solutions are analyzed for a large but finite system, the energies and momenta of low-energy spinons and holons are found to form towers just as in the TL model. The elements of a tower are characterized by integer numbers $n_{c,+}$, $n_{c,-}$, $n_{s,+}$, and $n_{s,-}$, which give the number of small-momentum excitations in the holon and spinon sectors, respectively. The positions of the towers depend on the number of extra particles $\delta N_{\pm,\sigma}$ added to the system near $\pm k_c$ with spin σ . We have

$$E = L\varepsilon_{0} + \hbar u_{c} \frac{2\pi}{L} \left(n_{c,+} + n_{c,-} + \Delta_{c,+} + \Delta_{c,-} - \frac{1}{12} \right) + \hbar u_{s} \frac{2\pi}{L} \left(n_{s,+} + n_{s,-} + \Delta_{s,+} + \Delta_{s,-} - \frac{1}{12} \right), \qquad (32.4.52)$$

where ε_0 is the ground-state energy per site in the thermodynamic limit and

$$P = \hbar k_{\rm F} J_{\rm c} + \hbar \frac{2\pi}{L} \left(n_{\rm c,+} - n_{\rm c,-} + \Delta_{\rm c,+} - \Delta_{\rm c,-} \right) + \hbar \frac{2\pi}{L} \left(n_{\rm s,+} - n_{\rm s,-} + \Delta_{\rm s,+} - \Delta_{\rm s,-} \right), \qquad (32.4.53)$$

with

$$\Delta_{c,\pm} = \frac{1}{16} \left(\frac{1}{\sqrt{K_c}} \delta N_c \pm \sqrt{K_c} J_c \right)^2,$$

$$\Delta_{s,\pm} = \frac{1}{16} \left(N_s \pm J_s \right)^2,$$

(32.4.54)

where δN_c is the total number of particles added to the system, N_s is the difference between the number of particles added with \uparrow and \downarrow spins, J_c and J_s are the charge and spin currents. The parameter K_c , which determines the critical exponents, is a function of the Hubbard U and the number of electrons per site, n_e . It can be calculated from an integral equation which is analogous to the integral equations obtained for the spinon and holon energies. In the absence of an external magnetic field $K_c = \xi^2(k_0)/2$, where $\xi(k_0)$ is obtained from

$$\xi(k) = 1 + \int_{-k_0}^{\kappa_0} \mathrm{d}k' \, \cos k' R(\sin k' - \sin k) \xi(k') \tag{32.4.55}$$



Fig. 32.31. Correlation parameter K_c of the Hubbard model as a function of n_e for several values of U/t

at $k = k_0$ with the kernel R(x) given in (32.4.28). The numerically evaluated values are displayed in Fig. 32.31.

Analytic expressions can be obtained in two limits. For small values of U we find

$$K_{\rm c} \approx 1 - \frac{U}{4\pi t \sin(\pi n_{\rm e}/2)},$$
 (32.4.56)

while in the large U limit

$$K_{\rm c} \approx \frac{1}{2} + \frac{4t \ln 2}{\pi U} \sin(\pi n_{\rm e}) \,.$$
 (32.4.57)

Although the one-dimensional Hubbard model does not possess conformal symmetry owing to the different velocities of holons and spinons, the concepts of conformal invariance can be applied to it due to the tower structure of the excitation spectrum. The quantities $\Delta_{c,\pm}$ and $\Delta_{s,\pm}$ can be identified with the scaling dimensions appearing in the exponents of the correlation functions. If an operator \mathcal{O} changes the number of particles with spin σ in the vicinity of the Fermi points $\pm k_{\rm F}$ by $\delta N_{\pm,\sigma}$, the asymptotic form of the correlation function is

$$\langle \mathcal{O}(x,t)\mathcal{O}^{\dagger}(0,0)\rangle \sim \frac{\mathrm{e}^{-\mathrm{i}k_{\mathrm{F}}J_{\mathrm{c}}x}}{(x-u_{\mathrm{c}}t)^{2\Delta_{\mathrm{c},+}}(x+u_{\mathrm{c}}t)^{2\Delta_{\mathrm{c},-}}(x-u_{\mathrm{s}}t)^{2\Delta_{\mathrm{s},+}}(x+u_{\mathrm{s}}t)^{2\Delta_{\mathrm{s},-}}}$$
(32.4.58)

32.4.5 Mapping Between the Hubbard and TL Models

The low-energy spectrum of the Hubbard model given in (32.4.52) and (32.4.53) has precisely the same structure as that of the TL model given in (32.3.98) and (32.3.100) except for the term -1/12 which gives the finite-size correction to the ground-state energy. That means that those physical properties of the two models that are determined by the low-energy excitations are identical, if a proper mapping is found between the Coulomb repulsion and

band filling $n_{\rm e}$ of the Hubbard model and the couplings $g_{2\rm c}$, $g_{2\rm s}$, $g_{4\rm c}$, and $g_{4\rm s}$ of the TL model. This mapping can be achieved by equating the parameters $u_{\rm c}$, $u_{\rm s}$, $K_{\rm c}$, and $K_{\rm s}$ calculated for the two models.

This does not imply that the charge and spin bosons of the TL model can be identified with the holons (antiholons) and spinons of the Hubbard model. Holons carry no spin and have charge +e (antiholons have charge -e), spinons are neutral and carry spin-1/2. Holons (antiholons) and spinons on the one hand and the TL bosons on the other hand simply offer alternative, but equivalent descriptions of the same low-energy physics in the regime where a linearized dispersion is a good approximation.

In the weak-coupling limit of the Hubbard model the velocities [see (32.4.39) and (32.4.44)] and the correlation parameter (32.4.56) can be written as

$$\begin{aligned} &\hbar u_{\rm c} \approx \hbar v_{\rm F} + \frac{U}{2\pi} ,\\ &\hbar u_{\rm s} \approx \hbar v_{\rm F} - \frac{U}{2\pi} ,\\ &K_{\rm c} \approx 1 - \frac{U}{2\pi \hbar v_{\rm F}} ,\end{aligned}$$
(32.4.59)

and $K_s = 1$ for any U. On the other hand, in the weak-coupling limit of the TL model the expansion of (32.3.83), (32.3.89), (32.3.86), and (32.3.92) give

$$\begin{split} \hbar u_{\rm c} &= \hbar v_{\rm F} \left[1 + \frac{g_{4\rm c}}{2\pi\hbar v_{\rm F}} - \frac{1}{2} \left(\frac{g_{2\rm c}}{2\pi\hbar v_{\rm F}} \right)^2 \right],\\ \hbar u_{\rm s} &= \hbar v_{\rm F} \left[1 + \frac{g_{4\rm s}}{2\pi\hbar v_{\rm F}} - \frac{1}{2} \left(\frac{g_{2\rm s}}{2\pi\hbar v_{\rm F}} \right)^2 \right],\\ K_{\rm c} &= 1 - \frac{g_{2\rm c}}{2\pi\hbar v_{\rm F}},\\ K_{\rm s} &= 1 - \frac{g_{2\rm s}}{2\pi\hbar v_{\rm F}}. \end{split}$$
(32.4.60)

Comparison of these equations yields the relationships

$$g_{2c} = U$$
, $g_{2s} = 0$, $g_{4c} = U$, $g_{4s} = -U$ (32.4.61)

between the couplings of the two models. When written in terms of $g_{i\parallel}$ and $g_{i\perp}$ we find

$$g_{2\parallel} = g_{2\perp} \approx U/2, \quad g_{4\parallel} \approx 0, \quad g_{4\perp} \approx U.$$
 (32.4.62)

In the large-U limit we have

$$g_{2\parallel} = g_{2\perp} \approx \frac{3\pi t}{2} \sin(\pi n_{\rm e}) ,$$

$$g_{4\parallel} \approx \frac{5\pi t}{2} \sin(\pi n_{\rm e}) - 4\pi t \sin(\pi n_{\rm e}/2) , \qquad (32.4.63)$$

$$g_{4\perp} \approx \frac{5\pi t}{2} \sin(\pi n_{\rm e}) .$$

For intermediate values of U the equivalent TL couplings can be obtained by comparing the numerically evaluated holon and spinon velocities and the parameter K_c with the corresponding expressions in the TL model. The results for $g_{2\parallel} = g_{2\perp}$ are shown in Fig. 32.32.



Fig. 32.32. (a) The couplings $g_{2\parallel} = g_{2\perp}$ in units of t which make the TL model equivalent to the Hubbard model with Coulomb repulsion U for various band fillings characterized by $n_{\rm e}$. (b) The same as in the left panel, but the equivalent couplings are plotted as a function of the band filling for several values of U, $U/t = 0.4, 0.8, 1.2, 1.6, 2, 4, 8, 16, \infty$ from bottom to top

As seen, the linear relationship between the TL couplings and U is rather well satisfied up to about $U/t \approx 1$, except for low band filling or when the band is almost half filled. In the first case, the curvature of the dispersion relation gives rise to a stronger renormalization, while in the second case the umklapp processes start to play a role.

32.5 Luttinger Liquids

The two models discussed above, the Tomonaga–Luttinger model and the onedimensional Hubbard model, display surprising similarities. The low-energy excitation spectrum is exhausted by soft bosonic excitations; fermionic quasiparticles are absent. The tower structure of the spectrum can be described by a few parameters. The scaling dimensions that determine the exponents of the power-law decay of the correlation functions can be calculated from the finite-size corrections to the energy. This similarity occurs despite the difference in the bare dispersion relation and in the type of interactions. F. D. M. HALDANE (1980) conjectured that this is not an accident. He demonstrated that the absence of fermionic quasiparticles, the existence of several branches of low-energy bosonic excitations with linear dispersion (characterized by the renormalized velocity u_i), the appearance of topological excitations with stiffness constant K_i , and the nonuniversal power-law decay of correlations, which is the consequence of the particularities of the excitation spectrum, are generic features of a large class of one-dimensional systems. The Luttinger model being the archetype of this behavior, he proposed the name *Luttinger liquid* for such systems. The term *Tomonaga–Luttinger liquid* is also used.

Before presenting the generic properties of Luttinger liquids we consider another example, the one-dimensional XXZ or Heisenberg–Ising model in the spinless-fermion representation and show that it exhibits similar behavior.

32.5.1 Low-Energy Spectrum of the XXZ Chain

We have seen in Chapter 15 that the s = 1/2 spin operators can be expressed in terms of spinless fermions with the aid of the Jordan–Wigner transformation. Applying transformation (15.2.62) to the one-dimensional anisotropic Heisenberg model the Hamiltonian becomes

$$\mathcal{H} = -J\sum_{i} \left[\frac{1}{2} \left(c_{i}^{\dagger} c_{i+1} + c_{i+1}^{\dagger} c_{i} \right) + \Delta \left(c_{i}^{\dagger} c_{i} - \frac{1}{2} \right) \left(c_{i+1}^{\dagger} c_{i+1} - \frac{1}{2} \right) \right], \quad (32.5.1)$$

where the parameter $\Delta = J_z/J_{xy}$ characterizes the anisotropy. In Fourier representation, apart from an additive constant we have

$$\mathcal{H} = -J \sum_{k} \left[\cos(ka) - \Delta \right] c_{k}^{\dagger} c_{k} - \frac{J\Delta}{N} \sum_{q} \cos(qa) \left(\sum_{k} c_{k+q}^{\dagger} c_{k} \right) \left(\sum_{k'} c_{k'-q}^{\dagger} c_{k'} \right),$$
(32.5.2)

where k runs over the Brillouin zone, $-\pi/a \le k \le \pi/a$.

We also know that the ground state is magnetically disordered in the range $-1 \le \Delta < 1$ in the absence of external magnetic field, that is

$$\langle S_i^z \rangle = \langle c_i^{\dagger} c_i \rangle - \frac{1}{2} = \frac{1}{N} \sum_k \langle c_k^{\dagger} c_k \rangle - \frac{1}{2} = 0, \qquad (32.5.3)$$

which means that exactly half of the allowed k states are occupied in the ground state. We can assume without restricting generality that J > 0. With this choice, the middle portion of the Brillouin zone, the region $-\pi/2a \le k \le \pi/2a$, is filled for $\Delta = 0.14$

The noninteracting system, $\Delta = 0$, corresponds to the XY model. We know from the Bethe-ansatz solution presented in Chapter 15 that the lowenergy part of the excitation spectrum is quite similar for finite Δ to that obtained for $\Delta = 0$. The elementary excitations are s = 1/2 spinons with linear dispersion relation and an anisotropy-dependent velocity, but they are always created in pairs. The measured excitation spectrum is a continuum of two-spinon excitations. Here we give a different treatment.

¹⁴ The states close to the zone boundary would be filled for J < 0. They can be shifted to the center of the Brillouin zone by the transformation $k \to k + \pi/a$.

We first consider the XY part of the Hamiltonian which gives the kinetic energy of the spinless fermions:

$$\mathcal{H} = -\frac{1}{2}J\sum_{i} \left[c_{i}^{\dagger}c_{i+1} + c_{i+1}^{\dagger}c_{i} \right] = -J\sum_{k}\cos(ka)c_{k}^{\dagger}c_{k} \,. \tag{32.5.4}$$

The physical properties are determined by the states close to the Fermi points $\pm k_{\rm F} = \pm \pi/2a$. We may therefore define a finite band (of width 2D in energy or $2k_{\rm c}$ in wave number) and keep only those states that are within this band. When the dispersion curve $-J \cos ka$ is linearized about the Fermi points, the velocity of the fermionic excitations is given by the relation $\hbar v_{\rm F} = Ja$. Separating the right- and left-moving fermions and introducing the bosonic densities in the same way as was done in the TL model we find

$$\mathcal{H}_0 = \sum_q \hbar v_{\rm F} |q| b_q^{\dagger} b_q + \frac{\pi \hbar v_{\rm F}}{2L} \left[(\delta N)^2 + \tilde{J}^2 \right], \qquad (32.5.5)$$

where $\delta N = \delta N_+ + \delta N_-$ and $\tilde{J} = \delta N_+ - \delta N_-$. The momentum operator is given by

$$\mathcal{P} = \sum_{q} \hbar q b_{q}^{\dagger} b_{q} + \hbar \sum_{\lambda} \lambda \left[k_{\rm F} + (\pi/L) \delta N_{\lambda} \right] \delta N_{\lambda}$$

$$= \sum_{q} \hbar q b_{q}^{\dagger} b_{q} + \hbar k_{\rm F} \tilde{J} + \hbar \frac{\pi}{L} \delta N \tilde{J} .$$
(32.5.6)

The spinless-fermion representation of the XY model is identical to a onecomponent TL model.

Strictly speaking the quantities δN_{\pm} are not well defined when δN is an odd number, that is an odd number of spins are reversed compared to the ground state. This is due to the shift of the allowed positions of k, which depend according to (15.5.122) and (15.5.123) on the parity of the number of reversed spins. The quantity δN can, however, be well defined as the change in the number of occupied states compared to the ground state. The quantity \tilde{J} is defined as the difference between the occupied states on the right and left sides of k-space. The Hamiltonian and the momentum operator can then be expressed in terms of these quantities in the form given above.

The energy and momentum eigenvalues for a finite chain are

$$E = \hbar v_{\rm F} \frac{2\pi}{L} \left(n_+ + n_- + \Delta_+ + \Delta_- \right)$$
(32.5.7)

and

$$P = \hbar k_{\rm F} \tilde{J} + \hbar \frac{2\pi}{L} \left(n_+ - n_- + \Delta_+ - \Delta_- \right), \qquad (32.5.8)$$

where

$$\Delta_{\pm} = \frac{1}{8} \left(\delta N \pm \tilde{J} \right)^2. \tag{32.5.9}$$

The excitation spectrum has a tower structure similar to the one shown in Fig. 32.10.

Taking now the terms proportional to Δ in the Hamiltonian, they describe an interaction between the spinless fermions. The momenta of both incoming and both outgoing particles are in the vicinity of one of the Fermi points in the physically relevant processes. The momentum transfer q is either small or of the order of $\pm 2k_{\rm F}$. The four possible processes are displayed in Fig. 32.33.



Fig. 32.33. Allowed scattering processes between one-dimensional spinless fermions. Right-moving fermions are denoted by solid lines and left-moving fermions by dashed lines

When two fermions from the neighborhood of the same Fermi point or a right- and a left-moving particle exchange a small momentum, they remain in the same branch after scattering. These are the forward-scattering processes retained in the TL model. Using again the notation $c_{k_{\rm F}+k}^{\dagger}$ ($c_{k_{\rm F}+k}$) and $d_{-k_{\rm F}+k}^{\dagger}$ ($d_{-k_{\rm F}+k}$) for the creation (annihilation) operator of the right- and left-moving particles, the forward-scattering processes can be written as

$$\mathcal{H}_{\rm fw} = -\frac{J\Delta}{N} \sum_{q} \cos(qa) \sum_{k} \left(c^{\dagger}_{k_{\rm F}+k+q} c_{k_{\rm F}+k} + d^{\dagger}_{-k_{\rm F}+k+q} d_{-k_{\rm F}+k} \right) \\ \times \sum_{k'} \left(c^{\dagger}_{k_{\rm F}+k'-q} c_{k_{\rm F}+k'} + d^{\dagger}_{-k_{\rm F}+k'-q} d_{-k_{\rm F}+k'} \right), \qquad (32.5.10)$$

where q is small. This interaction is between the long-wavelength components of the densities and can be written in terms of the boson operators defined for spinless fermions in analogy with (32.3.23). The forward-scattering processes can thus be written in the boson representation as

$$\mathcal{H}_{\rm fw} = -\frac{Ja\Delta}{2\pi} \sum_{q} |q| \left(b_q^{\dagger} + b_{-q} \right) \left(b_q + b_{-q}^{\dagger} \right)$$

$$= -\frac{Ja\Delta}{\pi} \sum_{q} |q| b_q^{\dagger} b_q - \frac{Ja\Delta}{2\pi} \sum_{q} |q| \left(b_q^{\dagger} b_{-q}^{\dagger} + b_{-q} b_q \right), \qquad (32.5.11)$$

where $\cos(qa)$ was approximated by unity for small q values, and a constant term has been omitted. The first term is the contribution of the Fock term. Being of the same form as the kinetic energy, it renormalizes the velocity of the bosons. The role of the second term will be discussed later.

A seemingly backward-scattering process is obtained when two oppositely moving particles exchange a large momentum of the order of $2k_{\rm F}$. The rightmoving particle is scattered into a left-moving state and vice versa. With a change of variables $q \rightarrow \pm 2k_{\rm F} + q$ the new q is small and the corresponding term in the Hamiltonian can be written in the form

$$\mathcal{H}_{\rm bw} = -\frac{J\Delta}{N} \sum_{q} \cos(\pi + qa) \sum_{k} c^{\dagger}_{k{\rm F}+k+q} d_{-k{\rm F}+k} \sum_{k'} d^{\dagger}_{-k{\rm F}+k'-q} c_{k{\rm F}+k'} -\frac{J\Delta}{N} \sum_{q} \cos(-\pi + qa) \sum_{k} d^{\dagger}_{-k{\rm F}+k+q} c_{k{\rm F}+k} \sum_{k'} c^{\dagger}_{k{\rm F}+k'-q} d_{-k{\rm F}+k'} .$$
(32.5.12)

With a further change of variables $q \to q + k' - k$ and a change of the order of the operators we find

$$\mathcal{H}_{\rm bw} = -\frac{J\Delta}{N} \sum_{q} \sum_{k'} c^{\dagger}_{k{\rm F}+k'+q} c_{k{\rm F}+k'} \sum_{k} d^{\dagger}_{-k{\rm F}+k-q} d_{-k{\rm F}+k} -\frac{J\Delta}{N} \sum_{q} \sum_{k} c^{\dagger}_{k{\rm F}+k-q} c_{k{\rm F}+k} \sum_{k'} d^{\dagger}_{-k{\rm F}+k'+q} d_{-k{\rm F}+k'}.$$
(32.5.13)

We may recognize in this representation the densities of right- and left-moving particles and this part of the Hamiltonian has the same form in terms of the bosonic operators,

$$\mathcal{H}_{\rm bw} = -\frac{Ja\Delta}{2\pi} \sum_{q} |q| \left(b_q^{\dagger} b_{-q}^{\dagger} + b_{-q} b_q \right), \qquad (32.5.14)$$

as the forward-scattering term. It is easy to understand why the backwardand forward-scattering terms give identical result for spinless fermions. Both the initial and the final states of the scattering process are the same. A particle from the neighborhood of $+k_{\rm F}$ is scattered by a particle from the neighborhood of $-k_{\rm F}$. One is scattered to the neighborhood of $+k_{\rm F}$ and the other to the neighborhood of $-k_{\rm F}$. Owing to the indistinguishability of the particles one cannot tell which particle is scattered to which side; therefore, no distinction can be made between forward and backward scattering. The Fock term corresponding to the renormalization of the velocity is missing in the boson representation, although it should be present if forward and backward scatterings are truly equivalent. This drawback of the naive bosonization can be corrected in a more careful treatment and we find

$$\mathcal{H}_{\rm bw} = -\frac{Ja\Delta}{\pi} \sum_{q} |q| b_q^{\dagger} b_q - \frac{Ja\Delta}{2\pi} \sum_{q} |q| \left(b_q^{\dagger} b_{-q}^{\dagger} + b_{-q} b_q \right).$$
(32.5.15)

Finally when two particles moving in the same direction are scattered to the opposite side, we are dealing with umklapp processes. When both the incoming and the outgoing particles are in the vicinity of the Fermi energy and the change in the total momentum is $\pm 4k_{\rm F}$, the conservation of quasimomentum can be satisfied only if the band is half filled, that is $k_{\rm F} = \pi/2a$ and the total incoming quasimomentum differs from the outgoing quasimomentum by $2\pi/a$, which is a vector of the reciprocal lattice. If the momentum transfer is written as $\pm 2k_{\rm F} + q$, the corresponding terms in the Hamiltonian are

$$\mathcal{H}_{u} = -\frac{J\Delta}{N} \sum_{q} \cos(\pi + qa) \sum_{k} c^{\dagger}_{k_{\mathrm{F}}+k+q} d_{-k_{\mathrm{F}}+k} \sum_{k'} c^{\dagger}_{k_{\mathrm{F}}+k'-q} d_{-k_{\mathrm{F}}+k'} -\frac{J\Delta}{N} \sum_{q} \cos(-\pi + qa) \sum_{k} d^{\dagger}_{-k_{\mathrm{F}}+k+q} c_{k_{\mathrm{F}}+k} \sum_{k'} d^{\dagger}_{-k_{\mathrm{F}}+k'-q} c_{k_{\mathrm{F}}+k'}.$$
(32.5.16)

They cannot be expressed simply in terms of the densities of right- and leftmoving particles, and will therefore be neglected for the moment. We will return later to the justification of this omission and to the role umklapp processes play.

The interaction between the spinless fermions can then be written in boson representation in the form

$$\mathcal{H}_{\text{int}} = -\frac{2Ja\Delta}{\pi} \sum_{q} |q| b_{q}^{\dagger} b_{q} - \frac{Ja\Delta}{\pi} \sum_{q} |q| \left(b_{q}^{\dagger} b_{-q}^{\dagger} + b_{-q} b_{q} \right)$$

$$= -\hbar v_{\text{F}} \frac{2\Delta}{\pi} \sum_{q} |q| b_{q}^{\dagger} b_{q} - \hbar v_{\text{F}} \frac{\Delta}{\pi} \sum_{q} |q| \left(b_{q}^{\dagger} b_{-q}^{\dagger} + b_{-q} b_{q} \right),$$
(32.5.17)

where the relationship $\hbar v_{\rm F} = Ja$ has been used. This expression contains only the contributions of the bosonic excitations, that is the $q \neq 0$ modes. We have to add the energy of topological excitations when the number of fermions changes in the branches:

$$\mathcal{H}' = -\frac{2Ja\Delta}{L} \left(\delta N_+ + \delta N_-\right)^2 = -\frac{2Ja\Delta}{L} \left(\delta N\right)^2.$$
(32.5.18)

The total Hamiltonian is the sum of (32.5.5), (32.5.17), and (32.5.18), that is

$$\mathcal{H} = \sum_{q} \hbar v_{\mathrm{F}} \left(1 - \frac{2\Delta}{\pi} \right) |q| b_{q}^{\dagger} b_{q} - \hbar v_{\mathrm{F}} \frac{\Delta}{\pi} \sum_{q} |q| \left(b_{q}^{\dagger} b_{-q}^{\dagger} + b_{-q} b_{q} \right) + \frac{\pi \hbar v_{\mathrm{F}}}{2L} \left(1 - \frac{4\Delta}{\pi} \right) (\delta N)^{2} + \frac{\pi \hbar v_{\mathrm{F}}}{2L} \tilde{J}^{2} \,.$$
(32.5.19)

The bosonic part of the Hamiltonian is bilinear but nondiagonal. Diagonalization can be achieved by a Bogoliubov-like canonical transformation which mixes the operators b_q^{\dagger} and b_{-q} . In analogy to (32.3.76) we introduce the operators 298 32 Fermion Liquids

$$\beta_q^{\dagger} = u_q b_q^{\dagger} + v_q b_{-q} ,$$

$$\beta_{-q} = u_q b_{-q} + v_q b_q^{\dagger} ,$$
(32.5.20)

for which bosonic commutation rules are assumed. Repeating the same steps as for the TL model, the Hamiltonian can be transformed to the form

$$\mathcal{H} = \sum_{q} \hbar u |q| \beta_{q}^{\dagger} \beta_{q} + \frac{\pi \hbar}{2L} \left[v_{\mathrm{N}} \left(\delta N \right)^{2} + v_{\mathrm{J}} \tilde{J}^{2} \right], \qquad (32.5.21)$$

with

$$\hbar u = \hbar v_{\rm F} \left[\left(1 - 2\Delta/\pi \right)^2 - \left(2\Delta/\pi \right)^2 \right]^{1/2} = Ja \left(1 - 4\Delta/\pi \right)^{1/2}, \qquad (32.5.22)$$

and

$$\hbar v_{\rm N} = Ja (1 - 4\Delta/\pi), \quad \hbar v_{\rm J} = Ja.$$
 (32.5.23)

Just as in the Tomonaga–Luttinger model [see (32.3.85) and (32.3.91)], the velocities $u, v_{\rm N}$, and $v_{\rm J}$ are not independent, they satisfy the relationship

$$u^2 = v_{\rm N} v_{\rm J}$$
. (32.5.24)

The quantity K defined by $K = u/v_{\rm N} = v_{\rm J}/u$ is then

$$K = (1 - 4\Delta/\pi)^{-1/2}.$$
 (32.5.25)

The low-energy part of the spectrum of the XXZ model is thus described by a Tomonaga–Luttinger-type Hamiltonian with one bosonic component.

When the eigenvalues are calculated for a finite chain, the spectrum has a tower structure. The energies can be written as

$$E = \hbar u \frac{2\pi}{L} \left(n_{+} + n_{-} + \Delta_{+} + \Delta_{-} \right)$$
(32.5.26)

and the momentum as

$$P = \hbar k_{\rm F} \tilde{J} + \hbar \frac{2\pi}{L} \left(n_+ - n_- + \Delta_+ - \Delta_- \right), \qquad (32.5.27)$$

where n_+ and n_- are integers, and

$$\Delta_{\pm} = \frac{1}{8} \left(\frac{1}{\sqrt{K}} \delta N \pm \sqrt{K} \tilde{J} \right)^2 \,. \tag{32.5.28}$$

These expressions were obtained after linearizing the $\cos qa$ spectrum. As explained in Chapter 15, the excitation spectrum of the one-dimensional anisotropic spin-1/2 Heisenberg chain can be calculated exactly with the Bethe ansatz. The leading terms to order 1/N for a finite chain of length L = Naare

$$E = L\varepsilon_0 + \hbar u \frac{2\pi}{L} \left(n_+ + n_- + \Delta_+ + \Delta_- - \frac{1}{12} \right)$$
(32.5.29)

with ε_0 the ground-state energy per site in an infinitely long chain and

$$P = \hbar k_{\rm F} \tilde{J} + \hbar \frac{2\pi}{L} \left(n_+ - n_- + \Delta_+ - \Delta_- \right) \,. \tag{32.5.30}$$

The term -1/12 is the finite-size correction to the ground-state energy, n_+ and n_- are integers, and u is determined by the anisotropy parameter Δ via

$$\hbar u = Ja \frac{\pi \sqrt{1 - \Delta^2}}{2 \left(\pi - \arccos \Delta\right)} \,. \tag{32.5.31}$$

The quantities Δ_{\pm} are related to the distribution of the (half-odd) integers I_j appearing in (15.5.98). We know that these numbers take consecutive values in the range $-N/4 < I_j < N/4$ in the ground state. The change in the number of positive and negative (half-odd) integers in an excited state is denoted by δN_+ and δN_- , respectively. Their symmetric and antisymmetric combinations,

$$\delta N = \delta N_{+} + \delta N_{-}, \qquad \tilde{J} = \delta N_{+} - \delta N_{-}$$
 (32.5.32)

appear in Δ_{\pm} in the form

$$\Delta_{\pm} = \frac{1}{8} \left(\frac{1}{\sqrt{K}} \delta N \pm \sqrt{K} \tilde{J} \right)^2, \qquad (32.5.33)$$

where 15

$$K = \frac{\pi}{2 \arccos \Delta} \,. \tag{32.5.34}$$

Comparison of the parameters u and K of the exact solution with that obtained in the approximate treatment can shed light on the accuracy of the bosonic approximation scheme. At $\Delta = 0$, where there is no interaction between the spinless fermions, the velocity of the bosons is equal to that of fermions. For small values of Δ , where $\arccos \Delta \approx \pi/2 - \Delta$, both the exact result and the bosonic treatment give the same corrections up to linear order:

$$\hbar u \approx Ja(1 - 2\Delta/\pi), \qquad K \approx 1 + 2\Delta/\pi.$$
 (32.5.35)

Deviations appear for larger Δ values, where higher order corrections have to be taken into account, indicating that the curvature of the true dispersion curve cannot be neglected in establishing the relationship between the parameters of the Heisenberg chain and of the equivalent TL model. The Heisenberg chain, at least in the low-energy sector, can still be mapped onto a TL model with effective couplings. In other words the effects of the curvature can be

¹⁵ The difference compared to (15.5.119) is due to a redefinition of the model. The antiferromagnetic side corresponds to $\Delta < 0$ in the present treatment, while we used the convention $\Delta > 0$ there.

eliminated by renormalizing the coupling constants. The mapping to the TL model breaks down at $\Delta = \pm 1$. The velocity of bosons vanishes at $\Delta = 1$ and a ferromagnetic transition takes place. The velocity remains finite at the isotropic antiferromagnetic point $\Delta = -1$; it is given by $\hbar u = Ja\pi$. Nevertheless, a new phase appears due to the umklapp processes neglected until now. As shown in Appendix L, umklapp processes are irrelevant in the planar regime, where K > 1/2. They can be eliminated by a renormalization group transformation discussed later in this chapter and the TL model with small-momentum transfer turns out to be a stable fixed point of the transformation. The umklapp processes become relevant for K < 1/2, that is for $\Delta < -1$, and generate a finite gap in the excitation spectrum.

The correlation functions of the spin-1/2 XXZ Heisenberg–Ising chain can be calculated directly in the spinless fermion representation in the continuum limit. The same results are obtained if the general expressions given for the TL model are applied to this one-component case. The exponents are related to the scaling dimensions Δ_{\pm} that depend on the anisotropy via K and on the number of particles added to the branches by the operator whose correlations are considered. The operator S^z in the correlation function $\langle S_l^z(t)S_0^z(0)\rangle$ does not change the number of reversed spins, $\delta N = 0$. It creates a particle–hole pair either with small momentum $(\tilde{J} = 0)$ or with $q \approx \pm 2k_{\rm F}$ $(\tilde{J} = 2)$. The leading terms in the correlation function are

$$\left\langle S_l^z(t)S_0^z(0)\right\rangle \approx \frac{A}{\pi^2} \frac{x^2 + u^2 t^2}{\left(x^2 - u^2 t^2\right)^2} + B \frac{\cos 2k_{\rm F} x}{\left(x^2 - u^2 t^2\right)^K},$$
 (32.5.36)

where x is the distance of the *l*th lattice point from the origin.

In calculating the correlation function $\langle S_l^+(t)S_0^-(0)\rangle$ we have to take into account that when a particle is removed from the system, the change in the parity of the number of particles leads to a rearrangement of the allowed k values, and the lowest energy state corresponds to a symmetric distribution of the momenta. $\delta N = 1$ does not imply $\tilde{J} = 1$. Instead of that we have $\tilde{J} = 0$ and $\tilde{J} = \pm 2$ for the lowest lying excitations. Accordingly the leading terms of the asymptotic form of the transverse correlation function are

$$\left\langle S_l^+(t)S_0^-(0) \right\rangle \approx A \frac{1}{\left(x^2 - u^2 t^2\right)^{1/4K}} + B \frac{x^2 + u^2 t^2}{x^2 - u^2 t^2} \frac{\cos 2k_F x}{\left(x^2 - u^2 t^2\right)^{K+1/4K}}.$$
(32.5.37)

32.5.2 Generic Properties

We are now in the position to collate the characteristic features of Luttinger liquids. The elementary excitations are bosonic collective density oscillations with a dispersion linear in |q| at long wavelengths. The slope of the dispersion curve defines the sound velocity u. If there are several branches of excitations, e.g., charge density and spin density oscillations for spin-1/2 fermions, these excitations do not interact (this is known under the name "spin-charge separation") and propagate with different velocities u_i . The number of particles and the current are conserved, and there are two topological excitations associated with each bosonic branch, corresponding to adding particles to the system or generating a current. The Hamiltonian of the *i*th component is

$$\mathcal{H}_{i} = \sum_{q} \hbar u_{i} |q| \beta_{qi}^{\dagger} \beta_{qi} + \frac{\pi \hbar}{4L} \left[v_{N_{i}} \left(\delta N_{i} \right)^{2} + v_{J_{i}} J_{i}^{2} \right], \qquad (32.5.38)$$

and the momentum operator is

$$\mathcal{P} = \sum_{q} \hbar q b_{qi}^{\dagger} b_{qi} + \hbar \left(k_{\rm F} + \frac{\pi}{2L} \delta N_i \right) J_i \,. \tag{32.5.39}$$

The velocities of the topological excitations are not independent; they obey

$$u_i^2 = v_{N_i} v_{J_i} \,. \tag{32.5.40}$$

The spectrum of low-energy bosonic excitations form towers about the points labeled by the integers δN_i and J_i . As a consequence, the correlation functions exhibit at T = 0 a power-law decay in the asymptotic regime, at long distances and times, with coupling-strength-dependent exponents. The exponents depend on the correlation parameters $K_i = u_i/v_{N_i} = v_{J_i}/u_i$.

The characteristic Kohn anomaly wave number $2k_{\rm F}$ varies linearly with the charge density. The Luttinger-liquid state becomes unstable when an integer multiple of $2k_{\rm F}$ is equal to the reciprocal-lattice vector $2\pi/a$.

This kind of behavior was originally found in the Tomonaga–Luttinger model with a strictly linear dispersion relation when the large-momentumtransfer processes were excluded. We may say in view of the exact results in the XXZ and Hubbard models that neither of these assumptions are necessary. A curvature in the dispersion relation may result in an interaction between the bosonic degrees of freedom, but this interaction is not relevant. It can be eliminated by a renormalization procedure leading to a Luttinger liquid with effective couplings. That is why a weak nearest-neighbor interaction in the extended Hubbard model does not destroy the Luttinger-liquid properties.

The problem of large-momentum-transfer and umklapp processes is more delicate. There is no good physical reason why these processes should be forbidden in realistic physical systems. In the Hubbard model, for example, the strength of the interaction is independent of the momentum transfer. The coupling constants of the backward and umklapp processes are the same as that for forward scattering. The umklapp processes, which play a role only in a half-filled model, seem to be relevant; they generate a gap in the excitation spectrum. On the other hand, backward scattering seems to be irrelevant; it does not seem to destroy the Luttinger-liquid behavior even when it is present. The relevance or irrelevance of couplings can be studied by a renormalization transformation. Here we will apply the procedure presented in Appendix M to derive the scaling equations of the one-dimensional electron gas and to demonstrate that backward scattering can indeed be eliminated.

32.5.3 Scaling Theory of the One-Dimensional Electron Gas

For the sake of simplicity we consider first non-half-filled systems and neglect the umklapp processes. The g_4 terms that lead to a trivial renormalization of the Fermi velocity will also be omitted. There are three independent couplings in an unpolarized system since the process with coupling $g_{1\parallel}$, where particles with the same spin are scattered backwards, cannot be distinguished from forward scattering with coupling $g_{2\parallel}$. The strength of this process is in fact $g_{1\parallel} - g_{2\parallel}$ owing to the different order of the operators in the two terms of the Hamiltonian. When the spins of the scattered particles are different, and the spin is conserved in the scattering process, the forward- and backwardscattering processes with coupling constants $g_{2\perp}$ and $g_{1\perp}$, respectively, can be distinguished.

Consider a scattering process in which the initial state

$$|i\rangle = c^{\dagger}_{k_{\rm F}+k_1\alpha} d^{\dagger}_{-k_{\rm F}+k_2\beta} |\Psi_{\rm FS}\rangle \tag{32.5.41}$$

with a right- and a left-moving electron outside the Fermi sea is scattered into the final state

$$|f\rangle = d^{\dagger}_{-k_{\rm F}+k_3\gamma} c^{\dagger}_{k_{\rm F}+k_4\delta} |\Psi_{\rm FS}\rangle. \qquad (32.5.42)$$

The matrix element of the interaction Hamiltonian between these states gives

$$\langle f | \mathcal{H}_{\text{int}} | i \rangle = \frac{1}{L} \left[(g_{1\parallel} - g_{2\parallel}) \delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\alpha\beta} + g_{1\perp} \delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\alpha,-\beta} - g_{2\perp} \delta_{\alpha\delta} \delta_{\beta\gamma} \delta_{\alpha,-\beta} \right].$$
(32.5.43)

The three terms correspond to the three processes discussed above.

Applying the procedure presented in Appendix M we decrease the bandwidth cutoff from $D = \hbar v_F k_c$ to $D - \delta D$. Processes in which the energies of some of the intermediate particles are in the narrow ranges $[-D, -D + \delta D]$ or $[D - \delta D, D]$ become now forbidden. Their missing contributions can be compensated by modifying the coupling constants. The original model and the new model with the smaller cutoff and modified couplings describe the same physical behavior if the matrix elements of the scattering matrix are identical at least for electrons near the Fermi energy.

The correction to the effective Hamiltonian of the new model up to second order in the coupling constants is

$$\delta \mathcal{H}_{\rm int}' = \mathcal{H}_{\rm int} P \frac{1}{z - \mathcal{H}_0} \mathcal{H}_{\rm int} , \qquad (32.5.44)$$

where z is the energy of the initial state and P is a projection operator that ensures that there is at least one electron in the neighborhood of the upper band edge, in the region $[D - \delta D, D]$, in the intermediate state, or at least one hole near the lower band edge, in the range $[-D, -D + \delta D]$. A lengthy but straightforward calculation yields
$$\langle f|\delta\mathcal{H}'_{\rm int}|i\rangle = -\frac{1}{L}\frac{1}{2\pi\hbar v_{\rm F}} \left[g_{1\perp}^2\delta_{\alpha\gamma}\delta_{\beta\delta}\delta_{\alpha\beta} + g_{1\perp}^2\delta_{\alpha\delta}\delta_{\beta\gamma}\delta_{\alpha,-\beta} + 2g_{1\perp}(g_{1\parallel} - g_{2\parallel} + g_{2\perp})\delta_{\alpha\gamma}\delta_{\beta\delta}\delta_{\alpha,-\beta}\right]\frac{\delta D}{D}.$$
(32.5.45)

The spin-dependent factors help to identify the contributions to the different processes. We find

$$\delta(g_{1\parallel} - g_{2\parallel}) = -\frac{1}{D} \frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \delta D ,$$

$$\delta g_{1\perp} = -\frac{1}{D} \frac{1}{\pi\hbar v_{\rm F}} g_{1\perp} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \delta D , \qquad (32.5.46)$$

$$\delta g_{2\perp} = -\frac{1}{D} \frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \delta D .$$

Linear combinations of these equations lead to the relations

$$\delta(g_{1\parallel} - g_{2\parallel} - g_{2\perp}) = 0,$$

$$\delta(g_{1\parallel} - g_{2\parallel} + g_{2\perp}) = -\frac{1}{D} \frac{1}{\pi \hbar v_{\rm F}} g_{1\perp}^2 \delta D,$$

$$\delta g_{1\perp} = -\frac{1}{D} \frac{1}{\pi \hbar v_{\rm F}} g_{1\perp}(g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \delta D.$$
(32.5.47)

The combination $g_{1\parallel} - g_{2\parallel} - g_{2\perp}$ is invariant under the renormalization transformation. The two other combinations scale together.

The new couplings are obtained by decreasing the cutoff by δD ; hence, for small changes in the cutoff and the couplings

$$\delta g_i = -\frac{\mathrm{d}g_i}{\mathrm{d}D}\delta D\,.\tag{32.5.48}$$

The flow equations of the effective couplings can be written in differential form

$$\frac{\mathrm{d}(g_{1\parallel} - g_{2\parallel})}{\mathrm{d}D} = \frac{1}{D} \frac{1}{2\pi\hbar v_{\mathrm{F}}} g_{1\perp}^{2},
\frac{\mathrm{d}g_{1\perp}}{\mathrm{d}D} = \frac{1}{D} \frac{1}{\pi\hbar v_{\mathrm{F}}} g_{1\perp}(g_{1\parallel} - g_{2\parallel} + g_{2\perp}), \qquad (32.5.49)
\frac{\mathrm{d}g_{2\perp}}{\mathrm{d}D} = \frac{1}{D} \frac{1}{2\pi\hbar v_{\mathrm{F}}} g_{1\perp}^{2}.$$

When the appropriate linear combinations are taken,

$$\frac{\mathrm{d}(g_{1\parallel} - g_{2\parallel} - g_{2\perp})}{\mathrm{d}D} = 0,$$

$$\frac{\mathrm{d}(g_{1\parallel} - g_{2\parallel} + g_{2\perp})}{\mathrm{d}D} = \frac{1}{D} \frac{1}{\pi \hbar v_{\mathrm{F}}} g_{1\perp}^{2},$$

$$\frac{\mathrm{d}g_{1\perp}}{\mathrm{d}D} = \frac{1}{D} \frac{1}{\pi \hbar v_{\mathrm{F}}} g_{1\perp}(g_{1\parallel} - g_{2\parallel} + g_{2\perp}).$$
(32.5.50)

The flow of the renormalized couplings as the cutoff is decreased is displayed in Fig. 32.34.



Fig. 32.34. Flow of the renormalized couplings of the one-dimensional electron gas

The line $g_{1\perp} = 0$ is a fixed line of the scaling equations. No backward scattering is generated by higher order processes if there is no backward scattering in the bare Hamiltonian. The couplings of the forward-scattering processes, $g_{1\parallel} - g_{2\parallel} - g_{2\perp}$ and $g_{1\parallel} - g_{2\parallel} + g_{2\perp}$, are marginal; they remain unrenormalized. That is why the critical exponents of the correlation functions of the TL model are not universal; they depend on the coupling constants. The stability of the fixed line is, however, different whether $g_{1\parallel} - g_{2\parallel} + g_{2\perp} \ge |g_{1\perp}|$ or $g_{1\parallel} - g_{2\parallel} + g_{2\perp} < |g_{1\perp}|$. In the former case, the scaling curves flow in from both sides to $g_{1\perp} = 0$ and $g_{1\parallel} - g_{2\parallel} + g_{2\perp}$ takes a finite nonuniversal value. The halfline $g_{1\perp} = 0, g_{1\parallel} - g_{2\parallel} + g_{2\perp} \ge 0$ is thus stable under renormalization when the bare couplings of the model satisfy the condition $g_{1\parallel} - g_{2\parallel} + g_{2\perp} \ge |g_{1\perp}|$. Even if the bare value of $g_{1\perp}$ is finite, that is backward scattering is present in the original model, the absolute values of the couplings decrease as the cutoff becomes smaller and $g_{1\perp}$ scales to zero. Backward scattering is irrelevant in this case, it is gradually transformed out, eliminated. The model can be mapped onto an equivalent model with modified cutoff and modified, renormalized values for the couplings of the forward-scattering processes but with no backward scattering.

The situation is different for $g_{1\parallel} - g_{2\parallel} + g_{2\perp} < |g_{1\perp}|$. As seen in Fig. 32.34, the scaling curves flow out, the couplings get stronger and stronger under renormalization. This happens also when the coupling $g_{1\perp}$ is arbitrarily small but finite provided that $g_{1\parallel} - g_{2\parallel} + g_{2\perp} < 0$. Backward scattering is then relevant: the model scales away from the TL model.

We mention, without doing the calculations here, that the combination $g_{1\parallel} - g_{2\parallel} - g_{2\perp}$ is not invariant when umklapp processes with coupling $g_{3\perp}$ are taken into account in a half-filled system. The scaling equations are

$$\frac{\mathrm{d}(g_{1\parallel} - g_{2\parallel} - g_{2\perp})}{\mathrm{d}D} = \frac{1}{D} \frac{1}{\pi \hbar v_{\mathrm{F}}} g_{3\perp}^2, \qquad (32.5.51)$$
$$\frac{\mathrm{d}g_{3\perp}}{\mathrm{d}D} = \frac{1}{D} \frac{1}{\pi \hbar v_{\mathrm{F}}} g_{3\perp} (g_{1\parallel} - g_{2\parallel} - g_{2\perp}).$$

Umklapp processes are irrelevant; they can be transformed out, if $g_{1\parallel} - g_{2\parallel} - g_{2\perp} \geq |g_{3\perp}|$. Otherwise they are relevant and drive the system toward the strong-coupling limit, away from Luttinger-liquid behavior.

We can now return to the problem of why the Hubbard model behaves as a Luttinger liquid in spite of the fact that backward-scattering processes are allowed in the bare Hamiltonian. Since the strength U of the interaction is independent of the momentum transfer and only electrons with opposite spins interact,

$$g_{1\parallel} = g_{2\parallel} = 0, \qquad g_{1\perp} = g_{2\perp} = U,$$
 (32.5.52)

which means that

$$g_{1\parallel} - g_{2\parallel} - g_{2\perp} = -U, \qquad g_{1\parallel} - g_{2\parallel} + g_{2\perp} = U, \qquad g_{1\perp} = U.$$
 (32.5.53)

When U is positive, $g_{1\perp}$ and $g_{1\parallel} - g_{2\parallel} + g_{2\perp}$ scale to zero according to the scaling equations, and $g_{1\parallel} - g_{2\parallel} - g_{2\perp}$ remains invariant. Hence in the fixed point of the renormalization transformation we have

$$g_{1\parallel}^* - g_{2\parallel}^* - g_{2\perp}^* = -U, \qquad g_{1\parallel}^* - g_{2\parallel}^* + g_{2\perp}^* = g_{1\perp}^* = 0.$$
 (32.5.54)

The solution of these equations is

$$g_{1\parallel}^* - g_{2\parallel}^* = -\frac{1}{2}U, \qquad g_{2\perp}^* = \frac{1}{2}U, \qquad g_{1\perp}^* = 0, \qquad (32.5.55)$$

and the fixed-point couplings can be chosen as

$$g_{1\parallel}^* = g_{1\perp}^* = 0, \qquad g_{2\parallel}^* = g_{2\perp}^* = \frac{1}{2}U.$$
 (32.5.56)

This shows that the backward-scattering terms of the Hubbard model are irrelevant; they can be transformed out. Only the forward-scattering processes survive. That is why the Hubbard model behaves like a Luttinger liquid.

The situation is different in the half-filled case, when umklapp processes have to be taken into account. The couplings between the spin degrees of freedom, $g_{1\perp}$ and $g_{1\parallel} - g_{2\parallel} + g_{2\perp}$, still scale in the same way as above. The backward scattering is irrelevant and the spin modes are soft bosons with linear dispersion curve. The bare couplings in the charge sector are

$$g_{1\parallel} - g_{2\parallel} - g_{2\perp} = -U, \qquad g_{3\perp} = U.$$
 (32.5.57)

The condition $g_{1\parallel} - g_{2\parallel} - g_{2\perp} \ge |g_{3\perp}|$ for the irrelevance of the umklapp terms is not satisfied in the Hubbard model and the renormalization transformation scales the couplings to strong values, away from Luttinger-liquid behavior. Although the present approximation, in which only the lowest order corrections were calculated to the scaling equations, does not allow one to calculate the fixed-point values in the strong-coupling limit and to determine the physical properties, it may not be surprising that the umklapp terms generate a gap in the charge sector, as will be discussed later.

32.5.4 Experimental Results

We have seen already in Chapter 7, where a selection of possible crystal structures was presented, that there exist materials in which the chemical binding is strongly anisotropic, as if they were built up from weakly coupled chains of atoms. Further examples will be shown in Chapter 33. Although the atoms form a regular three-dimensional lattice, the electrons can propagate in practically only one preferred direction, since the overlap between the wavefunctions of neighboring atoms is extremely weak in the other directions. These materials are quasi-one-dimensional from the point of view of electronic properties and can be modeled by a one-dimensional interacting electron gas. The theoretical results discussed until now are valid strictly speaking only for exactly one-dimensional models. We are never dealing with such an ideal situation when the behavior of quasi-one-dimensional systems of weakly coupled chains is studied. Nevertheless we can claim, based on experimental results and theoretical considerations, that there exists a temperature range, where the onedimensional features are dominant and Luttinger-liquid properties might be observed.

Below a certain crossover temperature T^* , where the thermal energy is comparable with the kinetic energy of the hopping between the chains, the coupling between the chains cannot be neglected. The electron system is then truly three dimensional. In strongly anisotropic systems another characteristic temperature T^{**} can be defined from the width of that portion of the band where the dispersion curve is well approximated by that of a one-dimensional model. When the overlap integrals between the wavefunctions of neighboring atoms are much weaker between the chains than within the chains, T^* may be much smaller than T^{**} , and there is an appreciable temperature interval between them where the properties are one-dimensional-like. Similarly, when frequency-dependent quantities are measured, the coupling between chains may distort the one-dimensional spectrum at very low energies, but there might be an intermediate frequency window where one-dimensional physics could be observed.

These crossover temperatures are not sharply defined and it is difficult to find experimental results where the non-Fermi-liquid behavior can be demonstrated in a wide temperature interval without symmetry breaking. Nevertheless, there are indications of one-dimensional behavior in quasi-onedimensional materials. The Bechgaard salts $[(TMTSF)_2X \text{ with } X=PF_6, AsF_6,$ and ClO₄] to be discussed in more detail in the next chapter are well-known examples. Although a gap is opened in their spectrum, the optical conductivity shows anomalous behavior at somewhat higher energies (higher frequencies), where the interchain couplings become ineffective. As shown in Fig. 32.35, the optical conductivity of Bechgaard salts has a power-law frequency dependence, $\sigma(\omega) \sim \omega^{-\nu}$, over more than a decade with an anomalous exponent, which is characteristic for a Luttinger liquid.



Fig. 32.35. Frequency-dependent optical conductivity of Bechgaard salts. The normalized conductivities are shown on a log–log scale. The solid line is a fit of the form $\sigma(\omega) \sim \omega^{-\nu}$ [Reprinted with permission from A. Schwartz et al., *Phys. Rev. B* 58, 1261 (1998). \bigcirc (1998) by the American Physical Society]

The single-particle excitation spectrum can be probed by angle-resolved photoemission spectroscopy (ARPES). The experimental spectra on TTF– TCNQ, which is another well-known example of quasi-one-dimensional organic conductors, indicate marked deviations from conventional metallic behavior. The unconventional features, namely the absence of a Fermi edge and the spectroscopic evidence for spin–charge separation, can be explained by the physics of Luttinger liquids.

Tunneling experiments are suitable to measure the density of states. The derivative of the current with respect to voltage is proportional to the convolution of the densities of states on the two sides. If the density of states is structureless on one side, the dI/dV signal measures the density of states of the other side directly. Figure 32.36 shows the dI/dV spectrum of the so-called purple bronze (Li_{0.9}Mo₆O₁₇), a highly anisotropic quasi-one-dimensional conductor.

The experimental result can be fit by a form

$$\frac{\mathrm{d}I}{\mathrm{d}V} \propto |V|^{\alpha} \tag{32.5.58}$$

with $\alpha = 0.6$. This corresponds to a density of states

$$\rho(\varepsilon) \propto |\varepsilon - \varepsilon_{\rm F}|^{\alpha},$$
(32.5.59)

which is precisely the functional form we obtained for the density of states of Luttinger liquids.



Fig. 32.36. The dI/dV spectrum of purple bronze at low temperatures near zero bias plotted in both (a) linear and (b) double logarithmic scale. The dashed lines are power-law fits with exponent $\alpha = 0.6$ [Reprinted with permission from J. Hager et al., *Phys. Rev. Lett.* 95, 186402 (2005). © (2005) by the American Physical Society]

An interesting development of the last decades was the discovery of carbon nanotubes, which are either metallic or insulating depending on the chirality of the tube. The low-energy part of the band structure of the metallic nanotubes can be well approximated by a multicomponent TL model. The voltage and temperature dependence of the conductance exhibit anomalous power-law behavior just as expected for a Luttinger liquid. The results of such measurements are shown in Fig. 32.37.



Fig. 32.37. Scaled differential conductance of differently contacted nanotubes [M. Bockrath et al., *Nature* 397, 598 (1999)]

32.5.5 Luttinger Liquids in Higher Dimensions

The Tomonaga–Luttinger model is by definition a one-dimensional model. There is no simple generalization to higher dimensions. The question whether Luttinger-liquid behavior is possible in higher dimensions or not remains an interesting and as yet unsolved problem. The question is especially relevant in connection with the attempts to understand the "normal-state" properties of high-temperature superconductors. The anomalous behavior above the superconducting state indicates that these layered, quasi-two-dimensional systems are not normal Fermi liquids. One possibility is that they behave as Luttinger liquids. Studying the two-dimensional Hubbard model and its generalizations may help to elucidate this problem. There are only a few exact statements about the two-dimensional Hubbard model. One can show that the half-filled model is not Fermi liquid for weak couplings apart from an exponentially small temperature region, but it is not Luttinger liquid since a gap is generated in the excitation spectrum. However, away from half-filling, the model can be shown to be Fermi liquid at least for weak couplings. Luttinger-liquid behavior can thus only be observed, if at all, in two-dimensional models with more complicated interactions.

32.6 Alternatives to Luttinger-Liquid Behavior

The Luttinger-liquid behavior discussed up to now is a generic feature of a large class of one-dimensional models, but it is only one possible low-energy state of one-dimensional Fermi systems. Although strictly one-dimensional systems may not undergo a phase transition at any finite temperature, brokensymmetry phases may appear in quasi-one-dimensional systems, as will be discussed in the next chapter. Here we will consider other alternatives with no broken symmetry.

32.6.1 Mott Insulator

Luttinger-liquid behavior was found in the repulsive Hubbard model away from half filling, when umklapp processes can be neglected. The umklapp processes were neglected also in our study of the TL model. The scaling approach predicted that the coupling of the umklapp term $(g_{3\perp})$ scales to strong coupling in the half-filled Hubbard model, indicating that this coupling is relevant, and the Luttinger-liquid state is not a stable fixed point.

The Hubbard model can be solved exactly in the half-filled $(n_e = 1)$ case as well. The parameter k_0 takes the value $k_0 = \pi$ and the equations for the root densities given in (32.4.27) can be solved in terms of Bessel functions to yield

$$\rho(k) = \frac{1}{2\pi} + \cos k \int_{-\infty}^{\infty} \frac{\mathrm{d}\xi}{2\pi} \frac{J_0(\xi) \cos(\xi \sin k)}{1 + \mathrm{e}^{2u|\xi|}},$$

$$\sigma(\lambda) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\xi}{2\pi} \frac{J_0(\xi)}{2\cosh(u\xi)} \mathrm{e}^{-\mathrm{i}\xi\lambda}.$$
(32.6.1)

The ground-state energy per site can be expressed in the form

$$E_0/N = -4t \int_0^\infty \frac{\mathrm{d}\xi}{\xi} \frac{J_0(\xi)J_1(\xi)}{1 + \mathrm{e}^{2u\xi}} \,. \tag{32.6.2}$$

Since the ground-state energy is an analytic function of u = U/4t for real U, except for U = 0, no phase transition occurs as a function of U for any U > 0.

Just as in a non-half-filled model, the excited states are combinations of spinons, holons, and antiholons, but the holons and antiholons of the half-filled model are different in nature from their counterparts in the non-half-filled case. The spinon dispersion relation is obtained by eliminating the parameter λ_s from the equations

$$\varepsilon_{\rm s}(\lambda_{\rm s}) = 2t \int_{0}^{\infty} \frac{\mathrm{d}\xi}{\xi} \frac{J_1(\xi)\cos(\xi\lambda_{\rm s})}{\cosh(\xi u)}, \qquad (32.6.3)$$
$$q(\lambda_{\rm s}) = 2 \int_{0}^{\infty} \frac{\mathrm{d}\xi}{\xi} \frac{J_0(\xi)\sin(\xi\lambda_{\rm s})}{\cosh(\xi u)}.$$

The holon dispersion curve can be calculated similarly from

$$\varepsilon_{\rm h}(k_{\rm h}) = 2t \cos k_{\rm h} + U/2 + 2t \int_{0}^{\infty} \frac{\mathrm{d}\xi}{\xi} \frac{J_{1}(\xi) \cos(\xi \sin k_{\rm h})}{\cosh(\xi u)} \mathrm{e}^{-\xi u} ,$$

$$q(k_{\rm h}) = k_{\rm h} + 2 \int_{0}^{\infty} \frac{\mathrm{d}\xi}{\xi} \frac{J_{0}(\xi) \sin(\xi \sin k_{\rm h})}{1 + \mathrm{e}^{2u\xi}}$$
(32.6.4)

by eliminating $k_{\rm h}$. The momentum of spinons covers only half of the Brillouin zone; it varies in the range $[-\pi/2, \pi/2]$ and a gapless spectrum is obtained. On the other hand, the momentum of holons covers the entire Brillouin zone, and the spectrum is gapped. For small q values

$$\varepsilon_{\rm h} = \sqrt{\Delta_0^2 + u_{\rm c}^2 q^2} \tag{32.6.5}$$

with

$$\Delta_0 = U/2 - 2t + 2t \int_0^\infty \frac{\mathrm{d}\xi}{\xi} \frac{J_1(\xi)\mathrm{e}^{-\xi U/4t}}{\cosh(\xi U/4t)} \,. \tag{32.6.6}$$

In the weak-coupling limit

$$\Delta_0 = \frac{4t}{\pi} \sqrt{U/t} e^{-2\pi t/U}, \qquad u_c = 2t$$
(32.6.7)

and in the strong-coupling limit

$$\Delta_0 = U/2 - 2t + 4\ln 2\frac{t^2}{U}, \qquad u_c = t\sqrt{U/t}. \qquad (32.6.8)$$

Antiholons were defined for a non-half-filled band in the ranges $[-\pi, -2k_{\rm F}]$ and $[\pi, 2k_{\rm F}]$. These regions shrink to zero in the half-filled case. Nevertheless, antiholons can be defined by studying excitations with an extra added particle. Since $N_{\rm e} \leq N$ was assumed from the very beginning, such states should be considered in the complementer space by studying the motion of $N_{\rm e} - 1$ holes through a lattice of doubly occupied sites. Removing a hole from the halffilled band creates a spinon and an antiholon. Antiholons are defined in the entire Brillouin zone and they have identical dispersion relation to holons by electron-hole symmetry. The same dispersion relation can be derived by considering particle-hole excitations in the half-filled band.

Although the gap in the holon and antiholon spectrum is exponentially small for weak Coulomb repulsion, it is finite for arbitrary finite U. While metallic behavior is found away from half filling in the one-dimensional Hubbard model, the half-filled model is nonmetallic for arbitrary positive values of the Coulomb repulsion. The critical value of U for the metal–insulator transition from the metalliclike free electron behavior at U = 0 to the gapped phase for U > 0 is $U_c = 0$, and the transition is of BKT type.

The field-theoretical treatment of the one-dimensional Fermi system given in Appendix L sheds more light on what happens in the half-filled case. The Hamiltonian of the TL model can be rewritten in terms of charge and spin phase fields and their conjugates in the form of a harmonic model,

$$\mathcal{H} = \frac{1}{2}\hbar u_{\rm c} \int \mathrm{d}x \left[K_{\rm c} \Pi_{\rm c}^2(x) + \frac{1}{K_{\rm c}} \left(\partial_x \phi_{\rm c}(x) \right)^2 \right] + \frac{1}{2}\hbar u_{\rm s} \int \mathrm{d}x \left[K_{\rm s} \Pi_{\rm s}^2(x) + \frac{1}{K_{\rm s}} \left(\partial_x \phi_{\rm s}(x) \right)^2 \right], \qquad (32.6.9)$$

and the umklapp term that depends only on the charge degrees of freedom gives rise to a term

$$\mathcal{H}_{\mathrm{u}} = \frac{2g_{3\perp}}{(2\pi\alpha)^2} \int \mathrm{d}x \cos\left(\sqrt{8\pi}\phi_{\mathrm{c}}(x)\right). \tag{32.6.10}$$

The spin part is unaffected; hence, the low-energy part of the spectrum of spin excitations is identical to that of the TL model. The spin bosons have linear dispersion relation and propagate with velocity u_s . Owing to the extra term the charge part is described by the *sine-Gordon model* well known in

field theory. It has a massive, gapped spectrum. The relevance or irrelevance of the umklapp term can be studied by analyzing the scaling dimension of the umklapp operator $\cos(\sqrt{8\pi}\phi_c(x))$. This operator transfers two right-moving particles to the left-moving branch, $\delta N_{+,\uparrow} = \delta N_{+,\downarrow} = 1$, $\delta N_{-,\uparrow} = \delta N_{-,\downarrow} = -1$, that is $J_c = 4$, $\delta N_c = N_s = J_s = 0$ and therefore $\Delta_{c,\pm} = K_c$ and $\Delta_{s,\pm} = 0$. The scaling dimension of the operator is $d = 2K_c$. Umklapp processes are marginal if d = 2, that is if $K_c = 1$. They are relevant for $K_c < 1$ and irrelevant for $K_c > 1$. The condition for the irrelevance is $g_{2c} < 0$ in the TL model. When the forward-scattering term with coupling $g_{1\parallel}$ is also taken into account, the umklapp term is relevant if

$$g_{2\parallel} - g_{1\parallel} + g_{2\perp} > 0. (32.6.11)$$

This is in agreement with the result of the scaling theory, where we saw that the fixed line $g_{3\perp}$ is unstable if $g_{1\parallel} - g_{2\parallel} - g_{2\perp} < 0$.

The $\cos(\sqrt{8\pi}\phi_c(x))$ term in the Hamiltonian pins the value of $\phi_c(x)$ when its coupling gets larger and larger under the scaling transformation. The lowenergy phase fluctuations are eliminated and a gap arises in the charge part of the spectrum leading to a nonmetallic behavior. This gap is a many-body effect and the insulating state is due to the interactions between electrons. It is for this reason that this phase is known as a *Mott insulator*.

32.6.2 Luther–Emery Liquid

We have seen that backward scattering is irrelevant if $g_{1\parallel} - g_{2\parallel} + g_{2\perp} \ge |g_{1\perp}|$, and the fixed line $g_{1\perp} = 0$ is stable for $g_{1\parallel} - g_{2\parallel} + g_{2\perp} > 0$. It becomes relevant for $g_{1\parallel} - g_{2\parallel} + g_{2\perp} < 0$. This result can be derived from the field-theoretic formulation of the one-dimensional electron gas in complete analogy with our previous considerations for the umklapp process. Backward scattering contributes a term

$$\mathcal{H}_{\rm bw} = \frac{2g_{1\perp}}{(2\pi\alpha)^2} \int \mathrm{d}x \cos\left(\sqrt{8\pi}\phi_{\rm s}(x)\right) \tag{32.6.12}$$

to the Hamiltonian in field-theoretical language. This operator is marginal if $K_{\rm s}$ equals unity, relevant for $K_{\rm s} < 1$ and irrelevant for $K_{\rm s} > 1$. Thus backward scattering becomes relevant for $g_{2\rm s} > 0$. This gives precisely the previous conditions when $g_{1\parallel}$ is also taken into account. A relevant backward scattering fixes the phase $\phi_{\rm s}$ and a gap appears in the spin part of the excitation spectrum. This is the case for U < 0 in the Hubbard model. The state with gapped spin excitations and gapless charge excitations is referred to as a Luther–Emery liquid.¹⁶ For the negative-U Hubbard model we get

$$\Delta_0^{(s)} = \frac{8}{\pi} t \sqrt{\frac{|U|}{t}} \sin^3(\pi n_e/2) e^{-2\pi t \sin(\pi n_e/2)/|U|}, \qquad (32.6.13)$$

¹⁶ A. LUTHER and V. J. EMERY, 1974.

for the spin gap from the Bethe ansatz in the weak-coupling limit. The opening of the gap is again exponentially slow; the transition to the Luther–Emery liquid at U = 0 is of Berezinskii–Kosterlitz–Thouless type.

In multicomponent Luttinger liquids, where there are several charge and spin modes, gaps may be generated in them independently and the phase may be characterized by the number of remaining gapless modes.

32.6.3 Phase separation

For strong Coulomb repulsion, when doubly occupied sites are forbidden, the half-filled Hubbard model is equivalent to a Heisenberg model. When the band is close to half filling, the so-called t-J model is obtained with a few holes propagating between the localized spins. Such a system behaves as a Luttinger liquid in one dimension for weak exchange coupling J. The elementary excitations are holons and spinons. For larger values of J/t the holon liquid becomes unstable and separates into a hole-rich and a hole-poor phase. Phase separation and stripe formation is a particularly interesting question in the non-Fermi-liquid phases of two-dimensional systems.

32.7 Quantum Hall Liquid

We mentioned already that the problem of an eventual non-Fermi-liquid behavior of the two-dimensional electron gas is an unsolved problem in general, even though many efforts have been devoted to it recently. It is well established, however, that in one special case, namely in strong magnetic field, the two-dimensional interacting electron gas is definitely not a Fermi liquid and the elementary excitations of the particular quantum liquid are unusual quasiparticles. They can be observed in the quantum Hall effect.

32.7.1 Fractional Quantum Hall Effect

It was shown in Chapter 24 that plateaus may be observed in the magneticfield dependence of the nondiagonal components of the conductivity of MOS-FET devices, where carriers are constrained to a narrow region near the interface forming a two-dimensional electron gas (2DEG). Similar plateaus are found when the conductivity is measured as a function of the charge density for a fixed magnetic field. When the electrons can move only parallel to the z = 0 plane and the magnetic field is oriented in the z-axis, σ_{xy} takes quantized values

$$\sigma_{xy} = \nu \frac{e^2}{h} \tag{32.7.1}$$

on the plateaus. The resistivity ρ_{xx} vanishes in the same regions.

The occurrence of plateaus with integer ν is known as the integer quantum Hall effect. It could be explained in the one-particle picture by assuming that the Landau levels become broadened in the presence of impurities and some of these states become localized. Plateaus appear in the nondiagonal elements of the conductivity and the resistivity vanishes, when the chemical potential falls into the range of localized states as the magnetic field or the charge density is varied.

Soon after the discovery of the integer quantum Hall effect, D. C. TSUI, H. L. STÖRMER, and A. C. GOSSARD^{17} observed a new plateau in a $\text{GaAs/Ga}_x \text{Al}_{1-x} \text{As}$ heterostructure at very low temperatures, below about 1 K, in very strong fields at $\rho_{xy} = 3h/e^2$. This corresponds to a value $\nu = 1/3$, that is to a one-third-filled lowest Landau level. The experimental results are shown in Fig. 32.38.



Fig. 32.38. First observation of the fractional quantum Hall effect at $\nu = 1/3$ [Reprinted with permission from D. C. Tsui, H. L. Stormer, and A. C. Gossard, *Phys. Rev. Lett.* 48, 1559 (1982). \bigcirc (1982) by the American Physical Society]

It soon turned out that fractional quantization of the Hall plateaus appear not only at $\nu = 1/3$, but at many other fractional ν values as well, e.g., at $\nu = 2/3, 2/5, 3/5, 3/7, 4/7$ with accuracy 10^{-3} – 10^{-5} . Similar effects could be observed at fractional values larger than unity, at $\nu = 4/3, 5/3, 9/7, 10/7, 11/7$. The plateaus are always accompanied by the vanishing of ρ_{xx} . Weaker anomalies could be seen at further $\nu = p/q$ values with q odd. Somewhat different

¹⁷ See the footnote on page 6 of Volume 1.

anomalies were found at $\nu = 1/2$ or 3/2. Figure 32.39 shows the anomalies for a multitude of ν values.



Fig. 32.39. Overview of diagonal resistivity ρ_{xx} and Hall resistance ρ_{xy} measured on a GaAs/AlGaAs heterostructure at about 100 mK up to 30 T. N indicates the Landau-level quantum number and ν is the filling factor [Reprinted with permission from R. Willett et al., *Phys. Rev. Lett.* **59**, 1776 (1987). \bigcirc (1987) by the American Physical Society]

These results arose enormous interest because the plateaus at fractional ν values are strong indications that the interaction between electrons opens gaps inside the Landau level for special fractional fillings. The situation is similar to the metal–insulator transition to be discussed later. Systems that would be metallic according to band structure calculations may turn out to be insulators since interactions destroy the single-particle picture and open a gap, a forbidden region, in the neighborhood of the Fermi energy.

32.7.2 Laughlin State

As the interaction between electrons seems to play an important role in the fractional quantum Hall effect we cannot content ourselves with the solution of the problem of noninteracting electrons in strong magnetic field as presented in Chapter 22. Instead of considering the Hamiltonian given in (22.1.1) we have to study the eigenvalue problem of the Hamiltonian

$$\mathcal{H} = \frac{1}{2m_{\rm e}} \sum_{i=1}^{N_{\rm e}} \left[\left(\boldsymbol{p}_i + e\boldsymbol{A}(\boldsymbol{r}_i) \right)^2 + V(\boldsymbol{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{\tilde{e}^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \qquad (32.7.2)$$

where the Coulomb repulsion between electrons and the potential of the neutralizing homogeneous background are explicitly taken into account. As the most pronounced effect appears at filling $\nu = 1/3$ of the lowest Landau level, we first consider this case.

The degeneracy of the Landau levels [see (22.1.25)] is given by

$$N_{\rm p} = \frac{L_x L_y}{2\pi l_{\rm H}^2} \,. \tag{32.7.3}$$

We assume that $N_{\rm e} = \frac{1}{3}N_{\rm p}$. When the interaction is neglected, the wavefunctions in the lowest (n = 0) Landau level can be written according to (22.1.88) in the symmetric gauge in the form

$$\psi_m(z) = (2\pi l_{\rm H}^2 2^m m!)^{-1/2} \left(\frac{z}{l_{\rm H}}\right)^m {\rm e}^{-|z|^2/4l_{\rm H}^2}$$
(32.7.4)

with z = x + iy. The quantum number *m* takes integer values from 0 to $N_{\rm p}-1$. The many-particle wavefunction of $N_{\rm e}$ electrons can be given as a linear combination of Slater determinants formed from the one-particle functions. In a magnetic field when $N_{\rm e}$ particles fill completely the lowest Landau level, a single Slater determinant can be constructed:

$$\Psi(z_1, z_2, \dots, z_{N_e}) = D(z_1, z_2, \dots, z_{N_e}) \exp\left(-\sum_{i=1}^{N_e} \frac{|z_i|^2}{4l_H^2}\right), \quad (32.7.5)$$

where, apart from a normalizing factor,

$$D(z_1, z_2, \dots, z_{N_e}) = \begin{vmatrix} 1 & z_1 & z_1^2 & \dots & z_1^{N_e - 1} \\ 1 & z_2 & z_2^2 & \dots & z_2^{N_e - 1} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & z_{N_e} & z_{N_e}^2 & \dots & z_{N_e}^{N_e - 1} \end{vmatrix}.$$
 (32.7.6)

This Vandermonde determinant can be written in the simple form

$$D(z_1, z_2, \dots, z_{N_e}) = \prod_{i>j} (z_i - z_j).$$
(32.7.7)

When the lowest Landau level is not completely filled, the wavefunction could be written as a linear combination of Slater determinants. Instead of that R. B. LAUGHLIN¹⁸ (1983) proposed to modify the wavefunction of the completely filled level by a Jastrow factor¹⁹ $f(z_i - z_j)$:

 $^{^{18}}$ See footnote on page 6 of Volume 1.

¹⁹ R. Jastrow, 1955.

$$\Psi = \prod_{i>j} (z_i - z_j) f(z_i - z_j) \exp\left(-\sum_{i=1}^{N_e} \frac{|z_i|^2}{4l_H^2}\right).$$
 (32.7.8)

This factor was invented to incorporate the effect of Coulomb repulsion between particles into the wavefunction, reducing thereby its contribution to the energy. The Pauli exclusion principle requires that $f(z_i - z_j)$ be an even function under the exchange of the coordinates. As the simplest choice LAUGHLIN proposed the function

$$\Psi = \prod_{i>j} (z_i - z_j)^{2p+1} \exp\left(-\sum_{i=1}^{N_e} \frac{|z_i|^2}{4l_H^2}\right).$$
(32.7.9)

When the product of the functions $(z_i - z_j)^{2p+1}$ is expanded in a power series, the wavefunction contains the $(2p + 1)(N_e - 1)$ th power of the coordinates of each particle. However, the highest power that may occur in the wavefunction of the lowest Landau level is $N_p - 1$ if it is formed from the one-particle functions (32.7.4). The Laughlin wavefunction can be used only if

$$N_{\rm e} < \frac{N_{\rm p}}{2p+1} \,. \tag{32.7.10}$$

The one-third-filled Landau level can thus be described by this wavefunction with p = 1. For somewhat larger filling (in somewhat weaker field for unchanged number of electrons) the Jastrow factor with power p = 1 may not occur for every pair of particles. On the other hand, when the filling factor is smaller (the field is stronger for unchanged number of electrons) also the power p = 2 may occur for some pairs. Similar arguments can be used for fillings $\nu = 1/(2p+1)$. This change in the character of the wavefunction at these particular fillings may give rise to a discontinuity in the chemical potential as a function of the filling (or magnetic field), implying that a finite energy is needed to add a particle: the ground state is incompressible at fillings $\nu = 1/(2p+1)$. At these particular fillings the ground state cannot be obtained from the ground state of the noninteracting two-dimensional electron gas by adiabatic continuation, hence this state is not a Fermi liquid. It is a new quantum liquid state of matter with particular properties. Electrons are not localized into a Wigner-crystal-like structure despite the repulsion between them; their spatial distribution is homogeneous and the state is liquidlike. This state of matter is referred to as the *quantum Hall liquid*.

Although the Laughlin wavefunction does not contain a variational parameter, it could be considered as the best available wavefunction at filling $\nu = 1/(2p + 1)$ of the lowest Landau level. Comparing it with the results of exact numerical calculations for systems with relatively small number of particles, it gives the ground-state energy with surprising accuracy, and its overlap with the exact ground-state wavefunction of finite systems is very close to unity.

32.7.3 Quasiparticles in the Quantum Hall Liquid

The ground state of the two-dimensional electron gas in a strong magnetic field is not a Fermi liquid and the low-lying excitations are not fermionic quasiparticles. LAUGHLIN constructed the wavefunction of the state containing one elementary excitation, a quasiparticle or a quasihole, and calculated the gap in their excitation spectrum. Moreover, he has shown that these quasiparticles have fractional charge, $e^* = e/(2p+1)$. Measurement of the current noise spectrum gave evidence that the charge of the elementary excitations is indeed fractional. Owing to this anomalous charge, these quasiparticles are neither bosons nor fermions. They obey an intermediate, fractional statistics depending on the charge and are called *anyons*. They play an important role at other fillings as well. The fractional quantum Hall effect at fillings $\nu = q/(2p+1)$ with q > 1 is explained in this theory as being due to a Laughlin-like state in the system of anyon quasiparticles. Thus, a hierarchical model can be built up for the series of anomalies.

Although the low-energy excitations are suppressed in the bulk, there are gapless excitations at the edge. We have seen already in Chapter 22 that edge states play an important role in the quantized Hall conductance. These edge states can be described as a chiral Luttinger liquid. Their treatment is beyond the scope of this brief presentation of the fractional quantum Hall effect.

A different approach has been proposed by J. K. JAIN (1989) to visualize the quasiparticles and to describe the fractional quantum Hall effect. He assumed that the quasiparticles of the two-dimensional electron system in strong magnetic field are composite fermions that are bound states of an electron of charge -e and an even number of magnetic flux quanta $2p\Phi_0^*$, where $\Phi_0^* = h/e$ is the flux quantum used in the Landau theory of electrons in strong magnetic field (it is twice the flux quantum used in superconductivity). When each quasiparticle carries such a flux, the N_e particles generate an internal field $\pm N_e 2p\Phi_0^*/F$. Subtracting it from the applied field B the effective field inside the sample is

$$B_{\rm eff} = B - N_{\rm e} 2p \Phi_0^* / F \,. \tag{32.7.11}$$

Taking into account the relationship

$$N_{\rm p} = \frac{B}{\Phi_0^*} F \tag{32.7.12}$$

between the magnetic induction and the degeneracy of the Landau level given in (22.1.27) we find

$$B_{\rm eff} = B(1 - 2pN_{\rm e}/N_{\rm p}). \qquad (32.7.13)$$

At the particular filling $\nu = 1/(2p+1)$ we have

$$B_{\rm eff} = B/(2p+1). \tag{32.7.14}$$

The effective field sensed by the composite fermions is much smaller than the applied magnetic field, the degeneracy of the Landau levels of quasiparticles is 2p + 1-times smaller than the usual degeneracy of the Landau levels, and thus $N_e = N_p/(2p+1)$ quasiparticles fill completely a quantized Landau level, although the same number of particles would fill the lowest Landau level only to a fraction 1/(2p+1) in the noninteracting case. Thus the fractional quantum Hall effect is the analog of the integer quantum Hall effect if the composite fermion quasiparticles are used instead of electrons. The anomalies at other fillings q'/(2p'+1) are explained by assuming that the composite fermions fill several sublevels into which the lowest Landau level is split by the interaction.

32.7.4 Anisotropic Hall Liquids

It was assumed in the foregoing treatment of the quantum Hall effect that the system remains homogeneous in space. Periodic variations of the charge, for which we will see examples in quasi-one-dimensional systems in the next chapter, were found numerically to be energetically unfavorable in two-dimensional interacting electron systems. Recently it has been found experimentally that the two-dimensional electron gas becomes anisotropic in not too strong magnetic fields at special fillings of the Landau levels. As seen in Fig. 32.40, the resistivity of GaAs/AlGaAs heterostructures exhibits strong anisotropy in fields of a few teslas at low temperatures, below 150 mK, at fillings $\nu = 9/2$, 11/2, 13/2, 15/2.



Fig. 32.40. Resistivity of the two-dimensional electron gas in a GaAs/AlGaAs heterostructure in two directions at T = 25 mK and the increase of the anisotropy as the temperature is lowered from T = 100 to 25 mK [Reprinted with permission from M. P. Lilly et al., *Phys. Rev. Lett.* 82, 394 (1999). \bigcirc (1999) by the American Physical Society]

It has been proposed that new quantum liquid phases may exist in the twodimensional electron gas with symmetries resembling the liquid-crystalline smectic and nematic phases. This would result in an anisotropy of the resistivity.

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33

Electronic Phases with Broken Symmetry

It was shown in the previous chapter that the normal Fermi-liquid state of an isotropic Fermi system is stable if the Landau parameters characterizing the interaction between quasiparticles satisfy the inequalities $F_l^{s(a)} > -(2l+1)$ for all l. Otherwise a characteristic physical quantity, e.g., the effective mass, the compressibility, the sound velocity, or the magnetic susceptibility, vanishes or diverges. When this happens, fluctuations are enhanced so drastically in the channel where the Pomeranchuk condition fails that the system undergoes a transition to a new phase. For example, a divergence in the paramagnetic susceptibility of the Fermi liquid indicates that a magnetic phase transition occurs to a magnetically ordered state.

The occupations of states with \uparrow and \downarrow spin orientations are identical in the paramagnetic phase both globally and locally. The paramagnetic state is invariant not only under spin reversal but also under rotation of all spins by the same angle. The continuous spin-rotation symmetry of the Hamiltonian, still retained in the paramagnetic state, is spontaneously broken at the transition to the magnetically ordered state. The \uparrow and \downarrow spin states are occupied differently in the ferromagnetic state, while the densities of spin-up and spin-down electrons oscillate in space with opposite phase in antiferromagnets.

Spontaneous breaking of a symmetry is a quite common phenomenon. As was mentioned in Chapter 6, it often happens that the state realized in nature (in mathematical terms the solution of the eigenvalue problem of the Hamiltonian) does not possess all symmetries of the Hamiltonian. An inhomogeneous charge distribution may result from a translationally invariant Hamiltonian. The crystalline state itself is a good example: the basic Hamiltonian is invariant under arbitrary, continuous translation, but the ground state possesses discrete translational symmetry only. Usually the spatial arrangement of the ions and the electronic subsystem display the same periodicity. When an inhomogeneous charge distribution occurs in the electronic subsystem with periodicity different from that of the underlying lattice, we speak of *charge-density waves*. It can also happen that the charge density has the same translational symmetry as the ions, but the spin density varies with a different spatial periodicity. We are then dealing with a *spin-density wave*.

Breaking of symmetry is usually not observed at high temperatures, since thermal fluctuations destroy any ordering. Order and breaking of a symmetry occurs at a well-defined temperature T_c , because symmetry cannot change continuously, as stated by the first theorem of condensed matter physics. A symmetry is either absent or present in a system. Transitions, where the new state can be characterized by an order parameter, are quite often of second order and T_c is the critical temperature, though first-order transitions are also common.

Some properties of the ordered phase are quite different from that of the high-temperature disordered symmetric phase. One reason is the difference in the spectrum of excited states. This spectrum depends strongly on the type of symmetry that is broken. The Goldstone theorem mentioned in Chapter 6 states that soft bosonic excitations have to show up in the ordered phase whenever a continuous symmetry is broken. The simplest example is that of acoustic phonons. The three acoustic branches that are always gapless and have linear dispersion relations in the long-wavelength limit are the consequences of breaking the continuous translational symmetry in the three directions of space. Similarly, gapless magnons are found in isotropic ferroand antiferromagnets, when the continuous spin-rotation symmetry of the Heisenberg Hamiltonian is broken.

Similar soft modes appear in the density-wave states of electronic systems owing to the broken translation or spin-rotation symmetry. In the superconducting state that will be studied in the next chapter, there are no collective Goldstone bosons since the long-range Coulomb interaction is not screened. For the same reason only the two transverse modes are soft in a Wigner crystal; the longitudinal excitations have finite energy.

We will first study the properties of the homogeneous ferromagnetic phase. We then turn to the inhomogeneous density-wave states, presenting first a mean-field theory and then a discussion of the soft collective modes. Some experimental results on density-wave materials will be discussed in this context at the end of this chapter.

The Hamiltonian may have less obvious symmetries, e.g., gauge symmetry, which is related to charge conservation. It is broken in the superconducting state which is one of the most studied broken-symmetry phases of fermion systems both experimentally and theoretically. A phenomenological description of superconductivity has already been given in Chapter 26, but the presentation of the microscopic theory was postponed because superconductivity is a true many-body effect which cannot be understood in the one-particle picture. Because of its importance a separate chapter will be devoted to it.

33.1 Ferromagnetic Instability

The interacting electron system was assumed to be unpolarized in most of the previous treatments, i.e., equal numbers of electrons occupy up- and down-spin states. Some of the calculations can easily be extended to polarized electron systems. As the simplest example we consider the ferromagnetic instability in the homogeneous electron gas and in the Hubbard model.

33.1.1 Ferromagnetism in the Homogeneous Electron Gas

Consider a homogeneous electron gas with $N_{\rm e}$ electrons, all with spin \uparrow . They fill a Fermi sphere of radius $k_{\rm F\uparrow}$ which can be determined from the relation

$$N_{\rm e} = \frac{V}{(2\pi)^3} \frac{4k_{\rm F\uparrow}^3 \pi}{3} \,. \tag{33.1.1}$$

Combining it with (16.2.24) where the Fermi wave number $k_{\rm F}$ of the unpolarized electron gas was given we find the relation $k_{\rm F\uparrow} = \sqrt[3]{2} k_{\rm F}$. If the radius r_0 belonging to an electron in real space is used [see (16.2.31)] we find

$$k_{\rm F\uparrow} = \left(\frac{9\pi}{2}\right)^{1/3} \frac{1}{r_0} \,. \tag{33.1.2}$$

The ground-state energy of the fully polarized homogeneous electron gas can be calculated in the Hartree–Fock approximation very simply without repeating the procedure used in Chapter 30. The kinetic energy is proportional to $k_{\rm F}^2$ and the exchange energy to $k_{\rm F}$ according to (30.1.13). Substituting $k_{\rm F\uparrow}$ in both terms we find

$$\frac{E_{\rm HF}}{N_{\rm e}} = \frac{\tilde{e}^2}{2a_0} \left[\frac{3}{5} \left(k_{\rm F\uparrow} a_0 \right)^2 - \frac{3}{2\pi} \left(k_{\rm F\uparrow} a_0 \right) \right] \\
= \frac{\tilde{e}^2}{2a_0} \left[\frac{3}{5} \left(\frac{9\pi}{2} \right)^{2/3} \left(\frac{a_0}{r_0} \right)^2 - \frac{3}{2\pi} \left(\frac{9\pi}{2} \right)^{1/3} \left(\frac{a_0}{r_0} \right) \right] \\
= \left[\frac{1.754}{r_{\rm s}^2} - \frac{0.577}{r_{\rm s}} \right] \frac{\tilde{e}^2}{a_0}$$
(33.1.3)

for the energy per particle. It is readily seen by comparing this expression with the energy of the unpolarized electron gas given in (30.1.13) that the polarized state has lower energy if $r_{\rm s} > 5.47$. If this estimate were correct, an appreciable number of metals would have magnetic ground states. That this is not so is a consequence of correlations. One finds in Monte Carlo calculations that the polarized state is favorable at much lower densities. A second-order transition to the partially polarized state occurs at $r_{\rm s} \approx 50$. The interacting electron gas becomes fully polarized at $r_{\rm s} \approx 106$, at the density where a first-order freezing

transition takes place to the paramagnetic body-centered cubic Wigner-crystal phase.¹ For Bloch electrons, especially in transition metals, where the narrow d-bands play an important role, the condition for magnetism can be satisfied more easily and magnetic instability may occur at much lower, physically more realistic densities.

33.1.2 Stoner Model

We have seen in Chapter 29 that the Hubbard model becomes unstable in the mean-field approximation if either the Coulomb repulsion is strong enough or the density of states is high enough at the Fermi energy. The stability condition of the paramagnetic state is $U\rho_{\sigma}(\varepsilon_{\rm F}) < 1$. Otherwise the susceptibility diverges and a magnetically ordered state may be formed in which the spin-rotation symmetry is broken. Assuming that this magnetic state is homogeneous, we arrive at the *Stoner model*² of metallic ferromagnetism. We consider here the properties of such a state.

When the Hubbard model is treated in the Hartree–Fock approximation, the renormalized one-particle energy can be written either as

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + U_{\mathrm{H}} \langle n_{i,-\sigma} \rangle \tag{33.1.4}$$

or equivalently in the form

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + \frac{U}{V} \sum_{\boldsymbol{k}'} \langle n_{\boldsymbol{k}',-\sigma} \rangle \,. \tag{33.1.5}$$

The expectation value $\langle n_{i,\sigma}\rangle$ is independent of the site index in the ferromagnetic state and the notation

$$n_{\sigma} = \langle n_{i,\sigma} \rangle \tag{33.1.6}$$

will be used. It is convenient to introduce the spin-symmetric and spin-antisymmetric combinations

$$n^{\rm s} = \frac{1}{2}(n_{\uparrow} + n_{\downarrow}), \qquad n^{\rm a} = \frac{1}{2}(n_{\uparrow} - n_{\downarrow}), \qquad (33.1.7)$$

and to measure the energy shift due to the polarization relative to

$$\widetilde{\varepsilon}_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}} + U_{\mathrm{H}} n^{\mathrm{s}}, \qquad (33.1.8)$$

which is equal to the spin-independent energy in the unpolarized state. We then have

¹ The phase diagram of the two-dimensional electron system is not so well established. The spin-polarized Fermi liquid is probably never the stable ground state without external magnetic field. The ferromagnetic triangular Wigner crystal has lower energy than the paramagnetic fluid phase for $r_{\rm s} > 33$, but an antiferromagnetic Wigner-crystal phase seems to intervene between the paramagnetic fluid and the ferromagnetic Wigner crystal for densities $31 < r_{\rm s} < 38$.

² E. C. Stoner, 1938.

$$\widetilde{\varepsilon}_{\boldsymbol{k}\sigma} = \widetilde{\varepsilon}_{\boldsymbol{k}} - \frac{1}{2} U_{\mathrm{H}} \left(n_{\sigma} - n_{-\sigma} \right), \qquad (33.1.9)$$

that is

$$\widetilde{\varepsilon}_{\mathbf{k}\uparrow} = \widetilde{\varepsilon}_{\mathbf{k}} - U_{\mathrm{H}}n^{\mathrm{a}}, \qquad \widetilde{\varepsilon}_{\mathbf{k}\downarrow} = \widetilde{\varepsilon}_{\mathbf{k}} + U_{\mathrm{H}}n^{\mathrm{a}}.$$
 (33.1.10)

The energy levels are shifted oppositely for the two spin orientations; the band splits into two subbands. This phenomenon is known as *exchange splitting*. The split bands are displayed in Fig. 33.1 for a very simple free-electron-like dispersion relation.



Fig. 33.1. Splitting of the energy band in a polarized electron gas (a) for partial polarization, (b) in a fully polarized state

The states are filled up to the same chemical potential in the subbands; hence, the Fermi momentum is different for spin-up and spin-down electrons. It may happen that the splitting is so large that all electrons are in the same subband and the other is empty. This situation corresponds to full polarization. We will assume in our further calculations that the polarization is only partial.

The energy shift and the asymmetry in the occupation numbers strongly depend on the Coulomb repulsion and have to be calculated self-consistently. This will then give the self-consistent value of magnetization, since the magnetic moment per site is given by

$$m = \frac{1}{2}g_{\rm e}\mu_{\rm B}(n_{\uparrow} - n_{\downarrow}) = g_{\rm e}\mu_{\rm B}n^{\rm a}$$
. (33.1.11)

The total number of electrons with spin σ is obtained from

$$N_{\sigma} = \sum_{\boldsymbol{k}} f_0(\tilde{\varepsilon}_{\boldsymbol{k}\sigma}) = V \int \tilde{\rho}_{\sigma}(\varepsilon) f_0(\varepsilon) \mathrm{d}\varepsilon , \qquad (33.1.12)$$

where $\tilde{\rho}_{\sigma}(\varepsilon)$ is the density of states for electrons with spin σ in the polarized state and f_0 is the Fermi distribution function. The bands are shifted rigidly in the polarized state in the mean-field approximation and we have

$$\tilde{\rho}_{\sigma}(\varepsilon) = \rho_{\sigma}(\varepsilon + \sigma U_{\rm H} n^{\rm a}), \qquad (33.1.13)$$

where $\rho_{\sigma}(\varepsilon)$ is the density of states per spin in the unpolarized state. Substituting this into (33.1.12) we get

$$N_{\uparrow} = V \int \rho_{\sigma}(\varepsilon + U_{\rm H}n^{\rm a}) f_{0}(\varepsilon) d\varepsilon = V \int \rho_{\sigma}(\varepsilon) \frac{1}{{\rm e}^{\beta(\varepsilon - U_{\rm H}n^{\rm a} - \mu)} + 1} d\varepsilon,$$

$$(33.1.14)$$

$$N_{\downarrow} = V \int \rho_{\sigma}(\varepsilon - U_{\rm H}n^{\rm a}) f_{0}(\varepsilon) d\varepsilon = V \int \rho_{\sigma}(\varepsilon) \frac{1}{{\rm e}^{\beta(\varepsilon + U_{\rm H}n^{\rm a} - \mu)} + 1} d\varepsilon.$$

The change in the number of electrons per site compared to the unpolarized state is given by

$$\begin{split} \delta n_{\uparrow} &= \frac{V}{N} \int \rho_{\sigma}(\varepsilon) \frac{1}{\mathrm{e}^{\beta(\varepsilon - U_{\mathrm{H}} n^{\mathrm{a}} - \mu)} + 1} \mathrm{d}\varepsilon - \frac{V}{N} \int \rho_{\sigma}(\varepsilon) \frac{1}{\mathrm{e}^{\beta(\varepsilon - \mu_{0})} + 1} \mathrm{d}\varepsilon, \\ (33.1.15) \\ \delta n_{\downarrow} &= \frac{V}{N} \int \rho_{\sigma}(\varepsilon) \frac{1}{\mathrm{e}^{\beta(\varepsilon + U_{\mathrm{H}} n^{\mathrm{a}} - \mu)} + 1} \mathrm{d}\varepsilon - \frac{V}{N} \int \rho_{\sigma}(\varepsilon) \frac{1}{\mathrm{e}^{\beta(\varepsilon - \mu_{0})} + 1} \mathrm{d}\varepsilon, \end{split}$$

where μ_0 is the chemical potential in the unpolarized state and μ is the chemical potential in the polarized state. At temperature T = 0

$$\delta n_{\uparrow} = \frac{V}{N} \int_{\mu_0}^{\mu+U_{\rm H}n^{\rm a}} \rho_{\sigma}(\varepsilon) \,\mathrm{d}\varepsilon \,, \qquad \delta n_{\downarrow} = \frac{V}{N} \int_{\mu_0}^{\mu-U_{\rm H}n^{\rm a}} \rho_{\sigma}(\varepsilon) \,\mathrm{d}\varepsilon \,. \tag{33.1.16}$$

The chemical potential μ can be determined from the condition that the total number of particles is unchanged, that is

$$\delta n_{\uparrow} + \delta n_{\downarrow} = 0. \qquad (33.1.17)$$

For an explicit calculation of the magnetization in the polarized state we expand the density of states about the Fermi energy $\mu_0 = \varepsilon_{\rm F}$ in the form

$$\rho_{\sigma}(\varepsilon) = \rho_{\sigma}(\varepsilon_{\rm F}) \left[1 + a(\varepsilon - \varepsilon_{\rm F}) + \frac{1}{2}b(\varepsilon - \varepsilon_{\rm F})^2 + \cdots \right].$$
(33.1.18)

For a free electron gas, where the density of states is given by (16.2.54),

$$a = \frac{1}{2\varepsilon_{\rm F}}, \qquad b = -\frac{1}{4\varepsilon_{\rm F}^2}. \tag{33.1.19}$$

The parameters are somewhat different in a more general case, but we assume that a second-order expansion is sufficient and b < 0. Inserting this expansion into (33.1.16) the leading correction in $n^{\rm a}$ gives

$$\mu = \mu_0 - \frac{1}{2}a(U_{\rm H}n^{\rm a})^2. \qquad (33.1.20)$$

The asymmetry n^{a} in the occupation number has to be determined self-consistently from the relation

$$n^{\rm a} = \frac{V}{2N} \int_{\mu-U_{\rm H}n^{\rm a}}^{\mu+U_{\rm H}n^{\rm a}} \rho_{\sigma}(\varepsilon) \,\mathrm{d}\varepsilon \,. \tag{33.1.21}$$

Using again the expanded form of the density of states, but keeping now the next-to-leading (cubic) corrections as well, we get

$$n^{\rm a} = \frac{V}{N} U_{\rm H} \rho_{\sigma}(\varepsilon_{\rm F}) \, n^{\rm a} \Big[1 - \frac{1}{2} \left(a^2 - \frac{1}{3} b \right) (U_{\rm H} n^{\rm a})^2 \Big].$$
(33.1.22)

A trivial solution of this equation is $n^{a} = 0$. The coefficient of the cubic term is negative for b < 0 and a nontrivial solution exists if

$$\frac{V}{N}U_{\rm H}\rho_{\sigma}(\varepsilon_{\rm F}) = U\rho_{\sigma}(\varepsilon_{\rm F}) > 1.$$
(33.1.23)

This is the condition for the occurrence of spontaneous magnetization. The critical value of the Coulomb repulsion is given by

$$U_{\rm c}\rho_{\sigma}(\varepsilon_{\rm F}) = 1 \tag{33.1.24}$$

in agreement with the stability condition of the paramagnetic phase derived earlier.

For U not much larger than the critical value, where the magnetization is small and the expansion in (33.1.22) is applicable, the saturation value of the magnetic moment per site takes the simple form

$$m_0 \propto \sqrt{1 - \frac{1}{U\rho_\sigma(\varepsilon_{\rm F})}} = \sqrt{\frac{U - U_{\rm c}}{U}}.$$
 (33.1.25)

With the parameters valid for a parabolic dispersion relation we have

$$m_0 = |g_e| \mu_B \frac{\sqrt{6\varepsilon_F}}{U_H} \sqrt{\frac{U - U_c}{U}}. \qquad (33.1.26)$$

33.1.3 Stoner Excitations

Just as in the paramagnetic phase, electron-hole pair excitations can be generated in the ferromagnetic state. These pairs created either in the spin-up or spin-down subbands form a similar continuum as in a paramagnet. Since the Fermi momenta are different for the two spin orientations, low-energy pairs can be generated up to a total momentum $2k_{F\uparrow}$ or $2k_{F\downarrow}$, respectively. These spin-conserving excitations (the spin of the electron compensates the missing spin due to the hole in the same subband) are not relevant for the magnetic properties. The temperature dependence of the magnetization is determined by spin-flip excitations, where electrons from an occupied state of the spin-up subband are excited to an empty state of the spin-down subband or vice versa. Such electron-hole pair excitations are displayed in Fig. 33.2. They are forbidden if the interaction processes in the Hamiltonian conserve the total spin. This is the case, e.g., in the Hubbard model. They can, however, be excited spontaneously when spin-orbit coupling is present. The angular momentum is transferred from the electron system to the lattice.



Fig. 33.2. Low-energy electron-hole pair excitations in the polarized electron gas with the electron and the hole in different subbands

The ground state of the polarized Fermi sea, denoted by $|\Psi_{\rm PFS}\rangle$, can be given in second quantization in the form

$$|\Psi_{\rm PFS}\rangle = \prod_{|\boldsymbol{k}| < k_{\rm F\uparrow}} c^{\dagger}_{\boldsymbol{k}\uparrow} \prod_{|\boldsymbol{k}'| < k_{\rm F\downarrow}} c^{\dagger}_{\boldsymbol{k}'\downarrow} |0\rangle . \qquad (33.1.27)$$

The wavefunction of the state with one excited electron-hole pair is

$$c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow}c_{\boldsymbol{k}\downarrow}|\Psi_{\mathrm{PFS}}\rangle$$
. (33.1.28)

The excitation energy is easily obtained in the mean-field approximation using (33.1.10) for the single-particle energies. We find

$$\hbar\omega_{\boldsymbol{q}} = \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} - \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow} = \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}} - \widetilde{\varepsilon}_{\boldsymbol{k}} - 2U_{\mathrm{H}}n^{\mathrm{a}}, \qquad (33.1.29)$$

or, if the magnetic moment per site is used,

$$\hbar\omega_{\boldsymbol{q}} = \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}} + \frac{2}{|g_{\rm e}|\mu_{\rm B}} U_{\rm H} m_0 \,. \tag{33.1.30}$$

For small values of \boldsymbol{q} this energy is equal to the exchange splitting between the subbands,

$$\Delta_0 = \frac{2}{|g_e|\mu_B} U_H m_0 \,. \tag{33.1.31}$$

The excitation energies form a continuum for finite q as seen in Fig. 33.3. These electron-hole pair excitations involving both the spin-up and the spin-down subbands are called *Stoner excitations*. Their continuum is the *Stoner continuum*.



Fig. 33.3. Continuum of electron–hole pair excitations when the electron and the hole are created in the oppositely polarized subbands

33.1.4 Stoner Model at Finite Temperatures

Thermally excited electron-hole pairs with spin reversal decrease the difference between the fillings of the two subbands at finite temperatures. This gives rise to a decrease of the exchange splitting and of the magnetization. A selfconsistent calculation of this decrease allows us to determine the temperature dependence of the magnetization. The temperature-dependent corrections to the integrals in (33.1.15) can be evaluated using the Sommerfeld expansion. For the chemical potential we obtain

$$\mu = \mu_0 - \frac{1}{2}a(U_{\rm H}n^{\rm a})^2 - \frac{\pi^2}{6}a(k_{\rm B}T)^2, \qquad (33.1.32)$$

and the asymmetry of the filling of the subbands has to be determined from

$$n^{a} = \frac{V}{N} U_{\rm H} \rho_{\sigma}(\varepsilon_{\rm F}) n^{a} \left[1 - \frac{1}{2} \left(a^{2} - \frac{1}{3} b \right) (U_{\rm H} n^{a})^{2} - \frac{\pi^{2}}{6} \left(a^{2} - b \right) (k_{\rm B} T)^{2} \right].$$
(33.1.33)

This leads to a quadratic temperature dependence of the magnetization:

$$M(T) = M_0 \left[1 - \left(\frac{T}{T_{\rm C}}\right)^2 \right]^{1/2}, \qquad (33.1.34)$$

where $T_{\rm C}$ is the Curie temperature which is obtained from (33.1.33) as the temperature where the magnetization vanishes. Using the parameters valid for a free-electron-like density of states we find

$$k_{\rm B}T_{\rm C} = \frac{2\sqrt{3}}{\pi} \varepsilon_{\rm F} \sqrt{1 - \frac{1}{U\rho_{\sigma}(\varepsilon_{\rm F})}} \,. \tag{33.1.35}$$

The situation is different if the ground state is fully polarized, that is if all electrons occupy the same subband, as shown in Fig. 33.1(b). Since the bottom of the empty subband is above the chemical potential, there are no low-energy electron-hole excitations between the subbands. If the minimum

excitation energy to the empty band is denoted by $\Delta \varepsilon_0$, the temperature dependence of the magnetization is given by

$$M(T) = M_0 \left(1 - B \mathrm{e}^{-\Delta \varepsilon_0 / k_\mathrm{B} T} \right).$$
(33.1.36)

33.1.5 Failure of the Stoner Model

Some of the results obtained in the Stoner model are not supported by experimental findings. A T^2 temperature dependence of the magnetization is not observed in itinerant ferromagnets at low temperatures, neither is an exponentially slow variation. Recall that a similar discrepancy was found in the mean-field treatment of the Heisenberg model and the measured $T^{3/2}$ dependence of the magnetization could be explained only in the spin-wave theory as coming from the thermally excited soft bosonic magnons with quadratic dispersion relation. That the same temperature dependence is observed in metallic ferromagnets is a strong indication that similar low-energy collective magnetic excitations exist there as well, in addition to the gapped electron-hole pairs. These excitations will be studied in the next section.

Another problem is related to the value of the Curie temperature. The thermal energy $k_{\rm B}T_{\rm C}$ is on the order of the Fermi energy according to (33.1.35), that is $T_{\rm C}$ should be on the order of $10^4 \, {\rm K}$, whereas the typical experimental values are one or two orders of magnitude smaller. The too high Curie temperature is the consequence of the mechanism assumed for the thermal destruction of magnetization in the Stoner model. Magnetism is calculated from the difference in the fillings of the subbands and this difference appears in the exchange splitting. When the magnetization vanishes at the Curie temperature, so does the exchange splitting as well as the local magnetic moment. The same number of spin-up and spin-down electrons sit on every site in the homogeneous paramagnetic phase. Since the exchange splitting is on the order of the Fermi energy at T = 0, high temperatures are needed to destroy it uniformly. The physical picture of a vanishing local magnetic moment in the paramagnetic phase is, however, in contradiction with the experimental findings. The susceptibility of metallic ferromagnets above their Curie points is not Pauli-like but displays a Curie–Weiss-like temperature dependence. This can be understood if we assume that the electron states remain locally polarized, on an atomic scale, even in the paramagnetic phase, but are disordered in space and fluctuate in time. The vanishing of the magnetization is due to the fluctuations in the direction rather than in the amplitude of the local moments. A proper treatment of these effects far exceeds the scope of this book, just as the treatment of the magnetic properties of materials based on a realistic band structure.

33.1.6 Spin Waves in the Ferromagnetic Electron Gas

We have seen earlier in Chapter 31 that if an electron gas is polarized by an external magnetic field, the continuum of electron-hole pair excitations starts at a finite energy. Collective excitations, called spin waves, appear below the continuum when $U\rho_{\sigma}(\varepsilon_{\rm F})$ is close to the critical value, although with a finite gap, because the breaking of the continuous rotational symmetry is not spontaneous in the polarized state but is implemented by the external field. Similar collective excitations corresponding to spin-density fluctuations are expected to appear in itinerant ferromagnets as well but now as soft Goldstone bosons. They, too, are called *spin waves*.

These collective excitations can be constructed by taking linear combinations of the states in which one electron-hole pair with opposite spins is excited [see (33.1.28)]. The state

$$|\Psi_{q}\rangle = \sum_{k} \phi_{kq} c^{\dagger}_{k+q\uparrow} c_{k\downarrow} |\Psi_{\text{PFS}}\rangle$$
(33.1.37)

is generated from the polarized ground state $|\Psi_{\rm PFS}\rangle$ by the operator

$$\alpha_{\boldsymbol{q}}^{\dagger} = \sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}\boldsymbol{q}} c_{\boldsymbol{k}+\boldsymbol{q}\uparrow}^{\dagger} c_{\boldsymbol{k}\downarrow}; \qquad (33.1.38)$$

hence, it can be considered as the creation operator of a spin wave. The annihilation operator is its Hermitian adjoint. The excited state contains one elementary excitation if

$$\left[\mathcal{H}, \alpha_{\boldsymbol{q}}^{\dagger}\right]_{-} = \hbar \omega_{\boldsymbol{q}} \alpha_{\boldsymbol{q}}^{\dagger}, \qquad (33.1.39)$$

that is the Hamiltonian can be transformed to the form

$$\mathcal{H} = \sum_{\boldsymbol{q}} \hbar \omega_{\boldsymbol{q}} \alpha_{\boldsymbol{q}}^{\dagger} \alpha_{\boldsymbol{q}} \tag{33.1.40}$$

describing a free gas of bosons with excitation energies $\hbar\omega_q$.

The coefficients ϕ_{kq} are fixed by the condition

$$\left[\mathcal{H}, \sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}\boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} c_{\boldsymbol{k}\downarrow}\right]_{-} = \hbar \omega_{\boldsymbol{q}} \sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}\boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} c_{\boldsymbol{k}\downarrow}, \qquad (33.1.41)$$

which follows from (33.1.39). Since the electron states are described in a momentum representation, it is convenient to consider also the Hamiltonian of the Hubbard model in a momentum representation:

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{U}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\downarrow} c_{\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}\uparrow} \,. \tag{33.1.42}$$

Using the results given in detail in Chapter 29 we find

$$\begin{bmatrix} \mathcal{H}, c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow} \end{bmatrix}_{-} = \left(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} \right) c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow} - \frac{U}{V} \sum_{\mathbf{k}'\mathbf{q}'} c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}'-\mathbf{q}'\uparrow}^{\dagger} c_{\mathbf{k}'\uparrow}^{\dagger} c_{\mathbf{k}-\mathbf{q}'\downarrow} - \frac{U}{V} \sum_{\mathbf{k}'\mathbf{q}'} c_{\mathbf{k}'+\mathbf{q}'\downarrow}^{\dagger} c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\uparrow}^{\dagger} c_{\mathbf{k}\downarrow}^{\dagger} c_{\mathbf{k}\downarrow} .$$
(33.1.43)

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Clearly, (33.1.41) cannot be exactly satisfied with any choice of ϕ_{kq} . States with one electron-hole pair will be mixed with states containing several pairs. $|\Psi_q\rangle$ can, however, be chosen so as to satisfy (33.1.41) approximately by applying a decoupling procedure in the commutator which replaces products of two operators in the four-operator terms in (33.1.43) with their expectation values. Care must be taken of the order of the operators. Every exchange of fermion operators gives a factor -1. Such a linearization gives

$$\begin{bmatrix} \mathcal{H}, c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow} \end{bmatrix}_{-} = (\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}}) c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow}$$

$$- \frac{U}{V} \sum_{\mathbf{k}'} \langle n_{\mathbf{k}'\uparrow} \rangle c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow} + \frac{U}{V} \sum_{\mathbf{q}'} \langle n_{\mathbf{k}+\mathbf{q}\uparrow} \rangle c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\uparrow}^{\dagger} c_{\mathbf{k}-\mathbf{q}'\downarrow}$$

$$+ \frac{U}{V} \sum_{\mathbf{k}'} \langle n_{\mathbf{k}'\downarrow} \rangle c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow} - \frac{U}{V} \sum_{\mathbf{k}'} \langle n_{\mathbf{k}\downarrow} \rangle c_{\mathbf{k}'+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}'\downarrow} .$$

$$(33.1.44)$$

In two of the terms you may recognize the Hartree–Fock correction to the quasiparticle energy. Incorporating them in the renormalized energies and changing the summation variable q' to k - k' we get

$$\begin{bmatrix} \mathcal{H}, c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow} \end{bmatrix}_{-} = \left(\widetilde{\varepsilon}_{\mathbf{k}+\mathbf{q}\uparrow} - \widetilde{\varepsilon}_{\mathbf{k}\downarrow} \right) c_{\mathbf{k}+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}\downarrow} - \frac{U}{V} \left(\langle n_{\mathbf{k}\downarrow} \rangle - \langle n_{\mathbf{k}+\mathbf{q}\uparrow} \rangle \right) \sum_{\mathbf{k}'} c_{\mathbf{k}'+\mathbf{q}\uparrow}^{\dagger} c_{\mathbf{k}'\downarrow} .$$
 (33.1.45)

Substitution of this expression into the left-hand side of (33.1.41) gives

$$\sum_{\boldsymbol{k}} \phi_{\boldsymbol{k}\boldsymbol{q}} \left(\hbar \omega_{\boldsymbol{q}} - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} + \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow} \right) c_{\boldsymbol{k}+\boldsymbol{q}\uparrow}^{\dagger} c_{\boldsymbol{k}\downarrow}$$

$$= \frac{U}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'} \left(\langle n_{\boldsymbol{k}+\boldsymbol{q}\uparrow} \rangle - \langle n_{\boldsymbol{k}\downarrow} \rangle \right) \phi_{\boldsymbol{k}\boldsymbol{q}} c_{\boldsymbol{k}'+\boldsymbol{q}\uparrow}^{\dagger} c_{\boldsymbol{k}'\downarrow} .$$
(33.1.46)

We may require – after a change of variables $k \leftrightarrow k'$ – that the equality

$$\phi_{\boldsymbol{k}\boldsymbol{q}}\big(\hbar\omega_{\boldsymbol{q}} - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} + \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow}\big) = \frac{U}{V}\sum_{\boldsymbol{k}'}\phi_{\boldsymbol{k}'\boldsymbol{q}}\big(\langle n_{\boldsymbol{k}'+\boldsymbol{q}\uparrow}\rangle - \langle n_{\boldsymbol{k}'\downarrow}\rangle\big)$$
(33.1.47)

holds for each k separately. To solve this equation we introduce the quantity

$$A_{\boldsymbol{q}} = \frac{U}{V} \sum_{\boldsymbol{k}'} \phi_{\boldsymbol{k}'\boldsymbol{q}} \big(\langle n_{\boldsymbol{k}'+\boldsymbol{q}\uparrow} \rangle - \langle n_{\boldsymbol{k}'\downarrow} \rangle \big). \tag{33.1.48}$$

The formal solution of (33.1.47) is

$$\phi_{\boldsymbol{k}\boldsymbol{q}} = \frac{A_{\boldsymbol{q}}}{\hbar\omega_{\boldsymbol{q}} - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}\uparrow} + \widetilde{\varepsilon}_{\boldsymbol{k}\downarrow}} \,. \tag{33.1.49}$$

Substitution of this expression into the definition of A_q leads to the selfconsistency condition

$$1 = \frac{U}{V} \sum_{\mathbf{k}'} \frac{\langle n_{\mathbf{k}'+\mathbf{q}\uparrow} \rangle - \langle n_{\mathbf{k}'\downarrow} \rangle}{\hbar \omega_{\mathbf{q}} - \tilde{\varepsilon}_{\mathbf{k}'+\mathbf{q}\uparrow} + \tilde{\varepsilon}_{\mathbf{k}'\downarrow}} \,. \tag{33.1.50}$$

When the occupation numbers are expressed in terms of the Fermi distribution functions we have

$$1 = \frac{U}{V} \sum_{\mathbf{k}'} \frac{f_0(\tilde{\varepsilon}_{\mathbf{k}'+\mathbf{q}\uparrow}) - f_0(\tilde{\varepsilon}_{\mathbf{k}'\downarrow})}{\hbar\omega_{\mathbf{q}} - \tilde{\varepsilon}_{\mathbf{k}'+\mathbf{q}\uparrow} + \tilde{\varepsilon}_{\mathbf{k}'\downarrow}}.$$
 (33.1.51)

The $\hbar \omega_q$ values satisfying this equation are the allowed excitation energies. The solutions can be found graphically, as was done already in many cases, by analyzing the behavior of the function

$$g(\omega) = \frac{U}{V} \sum_{\mathbf{k}'} \frac{f_0(\widetilde{\varepsilon}_{\mathbf{k}'+\mathbf{q}\uparrow}) - f_0(\widetilde{\varepsilon}_{\mathbf{k}\downarrow\downarrow})}{\hbar\omega - \widetilde{\varepsilon}_{\mathbf{k}'+\mathbf{q}\uparrow} + \widetilde{\varepsilon}_{\mathbf{k}\downarrow\downarrow}} \,. \tag{33.1.52}$$



Fig. 33.4. Graphical solution of (33.1.51) for the collective spin waves and the electron-hole excitations in the Stoner continuum

The function $g(\omega)$ displayed in Fig. 33.4 diverges every time when $\hbar \omega = \tilde{\epsilon}_{\mathbf{k}'+\mathbf{q}\uparrow} - \tilde{\epsilon}_{\mathbf{k}'\downarrow}$. The solutions of $g(\omega) = 1$ between subsequent singular points give the excitations in the Stoner continuum. In addition to these there is an extra solution below the continuum. This solution, which can be considered as a bound state of electron-hole pairs, corresponds to a collective spin-wave excitation. The full spectrum is displayed in Fig. 33.5.

The dispersion relation of spin waves can be obtained analytically for small values of ω and q by expanding the right-hand side of (33.1.51). Keeping only the leading terms when the exchange splitting Δ_0 is large compared to the spin-wave energy, we find



Fig. 33.5. Spin waves below the Stoner continuum in a ferromagnetic electron gas

$$\frac{U}{V} \sum_{\boldsymbol{k}'} \frac{f_0(\tilde{\varepsilon}_{\boldsymbol{k}'+\boldsymbol{q}\uparrow}) - f_0(\tilde{\varepsilon}_{\boldsymbol{k}'\downarrow})}{\hbar\omega_{\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}'+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}'} + 2U_{\rm H}n^{\rm a}} = 1 + \frac{\hbar\omega_{\boldsymbol{q}}}{\Delta_0} - Dq^2 \,, \qquad (33.1.53)$$

where the order of magnitude of D is $1/k_{\rm F}^2$. For a free-electron-like dispersion relation the prefactor is $D = 1/(12k_{\rm F}^2)$. Combining this expression with (33.1.50) we readily find that the spin waves have a quadratic dispersion relation,

$$\hbar\omega_{\boldsymbol{q}} \sim \Delta_0 (q/k_{\rm F})^2 \,, \tag{33.1.54}$$

just like magnons of the Heisenberg model of localized spins.

We can recognize on the right-hand side of (33.1.51) the quantity $\Sigma_{\perp}^{0}(\boldsymbol{q},\omega_{\boldsymbol{q}})$ defined in (29.8.52). Thus the dispersion relation of the spin waves has to be determined from

$$U\Sigma_{\perp}^{0}(\boldsymbol{q},\omega_{\boldsymbol{q}}) = 1 \tag{33.1.55}$$

in accordance with (31.4.12). Looking back at (29.8.54) we see that this relationship is equivalent to the statement that spin excitations can propagate in the system with frequency ω_q at a given q for which the transverse susceptibility diverges, i.e., the spin waves can be obtained from the poles of χ_{\perp} . The poles are at real frequencies for small values of q, indicating that the spin waves are well-defined excitations with infinite lifetime in this approximation. It is worthwhile to make a connection between these excitations and the overdamped spin-fluctuation modes, the paramagnons, found in nearly ferromagnetic metals when $U\rho_{\sigma}(\varepsilon_{\rm F})$ is close to the critical value. The paramagnons can also be obtained from the pole of the transverse susceptibility given in (31.4.2), but the pole is now pure imaginary. The spin fluctuations are overdamped, but can produce a relatively sharp peak in the cross section for magnetic scattering. Thus the paramagnons of nearly ferromagnetic metals are the precursors of spin waves (magnons), which are the soft Goldstone bosons of the ferromagnetic state.

33.1.7 Role of Spin Waves in the Ferromagnetic Electron Gas

The thermodynamic properties of ferromagnets, such as the temperature dependence of the heat capacity or the magnetization, are determined by the dispersion relation of the elementary excitations and their statistics. As seen in Fig. 33.5, spin waves are well-defined excitations for small momenta only where they are below the continuum of Stoner excitations. They merge into it at a momentum q_0 of the order of $\Delta_0/\hbar v_{\rm F}$. Δ_0 being proportional to the magnetization we have

$$q_{\rm c} \propto k_{\rm F} \sqrt{U \rho_{\sigma}(\varepsilon_{\rm F}) - 1}$$
. (33.1.56)

A crossover temperature can be defined as the temperature where the thermal energy is comparable with the maximum spin-wave energy. We find

$$k_{\rm B}T^* \propto \Delta_0 (q_{\rm c}/k_{\rm F})^2 \propto \varepsilon_{\rm F} \left[U \rho_\sigma(\varepsilon_{\rm F}) - 1 \right]^{3/2}.$$
 (33.1.57)

Spin waves are the dominant excitations below this energy. Their dispersion relation is similar to that of magnons in the Heisenberg model, and the thermodynamic behavior is qualitatively similar in the two cases at low temperatures, below T^* . The magnetization decreases as $T^{3/2}$ instead of T^2 found in (33.1.34). Based solely on measurements of macroscopic quantities, one cannot decide whether magnetism originates from localized moments or from itinerant electrons. However, measuring the magnetic form factor, and thereby the magnetic-moment density, by magnetic scattering of neutrons can give information about the nature of the magnetic moment.

When T exceeds the crossover temperature T^* , the damped spin waves within the Stoner continuum (indicated by the dashed line in Fig. 33.5) become the dominant thermal excitations. They are insensitive to the spontaneous magnetization and behave like paramagnons of large wave number, where the dispersion curve is cubic:

$$\hbar\omega \propto \varepsilon_{\rm F} (q/k_{\rm F})^3$$
. (33.1.58)

They are referred to as paramagnons even in the ferromagnetic state. It can be shown that they are responsible for destroying ferromagnetism. A selfconsistent calculation of the Curie temperature gives

$$k_{\rm B}T_{\rm C} \propto \Delta_0 \sqrt{\frac{\Delta_0}{\varepsilon_{\rm F}}} \propto \varepsilon_{\rm F} \left[U \rho_\sigma(\varepsilon_{\rm F}) - 1 \right]^{3/4},$$
 (33.1.59)

which is smaller than the mean-field result, but larger than the crossover temperature.

33.2 Itinerant Antiferromagnets

We assumed in our previous considerations that the magnetic moment is homogeneous in space. A simple justification can be found in the RPA. The susceptibility of the paramagnetic phase of the Hubbard model can be written according to (29.8.43) in the form 336 33 Electronic Phases with Broken Symmetry

$$\chi(\boldsymbol{q},\omega) = \frac{\frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\Sigma_0(\boldsymbol{q},\omega)}{1 - U\Sigma_0(\boldsymbol{q},\omega)},\qquad(33.2.1)$$

where Σ_0 is $-\frac{1}{2}$ times the Lindhard function, that is

$$\Sigma_0(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) - f_0(\varepsilon_{\boldsymbol{k}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \,. \tag{33.2.2}$$

We know from Chapter 29 that the Lindhard function has a very broad maximum at q = 0 in an isotropic three-dimensional system. The stability condition

$$U\Sigma_0(\boldsymbol{q},\omega) < 1 \tag{33.2.3}$$

of the paramagnetic phase fails first at q = 0 as U increases. That is why we expected a homogeneous magnetization in the broken-symmetry phase.

 $\Sigma_0(\boldsymbol{q},\omega)$ may have a different \boldsymbol{q} dependence when the dispersion relation deviates essentially from that of free electrons. We have seen in Chapter 29 that if the Fermi surface has the nesting property, the dielectric function (or the susceptibility) of the noninteracting system has a maximum at the nesting vector \boldsymbol{q}_0 . The paramagnetic phase becomes unstable at this \boldsymbol{q}_0 and the ordered magnetic phase is expected to display a periodic spatial variation corresponding to \boldsymbol{q}_0 .

33.2.1 Slater's Theory of Antiferromagnetism

Such a perfectly nested Fermi surface is found in the simple cubic lattice in the tight-binding approximation, where the dispersion relation has the form

$$\varepsilon_{\mathbf{k}} = \varepsilon_0 + \gamma \left(\cos k_x a + \cos k_y a + \cos k_z a \right) \tag{33.2.4}$$

if the band is half filled, i.e., ε_0 is equal to the Fermi energy. The Fermi surface is then given by the k vectors satisfying

$$\cos k_x a + \cos k_y a + \cos k_z a = 0. \tag{33.2.5}$$

It is readily seen from this equation and from Fig. 33.6, where the Fermi surface is displayed, that if \mathbf{k} is on the Fermi surface, then $\mathbf{k} + \mathbf{q}_0$ is also on the Fermi surface provided that \mathbf{q}_0 is one of the vectors $\mathbf{q}_0 = (\pi/a)(\pm 1, \pm 1, \pm 1)$, which are halves of a reciprocal-lattice vector. This means that if a piece of the Fermi surface is displaced by one of these vectors, perfect nesting is achieved. [The same perfect nesting is found in a square lattice for $\mathbf{q}_0 = (\pi/a)(\pm 1, \pm 1)$.]

The nesting property of the Fermi surface is even more spectacular for the body-centered cubic lattice with a half-filled tight-binding *s*-band. The electronic energy spectrum is given by

$$\varepsilon_{\mathbf{k}} = \varepsilon_0 + \gamma \cos(k_x a/2) \cos(k_y a/2) \cos(k_z a/2), \qquad (33.2.6)$$



Fig. 33.6. (a) Nested Fermi surface for the half-filled tight-binding band in a simple cubic lattice. (b) A section of the Fermi surface (cutting the Brillouin zone diagonally through the points R_1, R_2, R_3 , and R_4) with the nesting vector \boldsymbol{q}_0

and the Fermi surface is a regular cube. The opposite faces are separated by one of the vectors $\mathbf{q}_0 = (2\pi/a)(\pm 1, 0, 0), (2\pi/a)(0, \pm 1, 0), \text{ or } (2\pi/a)(0, 0, \pm 1),$ which are halves of a vector of the reciprocal lattice.

If the energies are measured from the Fermi energy in a system with perfectly nesting Fermi surface, the quantity $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \varepsilon_{\mathrm{F}}$ satisfies the relationship

$$\xi_{\boldsymbol{k}} = -\xi_{\boldsymbol{k}+\boldsymbol{q}_0} \tag{33.2.7}$$

for k vectors near the Fermi surface. It follows from this nesting property that the q dependence of the quantity $\Sigma_0(q, \omega)$ is similar to that of one-dimensional systems. $\Sigma_0(q, \omega)$ is singular at $q = q_0$ at zero temperature and this singularity is rounded off at finite temperatures: the peak is broadened and its height decreases with increasing temperature. The paramagnetic phase is stable at high temperatures and may become unstable below a critical temperature. Electrons in the localized Wannier states are expected to be polarized in the low-temperature phase. The spin-up and spin-down electrons order statically into two sublattices with the on-site occupation varying as

$$\langle n_{i\sigma} \rangle = \frac{1}{2} + \sigma n^{\mathrm{a}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}_{0} \cdot \boldsymbol{R}_{i}} , \qquad (33.2.8)$$

where $n^{\mathbf{a}}$ is the spin asymmetry in the site occupations, \mathbf{q}_0 is one of the nesting vectors, and the factor $e^{i\mathbf{q}_0\cdot\mathbf{R}_i}$ takes the value +1 and -1, respectively, on the two sublattices. In a simple cubic lattice, the periodicity of the magnetic structure is doubled in all three directions compared to the chemical cell, just as in a type G antiferromagnet shown in Fig. 14.2. The magnetic structure is face-centered cubic with primitive translation vectors $\mathbf{a}_1 = a(0, 1, 1), \mathbf{a}_2 = a(1, 0, 1)$, and $\mathbf{a}_3 = a(1, 1, 0)$; the volume of the magnetic cell is twice that of the chemical cell.

The magnetic primitive cell of the antiferromagnetic structure appearing in the body-centered cubic lattice owing to the nesting property coincides with the Bravais cell of the bcc lattice. The magnetic moment at the center and at the vertices are oriented oppositely, and the volume of the magnetic cell is again twice that of the chemical cell.

Inserting (33.2.8) into the mean-field approximation of the Hubbard Hamiltonian we get

$$\mathcal{H} = \sum_{\langle ij\rangle\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} - U_{\rm H} n^{\rm a} \sum_{i\sigma} \sigma e^{i\boldsymbol{q}_0 \cdot \boldsymbol{R}_i} n_{i\sigma} \,. \tag{33.2.9}$$

When transforming the operators of the Wannier states into the momentum representation it is convenient to use \boldsymbol{k} vectors that are in the Brillouin zone corresponding to the magnetic structure. Owing to the doubling of the primitive cell in the antiferromagnetic phase, the volume of the corresponding Brillouin zone is smaller and contains only N/2 allowed \boldsymbol{k} vectors. The annihilation operators of the Wannier states of the N sites should therefore be given in terms of the annihilation operators of the Bloch states in the form

$$c_{i\sigma} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}}' c_{\boldsymbol{k}\sigma} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{i}} + \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k}}' c_{\boldsymbol{k}+\boldsymbol{q}_{0}\sigma} \mathrm{e}^{\mathrm{i}(\boldsymbol{k}+\boldsymbol{q}_{0})\cdot\boldsymbol{R}_{i}}, \qquad (33.2.10)$$

where the prime indicates that the summation goes over the Brillouin zone of the magnetic state.

If the one-particle energies are measured from the chemical potential and (33.2.7) is made use of, we find

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma}' \left[\xi_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} - \xi_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}_{0}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}_{0}\sigma} - U_{\mathrm{H}} n^{\mathrm{a}} \sigma (c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}_{0}\sigma} + c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}_{0}\sigma} c_{\boldsymbol{k}\sigma}) \right]$$
(33.2.11)

apart from a constant term. This bilinear Hamiltonian can be diagonalized by a Bogoliubov transformation

$$\begin{aligned} \alpha_{\boldsymbol{k}\sigma}^{\dagger} &= u_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} + \sigma v_{\boldsymbol{k}} c_{\boldsymbol{k}+\boldsymbol{q}_{0}\sigma}^{\dagger} ,\\ \beta_{\boldsymbol{k}\sigma}^{\dagger} &= -\sigma v_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} + u_{\boldsymbol{k}} c_{\boldsymbol{k}+\boldsymbol{q}_{0}\sigma}^{\dagger} \end{aligned}$$
(33.2.12)

with real coefficients. The new operators obey fermionic anticommutation relations if

$$u_{k}^{2} + v_{k}^{2} = 1. (33.2.13)$$

Requiring the vanishing of the off-diagonal terms yields

$$u_{k}^{2} = \frac{1}{2} \left(1 - \frac{\xi_{k}}{E_{k}} \right), \quad v_{k}^{2} = \frac{1}{2} \left(1 + \frac{\xi_{k}}{E_{k}} \right), \quad u_{k}v_{k} = \frac{U_{H}n^{a}}{2E_{k}}, \quad (33.2.14)$$

where

$$E_{k} = \sqrt{\xi_{k}^{2} + (U_{\rm H} n^{\rm a})^{2}}, \qquad (33.2.15)$$

and the diagonal Hamiltonian is
$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \left[\left(-E_{\boldsymbol{k}} + \varepsilon_{\mathrm{F}} \right) \alpha_{\boldsymbol{k}\sigma}^{\dagger} \alpha_{\boldsymbol{k}\sigma}^{\dagger} + \left(E_{\boldsymbol{k}} + \varepsilon_{\mathrm{F}} \right) \beta_{\boldsymbol{k}\sigma}^{\dagger} \beta_{\boldsymbol{k}\sigma}^{\dagger} \right].$$
(33.2.16)

The negative energy states are completely filled in the ground state of the half-filled system. The ground-state wavefunction can be written in the form

$$|\Psi_{\rm AF}\rangle = \prod_{|\boldsymbol{k}| < k_{\rm F}} \alpha_{\boldsymbol{k}\uparrow}^{\dagger} \alpha_{\boldsymbol{k}\downarrow}^{\dagger} |0\rangle \,. \tag{33.2.17}$$

This state is separated from the first excited states by a gap $\Delta_0 = 2U_{\rm H}n^{\rm a}$. Although the spin-up and spin-down states of the α particles are filled equally, there is a spin imbalance in the filling of the states created by the operators $c^{\dagger}_{k\sigma}$. The sublattice magnetization has to be calculated self-consistently from

$$n^{\rm a} = \frac{4}{N} \sum_{k} u_{k} v_{k} = \frac{2}{N} \sum_{k} \frac{U_{\rm H} n^{\rm a}}{\sqrt{\xi_{k}^{2} + (U_{\rm H} n^{\rm a})^{2}}} \,.$$
(33.2.18)

The magnetically ordered state of one electron per atom on a bipartite lattice³ is an insulator. It is a consequence of the doubling of the unit cell due to the establishment of antiferromagnetic order and the concomitant halving of the Brillouin zone. The band is split into two, the lower band is completely filled, and a gap appears in the spectrum of charge excitations. There exist low-energy magnetic excitations, antiferromagnons, in the ordered phase, just as in isotropic antiferromagnets of localized spins, but it costs a finite energy to add a particle to the system. The finite charge gap is in agreement with our expectation for large on-site Coulomb repulsion. That an insulating state is found for arbitrary positive U is the consequence of the perfect nesting property of the Fermi surface at half filling. As the temperature is increased, the sublattice magnetization decreases together with the gap. The lower and upper bands merge at the Néel temperature, where antiferromagnetic ordering is destroyed, and a continuous (second-order) transition to a metallic Fermi liquid takes place. This is the so-called *Slater transition*,⁴ and the antiferromagnetic insulator is a *Slater insulator*.

33.2.2 Antiferromagnetic Exchange

A simple physical picture can be obtained about the formation of the antiferromagnetic state in the large-U limit of the half-filled Hubbard model, when U is much larger than the bandwidth. Taking a single orbital per site, a site can be empty, singly occupied by a spin-up or a spin-down electron, or doubly occupied by two electrons of opposite spins. Double occupancy is energetically

 $^{^3}$ A bipartite lattice, such as the simple cubic or body-centered cubic lattice, can be decomposed into two sublattices such that the nearest neighbors of a lattice site are located on the other sublattice.

⁴ J. C. Slater, 1951.

unfavorable for large U and it becomes forbidden in the limit $U \to \infty$. All sites are occupied by exactly one electron. They are frozen to the sites and are unable to move. Because their spin configuration can be arbitrary, the ground state is highly degenerate, with degeneracy 2^N for N sites.

When U is large but finite, most of the sites are still occupied by one electron, although electrons can hop to neighboring sites for a short time even if that site is occupied by another electron with opposite spin. Figure 33.7 shows a snapshot of a portion of the lattice before and after such hopping processes.



Fig. 33.7. Two-step exchange process in the half-filled Hubbard model

The energy of the intermediate state with one doubly occupied and one empty site is high; therefore, one of the electrons hops back to the empty site. When the electron that hopped there in the first place hops back, the original spin configuration is recovered. If, however, the other electron hops to the empty site, a new configuration is obtained in which two spins are reversed, exchanged. Such second-order processes lift the degeneracy of the spin configurations and the ground state may become ordered.

We can restrict ourselves to the Hilbert space of the 2^N disordered spin configurations by neglecting all higher lying states that are well separated in energy and cannot be excited thermally. This portion of the spectrum can be mapped onto the spectrum of a spin model, where the exchange of spins is described by an effective exchange coupling. Its strength can be calculated in second-order degenerate perturbation theory. An alternative procedure is to perform a canonical transformation as outlined in Appendix I. When the Coulomb repulsion is strong compared to the bandwidth, the hopping term of the Hamiltonian can be chosen as perturbation. The total Hamiltonian is then separated into two terms:

$$\mathcal{H}_0 = U_{\rm H} \sum_i n_{i\uparrow} n_{i\downarrow} , \qquad \lambda \mathcal{H}_1 = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} . \qquad (33.2.19)$$

The hopping term is eliminated if the operator S in the canonical transformation

$$\widetilde{\mathcal{H}} = \mathrm{e}^{S} \mathcal{H} \mathrm{e}^{-S} \tag{33.2.20}$$

is chosen to satisfy the relation

$$\lambda \mathcal{H}_1 + [S, \mathcal{H}_0]_{-} = 0. \qquad (33.2.21)$$

The leading terms of the transformed Hamiltonian are then

$$\widetilde{\mathcal{H}} = \mathcal{H}_0 + \frac{1}{2} \left[S, \lambda \mathcal{H}_1 \right]_- + \cdots .$$
(33.2.22)

The matrix elements of the effective Hamiltonian between the degenerate configurations $|m\rangle$ and $|n\rangle$ with energy E_0 are given according to (I.1.14) by

$$\langle n|\widetilde{\mathcal{H}}|m\rangle = \langle n|\mathcal{H}_0|m\rangle - \sum_k \frac{\langle n|\lambda\mathcal{H}_1|k\rangle\langle k|\lambda\mathcal{H}_1|m\rangle}{E_k - E_0} + \cdots, \qquad (33.2.23)$$

where $|k\rangle$ denotes the intermediate states. They are finite in a second-order calculation if the spin configurations in states $|m\rangle$ and $|n\rangle$ differ at most on two sites. We can pick two neighboring sites *i* and *j* since nothing happens with the rest of the lattice. The state $c_{i\sigma}^{\dagger}c_{j\sigma'}^{\dagger}|0\rangle$ will be denoted by $|\Psi_{\sigma\sigma'}\rangle$. Calculating the matrix elements between $|\Psi_{\uparrow\uparrow}\rangle$, $|\Psi_{\uparrow\downarrow}\rangle$, and $|\Psi_{\downarrow\downarrow}\rangle$ it is readily seen that the effective Hamiltonian is equivalent to a Heisenberg-like spin model in the restricted Hilbert space.

If the electrons have identical spins on the two neighboring sites, hopping cannot occur. Acting with \mathcal{H}_1 on such a state gives zero. Hence

$$\langle \Psi_{\uparrow\uparrow} | \widetilde{\mathcal{H}} | \Psi_{\uparrow\uparrow} \rangle = \langle \Psi_{\downarrow\downarrow} | \widetilde{\mathcal{H}} | \Psi_{\downarrow\downarrow} \rangle = 0.$$
 (33.2.24)

If the electrons have opposite spins, one of the electrons can hop to the other site. The intermediate state has a doubly occupied and an empty site. There are two possibilities for the intermediate states:

$$|k\rangle = c_{i\uparrow}^{\dagger} c_{i\downarrow}^{\dagger} |0\rangle, \qquad |k'\rangle = c_{j\uparrow}^{\dagger} c_{j\downarrow}^{\dagger} |0\rangle. \qquad (33.2.25)$$

Owing to the double occupancy of a site the energy of the intermediate state is higher by $U_{\rm H}$ compared to the states in which all sites are singly occupied. Thus (33.2.23) gives

$$\langle \Psi_{\uparrow\downarrow} | \tilde{\mathcal{H}} | \Psi_{\uparrow\downarrow} \rangle = -\frac{\langle \Psi_{\uparrow\downarrow} | \lambda \mathcal{H}_1 | k \rangle \langle k | \lambda \mathcal{H}_1 | \Psi_{\uparrow\downarrow} \rangle}{E_k - E_0} - \frac{\langle \Psi_{\uparrow\downarrow} | \lambda \mathcal{H}_1 | k' \rangle \langle k' | \lambda \mathcal{H}_1 | \Psi_{\uparrow\downarrow} \rangle}{E_{k'} - E_0}$$

$$= -\frac{2t^2}{U_{\rm H}}$$
(33.2.26)

for the diagonal matrix element.

The off-diagonal matrix element between $|\Psi_{\uparrow\downarrow}\rangle$ and $|\Psi_{\downarrow\uparrow}\rangle$ is also finite. It corresponds to the spin exchange mentioned above. This process gives a contribution similar to the diagonal matrix element, apart from a factor -1 which comes from the different order of the fermion operators. We find

$$\langle \Psi_{\uparrow\downarrow} | \widetilde{\mathcal{H}} | \Psi_{\downarrow\uparrow} \rangle = \frac{2t^2}{U_{\rm H}} \,.$$
 (33.2.27)

The same matrix elements are obtained when the s = 1/2 Heisenberg exchange Hamiltonian

$$\widetilde{\mathcal{H}} = -2J\boldsymbol{s}_i \cdot \boldsymbol{s}_j + \frac{1}{2}J \tag{33.2.28}$$

acts on the spins of the electrons, provided that the strength of the effective exchange coupling is

$$J = -2\frac{t^2}{U_{\rm H}}\,.\tag{33.2.29}$$

The Coulomb repulsion $U_{\rm H}$ being positive, the coupling constant J is negative and the effective exchange is antiferromagnetic. We conclude that in the large-U limit, where the lowest 2^N states of the Hilbert space are well separated from the higher lying ones, the low-energy physics of the Hubbard model is equivalent to that of a spin-1/2 Heisenberg antiferromagnet described by the Hamiltonian

$$\widetilde{\mathcal{H}} = -J \sum_{\langle i,j \rangle} \boldsymbol{s}_i \cdot \boldsymbol{s}_j \tag{33.2.30}$$

with the exchange coupling between nearest-neighbor sites $\langle i, j \rangle$ given above.

The Néel temperature, where the antiferromagnetic order is destroyed, is of order $J/k_{\rm B}$. The Hartree–Fock theory, on the other hand, gives a Néel temperature, which, just as in the Stoner model, is of order $U/k_{\rm B}$. This discrepancy is due to the absence of correlations in the Hartree–Fock approach. The true ordering temperature is $T_{\rm N} \propto J/k_{\rm B}$, but the moments survive in the paramagnetic state. They would be thermally destroyed at a much higher temperature of order $U/k_{\rm B}$.

33.3 Spin-Density Waves

The itinerant antiferromagnetism occurring in the half-filled tight-binding model in a simple cubic or body-centered cubic lattice is a special example of more general situations where the Stoner condition $U\Sigma_0(\boldsymbol{q},\omega) < 1$ for the stability of the paramagnetic phase readily fails due to the nesting property of the Fermi surface. $\Sigma_0(\boldsymbol{q},\omega)$ exhibits a sharp maximum at the nesting vector \boldsymbol{q}_0 with the peak height increasing with decreasing temperature. The instability occurs at this wave vector at the temperature where $U\Sigma_0(\boldsymbol{q}_0,0)=1$ and the system orders magnetically into an inhomogeneous state breaking the continuous translational symmetry. The total magnetization vanishes, but a spatially oscillating magnetic-moment density appears below the transition point. The variations in space are characterized by the wave vector q_0 . Such a state is known as *spin-density-wave* (SDW) state. The archetypal example is chromium, an itinerant antiferromagnet, where - as predicted by A. W. OVERHAUSER (1962) – the incommensurate spin-density wave appearing at $T_{\rm N} = 311 \, {\rm K}$ is characterized by a wave vector determined by the nesting properties of the Fermi surface. The stability condition of the paramagnetic phase fails especially easily in strongly anisotropic, quasi-one-dimensional materials built up from weakly coupled chains. To get a simple physical picture of the formation of the SDW a one-dimensional model will be studied. We will return to the role of interchain couplings after a similar treatment of charge-density waves.

33.3.1 Susceptibility of the One-Dimensional Model

We consider the usual expression

$$\Sigma_0(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}}) - f_0(\varepsilon_{\boldsymbol{k}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta}$$
(33.3.1)

for the spin-density–spin-density response function. A linear dispersion relation given in (32.3.1) with a scalar k will be used in the neighborhood of the Fermi points $\pm k_{\rm F}$. When the energy measured from the chemical potential, $\xi_k = \varepsilon_k - \mu$, is used we have

$$\Sigma_0(q,\omega) = \frac{1}{L} \sum_k \frac{f_0(\xi_{k+q}) - f_0(\xi_k)}{\hbar\omega - \xi_{k+q} + \xi_k + \mathrm{i}\delta} \,. \tag{33.3.2}$$

We will evaluate it at finite temperatures for wave numbers near $q = 2k_{\rm F}$.

Precisely at $q = 2k_{\rm F}$ the relationship

$$\xi_{k+2k_{\rm F}} = -\xi_k \tag{33.3.3}$$

is satisfied for the linearized spectrum if k is near $-k_{\rm F}$ and $k + 2k_{\rm F}$ is near $+k_{\rm F}$. The response function of the noninteracting one-dimensional electron gas is then given at $\omega = 0$ by

$$\Sigma_0(2k_{\rm F}) = \frac{1}{L} \sum_{k<0} \frac{f_0(-\xi_k) - f_0(\xi_k)}{2\xi_k} \,. \tag{33.3.4}$$

Summation goes over wave numbers near $-k_{\rm F}$. Note that half filling of the band is not needed for the nesting property to hold in the one-dimensional model. The results are qualitatively similar in the half-filled case although a factor of 2 appears in some of the formulas. This is because $2k_{\rm F}$ and $-2k_{\rm F}$ are equivalent, they differ by the reciprocal-lattice vector $2\pi/a$, and the summation has to be extended to the region k > 0.

When replacing the sum by an integral, only half of the density of states has to be taken for a non-half-filled band. Assuming a symmetric band with bandwidth 2D around the Fermi energy and approximating the density of states with

$$\rho_{\sigma}(\varepsilon_{\rm F}) = \frac{m_{\rm e}}{\pi \hbar^2 k_{\rm F}} = \frac{1}{\pi \hbar v_{\rm F}} \,, \qquad (33.3.5)$$

its value at the Fermi energy, we have

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$$\Sigma_0(2k_{\rm F}) = \frac{1}{2}\rho_\sigma(\varepsilon_{\rm F}) \int_{-D}^{D} \mathrm{d}\xi \frac{f_0(-\xi) - f_0(\xi)}{2\xi} \,. \tag{33.3.6}$$

Making use of the relation

$$\frac{1}{e^x + 1} = \frac{1}{2} \left(1 - \tanh \frac{x}{2} \right) \tag{33.3.7}$$

for the Fermi distribution function gives

$$\Sigma_{0}(2k_{\rm F}) = \frac{1}{2}\rho_{\sigma}(\varepsilon_{\rm F}) \int_{-D}^{D} \frac{\mathrm{d}\xi}{2\xi} \tanh \frac{\xi}{2k_{\rm B}T}$$

$$= \frac{1}{2}\rho_{\sigma}(\varepsilon_{\rm F}) \int_{0}^{D} \frac{\mathrm{d}\xi}{\xi} \tanh \frac{\xi}{2k_{\rm B}T}.$$
(33.3.8)

By introducing the variable $x = \frac{\xi}{2k_{\rm B}T}$ we have

$$\Sigma_0(2k_{\rm F}) = \frac{1}{2}\rho_\sigma(\varepsilon_{\rm F}) \int_0^{D/2k_{\rm B}T} \frac{\mathrm{d}x}{x} \tanh x \,. \tag{33.3.9}$$

When the thermal energy is much smaller than the bandwidth, which is usually the case, the function $\tanh x$ is near unity over a large part of the domain of integration, and it can be approximated by

$$\tanh x \approx \begin{cases} x & \text{for } 0 \le x \le 1, \\ 1 & \text{for } x \ge 1, \end{cases}$$
(33.3.10)

and the integral can be estimated to give

$$\int_{0}^{D/2k_{\rm B}T} \frac{\mathrm{d}x}{x} \tanh x \approx \ln \frac{D}{2k_{\rm B}T} + 1 = \ln \frac{\mathrm{e}D}{2k_{\rm B}T}, \qquad (33.3.11)$$

which shows that the integral is logarithmically singular. To get a better estimate of the constant term we integrate by parts:

$$\int_{0}^{D/2k_{\rm B}T} \frac{\mathrm{d}x}{x} \tanh x = \ln \frac{D}{2k_{\rm B}T} - \int_{0}^{D/2k_{\rm B}T} \frac{\ln x}{\cosh^2 x} \,\mathrm{d}x \,. \tag{33.3.12}$$

The value of the remaining integral is known if it is performed up to infinity:

$$\int_{0}^{\infty} \frac{\ln x}{\cosh^2 x} \,\mathrm{d}x = -\ln\frac{4\,\mathrm{e}^{\gamma}}{\pi}\,,\qquad(33.3.13)$$

where $\gamma = 0.5772...$ is the Euler-Mascheroni constant defined in (C.3.32) and $C = e^{\gamma} = 1.781...$ Thus

$$\int_{0}^{D/2k_{\rm B}T} \frac{\mathrm{d}x}{x} \tanh x = \ln \frac{2\mathrm{e}^{\gamma}D}{\pi k_{\rm B}T}$$
(33.3.14)

and

$$\Sigma_0(2k_{\rm F}) = \frac{1}{2}\rho_\sigma(\varepsilon_{\rm F}) \ln \frac{2\mathrm{e}^{\gamma}D}{\pi k_{\rm B}T}.$$
(33.3.15)

The calculations cannot be done exactly for arbitrary values of q at finite temperatures. Writing the wave number in the form $q = 2k_{\rm F} + q'$, for small values of q' and ω we get

$$\Sigma_{0}(2k_{\rm F}+q',\omega) = \frac{1}{2}\rho_{\sigma}(\varepsilon_{\rm F})\left\{\ln\frac{2\mathrm{e}^{\gamma}D}{\pi k_{\rm B}T} + \psi\left(\frac{1}{2}\right)$$

$$-\frac{1}{2}\left[\psi\left(\frac{1}{2} + \frac{\mathrm{i}\hbar(v_{\rm F}q'-\omega)}{4\pi k_{\rm B}T}\right) + \psi\left(\frac{1}{2} - \frac{\mathrm{i}\hbar(v_{\rm F}q'+\omega)}{4\pi k_{\rm B}T}\right)\right]\right\},$$
(33.3.16)

where ψ is the digamma function defined in (C.3.30). The sharp peak at $q = 2k_{\rm F}$ is rounded off more and more as the temperature increases. This is depicted in Fig. 33.8.



Fig. 33.8. Rounding of the $q = \pm 2k_{\rm F}$ singularity in the spin density–spin density response function of the one-dimensional electron gas at finite temperatures

If the Coulomb interaction is taken into account in the RPA, the $2k_{\rm F}$ component of the susceptibility takes the form

$$\chi(2k_{\rm F}) = \frac{\frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\Sigma_0(2k_{\rm F})}{1 - U\Sigma_0(2k_{\rm F})} = \frac{\frac{1}{2}g_{\rm e}^2\mu_{\rm B}^2\mu_0\chi^0(2k_{\rm F})}{1 - \frac{1}{2}U\rho_{\sigma}(\varepsilon_{\rm F})\ln\frac{2{\rm e}^{\gamma}D}{\pi k_{\rm B}T}}.$$
 (33.3.17)

As will be discussed later, the application of the RPA cannot be justified in a strictly one-dimensional system. It does, however, give a good estimate of the role of magnetic fluctuations in quasi-one-dimensional materials.

The susceptibility is positive at high temperatures and the system is paramagnetic. The paramagnetic phase becomes unstable at a critical temperature $T_{\rm c}$ where

$$1 = U\Sigma_0(2k_{\rm F}) = \frac{1}{2}U\rho_\sigma(\varepsilon_{\rm F})\ln\frac{2{\rm e}^{\gamma}D}{\pi k_{\rm B}T_{\rm c}},\qquad(33.3.18)$$

from which we have

$$k_{\rm B}T_{\rm c} = 2\frac{{\rm e}^{\gamma}}{\pi}D\,{\rm e}^{-2/U\rho_{\sigma}(\varepsilon_{\rm F})} = 1.134D\,{\rm e}^{-2/U\rho_{\sigma}(\varepsilon_{\rm F})}\,.$$
 (33.3.19)

33.3.2 The Spin-Density-Wave Ground State

As the temperature is lowered, the stability condition fails first at a finite $T_{\rm c}$ at frequency $\omega = 0$ and wave number $q = \pm 2k_{\rm F}$. We may therefore assume that a static ordered state appears below $T_{\rm c}$ in which the magnetic-moment density varies periodically in space with wavelength $\lambda = 2\pi/2k_{\rm F}$. The $\pm 2k_{\rm F}$ Fourier components of the magnetic-moment density are finite,

$$\langle m(\pm 2k_{\rm F}) \rangle \neq 0,$$
 (33.3.20)

and they can serve as the order parameter.

The magnetic-moment density is proportional to the z-component of the spin density which can be written in second quantization in the form

$$\left\langle s^{z}(\pm 2k_{\rm F})\right\rangle = \frac{1}{2} \sum_{k} \left[\left\langle c_{k\uparrow}^{\dagger} c_{k\pm 2k_{\rm F}\uparrow} \right\rangle - \left\langle c_{k\downarrow}^{\dagger} c_{k\pm 2k_{\rm F}\downarrow} \right\rangle \right].$$
(33.3.21)

The charge density remains homogeneous in the magnetically ordered phase,

$$\langle n(q) \rangle \equiv \sum_{k\sigma} \left\langle c_{k\sigma}^{\dagger} c_{k+q\sigma} \right\rangle = N_{\rm e} \delta_{q,0} \,,$$
 (33.3.22)

which implies that

$$\sum_{k} \left\langle c_{k\uparrow}^{\dagger} c_{k\pm 2k_{\rm F}\uparrow} \right\rangle = -\sum_{k} \left\langle c_{k\downarrow}^{\dagger} c_{k\pm 2k_{\rm F}\downarrow} \right\rangle, \qquad (33.3.23)$$

and thus

$$\langle s^{z}(\pm 2k_{\rm F})\rangle = \sum_{k} \langle c^{\dagger}_{k\uparrow}c_{k\pm 2k_{\rm F}\uparrow}\rangle.$$
 (33.3.24)

It is readily shown by a change of variables that

$$\sum_{k} \left\langle c_{k\sigma}^{\dagger} c_{k\pm 2k_{\rm F}\sigma} \right\rangle = \sum_{k} \left\langle c_{k\sigma}^{\dagger} c_{k\mp 2k_{\rm F}\sigma} \right\rangle^{*} \tag{33.3.25}$$

and

$$\langle s^z(\pm 2k_{\rm F})\rangle = \langle s^z(\mp 2k_{\rm F})\rangle^*.$$
 (33.3.26)

All other Fourier components vanish. The magnetic-moment density can be written as

$$m(x) = \frac{1}{V} \left[\langle m(2k_{\rm F}) \rangle e^{i2k_{\rm F}x} + \langle m(-2k_{\rm F}) \rangle e^{-i2k_{\rm F}x} \right]$$

$$= \frac{2}{V} \left| \langle m(2k_{\rm F}) \rangle \right| \cos(2k_{\rm F}x + \phi), \qquad (33.3.27)$$

where ϕ is the phase of the complex order parameter. The spin density of the one-dimensional model displays $2k_{\rm F}$ oscillations in the spin-density-wave state. Both the continuous translation symmetry and the SU(2) symmetry of spin rotation are broken in this phase.

Note that the wavelength of the spin-density wave is determined by the number of electrons, i.e., by the filling of the band, via $k_{\rm F}$. The filling can be arbitrary, it can be changed continuously by adding carriers to the system, and the wavelength is not related in any way to the periodicity of the lattice. When the ratio of the wavelength $\lambda = \pi/k_{\rm F}$ and the lattice constant is an irrational number, we speak of *incommensurate* spin-density wave. When the ratio is a rational number, the SDW is *commensurate* with the lattice. Writing the Fermi wave number in the form

$$k_{\rm F} = \frac{\pi}{a} \frac{n}{m} \tag{33.3.28}$$

with m and n integers, m is the order of commensurability. The spin-density wave interacts with the underlying lattice, but this effect averages out in the incommensurate situation where all atoms experience a different phase of the SDW. That is why the phase can be arbitrary in this case. Commensurability effects will be discussed in the next section in connection with charge-density waves.

Note also that the expectation value of the electron density with spin σ ,

$$n_{\sigma}(x) = \frac{1}{L} \sum_{k} \left\langle c_{k\sigma}^{\dagger} c_{k+2k_{\mathrm{F}}\sigma} \right\rangle \mathrm{e}^{\mathrm{i}2k_{\mathrm{F}}x} + \frac{1}{L} \sum_{k} \left\langle c_{k\sigma}^{\dagger} c_{k-2k_{\mathrm{F}}\sigma} \right\rangle \mathrm{e}^{-\mathrm{i}2k_{\mathrm{F}}x} \,, \quad (33.3.29)$$

and the magnetic-moment density can be calculated by expressing the creation and annihilation operators of electrons in terms of the quasiparticle operators to be introduced in the next section. The result is

$$n_{\uparrow}(x) = \frac{1}{2} n_{\rm e} \left[1 + \frac{\Delta}{\hbar v_{\rm F} k_{\rm F} U \rho_{\sigma}(\varepsilon_{\rm F})} \cos(2k_{\rm F} x + \phi) \right],$$

$$n_{\downarrow}(x) = \frac{1}{2} n_{\rm e} \left[1 - \frac{\Delta}{\hbar v_{\rm F} k_{\rm F} U \rho_{\sigma}(\varepsilon_{\rm F})} \cos(2k_{\rm F} x + \phi) \right].$$
(33.3.30)

The value of Δ will be evaluated later. The up- and down-spin electron densities oscillate in opposite phase producing a net oscillation in the magnetic moment, but no oscillation in the total density.

33.3.3 One-Particle Excitation in the SDW State

Forgetting about the lattice and considering only the SDW, it has a discrete translational symmetry. It is invariant under translations by integer multiples of $\lambda = \pi/k_{\rm F}$. The electrons feel an effective potential with such a period and this effective potential modifies the dispersion relation of one-particle excitations. Its effect is best seen if the electron states are described in the Brillouin zone of the corresponding reciprocal lattice.

The reciprocal-lattice vectors are integer multiples of $2\pi/\lambda = 2k_{\rm F}$, and the boundaries of the new Brillouin zone are precisely at the Fermi points, $\pm k_{\rm F}$. The effect of the periodic potential is usually strongest at the zone boundary and the lifting of degeneracy often leads to the opening of a gap there. We may therefore expect the opening of a gap in the charge excitations. Since the zone boundary coincides with the Fermi momenta, the opening of a gap there should imply a Slater-type metal-insulator transition.

We apply the mean-field approximation to calculate the excitation spectrum. Writing the on-site repulsion of the Hubbard model in the momentum representation, the four-operator term is decoupled as usual to yield

$$c_{k+q\uparrow}^{\dagger}c_{k'-q\downarrow}^{\dagger}c_{k\downarrow}c_{k\uparrow} \approx \langle c_{k'-q\downarrow}^{\dagger}c_{k\downarrow} \rangle c_{k+q\uparrow}^{\dagger}c_{k\uparrow} + \langle c_{k+q\uparrow}^{\dagger}c_{k\uparrow} \rangle c_{k'-q\downarrow}^{\dagger}c_{k\downarrow} \\ - \langle c_{k'-q\downarrow}^{\dagger}c_{k\downarrow} \rangle \langle c_{k+q\uparrow}^{\dagger}c_{k\uparrow} \rangle.$$
(33.3.1)

According to our earlier considerations the q = 0 and $q = \pm 2k_{\rm F}$ components of $\langle n_{\sigma}(q) \rangle$ are nonvanishing. Neglecting the constant terms that contribute to the total energy but are not relevant for the spectrum, after appropriate changes of variables we find

$$\mathcal{H} = \sum_{k\sigma} \varepsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} + \frac{U_{\rm H}}{N} \sum_{kk'} \left(\langle c^{\dagger}_{k'\uparrow} c_{k'\uparrow} \rangle c^{\dagger}_{k\downarrow} c_{k\downarrow} + \langle c^{\dagger}_{k'\downarrow} c_{k'\downarrow} \rangle c^{\dagger}_{k\uparrow} c_{k\uparrow} \right)$$

$$+ \langle c^{\dagger}_{k'+2k_{\rm F}\uparrow} c_{k'\uparrow} \rangle c^{\dagger}_{k-2k_{\rm F}\downarrow} c_{k\downarrow} + \langle c^{\dagger}_{k'+2k_{\rm F}\downarrow} c_{k'\downarrow} \rangle c^{\dagger}_{k-2k_{\rm F}\uparrow} c_{k\uparrow}$$

$$+ \langle c^{\dagger}_{k'-2k_{\rm F}\uparrow} c_{k'\uparrow} \rangle c^{\dagger}_{k+2k_{\rm F}\downarrow} c_{k\downarrow} + \langle c^{\dagger}_{k'-2k_{\rm F}\downarrow} c_{k'\downarrow} \rangle c^{\dagger}_{k+2k_{\rm F}\uparrow} c_{k\uparrow} \right).$$
(33.3.32)

The terms coming from the q = 0 component give the Hartree–Fock correction to the one-particle energies. The remaining terms can be written in a more concise form if we introduce the notation

$$\Delta = \frac{U_{\rm H}}{N} \sum_{k'} \left\langle c^{\dagger}_{k'-2k_{\rm F}\downarrow} c_{k'\downarrow} \right\rangle = -\frac{U_{\rm H}}{N} \sum_{k'} \left\langle c^{\dagger}_{k'-2k_{\rm F}\uparrow} c_{k'\uparrow} \right\rangle. \tag{33.3.33}$$

Using (33.3.25) we find

$$\mathcal{H} = \sum_{k\sigma} \widetilde{\varepsilon}_k c^{\dagger}_{k\sigma} c_{k\sigma} + \sum_k \left(-\Delta^* c^{\dagger}_{k-2k_{\rm F}\downarrow} c_{k\downarrow} + \Delta^* c^{\dagger}_{k-2k_{\rm F}\uparrow} c_{k\uparrow} - \Delta c^{\dagger}_{k+2k_{\rm F}\downarrow} c_{k\downarrow} + \Delta c^{\dagger}_{k+2k_{\rm F}\uparrow} c_{k\uparrow} \right).$$
(33.3.34)

The same unperturbed dispersion relation is assumed as in the Tomonaga– Luttinger model shown in Fig. 32.6 with a band symmetric to the Fermi energy with bandwidth 2D. The interaction mixes the right- and left-moving electrons. The summation over k in the interaction terms is restricted to the neighborhood of either $+k_{\rm F}$ or $-k_{\rm F}$ depending on whether the wave number of the other operator is $k - 2k_{\rm F}$ or $k + 2k_{\rm F}$. If the wave numbers are measured from the Fermi points $\pm k_{\rm F}$, and the notations c and d are used for the right and the left movers, respectively, we have

$$\mathcal{H} = \sum_{k\sigma} \left(\widetilde{\varepsilon}_{k_{\mathrm{F}}+k} c^{\dagger}_{k_{\mathrm{F}}+k,\sigma} c_{k_{\mathrm{F}}+k,\sigma} + \widetilde{\varepsilon}_{-k_{\mathrm{F}}+k} d^{\dagger}_{-k_{\mathrm{F}}+k,\sigma} d_{-k_{\mathrm{F}}+k,\sigma} \right) + \sum_{k} \left(-\Delta^{*} d^{\dagger}_{-k_{\mathrm{F}}+k\downarrow} c_{k_{\mathrm{F}}+k\downarrow} + \Delta^{*} d^{\dagger}_{-k_{\mathrm{F}}+k\uparrow} c_{k_{\mathrm{F}}+k\uparrow} - \Delta c^{\dagger}_{k_{\mathrm{F}}+k\downarrow} d_{-k_{\mathrm{F}}+k\downarrow} + \Delta c^{\dagger}_{k_{\mathrm{F}}+k\uparrow} d_{-k_{\mathrm{F}}+k\uparrow} \right).$$

$$(33.3.35)$$

This expression is bilinear in the creation and annihilation operators and can be diagonalized by a unitary transformation. Instead of applying the general procedure outlined in Appendix I we make an inverse transformation. New states are combined out of the states of right- and left-moving particles and the Hamiltonian is required to be diagonal in terms of the new operators.

For this we rewrite the Hamiltonian by introducing the column vector

$$\begin{pmatrix} c_{k_{\rm F}+k,\sigma} \\ d_{-k_{\rm F}+k,\sigma} \end{pmatrix}$$
(33.3.36)

and its adjoint, the row vector

$$\left(c_{k_{\mathrm{F}}+k,\sigma}^{\dagger} d_{-k_{\mathrm{F}}+k,\sigma}^{\dagger}\right). \tag{33.3.37}$$

The Hamiltonian then takes the form

$$\mathcal{H} = \sum_{k\sigma} \left(c^{\dagger}_{k_{\mathrm{F}}+k,\sigma} d^{\dagger}_{-k_{\mathrm{F}}+k,\sigma} \right) \begin{pmatrix} \widetilde{\varepsilon}_{k_{\mathrm{F}}+k} & \sigma \Delta \\ \sigma \Delta^* & \widetilde{\varepsilon}_{-k_{\mathrm{F}}+k} \end{pmatrix} \begin{pmatrix} c_{k_{\mathrm{F}}+k,\sigma} \\ d_{-k_{\mathrm{F}}+k,\sigma} \end{pmatrix}. \quad (33.3.38)$$

The annihilation and creation operators of the new states are defined by

$$\begin{pmatrix} \alpha_{k\sigma} \\ \beta_{k\sigma} \end{pmatrix} = \begin{pmatrix} u_{k\sigma} & v_{k\sigma} \\ -v_{k\sigma}^* & u_{k\sigma}^* \end{pmatrix} \begin{pmatrix} c_{kF+k,\sigma} \\ d_{-kF+k,\sigma} \end{pmatrix}$$
(33.3.39)

and

$$\left(\alpha_{k\sigma}^{\dagger} \beta_{k\sigma}^{\dagger}\right) = \left(c_{k_{\mathrm{F}}+k,\sigma}^{\dagger} d_{-k_{\mathrm{F}}+k,\sigma}^{\dagger}\right) \begin{pmatrix}u_{k\sigma}^{*} - v_{k\sigma}\\ v_{k\sigma}^{*} & u_{k\sigma}\end{pmatrix}.$$
(33.3.40)

The transformation is unitary, with the new operators obeying fermionic anticommutation rules, if

$$|u_{k\sigma}|^2 + |v_{k\sigma}|^2 = 1. (33.3.41)$$

Inverting the transformation yields

$$\begin{pmatrix} c_{k_{\rm F}+k,\sigma} \\ d_{-k_{\rm F}+k,\sigma} \end{pmatrix} = \begin{pmatrix} u_{k\sigma}^* - v_{k\sigma} \\ v_{k\sigma}^* & u_{k\sigma} \end{pmatrix} \begin{pmatrix} \alpha_{k\sigma} \\ \beta_{k\sigma} \end{pmatrix},$$

$$\left(c_{k_{\rm F}+k,\sigma}^{\dagger} d_{-k_{\rm F}+k,\sigma}^{\dagger} \right) = \left(\alpha_{k\sigma}^{\dagger} \beta_{k\sigma}^{\dagger} \right) \begin{pmatrix} u_{k\sigma} & v_{k\sigma} \\ -v_{k\sigma}^* & u_{k\sigma}^* \end{pmatrix}.$$
(33.3.42)

Substituting these expressions into the mean-field Hamiltonian (33.3.38) the diagonalization condition can be written in terms of the matrices as

$$\begin{pmatrix} E_{k\sigma}^{(1)} & 0 \\ 0 & E_{k\sigma}^{(2)} \end{pmatrix} = \begin{pmatrix} u_{k\sigma} & v_{k\sigma} \\ -v_{k\sigma}^* & u_{k\sigma}^* \end{pmatrix} \begin{pmatrix} \widetilde{\varepsilon}_{k_{\rm F}+k} & \sigma\Delta \\ \sigma\Delta^* & \widetilde{\varepsilon}_{-k_{\rm F}+k} \end{pmatrix} \begin{pmatrix} u_{k\sigma}^* - v_{k\sigma} \\ v_{k\sigma}^* & u_{k\sigma} \end{pmatrix}.$$
(33.3.43)

The coefficient $u_{k\sigma}$ can be chosen to be independent of σ , while $v_{k\sigma} = \sigma v_k$. The off-diagonal terms vanish if

$$(\widetilde{\varepsilon}_{k_{\mathrm{F}}+k} - \widetilde{\varepsilon}_{-k_{\mathrm{F}}+k})u_{k}v_{k} - \Delta u_{k}^{2} + \Delta^{*}v_{k}^{2} = 0.$$
(33.3.44)

Although this equation can be satisfied by real coefficients and real Δ , complex coefficients should be allowed for if we are interested in the wavefunction of the system. Since only the relative phase of u_k and v_k is relevant, u_k can be chosen real and the phase of v_k coincides with the phase of Δ . [It is the same phase that appeared in (33.3.27).] Self-consistency of the equations requires that this phase be independent of k, that is

$$v_k = |v_k| \mathrm{e}^{\mathrm{i}\phi}, \qquad \Delta = |\Delta| \mathrm{e}^{\mathrm{i}\phi}.$$
 (33.3.45)

The coefficients are chosen in the form

$$u_k = \cos \theta_k , \qquad |v_k| = \sin \theta_k \tag{33.3.46}$$

to satisfy (33.3.41). Simple algebra yields

$$u_k^2 = \frac{1}{2} \left[1 + \frac{\xi_k}{\sqrt{\xi_k^2 + |\Delta|^2}} \right], \qquad |v_k|^2 = \frac{1}{2} \left[1 - \frac{\xi_k}{\sqrt{\xi_k^2 + |\Delta|^2}} \right], \qquad (33.3.47)$$

where

$$\xi_k = \frac{\widetilde{\varepsilon}_{k_{\rm F}+k} - \widetilde{\varepsilon}_{-k_{\rm F}+k}}{2} \,. \tag{33.3.48}$$

The value of $|\Delta|^2$ will be evaluated later. The k dependence of the coefficients is displayed in Fig. 33.9.



Fig. 33.9. Variations of the coefficients u_k and v_k as a function of the wave number

The diagonalization transformation leads to the Hamiltonian

$$\mathcal{H} = \sum_{k\sigma} \left(E_{k\sigma}^{(1)} \alpha_{k\sigma}^{\dagger} \alpha_{k\sigma} + E_{k\sigma}^{(2)} \beta_{k\sigma}^{\dagger} \beta_{k\sigma} \right)$$
(33.3.49)

with

$$E_{k\sigma}^{(1)} = \widetilde{\varepsilon}_{k_{\mathrm{F}}+k} |u_k|^2 + \widetilde{\varepsilon}_{-k_{\mathrm{F}}+k} |v_k|^2 + \Delta u_k v_k^* + \Delta^* u_k^* v_k ,$$

$$E_{k\sigma}^{(2)} = \widetilde{\varepsilon}_{k_{\mathrm{F}}+k} |v_k|^2 + \widetilde{\varepsilon}_{-k_{\mathrm{F}}+k} |u_k|^2 - \Delta u_k v_k^* - \Delta^* u_k^* v_k .$$
(33.3.50)

The operators α_k^{\dagger} and β_k^{\dagger} are the creation operators of quasiparticles, and the SDW state can be described in this approximation as a noninteracting gas of these quasiparticles. The right- and left-moving electrons are mixed with equal weight in the α and β particles at k = 0. The weight of right movers is larger in the α particles, and the β particles are more left-moving-like, for k > 0. The situation is reversed for negative k.

Using the explicit expressions for u_k and v_k we get

$$E_{k\sigma}^{(1)} = \frac{\widetilde{\varepsilon}_{k_{\rm F}+k} + \widetilde{\varepsilon}_{-k_{\rm F}+k}}{2} + \sqrt{\left(\frac{\widetilde{\varepsilon}_{k_{\rm F}+k} - \widetilde{\varepsilon}_{-k_{\rm F}+k}}{2}\right)^2 + |\Delta|^2},$$

$$E_{k\sigma}^{(2)} = \frac{\widetilde{\varepsilon}_{k_{\rm F}+k} + \widetilde{\varepsilon}_{-k_{\rm F}+k}}{2} - \sqrt{\left(\frac{\widetilde{\varepsilon}_{k_{\rm F}+k} - \widetilde{\varepsilon}_{-k_{\rm F}+k}}{2}\right)^2 + |\Delta|^2}$$
(33.3.51)

for the energies of the new particles. With the linearized dispersion relation near $\pm k_{\rm F},$ where

$$\widetilde{\varepsilon}_{k_{\rm F}+k} = \mu + \xi_k = \mu + \hbar v_{\rm F} k ,
\widetilde{\varepsilon}_{-k_{\rm F}+k} = \mu - \xi_k = \mu - \hbar v_{\rm F} k ,$$
(33.3.52)

we find

$$E_{k\sigma}^{(1)} = \mu + \sqrt{\xi_k^2 + |\Delta|^2} = \mu + \sqrt{(\hbar v_{\rm F} k)^2 + |\Delta|^2},$$

$$E_{k\sigma}^{(2)} = \mu - \sqrt{\xi_k^2 + |\Delta|^2} = \mu - \sqrt{(\hbar v_{\rm F} k)^2 + |\Delta|^2}.$$
(33.3.53)



Fig. 33.10. Dispersion relation of one-particle excitations in the spin-density-wave state. (a) In the representation where the wave number is measured from the zone boundary $\pm k_{\rm F}$. (b) In the extended-zone scheme, shifting the wave numbers by $\pm k_{\rm F}$

Figure 33.10(a) shows this spectrum for small values of k. Its most relevant feature is the opening of a gap of width 2Δ at k = 0.

Noting that the Brillouin zone in the SDW state extends from $-k_{\rm F}$ to $k_{\rm F}$ it is convenient to redefine the new particles to have wave numbers near $\pm k_{\rm F}$ via

$$\begin{pmatrix} \alpha_{-k_{\rm F}+k,\sigma} \\ \beta_{-k_{\rm F}+k,\sigma} \end{pmatrix} = \begin{pmatrix} u_{k\sigma} & v_{k\sigma} \\ -v_{k\sigma}^* & u_{k\sigma}^* \end{pmatrix} \begin{pmatrix} c_{k_{\rm F}+k,\sigma} \\ d_{-k_{\rm F}+k,\sigma} \end{pmatrix}$$
(33.3.54)

for k > 0 and

$$\begin{pmatrix} \alpha_{k_{\rm F}+k,\sigma} \\ \beta_{k_{\rm F}+k,\sigma} \end{pmatrix} = \begin{pmatrix} u_{k\sigma} \ v_{k\sigma} \\ -v_{k\sigma}^* \ u_{k\sigma}^* \end{pmatrix} \begin{pmatrix} c_{k_{\rm F}+k,\sigma} \\ d_{-k_{\rm F}+k,\sigma} \end{pmatrix}$$
(33.3.55)

for k < 0. A simple picture is obtained for the dispersion relation when it is displayed in the extended-zone scheme [see Fig. 33.10(b)]. As expected, a gap opens up at the zone boundaries compared to the free particle spectrum. The states are doubly degenerate and spin independent. The number of allowed states in the lower band is equal to the number of electrons in the system. The originally metallic system becomes an insulator in the SDW state. Contrary to band insulators where the position of the gap is determined by the underlying lattice, it is fixed in the SDW state by the number of electrons. The gap always opens at $\pm k_{\rm F}$. Adding electrons to the system modifies the value of the Fermi momentum and the system remains insulating.

33.3.4 The Energy Gap

The quantity Δ defined in (33.3.33) is an effective potential that scatters right-moving electrons into left-moving states and vice versa. It appears in the parameters u_k and v_k and through them in the excitation energies and the gap. Its value can be calculated from a self-consistency condition.

Using the notation c and d for right and left movers, Δ is given by

$$\Delta = \frac{U_{\rm H}}{N} \sum_{k'} \left\langle d^{\dagger}_{-k_{\rm F}+k'\downarrow} c_{k_{\rm F}+k'\downarrow} \right\rangle.$$
(33.3.56)

If these operators are expressed in terms of the quasiparticle operators using (33.3.42) we have

$$\Delta = \frac{U_{\rm H}}{N} \sum_{k} u_k^* v_k \left[\left\langle \beta_{k\downarrow}^{\dagger} \beta_{k\downarrow} \right\rangle - \left\langle \alpha_{k\downarrow}^{\dagger} \alpha_{k\downarrow} \right\rangle \right]. \tag{33.3.57}$$

The states with energy $E_{k\sigma}^{(1)}$ created by the operators $\alpha_{k\sigma}^{\dagger}$ are all empty in the ground state, while the lower band with energies $E_{k\sigma}^{(2)}$ is completely filled. This gives

$$\Delta = \frac{U_{\rm H}}{N} \sum_{k} u_k^* v_k \,. \tag{33.3.58}$$

With the aid of (33.3.47) we find

$$\Delta = \frac{U_{\rm H}}{N} \sum_{k} \frac{1}{2} \frac{\Delta}{\sqrt{\xi_k^2 + |\Delta|^2}} \,. \tag{33.3.59}$$

A trivial solution is $\Delta = 0$. A nontrivial solution can be obtained for a repulsive $(U_{\rm H} > 0)$ Coulomb term from

$$1 = \frac{U_{\rm H}}{N} \sum_{k} \frac{1}{2} \frac{1}{\sqrt{\xi_k^2 + |\Delta|^2}} \,. \tag{33.3.60}$$

This gives the energetically stable broken-symmetry phase. Replacing the summation over k by integration over energy, taking again only half of the density of states per spin [the sum over k' in (33.3.33) goes over the wave numbers of right-moving particles only] we have

$$1 = U \int d\xi \, \frac{1}{4} \rho_{\sigma}(\xi) \frac{1}{\sqrt{\xi^2 + |\Delta|^2}}, \qquad (33.3.61)$$

where $U = U_{\rm H} V/N$. Integration can be performed for a symmetric unperturbed band of width 2D with a constant density of states. We get

$$1 = \frac{1}{4}U\rho_{\sigma}(\varepsilon_{\rm F})\int_{-D}^{D}\frac{\mathrm{d}\xi}{\sqrt{\xi^{2}+|\Delta|^{2}}} = \frac{1}{2}U\rho_{\sigma}(\varepsilon_{\rm F})\operatorname{arsinh}\frac{D}{|\Delta|}.$$
 (33.3.62)

This gives

$$|\Delta| = \frac{D}{\sinh(2/U\rho_{\sigma}(\varepsilon_{\rm F}))}.$$
(33.3.63)

In the weak-coupling limit $U\rho_{\sigma}(\varepsilon_{\rm F}) \ll 1$ the expression for the gap reduces to

$$|\Delta| = 2D \mathrm{e}^{-2/U\rho_{\sigma}(\varepsilon_{\mathrm{F}})}.$$
(33.3.64)

Combining it with (33.3.19) obtained for the critical temperature we get

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$$\frac{\mathrm{e}^{\gamma}}{\pi}|\Delta| = k_{\mathrm{B}}T_{\mathrm{c}}\,.\tag{33.3.65}$$

The ratio of the energy gap and the critical temperature,

$$\frac{2|\Delta|}{k_{\rm B}T_{\rm c}} = \frac{2\pi}{{\rm e}^{\gamma}} = 3.528\dots, \qquad (33.3.66)$$

is a universal quantity independent of the material properties. This is not surprising since both quantities are determined from similar integrals. The critical temperature is obtained from the condition $1 = U \Sigma_0(2k_{\rm F})$ which leads to

$$1 = \frac{1}{2} U \rho_{\sigma}(\varepsilon_{\rm F}) \int_{0}^{D} \frac{\mathrm{d}\xi}{\xi} \tanh \frac{\xi}{2k_{\rm B}T_{\rm c}}, \qquad (33.3.67)$$

while the gap is determined from

$$1 = \frac{1}{2} U \rho_{\sigma}(\varepsilon_{\rm F}) \int_{0}^{D} \frac{\mathrm{d}\xi}{\sqrt{\xi^{2} + |\Delta|^{2}}} \,. \tag{33.3.68}$$

The Coulomb repulsion and the density of states drop out in the comparison. Since the bandwidth is much larger than $k_{\rm B}T_{\rm c}$ or Δ , the high-energy states give identical contributions to the integrals, and thus the value of D is also irrelevant.

Relationship (33.3.57) allows us to extend the calculation of the energy gap to finite temperatures. Since the quasiparticles are fermions and their thermal occupation is given by the Fermi distribution function, we have

$$\Delta(T) = \frac{U_{\rm H}}{N} \sum_{k} u_k^* v_k \left[f_0(E_{k\downarrow}^{(2)}) - f_0(E_{k\downarrow}^{(1)}) \right].$$
(33.3.69)

Expressing the Fermi functions in terms of $\tanh x$ using (33.3.7) we find

$$\Delta = \frac{U_{\rm H}}{N} \sum_{k} \frac{\Delta}{2\sqrt{\xi_k^2 + |\Delta|^2}} \tanh \frac{\sqrt{\xi_k^2 + |\Delta|^2}}{2k_{\rm B}T}.$$
(33.3.70)

The nontrivial solution has to satisfy the equation

$$1 = \frac{U_{\rm H}}{N} \sum_{k} \frac{\tanh \frac{\sqrt{\xi_k^2 + |\Delta|^2}}{2k_{\rm B}T}}{2\sqrt{\xi_k^2 + |\Delta|^2}} \,. \tag{33.3.71}$$

As the temperature increases, the gap diminishes and vanishes at a critical temperature $T_{\rm c}$ which can be determined from

$$1 = \frac{U_{\rm H}}{N} \sum_{k} \frac{\tanh \frac{|\xi_k|}{2k_{\rm B}T_{\rm c}}}{2|\xi_k|} \,. \tag{33.3.72}$$

Only the trivial solution $\Delta = 0$ survives above T_c .

This equation, obtained from the vanishing of the gap as the temperature increases in the ordered phase, is identical to the equation obtained from the instability condition $1 = U\Sigma_0(2k_{\rm F})$ as the temperature is decreased in the high-temperature phase. The same $T_{\rm c}$ given in (33.3.19) is found.

The temperature dependence of the gap can be calculated from (33.3.71). Near the critical point we find

$$\Delta(T) \propto \sqrt{T_{\rm c} - T} \,, \tag{33.3.73}$$

which is typical for the temperature dependence of the order parameter in mean-field theories. The thermodynamic behavior in the ordered phase can also be determined. We do not go into these details here and will return to these problems in our study of superconductivity in Chapter 34, where formally rather similar equations are obtained. The same results apply to density-wave systems as well.

33.3.5 Collective Excitations

The single-particle excitations were found to have a finite gap. We expect in fact two soft Goldstone modes in the ordered phase since two continuous symmetries are broken. The breaking of the translational symmetry implies the existence of acoustic-phonon-like excitations. The nature of this excitation can be understood if we recall that an incommensurate SDW can slide freely, without cost of energy, over the lattice, which means that the uniform phase can be arbitrarily chosen. Long-wavelength fluctuations of the phase, which correspond to slow variations of the wavelength of the SDW, cost a small energy. These modes are known as *phasons*. On the other hand, the breaking of the spin-rotation symmetry should lead to spin-wave-like excitations. To get their dispersion relation the dynamics of the SDW has to be studied. They are obtained in a microscopic theory from the poles of the dynamical susceptibility.

Both the amplitude and the phase of the order parameter may fluctuate in space and time. These variations can be described by taking a form

$$\Delta(x,t) = \left[\Delta_0 + \delta(x,t)\right] e^{i\phi'(x,t)}, \qquad (33.3.74)$$

where Δ_0 is the equilibrium value of the order parameter which – apart from a factor containing the Coulomb interaction – is related to the expectation value of the spin density:

$$\Delta_0 \propto \langle s^z(2k_{\rm F}) \rangle = \frac{1}{2} \sum_k \left[\left\langle c_{k\uparrow}^{\dagger} c_{k+2k_{\rm F}\uparrow} \right\rangle - \left\langle c_{k\downarrow}^{\dagger} c_{k+2k_{\rm F}\downarrow} \right\rangle \right].$$
(33.3.75)

The long-wavelength fluctuations of the order parameter are related to the $2k_{\rm F} + q$ Fourier components of the spin density with small q values, that is to

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$$\Delta(q,t) \propto \langle s^{z}(2k_{\rm F}+q,t)\rangle = \frac{1}{2} \sum_{k} \left[\left\langle c_{k\uparrow}^{\dagger}(t)c_{k+2k_{\rm F}+q\uparrow}(t) \right\rangle - \left\langle c_{k\downarrow}^{\dagger}(t)c_{k+2k_{\rm F}+q\downarrow}(t) \right\rangle \right]$$
(33.3.76)

To lowest order in the fluctuations, the variations in the amplitude are given by the symmetric combinations of $\langle s^z(2k_{\rm F}+q,t)\rangle$ and $\langle s^z(-2k_{\rm F}-q,t)\rangle$ while the phase fluctuations are connected to the antisymmetric combination:

$$\sigma_{\rm A}(q,t) \equiv \langle s^z(2k_{\rm F}+q,t)\rangle + \langle s^z(-2k_{\rm F}-q,t)\rangle = 2\left[\Delta_0 + \delta(q,t)\right],$$

$$\sigma_{\phi}(q,t) \equiv \langle s^z(2k_{\rm F}+q,t)\rangle - \langle s^z(-2k_{\rm F}-q,t)\rangle = 2i\phi'(q,t)\Delta_0.$$
(33.3.77)

The system exhibits spontaneous collective excitations for q, ω values for which the generalized susceptibilities

$$\Pi_{\sigma_{A}\sigma_{A}}(q,\omega) = -\frac{i}{\hbar} \frac{1}{L} \int_{0}^{\infty} dt e^{i\omega t} \left\langle \left[\sigma_{A}(q,t), \sigma_{A}(-q,0) \right]_{-} \right\rangle, \\
\Pi_{\sigma_{\phi}\sigma_{\phi}}(q,\omega) = -\frac{i}{\hbar} \frac{1}{L} \int_{0}^{\infty} dt e^{i\omega t} \left\langle \left[\sigma_{\phi}(q,t), \sigma_{\phi}(-q,0) \right]_{-} \right\rangle$$
(33.3.78)

are singular. Without going into details we note that the phase modes, the phasons, have a linear dispersion relation,

$$\hbar\omega_{\phi}(q) = \hbar v_{\rm F} \left[1 + U \rho_{\sigma}(\varepsilon_{\rm F}) \right] q \,. \tag{33.3.79}$$

The group velocity is close to the Fermi velocity at low temperatures, decreases with increasing temperature, and vanishes at the critical temperature. The amplitude fluctuations, called *amplitudons*, are not soft. Their dispersion relation is

$$\hbar\omega_{\rm A}(q) = \sqrt{(2\Delta)^2 + (\hbar v_{\rm F} q)^2}.$$
 (33.3.80)

Their minimum energy is the same as that of electron–hole excitations across the gap.

Spin waves, the other soft Goldstone modes, can be obtained by calculating the singularity in the transverse susceptibility. One finds a linear dispersion relation,

$$\hbar\omega(q) \propto J_{\rm eff}q\,,\tag{33.3.81}$$

with an effective exchange coupling

$$J_{\text{eff}}a = \frac{1}{2}\hbar v_{\text{F}} \left[1 - U\rho_{\sigma}(\varepsilon_{\text{F}}) \right]^{1/2}$$
(33.3.82)

in the weak-coupling limit, while $J_{\rm eff} \propto t^2/U$ in the strong-coupling limit.

Alternatively, one can study the dynamics phenomenologically, starting from a time-dependent Ginzburg–Landau free energy density. A somewhat more detailed discussion will be given in the next section in connection with charge-density waves.

33.4 Charge-Density Waves

It is clear from our earlier considerations that the spin-density waves appearing under favorable conditions (in systems where the Fermi surface has the nesting property) are due to the Coulomb repulsion between electrons. The same interaction suppresses charge-density fluctuations. This can easily be seen by looking at the RPA form of the density-density response function,

$$\Pi(\boldsymbol{q},\omega) = \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - U\Pi_0(\boldsymbol{q},\omega)}, \qquad (33.4.1)$$

if we recall that $\Pi_0(\boldsymbol{q},\omega) = -2\Sigma_0(\boldsymbol{q},\omega)$ and the static, long-wavelength limit, $\Pi_0(0,0)$, is equal to $-\rho(\varepsilon_{\rm F})$. An attractive interaction, on the other hand, can enhance charge fluctuations and eventually lead to the instability of the homogeneous state against the formation of static periodic charge oscillations known as *charge-density waves* (CDWs). We know from Chapter 23, where the consequences of electron-phonon interactions were studied, that the process, in which the phonon emitted by an electron is absorbed by another electron, is equivalent to an effective attractive interaction between the two electrons. This attraction is responsible for the formation of Cooper pairs and for superconductivity in conventional superconductors. Phonons mediate the interaction, but they are not directly involved in the anomalous electrodynamic properties. That is why the microscopic theory of this phenomenon can be formulated, as will be done in the next chapter, to a large extent by treating the electrons only. Phonons and electrons play equally important roles in charge-density waves and we have to start the theoretical description with a Hamiltonian that contains explicitly the kinetic energy of both electrons and phonons as well as their interactions. For the sake of simplicity we will use the Hamiltonian of the Fröhlich model [see (23.3.43)] with a single longitudinal acoustic phonon branch, but with the electron spin included. In the conventional notation

$$\mathcal{H} = \sum_{k\sigma} \varepsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} + \sum_{q} \hbar \omega_q a^{\dagger}_{q} a_{q} + \frac{1}{\sqrt{L}} \sum_{kq\sigma} g_q c^{\dagger}_{k+q\sigma} c_{k\sigma} \left(a_q + a^{\dagger}_{-q} \right). \quad (33.4.2)$$

This interaction can be interpreted as if phonons generated an effective potential

$$\Phi(\boldsymbol{q}) = \sqrt{L}g_{\boldsymbol{q}} \left(a_{\boldsymbol{q}} + a_{-\boldsymbol{q}}^{\dagger} \right)$$
(33.4.3)

that couples to the electron density n(-q).

33.4.1 Peierls Transition

We have seen in Chapter 23 that the energy of phonons is renormalized due to electron-phonon interaction, and this effect is strongest at $q = 2k_{\rm F}$. This is the Kohn anomaly. The change in the energy was calculated in second order of perturbation theory, since the frequency shift is relatively small under normal conditions in three-dimensional materials. The correction to the energy can be so big, the softening of the phonon so drastic, in quasi-onedimensional systems that the renormalized phonon energy vanishes, and a structural transition takes place. This is the *Peierls instability*, also known as *Peierls–Fröhlich instability*.⁵ Low-order perturbation theory is no longer applicable and a better procedure must be found to see what happens to the phonon and the electron systems around the transition point.

The simplest procedure is to write the equation of motion for the operators a_q and a_{-q}^{\dagger} that couple to the electron density. The most relevant phonons are the ones near $q = \pm 2k_{\rm F}$. The coupling constant will be taken real and independent of the wave number. We find

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}a_{q} = -\hbar\omega_{q}a_{q} - \frac{1}{\sqrt{L}}\sum_{k\sigma}gc_{k-q\sigma}^{\dagger}c_{k\sigma},$$

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}a_{-q}^{\dagger} = \hbar\omega_{-q}a_{-q}^{\dagger} + \frac{1}{\sqrt{L}}\sum_{k\sigma}gc_{k-q\sigma}^{\dagger}c_{k\sigma}.$$
(33.4.4)

Since the phonon frequency is an even function of q, the sum of the left- and right-hand sides gives

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}\left(a_q + a_{-q}^{\dagger}\right) = -\hbar\omega_q\left(a_q - a_{-q}^{\dagger}\right). \tag{33.4.5}$$

If this equation is differentiated once more with respect to time we get

$$\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}\right)^2 \left(a_q + a_{-q}^{\dagger}\right) = \left(\hbar\omega_q\right)^2 \left(a_q + a_{-q}^{\dagger}\right) + \frac{2\hbar\omega_q}{\sqrt{L}} \sum_{k\sigma} gc_{k-q\sigma}^{\dagger}c_{k\sigma} \,. \tag{33.4.6}$$

The second term on the right-hand side contains n(q), the Fourier transform of the electron density. In a mean-field approximation it can be replaced with its expectation value and this quantity can be calculated to linear order in the electron-phonon coupling. Since the effective potential $\Phi(q)$ couples to the electron density, the proportionality factor $\Pi(q)$ in

$$\langle n(q) \rangle = \Pi(q)\Phi(q) \tag{33.4.7}$$

is the density–density response function according to linear response theory. With this approximation

$$\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}\right)^2 \left(a_q + a_{-q}^{\dagger}\right) = \left(\hbar\omega_q\right)^2 \left(a_q + a_{-q}^{\dagger}\right) + 2\hbar\omega_q g^2 \Pi(q) \left(a_q + a_{-q}^{\dagger}\right).$$
(33.4.8)

For a harmonic time dependence with frequency $\widetilde{\omega}_q$ this equation gives

⁵ R. E. Peierls, 1955, H. Fröhlich, 1954.

$$(\hbar\widetilde{\omega}_q)^2 = \left(\hbar\omega_q\right)^2 + 2\hbar\omega_q g^2 \Pi(q), \qquad (33.4.9)$$

from which the renormalized energy of phonons, $\hbar \tilde{\omega}_q$, can be calculated. If the interaction between electrons is neglected, $\Pi(q)$ is replaced with its value for a free electron gas. An analytic expression for wave numbers close to $2k_{\rm F}$ can be inferred from (33.3.16) through the relationship $\Pi_0 = -2\Sigma_0$. We have

$$\Pi_{0}(\pm 2k_{\rm F} + q', \omega) = -\frac{1}{\pi \hbar v_{\rm F}} \Biggl\{ \ln \frac{2\mathrm{e}^{\gamma} D}{\pi k_{\rm B} T} + \psi(\frac{1}{2})$$

$$-\frac{1}{2} \Biggl[\psi \Bigl(\frac{1}{2} + \frac{\mathrm{i}\hbar (v_{\rm F} q' - \omega)}{4\pi k_{\rm B} T} \Bigr) + \psi \Bigl(\frac{1}{2} - \frac{\mathrm{i}\hbar (v_{\rm F} q' + \omega)}{4\pi k_{\rm B} T} \Bigr) \Biggr] \Biggr\}.$$
(33.4.10)

We then find

$$\left(\hbar\tilde{\omega}_{2k_{\mathrm{F}}+q'}\right)^{2} = \left(\hbar\omega_{2k_{\mathrm{F}}}\right)^{2} - 2\hbar\omega_{2k_{\mathrm{F}}}g^{2}\rho_{\sigma}(\varepsilon_{\mathrm{F}})\ln\frac{2\mathrm{e}^{\gamma}D}{\pi k_{\mathrm{B}}T} + 2\hbar\omega_{2k_{\mathrm{F}}}g^{2}\rho_{\sigma}(\varepsilon_{\mathrm{F}})\frac{7\zeta(3)}{16\pi^{2}}\frac{v_{\mathrm{F}}^{2}q'^{2}}{k_{\mathrm{B}}^{2}T^{2}}.$$
(33.4.11)

The softening of phonons near $q = 2k_{\rm F}$ as the temperature is lowered is seen in Fig. 33.11.



Fig. 33.11. Softening of phonons near $q = 2k_{\rm F}$ due to electron-phonon interaction in one-dimensional systems

The static charge-density wave appears at the temperature where the renormalized phonon frequency vanishes first at $2k_{\rm F}$. The critical temperature of the Peierls transition is given by

$$k_{\rm B}T_{\rm c} = \frac{2{\rm e}^{\gamma}}{\pi}D{\rm e}^{-1/\lambda},$$
 (33.4.12)

where

$$\lambda = \frac{2g^2 \rho_\sigma(\varepsilon_{\rm F})}{\hbar \omega_{2k_{\rm F}}} \tag{33.4.13}$$

is the dimensionless coupling constant.

33.4.2 The CDW State

The zero-energy $q = 2k_{\rm F}$ phonons may be excited in macroscopic number at the transition point. The new phase below T_c may be considered as their Bose condensate. Following the Bogoliubov theory⁶ of superfluidity we assume that the operators $a_{\pm 2k_{\rm F}}$ and $a_{\pm 2k_{\rm F}}^{\dagger}$, which change the number of particles in the condensate by one, behave as *c*-numbers; they have a finite mean value,

$$\left\langle a_{\pm 2k_{\rm F}} \right\rangle \neq 0. \tag{33.4.14}$$

The complex quantity

$$\Delta = |\Delta| e^{i\phi} = \frac{1}{\sqrt{L}} g \left[\left\langle a_{2k_{\rm F}} \right\rangle + \left\langle a_{-2k_{\rm F}}^{\dagger} \right\rangle \right]$$
(33.4.15)

can then serve as an order parameter.

The finite value of $\langle a_{\pm 2k_{\rm F}} \rangle$ implies that the atoms are displaced from their equilibrium positions and a static lattice deformation occurs with wave number $2k_{\rm F}$. The displacement of ions is given according to (12.1.39) by

$$\langle u(R_n) \rangle = \sqrt{\frac{\hbar}{2MN\omega_{2k_{\rm F}}}} \left[\left(\langle a_{2k_{\rm F}} \rangle + \langle a_{-2k_{\rm F}}^{\dagger} \rangle \right) e^{i2k_{\rm F}R_n} + {\rm c.c.} \right]$$

$$= \sqrt{\frac{\hbar L}{2MN\omega_{2k_{\rm F}}}} \frac{2|\Delta|}{g} \cos(2k_{\rm F}R_n + \phi) \,.$$

$$(33.4.16)$$

The new periodicity (with repetition length $\pi/k_{\rm F}$) of the ion positions results in a rearrangement of the electron states. The primitive vector of the reciprocal lattice is $2k_{\rm F}$ and the boundaries of the new Brillouin zone are at $\pm k_{\rm F}$. Just as in the SDW state, we expect a gap to open at the zone boundary. This gap transforms the metal into insulator.

To calculate the electronic energy spectrum we consider the Fröhlich Hamiltonian in the mean-field approximation where the phonon creation and annihilation operators are replaced with their expectation values. With the notation introduced in (33.4.15) we get

$$\mathcal{H} = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k\sigma} \left(\Delta^* c_{k-2k_{\rm F}\sigma}^{\dagger} c_{k\sigma} + \Delta c_{k\sigma}^{\dagger} c_{k-2k_{\rm F}\sigma} \right)$$
(33.4.17)

for the electronic part of the Hamiltonian. Separating the contributions of the right- and left-moving electrons in the kinetic energy, we have

$$\mathcal{H} = \sum_{k\sigma} \left(\varepsilon_{k_{\mathrm{F}}+k} c^{\dagger}_{k_{\mathrm{F}}+k,\sigma} c_{k_{\mathrm{F}}+k,\sigma} + \varepsilon_{-k_{\mathrm{F}}+k} d^{\dagger}_{-k_{\mathrm{F}}+k,\sigma} d_{-k_{\mathrm{F}}+k,\sigma} \right) + \sum_{k\sigma} \left(\Delta^{*} d^{\dagger}_{-k_{\mathrm{F}}+k,\sigma} c_{k_{\mathrm{F}}+k,\sigma} + \Delta c^{\dagger}_{k_{\mathrm{F}}+k,\sigma} d_{-k_{\mathrm{F}}+k,\sigma} \right).$$
(33.4.18)

⁶ N. N. Bogoliubov, 1947.

In matrix notation

$$\mathcal{H} = \sum_{k\sigma} \left(c_{k_{\mathrm{F}}+k,\sigma}^{\dagger} d_{-k_{\mathrm{F}}+k,\sigma}^{\dagger} \right) \begin{pmatrix} \varepsilon_{k_{\mathrm{F}}+k} & \Delta \\ \Delta^{*} & \varepsilon_{-k_{\mathrm{F}}+k} \end{pmatrix} \begin{pmatrix} c_{k_{\mathrm{F}}+k,\sigma} \\ d_{-k_{\mathrm{F}}+k,\sigma} \end{pmatrix}. \quad (33.4.19)$$

Comparison with (33.3.38) shows that this Hamiltonian can be diagonalized in terms of the operators α_k^{\dagger} and β_k^{\dagger} defined in (33.3.39) and (33.3.40), with the only difference that both $u_{k\sigma}$ and $v_{k\sigma}$ are spin independent. The creation operators of the new particles are defined by

$$\left(\alpha_{k\sigma}^{\dagger}\beta_{k\sigma}^{\dagger}\right) = \left(c_{kF+k,\sigma}^{\dagger}d_{-kF+k,\sigma}^{\dagger}\right) \begin{pmatrix}u_{k}^{*}-v_{k}\\v_{k}^{*}&u_{k}\end{pmatrix},$$
(33.4.20)

where u_k can be taken as real and

$$u_k^2 + |v_k|^2 = 1 (33.4.21)$$

from unitarity. The off-diagonal terms of the transformed Hamiltonian vanish if

$$u_k^2 = \frac{1}{2} \left[1 + \frac{\xi_k}{\sqrt{\xi_k^2 + |\Delta|^2}} \right], \qquad |v_k|^2 = \frac{1}{2} \left[1 - \frac{\xi_k}{\sqrt{\xi_k^2 + |\Delta|^2}} \right], \qquad (33.4.22)$$

with

$$\xi_k = \frac{\varepsilon_{k_{\rm F}+k} - \varepsilon_{-k_{\rm F}+k}}{2}, \qquad (33.4.23)$$

and the diagonal terms give

$$E_{k\sigma}^{(1)} = \frac{\varepsilon_{k_{\rm F}+k} + \varepsilon_{-k_{\rm F}+k}}{2} + \sqrt{\left(\frac{\varepsilon_{k_{\rm F}+k} - \varepsilon_{-k_{\rm F}+k}}{2}\right)^2 + |\Delta|^2},$$

$$E_{k\sigma}^{(2)} = \frac{\varepsilon_{k_{\rm F}+k} + \varepsilon_{-k_{\rm F}+k}}{2} - \sqrt{\left(\frac{\varepsilon_{k_{\rm F}+k} - \varepsilon_{-k_{\rm F}+k}}{2}\right)^2 + |\Delta|^2}$$
(33.4.24)

for the one-particle energies. This spectrum has the same form as in an SDW state. A gap opens in the spectrum at k = 0 (at $\pm k_{\rm F}$ in the original momenta) and the CDW state is insulating.

So far we have shown that the ions are displaced in the CDW state. We now show that a similar spatial variation occurs in the electron density, thereby justifying the name of charge-density wave. The electron density is calculated from the expression

$$\rho(x) = -e \sum_{\sigma} \langle \Psi_0 | \hat{\psi}^{\dagger}_{\sigma}(x) \hat{\psi}_{\sigma}(x) | \Psi_0 \rangle , \qquad (33.4.25)$$

where $|\Psi_0\rangle$ is the ground-state wavefunction of the CDW. The lower band is fully occupied and the upper band is empty in the ground state, that is

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$$|\Psi_0\rangle = \prod_{-k_{\rm F} \le k \le k_{\rm F}} \beta_{k\uparrow}^{\dagger} \beta_{k\downarrow}^{\dagger} |0\rangle , \qquad (33.4.26)$$

and $\hat{\psi}_{\sigma}(x)$ is the electronic field operator:

$$\hat{\psi}_{\sigma}(x) = \frac{1}{\sqrt{L}} \sum_{k} \left[c_{k_{\rm F}+k,\sigma} \mathrm{e}^{\mathrm{i}(k_{\rm F}+k)x} + d_{-k_{\rm F}+k,\sigma} \mathrm{e}^{-\mathrm{i}(k_{\rm F}-k)x} \right].$$
(33.4.27)

The ground-state expectation value can be easily calculated if the operators c and d are expressed in terms of α and β . In the weak-coupling limit we find

$$\rho(x) = \rho_0 \left[1 + \frac{\Delta}{\hbar v_{\rm F} k_{\rm F} \lambda} \cos(2k_{\rm F} x + \phi) \right], \qquad (33.4.28)$$

where ρ_0 is the homogeneous charge density in the metallic phase.

Similar to spin-density waves, we can distinguish commensurate and incommensurate charge-density waves. Obviously one can always find a commensurate density wave close to any incommensurate situation such that the wavelengths differ only a little. We might expect that their physical properties, too, differ only a little. This is not the case when the order of commensurability is small, $m = 2, 3, 4, \ldots$. Energy is gained in the commensurate situation when the maxima and minima of the density wave occupy special positions with respect to the lattice sites. This energy gain pins the phase of the CDW. The effect is strongest for low orders of commensurability and gives rise to a deformation of the lattice. For half-, one-third-, two-thirds-, quarter-, or three-quarters-filled bands, where the period of density oscillations is precisely twice, three times, or four times bigger than the lattice constant, it may be energetically favorable for the lattice to deform by doubling, tripling, or quadrupling this period.

33.4.3 Determination of the Gap

The self-consistent calculation of the energy gap cannot be done in the same way as for SDW, since the gap in the electronic excitation spectrum of the CDW state is defined in terms of the expectation value of the creation and annihilation operators of $\pm 2k_{\rm F}$ phonons. The gap can be obtained from the minimum of the total energy. The electronic contributions, including the renormalization due to electron-phonon interaction, come from the energy of the completely filled lower band. Taking, as usual, a finite bandwidth $2D = 2\hbar v_{\rm F}k_{\rm c}$ we have

$$E_{\rm e} = 2 \sum_{k=-k_{\rm c}}^{k_{\rm c}} E_k^{(2)}, \qquad (33.4.29)$$

where

$$E_k^{(2)} = \varepsilon_{\rm F} - \left[(\hbar v_{\rm F} k)^2 + |\Delta|^2 \right]^{1/2}.$$
 (33.4.30)

This energy can be evaluated by converting the sum to an integral. Neglecting the constant term $N_{\rm e}\varepsilon_{\rm F}$ we find

$$E_{\rm e} = -\frac{L}{\pi} \int_{-k_{\rm c}}^{k_{\rm c}} \left[(\hbar v_{\rm F} k)^2 + |\Delta|^2 \right]^{1/2} dk$$

$$= -\frac{L}{\pi \hbar v_{\rm F}} \left[D\sqrt{D^2 + |\Delta|^2} + |\Delta|^2 \operatorname{arsinh} \frac{D}{|\Delta|} \right].$$
(33.4.31)

In the weak-coupling limit it yields

$$E_{\rm e} = -L\rho_{\sigma}(\varepsilon_{\rm F}) \left[D^2 + |\Delta|^2 \ln \frac{2D}{|\Delta|} + \mathcal{O}\left(|\Delta|^2\right) \right], \qquad (33.4.32)$$

where we made use of the relation $\rho_{\sigma}(\varepsilon_{\rm F}) = 1/(\pi \hbar v_{\rm F})$. The correction $|\Delta|^2 \ln |\Delta|$ comes from the opening of the gap. Since the energy of the filled states is pushed downward by the interaction, the electronic energy is always lower in the gapped CDW state than in the homogeneous state. Moreover, this energy reduction is always larger in absolute value than the increase in the lattice energy due to the deformation. This elastic term is obtained from the expectation value of

$$\mathcal{H}_{\rm ph} = \sum_{\boldsymbol{q}} \hbar \omega_{\boldsymbol{q}} a_{\boldsymbol{q}}^{\dagger} a_{\boldsymbol{q}} \,. \tag{33.4.33}$$

Owing to the macroscopic occupation of the phonon states with wave numbers $\pm 2k_{\rm F}$, a reasonable estimate of the elastic energy is

$$E_{\rm ph} = \left\langle \mathcal{H}_{\rm ph} \right\rangle = 2\hbar\omega_{2k_{\rm F}} \left| \left\langle a_{2k_{\rm F}}^{\dagger} \right\rangle \right|^2. \tag{33.4.34}$$

In terms of the order parameter Δ and the dimensionless coupling constant λ we have

$$E_{\rm ph} = L\hbar\omega_{2k_{\rm F}}\frac{|\Delta|^2}{2g^2} = L\rho_{\sigma}(\varepsilon_{\rm F})\frac{|\Delta|^2}{\lambda}.$$
(33.4.35)

This quadratic term is indeed always smaller than the decrease in the electronic energy. Thus the one-dimensional electron-phonon system is always unstable against lattice distortion. The deformation of the lattice is such that the boundaries of the new Brillouin zone coincide with the Fermi points; a gap opens there and the system becomes insulating. Minimization of the total energy gives

$$|\Delta| = 2De^{-1/\lambda}.$$
 (33.4.36)

Note that the same universal number is obtained for the ratio of the gap and $k_{\rm B}T_{\rm c}$ as for spin-density waves [see (33.3.66)].

The gap was calculated at T = 0. It can also be evaluated at finite temperatures. Due to the formal similarity between the theory of superconductivity and density waves we refer to the results presented in the next chapter.

33.4.4 Collective Excitations

The one-particle excitations were calculated by assuming a rigid periodic lattice distortion, but phase and amplitude fluctuations of the order parameter

$$\Delta(x,t) = \left[\Delta + \delta(x,t)\right] e^{i\phi(x,t)}$$
(33.4.37)

may also be described in terms of collective excitations, just like in the SDW state. Fluctuations can be studied microscopically by calculating the response functions

$$\Pi_{n_{\mathrm{A}}n_{\mathrm{A}}}(q,\omega) = -\frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{e}^{\mathrm{i}\omega t} \left\langle \left[n_{\mathrm{A}}(q,t), n_{\mathrm{A}}(-q,0) \right]_{-} \right\rangle$$
(33.4.38)

and

$$\Pi_{n_{\phi}n_{\phi}}(q,\omega) = -\frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{e}^{\mathrm{i}\omega t} \Big\langle \left[n_{\phi}(q,t), n_{\phi}(-q,0) \right]_{-} \Big\rangle,$$
(33.4.39)

where

$$n_{\rm A}(q) = n(2k_{\rm F} + q) + n(-2k_{\rm F} + q), n_{\phi}(q) = n(2k_{\rm F} + q) - n(-2k_{\rm F} + q)$$
(33.4.40)

are the symmetric and antisymmetric combinations of the $\pm 2k_{\rm F}$ Fourier components of the density and as such they are related to the amplitude and phase fluctuations.

In an incommensurate CDW, where the phase is not pinned to the lattice, the energy of phase fluctuations is low in the long-wavelength limit. In contrast to SDW, the electrons oscillate together with the ions in a CDW. The inertia of the ions can be taken into account by an effective mass

$$m^* = m_{\rm e} \left(1 + \frac{4|\Delta|^2}{\lambda \hbar^2 \omega_{2k_{\rm F}}^2} \right) \tag{33.4.41}$$

of the moving CDW, where λ is the dimensionless coupling of the electron–phonon interaction, in terms of which the energy of phasons is given by

$$\hbar\omega_{\phi} = \left(\frac{m_{\rm e}}{m^*}\right)^{1/2} \hbar v_{\rm F} q \,. \tag{33.4.42}$$

The ratio $m^*/m_{\rm e}$ can be quite large.⁷ It is about $m^*/m_{\rm e} \approx 10^3$ in the Krogmann salt at low temperatures, and it is about 60 in TTF–TCNQ. Thus the phason velocity

$$v_{\phi} = v_{\rm F} \left(\frac{m_{\rm e}}{m^*}\right)^{1/2}$$
 (33.4.43)

⁷ There is no similar mass enhancement in SDW, since it does not couple to the lattice. That is why the phason velocity is $v_{\rm F}$ in SDW.

is much smaller than the Fermi velocity. As the temperature approaches the transition temperature from below, the order parameter and the mass enhancement decrease, while the phason velocity increases.

The oscillations of the amplitude of a density wave are accompanied by periodic charge accumulations or depletions. Hence the energy of *amplitudons* is finite even in the long-wavelength limit. At low temperatures we find

$$\hbar\omega_{\rm A} = \left[\lambda\hbar^2\omega_{2k_{\rm F}}^2 + \frac{1}{3}\frac{m_{\rm e}}{m^*}\hbar^2 v_{\rm F}^2 q^2\right]^{1/2}.$$
 (33.4.44)

It is instructive to plot the dispersion relation of phasons and amplitudons in the extended-zone scheme, as seen in Fig. 33.12, shifting the wave numbers by $2k_{\rm F}$. Comparison with Fig. 33.11, which shows the vanishing of the frequency of $2k_{\rm F}$ phonons at $T_{\rm c}$, justifies the interpretation that the phason and the amplitudon branches are the continuations of the soft phonon branch to temperatures below $T_{\rm c}$. The single branch of soft phonons splits into two below the transition temperature owing to the change in the periodicity. The phason branch remains soft, corresponding to acoustic oscillations, and a gap opens in the amplitudon branch which is the analog of optical excitations.



Fig. 33.12. Dispersion curves of phasons and amplitudons in the extended-zone scheme

Note that phasons are soft only in incommensurate CDWs, where the ionic background can be considered as a uniform but deformable continuum. It is only in this case that the phase can be arbitrarily chosen. This is not so in the commensurate situation where the phase is pinned to the lattice. The charge accumulations and depletions are arranged relative to the ionic positions in such a way as to minimize the energy. Fluctuations around the energy minimum cost finite energy and phasons are no longer soft even in the long-wavelength limit.

33.4.5 Dynamics of Charge-Density Waves

Because of their low energy, fluctuations of the phase are more relevant than amplitude variations in CDW systems. They determine the dynamics. We assume now that the phase may vary in space and time and will study the equations governing these variations.

The variations of the charge density are written in the form

$$\rho(x,t) = \rho_0 + \delta\rho \cos[2k_{\rm F}x + \phi(x,t)]$$
(33.4.45)

with a position- and time-dependent phase. For slow variations of the phase the spatial oscillations can be characterized by a local effective wavelength which can be defined by

$$2k_{\rm F}\lambda_{\rm eff} + \phi(\lambda_{\rm eff}, t) - \phi(0, t) = 2\pi , \qquad (33.4.46)$$

that is

$$\left[2k_{\rm F} + \frac{\partial\phi(x,t)}{\partial x}\right]\lambda_{\rm eff} = 2\pi. \qquad (33.4.47)$$

Alternatively, an effective Fermi wave number can be introduced via

$$2k_{\rm F,eff} = 2k_{\rm F} + \frac{\partial\phi(x,t)}{\partial x}.$$
(33.4.48)

That means that the local variation of the Fermi wave number is

$$\delta k_{\rm F}(x,t) = \frac{1}{2} \frac{\partial \phi(x,t)}{\partial x} \,. \tag{33.4.49}$$

In a semiclassical description this leads to a locally varying electronic band structure, where the Fermi points and the zone boundaries are shifted to

$$\pm \left[k_{\rm F} + \frac{1}{2} \frac{\partial \phi(x, t)}{\partial x}\right]. \tag{33.4.50}$$

Electrons fill the lower band completely, leaving the upper band empty. This implies that the electron density varies as

$$\delta n_{\rm e}(x,t) = \frac{2}{\pi} \delta k_{\rm F}(x,t) = \frac{1}{\pi} \frac{\partial \phi(x,t)}{\partial x}, \qquad (33.4.51)$$

and the local pileup of the electric charge is given by

$$\delta\rho(x,t) = -\frac{e}{\pi} \frac{\partial\phi(x,t)}{\partial x} \,. \tag{33.4.52}$$

In deriving these expressions we have taken into account that the spacing between the allowed k values is $2\pi/L$, one factor of 2 coming from the two Fermi points and another from the spin.

Temporal variations of the phase correspond to a displacement of the CDW, as if it moved along the chain. The drift velocity of this motion can be obtained from the equation

$$2k_{\rm F}x + \phi(x,t) = \text{const}$$
 (33.4.53)

that determines the motion of points with a fixed phase. We find

$$v_{\rm dr} = -\frac{1}{2k_{\rm F}} \frac{\partial \phi(x,t)}{\partial t} \,. \tag{33.4.54}$$

The particle-current density carried by the sliding CDW is

$$j_n = n_{\rm e} v_{\rm dr} \,.$$
 (33.4.55)

If all electrons are condensed into the CDW, the particle density is related to the Fermi wave number via

$$n_{\rm e} = \frac{2k_{\rm F}}{\pi} \,. \tag{33.4.56}$$

The particle-current density carried by the CDW is then

$$j_n = \frac{2k_{\rm F}}{\pi} \left(-\frac{1}{2k_{\rm F}} \frac{\partial \phi(x,t)}{\partial t} \right) = -\frac{1}{\pi} \frac{\partial \phi(x,t)}{\partial t} \,, \tag{33.4.57}$$

and the electric-current density is

$$j = \frac{e}{\pi} \frac{\partial \phi(x, t)}{\partial t} \,. \tag{33.4.58}$$

Note that the charge and current densities satisfy the continuity equation

$$\frac{\partial \rho(x,t)}{\partial t} + \frac{\partial j(x,t)}{\partial x} = 0. \qquad (33.4.59)$$

In order to get an explicit expression for the current and the conductivity, we have to find the equation that governs the spatial and temporal variations of the phase. It can be derived from the Lagrangian containing the kinetic energy arising from the temporal variations of the phase and the elastic energy coming from the spatial deformations.

Taking an effective mass m^* that contains the renormalization effect of the comoving ions, the kinetic energy of the electron condensate moving with velocity $v_{\rm dr}$ is given by

$$T = n_{\rm e} \frac{1}{2} m^* v_{\rm dr}^2 \,. \tag{33.4.60}$$

Combining this expression with (33.4.54) and (33.4.56) we have

$$T = \frac{m^*}{4\pi k_{\rm F}} \left(\frac{\partial \phi(x,t)}{\partial t}\right)^2.$$
(33.4.61)

The deformation energy can be estimated if we recall that the Fermi points are shifted by (33.4.49) and the states of the lower band are filled between the Fermi points. The local change in the number of particles is given by

$$4\delta k_{\rm F} \frac{L}{2\pi} = L \frac{1}{\pi} \frac{\partial \phi(x,t)}{\partial x} , \qquad (33.4.62)$$

and the mean energy of these particles measured from the Fermi energy is $\frac{1}{2}\hbar v_{\rm F} \delta k_{\rm F}$. Hence the deformation energy per unit length is

$$E_{\rm def} = \frac{\hbar v_{\rm F}}{4\pi} \left(\frac{\partial \phi(x,t)}{\partial x}\right)^2 = \frac{\hbar^2 k_{\rm F}}{4\pi m_{\rm e}} \left(\frac{\partial \phi(x,t)}{\partial x}\right)^2. \tag{33.4.63}$$

Although this estimate was obtained for a gapless spectrum, it is expected to hold in the CDW state as well. The Lagrangian is then

$$\mathcal{L} = \frac{m^*}{4\pi k_{\rm F}} \left(\frac{\partial \phi}{\partial t}\right)^2 - \frac{\hbar^2 k_{\rm F}}{4\pi m_{\rm e}} \left(\frac{\partial \phi}{\partial x}\right)^2$$
$$= \frac{m^*}{4\pi k_{\rm F}} \left[\left(\frac{\partial \phi}{\partial t}\right)^2 - \left(\frac{\hbar k_{\rm F}}{m_{\rm e}}\right)^2 \frac{m_{\rm e}}{m^*} \left(\frac{\partial \phi}{\partial x}\right)^2 \right].$$
(33.4.64)

The equation of motion obtained from the Euler-Lagrange equation,

$$\frac{\partial}{\partial t}\frac{\partial \mathcal{L}}{\partial \phi_t} + \frac{\partial}{\partial x}\frac{\partial \mathcal{L}}{\partial \phi_x} - \frac{\partial \mathcal{L}}{\partial \phi} = 0, \qquad (33.4.65)$$

where

$$\phi_t = \frac{\partial \phi}{\partial t}$$
 and $\phi_x = \frac{\partial \phi}{\partial x}$, (33.4.66)

is a wave equation,

$$\frac{\partial^2 \phi}{\partial t^2} - v_{\rm F}^2 \frac{m_{\rm e}}{m^*} \frac{\partial^2 \phi}{\partial x^2} = 0, \qquad (33.4.67)$$

which describes the propagation of the CDW with the phason velocity given in (33.4.42). The equations derived here will be used in studying the motion of the CDW in an external electric field.

33.4.6 Topological Excitations

The collective excitations were obtained on the assumption that the oscillations of the order parameter are small. Other types of excitations, where the deformations of the order parameter are not small, may also exist in CDWs. First, we consider such excitations in commensurate systems. For simplicity we visualize them in a half-filled model with one electron per atom. The Fermi points are at $k_{\rm F} = \pm \pi/2a$ and the $2k_{\rm F}$ instability of the lattice gives rise to a doubling of the periodicity. The phase of the CDW cannot be arbitrary; it is pinned to the lattice. There are two degenerate configurations for the lattice deformation displayed in Fig. 33.13.

The energy minima correspond to phases differing by π . In the case of *m*-fold commensurability there are *m* degenerate ground states with phases differing by $2\pi/m$. The pinning of the phase is due to the commensurability energy

$$E_{\rm comm} \propto 1 - \cos(m\phi) \,. \tag{33.4.68}$$



Fig. 33.13. Two equivalent deformation patterns and the corresponding CDWs in the dimerized lattice

When the phase varies by a nonzero integer multiple of $2\pi/m$ between the two ends of the chain, the lattice deformations at the two ends correspond to different deformation patterns and a domain wall of finite width has to appear between them. Such situations are seen in Fig. 33.14.



Fig. 33.14. Solitons between oppositely dimerized domains. The density wave is compressed or stretched in the domain wall

The domain walls are topological excitations. Their existence is related to the boundary condition, to the phase difference between the two ends. They cannot decay, but can propagate with a finite velocity along the chain. The effect of the lattice can be taken into account in the classical description by adding the commensurability energy to the deformation energy (33.4.63) in the Lagrangian. This leads to the equation of motion

$$\frac{\partial^2 \phi(x,t)}{\partial t^2} - v_\phi^2 \frac{\partial^2 \phi(x,t)}{\partial x^2} + \frac{\omega_0^2}{m} \sin m\phi(x,t) = 0$$
(33.4.69)

known as the *sine-Gordon equation*. It has solitary wave solutions, propagating kinks, of the form

$$\phi(x,t) = \frac{4}{m} \arctan e^{\gamma \omega_0(\pm x - vt)/v_\phi}, \qquad (33.4.70)$$

where $\gamma = (1 - v^2/v_{\phi}^2)^{-1/2}$. The kink, the rapid variation of the phase by $2\pi/m$, can propagate with any velocity less than the phason velocity. The corresponding topological excitations in the CDW state are know as *solitons*.

Solitons have rather unusual, reversed spin-charge relations. Unlike an electron, which has charge -e and spin s = 1/2, a soliton has no charge and s = 1/2 or charge $\pm e$ and no spin. To show this we can repeat the derivation of (33.4.51) that gives the electron density accumulated due to the deformation of the phase, but now separately for the two spin orientations. If the phase variations are different for the up- and down-spin electrons, we find

$$\delta n_{\uparrow}(x) = \frac{1}{\pi} \delta k_{\mathrm{F}\uparrow}(x) = \frac{1}{2\pi} \frac{\mathrm{d}\phi_{\uparrow}(x)}{\mathrm{d}x},$$

$$\delta n_{\downarrow}(x) = \frac{1}{\pi} \delta k_{\mathrm{F}\downarrow}(x) = \frac{1}{2\pi} \frac{\mathrm{d}\phi_{\downarrow}(x)}{\mathrm{d}x}$$
(33.4.71)

and

$$\delta \rho_{\uparrow}(x) = -\frac{e}{\pi} \delta k_{\mathrm{F}\uparrow}(x) = -\frac{e}{2\pi} \frac{\mathrm{d}\phi_{\uparrow}(x)}{\mathrm{d}x} ,$$

$$\delta \rho_{\downarrow}(x) = -\frac{e}{\pi} \delta k_{\mathrm{F}\downarrow}(x) = -\frac{e}{2\pi} \frac{\mathrm{d}\phi_{\downarrow}(x)}{\mathrm{d}x} .$$
(33.4.72)

We consider a deformed CDW in which the phase changes by $\pm \pi$ between $-\infty$ and $+\infty$ and varies relatively sharply at the position of the soliton, but the width of the domain wall, the region over which the phase varies by $\pm \pi$, is large compared to the wavelength of the CDW. The extra charge accumulated in the domain wall is the line integral of the charge density. Since

$$\Delta \rho_{\uparrow} = -\frac{e}{2\pi} \Delta \phi_{\uparrow} = -\frac{e}{2\pi} \left[\phi_{\uparrow}(\infty) - \phi_{\uparrow}(-\infty) \right],$$

$$\Delta \rho_{\downarrow} = -\frac{e}{2\pi} \Delta \phi_{\downarrow} = -\frac{e}{2\pi} \left[\phi_{\downarrow}(\infty) - \phi_{\downarrow}(-\infty) \right],$$
(33.4.73)

the total accumulated charge is

$$\Delta \rho = -\frac{e}{2\pi} \left(\Delta \phi_{\uparrow} + \Delta \phi_{\downarrow} \right). \tag{33.4.74}$$

If the phases of the two component waves vary in the same way, with π or $-\pi$ for both spin orientations, the charge of the soliton is -e or +e. Since the phase difference between the spin-up and spin-down electron densities vanishes along the entire chain, this charged soliton has no spin.

The situation is different when the phases of the spin-up and spin-down components of the density wave vary oppositely in the domain wall; one varies by π , the other by $-\pi$. One of the component waves is stretched, the other is compressed. The \uparrow spin and \downarrow spin electron densities are in registry with each other and with the underlying lattice at the two ends if

$$\left[\phi_{\uparrow}(\infty) - \phi_{\uparrow}(-\infty)\right] - \left[\phi_{\downarrow}(\infty) - \phi_{\downarrow}(-\infty)\right] = 2\pi n \qquad (33.4.75)$$

with n an integer. In the present case $n = \pm 1$. No charge is accumulated in the domain wall; this soliton is neutral. On the other hand, the spin density

$$s^{z}(x) = \frac{1}{2} \left[\delta n_{\uparrow}(x) - \delta n_{\downarrow}(x) \right]$$
(33.4.76)

is finite inside the domain wall and the spin of the neutral soliton calculated from

$$s^{z} = \frac{1}{2} \frac{1}{2\pi} \left(\Delta \phi_{\uparrow} - \Delta \phi_{\downarrow} \right) \tag{33.4.77}$$

is $s^z = \pm 1/2$. This is a spin soliton. It should be emphasized that these solitons cannot be generated thermally individually, neither by adding a single electron to the system, owing to their topological nature. They are always created in pairs, such that their total charge and spin correspond to the usual quantum numbers of electrons. However, unlike classical soliton solutions of the sine-Gordon equations, solitons of a deformable CDW interact. A charge and a spin soliton attract each other and form a polaron with usual spin–charge relation.

Fractionally charged solitons exist in CDWs with higher order commensurability. When the band is one-third filled, the Fermi wave number is $k_{\rm F} = \pi/(3a)$ and the wavelength of the CDW is 3a. Owing to the tripling of the primitive cell, there are three degenerate CDW ground states with phases differing by $\pm 2\pi/3$. Soliton configurations may appear in which $\Delta \phi_{\uparrow}$ and $\Delta \phi_{\downarrow}$ take values $\pm 2\pi/3$ or $\pm 4\pi/3$ with restriction (33.4.75). The charge of the soliton may be fractional, one-third, or two-thirds of the elementary charge. The spin of the soliton with $\Delta \rho = \pm e/3$ is $s^z = \pm 1/2$ and the soliton with charge $\Delta \rho = \pm 2e/3$ is spinless. In general, in an *m*-fold commensurate CDW the charge of the soliton may be a fraction $\pm 2/m$ of the elementary charge.

Solitons exist in SDW as well. The spin-up and spin-down component waves do not have the same phase far from the soliton. However, their variations between the two sides have to satisfy (33.4.75), which is simply a symmetry requirement. A similar reversed spin-charge relation is found as for solitons in a CDW. A new type of soliton appears when the vector nature of the spin is taken into account. The unit vector e(x) in

$$\boldsymbol{S}(x) = \boldsymbol{e}(x)s\cos(2k_{\rm F}x + \phi) \tag{33.4.78}$$

may rotate from e_0 to $-e_0$ as we move along the chain. Such a domain wall is known as *polarization soliton*.

The solitons discussed until now are due to deformations of the phase of the CDW. Another type of soliton, called *amplitude soliton*, may appear in incommensurate CDW systems with continuous degeneracy. Adding an electron to the system, this particle, instead of occupying a state of the empty upper band, distorts the CDW. It introduces a phase slip π by modifying the amplitude of the CDW and becomes localized or self-trapped. It carries a spin s = 1/2 but no charge. The charge of the extra electron is compensated by the distortion of the electronic wavefunctions of the valence band. The position dependence of the order parameter is described by

$$\Delta(x) = \Delta \tanh(x/\xi) e^{i\phi}$$
(33.4.79)

with the width of the domain wall given by $\xi = \hbar v_{\rm F}/\Delta$. The amplitude goes through zero at the position of the soliton, as seen in Fig. 33.15.



Fig. 33.15. Amplitude soliton in an incommensurate CDW

The same variations are observed in the ionic displacement between the two ends,

$$\langle u(R_n)\rangle = \sqrt{\frac{\hbar L}{2MN\omega_{2k_{\rm F}}}} \frac{2|\Delta|}{g} \tanh\left(\frac{x}{\xi}\right) \cos(2k_{\rm F}R_n + \phi).$$
 (33.4.80)

The energy level of the electron is right in the middle of the gap (midgap state). When the energy associated with the deformation of the lattice is also taken into account, the excitation energy to create a soliton is found to be

$$\varepsilon = \frac{2\Delta}{\pi} \,. \tag{33.4.81}$$

These solitons, which can be created individually, have been observed in tunneling experiments. As seen in Fig. 33.16, an extra peak appears at voltages $eV = \pm 2\Delta/\pi$ in addition to the peaks at $\pm 2\Delta$ corresponding to interband tunneling across the gap.



Fig. 33.16. Tunneling conductivity dI/dV of NbSe₃ (*a*) in transverse geometry, at various magnetic fields, and (*b*) in longitudinal geometry, at various temperatures [Reprinted with permission from Yu. I. Latyshev et al., *Phys. Rev. Lett.* **95**, 266402 (2005). \bigcirc (2005) by the American Physical Society]

33.4.7 Soliton Lattice

An interesting situation occurs when the CDW is incommensurate but its wavelength is close to a low-order commensurate value,

$$\lambda \approx \lambda_0 = a \frac{m}{n} \tag{33.4.82}$$

with small integer m and n. The repetition distance of the commensurate CDW is $n\lambda_0$, if measured in the wavelength of the CDW, while it is ma, if measured in lattice constant units. The wave number $2k_{\rm F}$ of the incommensurate CDW can be written as

$$2k_{\rm F} = 2k_{\rm F}^0 + \delta q \,, \tag{33.4.83}$$

where $2k_{\rm F}^0 = (2\pi/a)(n/m)$, and $\delta q = 2(k_{\rm F} - k_{\rm F}^0)$ is small compared to $2k_{\rm F}^0$. The factor describing the spatial oscillations of the incommensurate CDW can be written as

$$\cos(2k_{\rm F}x + \phi_0) = \cos(2k_{\rm F}^0x + \delta q \, x + \phi_0). \qquad (33.4.84)$$

This variation of the oscillating function can be interpreted as a slow variation of the phase

$$\phi(x) = \delta q \, x + \phi_0 \tag{33.4.85}$$

of the commensurate CDW with wave vector $2k_{\rm F}^0$. This variation is shown in Fig. 33.17(a).



Fig. 33.17. Variations of the phase in an incommensurate CDW: (a) relative to a nearby commensurate case and (b) in the soliton lattice

We know that the energy of a commensurate CDW is lower than that of an incommensurate CDW with nearly identical wavelength, and the commensurability energy decreases with increasing order of commensurability. It may be energetically favorable to deform the homogeneous CDW by pinning its phase to the lattice over large segments. The wavelength is λ_0 there and $\phi(x)$ varies relatively sharply between the segments.

An *m*-fold commensurate CDW has *m* equivalent, degenerate positions relative to the lattice. They are displaced by one lattice constant relative to each other and their phases differ by multiples of $2\pi/m$. The deformation of the incommensurate CDW and the energy increase due to this distortion are smallest if the phase difference between neighboring commensurate segments is just $2\pi/m$.⁸ Such a situation is shown schematically in Fig. 33.18.



Fig. 33.18. Rigid CDW of wavelength slightly larger than 2a and a deformable CDW with a discommensuration between two commensurate domains with wavelength 2a

The deformed CDW contains commensurate regions separated by shorter incommensurate regions, domain walls, also known as *discommensurations*. On the other hand it can be viewed as containing a periodic array of solitons. This explains the name *soliton lattice* for this configuration. Figure 33.17(b) shows the variation of the phase in the soliton lattice. The distance d between solitons is determined by the difference of the wavelengths of the commensurate and incommensurate CDW and the order of commensurability. The change of the phase on large distances should on the average be equal to the phase change in the rigid incommensurate CDW. Since the phase remains unchanged in the commensurate regions and varies by $2\pi/m$ within the soliton, we have

$$\delta q \, d = 2\pi/m \,. \tag{33.4.86}$$

If the phase changes in the same way for both spin orientations, a charge -2e/m is accumulated in the soliton. It compensates the charge redistribution caused by the commensurate regions.

No soliton lattice has ever been observed experimentally in incommensurate CDW systems probably owing to the coupling between the chains. The deformation of the CDW costs too high an energy due to the Coulomb interaction between the electronic charges forming the CDW on the chains and the counterions sitting between the chains.

⁸ The wavelength in the deformed region is smaller than λ_0 if $2k_{\rm F} > q_0$. It is larger than λ_0 if $2k_{\rm F} < q_0$.
33.4.8 Electrodynamics of Charge-Density Waves

An incommensurate CDW can slide freely, without cost of energy, in an ideal lattice. This led FRÖHLICH⁹ to the idea that the CDW state is not an insulator, but it is in fact superconducting. It soon turned out that this is not so in real materials. In our previous discussion of the CDW state the lattice was assumed ideal, defectless. That is why the phase of the CDW can be arbitrary in an incommensurate situation and the phason modes are gapless. Impurities have a profound effect on the CDW state. The system loses translational invariance in their presence; the appearance of a CDW does not break a continuous symmetry and soft bosons should not appear. Phasons have a finite frequency even in the limit $q \rightarrow 0$. To understand it in more physical terms we recall that impurities interact with the charges accumulating in the CDW with a Coulomb interaction and can pin the phase at the position of the impurity. This gives rise to unusual electrodynamic properties of the CDW state.

When an external electric field E is switched on, it interacts with the local charge density. The energy density that has to be added to the Lagrangian (33.4.64) is given by

$$\varepsilon(x,t) = \delta\rho(x,t)\varphi(x,t) = -\frac{e}{\pi}\frac{\partial\phi(x,t)}{\partial x}\varphi(x,t), \qquad (33.4.87)$$

where $\varphi(x,t)$ is the scalar potential. The equation of motion then becomes

$$\frac{\partial^2 \phi}{\partial t^2} - v_{\rm F}^2 \frac{m_{\rm e}}{m^*} \frac{\partial^2 \phi}{\partial x^2} = \frac{2k_{\rm F}e}{m^*} E. \qquad (33.4.88)$$

For a periodic variation of the electric field, $E = E(k, \omega) \exp(ikx - i\omega t)$, the phase and the current will have similar periodic variations. Inserting the solution for $\phi(k, \omega)$ into (33.4.58) we get

$$\sigma(k,\omega) = \frac{n_{\rm e}e^2}{m^*} \frac{{\rm i}\omega}{\omega^2 - v_{\rm F}^2 \frac{m_{\rm e}}{m^*} k^2}$$
(33.4.89)

for the conductivity of the CDW. In the long-wavelength limit

$$\sigma(\omega) = i \frac{n_e e^2}{m^*} \frac{1}{(\omega + i\delta)}, \qquad (33.4.90)$$

where δ is a positive infinitesimal. It ensures the correct analytical properties. The real and imaginary parts,

$$\operatorname{Re} \sigma(\omega) = \pi \frac{n_{e}e^{2}}{m^{*}} \,\delta(\omega) \,, \qquad \operatorname{Im} \sigma(\omega) = \frac{n_{e}e^{2}}{m^{*}\omega} \,, \qquad (33.4.91)$$

satisfy the Kramers–Kronig relations. This is precisely the result of the Drude model in the limit of infinitely long relaxation time, with the difference that

⁹ H. Fröhlich, 1954.

the effective mass m^* appears in place of the electron mass $m_{\rm e}$. The infinitely narrow and high Drude peak means infinite conductivity. This would be the Fröhlich superconductivity.

It is never observed. Impurities and defects that are always present in real materials hinder the free sliding of the CDW. The phase is pinned at the position of the randomly distributed impurities, and the periodic CDW is deformed statically. Assuming that the interaction between the impurities and the CDW is local, the effect of interaction can be given by the Hamiltonian

$$\mathcal{H} = \frac{\hbar v_{\rm F}}{4\pi} \int \mathrm{d}x \left(\frac{\partial \phi}{\partial x}\right)^2 - V_0 \delta \rho \sum_i \cos[2k_{\rm F} x_i + \phi(x_i)], \qquad (33.4.92)$$

where the first term describes the energy due to the deformation, V_0 in the second term is the strength of the impurity potential, and $\delta\rho$ is the amplitude of the CDW. If the impurity potential is strong, the phase is deformed in the neighborhood of each impurity rather strongly to gain the largest energy. The phase is pinned and the CDW cannot freely slide. Impurity pinning occurs for weak impurity potential as well. Although the phase is deformed less, it adjusts itself to the impurity configuration on the average. Not only the Fröhlich superconductivity is killed in both cases, but also the electrons condensed into the CDW give no contribution to the current for small biases. Another consequence of impurity pinning is the generation of a gap in the phason spectrum at q = 0.

When the phase deviates from the value determined by the impurities, a restoring force pulls the CDW back to its initial position. As the simplest approximation we assume a harmonic force. The phase could oscillate around its pinned value by a frequency ω_0 . Introducing a relaxation time τ^* due to friction, the variations of the phase are described in the presence of an external electric field by the equation

$$\frac{\partial^2 \phi}{\partial t^2} + \frac{1}{\tau^*} \frac{\partial \phi}{\partial t} + \omega_0^2 \phi = \pi \frac{n_{\rm e} e}{m^*} E \,. \tag{33.4.93}$$

Its solution gives

$$\operatorname{Re} \sigma(\omega) = \frac{n_{e}e^{2}\tau^{*}}{m^{*}} \frac{(\omega/\tau^{*})^{2}}{(\omega_{0}^{2} - \omega^{2})^{2} + (\omega/\tau^{*})^{2}},$$

$$\operatorname{Im} \sigma(\omega) = \frac{n_{e}e^{2}\tau^{*}}{m^{*}} \frac{(\omega^{2} - \omega_{0}^{2})\omega/\tau^{*}}{(\omega_{0}^{2} - \omega^{2})^{2} + (\omega/\tau^{*})^{2}}.$$
(33.4.94)

The frequency dependence of the real part of the conductivity is shown in Fig. 33.19(b). Comparing it with the result valid for a clean sample we find that the peak due to the collective modes is shifted to the frequency ω_0 . The spectral weight of the collective modes is suppressed by the large effective mass m^* of the CDW motion. Nearly all contribution comes from single-particle excitations. The situation is reversed in SDW systems. The band mass is not



Fig. 33.19. Frequency dependence of the real part of the optical conductivity: (a) in an ideal CDW and (b) in the presence of impurities

enhanced by the ions and the dominant contribution to the optical conductivity comes from the collective excitations.

The figure also shows the contributions of one-particle excitations to the optical conductivity. The minimum energy of excitations across the gap being 2Δ , they contribute to the optical conductivity above a frequency threshold $2\Delta/\hbar$.

We remark already here that although impurities kill the Fröhlich superconductivity, they cannot destroy conventional superconductivity. Cooper pairs form a particular condensate which is very different from the condensed state in CDW. The impurity potential can hardly influence the superconducting pairs. The situation is different for magnetic impurities. They lower the value of the order parameter appreciably, but do not kill superconductivity completely.

33.4.9 The Role of Fluctuations and Interchain Couplings

Our previous calculations for both charge- and spin-density waves were done in the mean-field approximation. The RPA for the magnetic susceptibility, the summation of the contribution of the simple series of bubbles, is equivalent to this approximation. That is why a finite transition temperature was obtained, although we know from statistical physics that no phase transitions can take place at finite temperatures in strictly one-dimensional systems unless the forces are long ranged. The energy of the disordered phase is higher than that of the ordered phase, but this is compensated by the term -TS in the free energy owing to the increased entropy. The fluctuations neglected in the mean-field theory are so large in one-dimensional systems that they destroy long-range order at any finite temperature.

To go beyond mean-field approximation, we would have to sum the contribution of a much larger class of diagrams. The effect of fluctuations can be taken into account much simpler in a generalized Ginzburg–Landau-type theory, expanding the free energy functional in terms of the order parameter and its gradient. The order parameter Δ being a complex quantity, the free energy density of a homogeneous system could be written in the neighborhood of the transition temperature as 378 33 Electronic Phases with Broken Symmetry

$$f = f_0 + A(T)|\Delta|^2 + B(T)|\Delta|^4 + \cdots .$$
 (33.4.95)

When the order parameter fluctuates in space, a gradient term should appear as in (14.5.17) or as in the Ginzburg–Landau theory of superconductivity. We have

$$f(x) = f_0 + A(T)|\Delta(x)|^2 + B(T)|\Delta(x)|^4 + C(T) \left|\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x}\right|^2 + \cdots \quad (33.4.96)$$

In Fourier representation, assuming that the Fourier components slightly away from $2k_{\rm F}$ are finite, we have the form

$$f[\Delta_q] = f_0 + A(T)|\Delta_q|^2 + B(T)|\Delta_q|^4 + C(T)(q - 2k_{\rm F})^2|\Delta_q|^2 + \cdots$$
(33.4.97)

The coefficients of the expansion can be calculated from the microscopic theory, similar to the microscopic derivation of the Ginzburg–Landau functional and of the Ginzburg–Landau equations in the theory of superconductivity (see the next chapter), but starting now with the Fröhlich Hamiltonian. We find

$$A(T) = \rho_{\sigma}(\varepsilon_{\rm F}) \ln(T/T_{\rm c}) \approx \rho_{\sigma}(\varepsilon_{\rm F})(T - T_{\rm c})/T_{\rm c},$$

$$B(T) = \rho_{\sigma}(\varepsilon_{\rm F})7\zeta(3)/(4\pi k_{\rm B}T)^2,$$

$$C(T) = \rho_{\sigma}(\varepsilon_{\rm F})\xi_0^2(T)$$
(33.4.98)

with $\xi_0^2(T) = 7\zeta(3)\hbar^2 v_{\rm F}^2/(4\pi k_{\rm B}T)^2$, and $T_{\rm c}$ the mean-field transition temperature given in (33.4.12).

A somewhat tedious calculation gives the result that the amplitude of the order parameter fluctuates about zero above the mean-field transition temperature. The amplitude would take a finite value at lower temperatures, where the minimum of the free energy density is at a finite $|\Delta|$; however, the phase of the order parameter is free to rotate and the order parameter averages out owing to phase fluctuations. The correlation function of the order parameter decays exponentially with distance as

$$\langle \Delta^*(x)\Delta(0)\rangle \propto \mathrm{e}^{-x/\xi_{\parallel}},$$
(33.4.99)

where the correlation length ξ_{\parallel} along the chain diverges as 1/T in the limit $T \to 0$. This shows that fluctuations do in fact wash out ordering at finite temperatures. Strictly speaking the Peierls transition occurs at T = 0. However, the correlation length becomes very large at about a quarter of the mean-field $T_{\rm c}$, and a pseudogap appears in the density of states, as seen in Fig. 33.20. Weak interchain couplings may drive the system into the ordered state.

The interaction between chains is the Coulomb interaction in CDW systems. It is energetically favorable to have a phase difference π between neighboring chains. This coupling diminishes the fluctuations and allows ordering at finite temperatures. Coulomb interaction does not play a dominant role in SDW materials, but interchain hopping can couple chains. The nesting property of the Fermi surface is not destroyed if the hopping matrix element is



Fig. 33.20. Forbidden region in the density of states at T = 0 and its smearing at finite T due to thermal fluctuations [Reprinted with permission from P. A. Lee, T. M. Rice, and P. W. Anderson, *Phys. Rev. Lett.* 31, 462 (1973). \bigcirc (1973) by the American Physical Society]

much smaller between chains than between molecules along the chain, and this interchain coupling can stabilize the density wave at low temperatures.

We might expect three-dimensional ordering to occur at the temperature where the thermal energy is comparable with the energy of the bare interchain coupling. In estimating this energy we should, however, take into account that the coherence length ξ_{\parallel} along the chain would diverge at T = 0. The coupling between the large coherent regions yields a T_c which is higher than the naive estimate.

In reality, the transition occurs at the temperature where the appropriate response function (the density–density response function for the CDW and the spin-density–spin-density response function for the SDW) first diverges. These response functions can be written in the form

$$\Pi(\boldsymbol{q},\omega) = \frac{\Pi(\boldsymbol{q},\omega)}{1 - (4\pi\tilde{e}^2/q^2)\widetilde{\Pi}(\boldsymbol{q},\omega)}$$
(33.4.100)

for an electron system interacting via the bare Coulomb repulsion, while for the spin density in the Hubbard model

$$\Sigma(\boldsymbol{q},\omega) = \frac{\widetilde{\Sigma}(\boldsymbol{q},\omega)}{1 - U\widetilde{\Sigma}(\boldsymbol{q},\omega)}, \qquad (33.4.101)$$

where $\widetilde{\Pi}(\boldsymbol{q},\omega)$ and $\widetilde{\Sigma}(\boldsymbol{q},\omega)$ are the irreducible parts of these response functions. Assuming that the weak interchain coupling can be treated in a mean-field approximation, we have 380 33 Electronic Phases with Broken Symmetry

$$\Pi_{\rm 3d}(\boldsymbol{q},\omega) = \frac{\Pi_{\rm 1d}(q_{\parallel},\omega)}{1 - c_{\perp}(\boldsymbol{q}_{\perp})\Pi_{\rm 1d}(q_{\parallel},\omega)}$$
(33.4.102)

and

$$\Sigma_{\rm 3d}(\boldsymbol{q},\omega) = \frac{\Sigma_{\rm 1d}(\boldsymbol{q}_{\parallel},\omega)}{1 - c_{\perp}(\boldsymbol{q}_{\perp})\Sigma_{\rm 1d}(\boldsymbol{q}_{\parallel},\omega)},\qquad(33.4.103)$$

where $c_{\perp}(\boldsymbol{q}_{\perp})$ is the Fourier transform of the interchain coupling, while $\Pi_{1\mathrm{d}}(q_{\parallel},\omega)$ and $\Sigma_{1\mathrm{d}}(q_{\parallel},\omega)$ are the response functions for the chains. The latter are divergent at T = 0 at wave number $q_{\parallel} = 2k_{\mathrm{F}}$; hence, the three-dimensional response diverges at a finite temperature $T_{3\mathrm{d}}$ where

$$1 = c_{\perp}(\boldsymbol{q}_{\perp}) \Pi_{1d}(2k_{\rm F}, \omega = 0, T_{3d})$$
(33.4.104)

or

$$1 = c_{\perp}(\boldsymbol{q}_{\perp}) \Sigma_{1d}(2k_{\rm F}, \omega = 0, T_{3d}). \qquad (33.4.105)$$

A static density wave occurs along the chains at this temperature. The phase relations between neighboring chains, the periodicity perpendicular to the chains, is given by q_{\perp} . In most cases this perpendicular structure is commensurate with the lattice, but it could be incommensurate.

The correlation function of the order parameter decays exponentially above the transition point, but the correlation length is drastically different along the chains or perpendicular to them:

$$\langle \Delta(\mathbf{r})\Delta(0)\rangle \propto \frac{\mathrm{e}^{-r_{\mathrm{eff}}}}{r_{\mathrm{eff}}},$$
 (33.4.106)

where

$$r_{\rm eff} = \left[\left(\frac{x}{\xi_{\parallel}}\right)^2 + \left(\frac{\boldsymbol{r}_{\perp}}{\xi_{\perp}}\right)^2 \right]^{1/2} \,. \tag{33.4.107}$$

Both correlation lengths diverge at the true ordering temperature. The perpendicular correlation length might become comparable with the distance between chains at some higher temperature T^* , which is still below the mean-field transition temperature. This is the crossover temperature, where the system loses its three-dimensional character and can be treated as quasi-one-dimensional.

33.5 Density Waves in Quasi-One-Dimensional Materials

The one-dimensional models of the electron-phonon system or that of the interacting electron gas are not just of theoretical interest. We know from Chapter 5 that chainlike structures are not uncommon in nature. Several classes of materials, both organic and inorganic compounds, built up of weakly coupled chains have been discovered from the 1970s on. If the distance between neighboring chains is very much larger than between the atoms within a chain, the wavefunction overlap between chains is much smaller than from atom to atom along the chain. The electronic properties of such materials are strongly anisotropic because electrons can propagate practically only along the chains with only occasional hopping between them. The ratio of the conductivities measured parallel and perpendicular to the chains, $\sigma_{\parallel}/\sigma_{\perp}$, can be as high as 10^5 corresponding to a ratio $t_{\parallel}/t_{\perp} \approx 10^2 - 10^3$ of the overlap integrals. First, we present some characteristic classes of quasi-one-dimensional materials possessing a density-wave ground state and then present some peculiarities of their transport properties.

33.5.1 Quasi-One-Dimensional Materials

One of the first quasi-one-dimensional material studied in detail is the Krogmann salt¹⁰ of composition K₂Pt(CN)₄X_{0.3} · 3H₂O (KCP) where X = Cl or Br. The Pt²⁺ ions are close to each other at a distance 2.89 Å along one of the crystallographic axes. The overlap between the wavefunctions of *d*-electrons is strong in this direction. The Pt–Pt distance being almost four times as big in the perpendicular directions, the overlap is negligibly small. The ratio of the conductivities along the chain and perpendicular to it is about $\sigma_{\parallel}/\sigma_{\perp} \approx 10^5$. The halogens only serve as a reservoir of carriers. They remove electrons from the highest occupied band of the otherwise insulating material transforming it into a hole conductor. The Krogmann salt exhibits static incommensurate density waves on the chains below 100 K with a phase difference π between neighboring chains, although, surprisingly, no sharp transition could be observed. A giant Kohn anomaly, seen in Fig. 33.21, is found in the dispersion relation of longitudinal acoustic phonons already at room temperature.



Fig. 33.21. Dispersion curve of LA phonons in $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ in the [001] direction at room temperature [Reprinted with permission from B. Renker et al., *Phys. Rev. Lett.* 30, 1144 (1973). \bigcirc (1973) by the American Physical Society]

¹⁰ K. Krogmann, 1969.

It was discovered in the early 1970s that there is a large class of organic compounds built up from two kinds of large planar molecules: donors and acceptors, in such a way that the molecules of the same type are stacked upon each other forming segregated chains. Due to the electron transfer between the donors and acceptors these compounds are known as *charge-transfer complexes* or *donor–acceptor salts*. The most famous example is TTF–TCNQ (tetrathiafulvalene–tetracyanoquinodimethane). The arrangement of the molecules in the crystal structure is shown in Fig. 33.22, viewed from the direction of the stacks and perpendicular to it.



Fig. 33.22. Crystal structure of TTF-TCNQ viewed from two directions

Substituting selenium for sulfur in TTF we get TSF (tetraselenafulvalene). When methyl ($-CH_3$) groups are attached to the TTF or TSF molecules, we get the molecules TMTTF (tetramethyltetrathiafulvalene) or TMTSF (tetramethyltetraselenafulvalene). HMTSF (hexamethylenetetraselenafulvalene) is obtained by substituting methylene ($-CH_2-$) groups in place of hydrogen atoms. An even larger polycyclic donor molecule is BEDT-TTF [bis(ethylenedithio) tetrathiafulvalene]. On the other hand, when methyl or ethyl groups are attached to the benzene ring in TCNQ, we get the molecules MTCNQ (methyl-TCNQ), DMTCNQ (dimethyl-TCNQ), or DETCNQ (diethyl-TCNQ). The acceptors TNAP (tetracyanonaphthoquinodimethane) and TCNDQ (tetracyanodiphenoquinodimethane) contain two benzene rings. Figure 33.23 shows a few typical donor and acceptor molecules. The charge-transfer complexes built up from the derivatives of the parent molecules TTF and TCNQ possess similar crystal structures where the donors and acceptors form segregated stacks. The structure of HMTTF–TCNQ was already shown in Fig. 7.24 as a typical chainlike structure.



Fig. 33.23. Planar (a) donor and (b) acceptor molecules that form linear-chain charge-transfer complexes. The carbon atoms and the hydrogens attached to the rings are not marked

Both the TTF and the TCNQ molecule are neutral with closed outer shells. However, TTF, as a donor, can readily give an electron away and TCNQ, as an acceptor, can easily accept an extra electron to become an open shell anion. This electron transfer takes place in the TTF–TCNQ crystal resulting in partially filled π -orbitals making this compound an organic conductor. The conductivity is, however, strongly anisotropic, since the overlap is mainly in the chain direction. TTF–TCNQ behaves as a quasi-one-dimensional metal. The room-temperature conductivity along the chain is only of order $10^4 (\Omega m)^{-1}$, but it increases with decreasing temperature much faster than in normal metals. Depending on sample quality it may reach a peak value of almost $10^7 (\Omega m)^{-1}$ before it starts to drop suddenly with an exponential temperature dependence (Arrhenius law¹¹) typical for semiconductors due to the opening of the Peierls gap. This is seen in Fig. 33.24(*a*) which shows the temperature dependence of the conductivity of several TTF–TCNQ samples.

The formation of a CDW and the transition from metallic to semiconducting behavior is typical for quasi-one-dimensional charge-transfer salts. The transition temperature, the value of the gap, and the wave vector q_0 of the CDW are given in Table 33.1 for some of them. The wave vector is given in terms of its components in the coordinate system spanned by the primitive vectors of the reciprocal lattice, a^* , b^* , c^* .

¹¹ S. ARRHENIUS, 1889. SVANTE AUGUST ARRHENIUS (1859–1927) was awarded the Nobel Prize in chemistry in 1903 "in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation".



Fig. 33.24. (a) Temperature dependence of the conductivity of several TTF-TCNQ samples [A. J. Heeger and A. F. Garito, in *Low-Dimensional Cooperative Phenomena*, Ed. by H. J. Keller, Plenum Press (1975)]. (b) Temperature dependence of the wave number of the CDW in TTF-TCNQ [W. D. Ellenson et al., *Solid State Commun.* 20, 53 (1976)]

Table 33.1. Critical temperature T_c of the CDW formation, the value of the gap, the dimensionless ratio $2\Delta/k_{\rm B}T_c$, and the wave vector \boldsymbol{q}_0 in units of the primitive vectors of the reciprocal lattice for some charge-transfer complexes

Compound	$T_{\rm c}({\rm K})$	$2\Delta(\mathrm{eV})$	$2\Delta/k_{\rm B}T_{\rm c}$	$oldsymbol{q}_0$
TTF-TCNQ	54			(1/2, 0.295, 0)
	38	0.04	12.1	(1/4, 0.295, 0)
TSF-TCNQ	29	0.02	8.6	(1/2, 0.317, 0)
HMTSF-TCNQ	24			(0, 0.37, 0)
HMTTF-TCNQ	43	0.04	11.2	(0.420, 0.360, 0)

In several cases there are two or even three subsequent phase transitions as the temperature is lowered. Further phases may appear under pressure. In TTF–TCNQ, for example, the a^* component of the wave vector takes the value $q_a = 1/2$ at the CDW ordering temperature $T_{c1} = 54$ K, which means that the periodicity is doubled in the a direction in the CDW state. As seen in Fig. 33.24(b), this component remains constant down to about $T_{c2} = 49$ K where it starts to decrease. Finally, it jumps to the value $q_a = 1/4$ at $T_{c3} = 38$ K and is locked there. The periodicity is quadrupled in the *a* direction in the low-temperature phase.

Another much studied class of quasi-one-dimensional materials is that of the *Bechgaard salts*.¹² Their composition is $(TMTSF)_2X$ with $X = PF_6$, AsF_6 , TaF_6 , NO_3 , BF_4 , ClO_4 , or ReO_4 .¹³ The molecules TMTSF are stacked to form conducting chains while the inorganic anions are well separated and only serve as a charge reservoir. The crystal structure is shown in Fig. 33.25. The temperature dependence of the resistivity gives clear indication of a metal-nonmetal transition in all of them.



Fig. 33.25. Crystal structure of (TMTSF)₂PF₆ viewed from two crystallographic directions [N. Thorup et al., *Acta Cryst.* B**37**, 1236 (1981)]

Perhaps the most studied Bechgaard salt is $(TMTSF)_2PF_6$ with a transition temperature $T_c = 12 \text{ K}$ to an SDW state. A similar transition is observed in the salts with anions AsF_6^- , SbF_6^- , and NO_3^- with almost identical critical points. Their magnetic properties are similar to antiferromagnets possessing localized spins and described by the Heisenberg Hamiltonian. This is best seen

¹² K. BECHGAARD, 1980. A particularly interesting feature of Bechgaard salts is that they were the first known organic superconductors. We will return briefly to the physics of organic superconductors in the next chapter.

 $^{^{13}}$ The salts (TMTTF)₂X are known as Fabre salts. J. M. FABRE, 1982.

when the temperature dependence of the susceptibility of $(TMTSF)_2AsF_6$ shown in Fig. 33.26 is compared with the theoretical result given in Fig. 14.14 for an anisotropic antiferromagnet. The susceptibility depends on the orientation of the external magnetic field relative to the sublattice magnetization. The parallel susceptibility vanishes at T = 0, while the perpendicular component remains finite, just as in a Heisenberg antiferromagnet.



Fig. 33.26. Temperature dependence of the static spin susceptibility of a single crystal (TMTSF)₂AsF₆ with field applied parallel to three crystallographic directions, a, b^* , and c^* [Reprinted with permission from K. Mortensen, Y. Tomkiewicz, and K. Bechgaard, *Phys. Rev. B* **25**, 3319 (1982). \bigcirc (1982) by the American Physical Society]

A spin-density wave appears below $T_c = 20 \text{ K}$ in several other salts, e.g., in (MDT-TTF)₂Au(CN)₂ where MDT-TTF stands for methylenedithiotetrathiafulvalene and in (DMET)₂Au(CN)₂ where DMET stands for dimethyl-(ethylenedithio)diselenadithiafulvalene.

Density waves are found in inorganic compounds as well. One typical example is the group of transition-metal trichalcogenides. Their composition is MX_3 , where M = Nb or Ta, and X = S or Se. The tetrachalcogenides $(MX_4)_n Y$ with Y = I, Br, Cl, and n = 2, 3, 10/3, 4 exhibit similar behavior. Their structure is shown in Fig. 33.27. Finally a third group is formed by the oxides of molybdenum (blue bronze) with composition $A_{0.3}MoO_3$ (A = K, Rb). A CDW is formed in many of these materials at relatively high temperatures. Characteristic data for some of them, the critical temperature, the gap, and the wave vector of the CDW are given in Table 33.2.



Fig. 33.27. Crystal structure of linear-chain tri- and tetrachalcogenides

Table 33.2. The critical temperature, the value of the gap, the dimensionless ratio $2\Delta/k_{\rm B}T_c$, and the wave vector in units of the primitive vectors of the reciprocal lattice for some CDW materials

Compound	$T_{\rm c}({\rm K})$	$2\Delta(\mathrm{eV})$	$2\Delta/k_{\rm B}T_{\rm c}$	$oldsymbol{q}_0$
KCP	189	0.12	7.41	(1/2, 1/2, 0.3)
NbS_3	340	0.38	13.3	(1/2, 0.298, 0)
NbSe ₃	145			(0, 0.243, 0)
	59	0.06	11.9	(1/2, 0.259, 1/2)
TaS_3 (monoclinic)	240			(0, 0.254, 0)
	160	0.16	11.9	(1/2, 0.245, 1/2)
TaS_3 (orthorhombic)	216	0.14	7.44	(1/2, 1/8, 1/4)
$(TaSe_4)_2I$	263	0.24	11.4	(0.05, 0.05, 0.085)
$(NbSe_4)_{10}I_3$	285	0.34	13.7	(0, 0, 0.487)
$\mathrm{K}_{0,3}\mathrm{MoO}_3$	183	0.079	5.03	(0, 0.748, 1/2)

It should not surprise us that the measured value of the dimensionless ratio $2\Delta/k_{\rm B}T_{\rm c}$ is much larger than the theoretical prediction in the mean-field approximation. As mentioned earlier the transition to the true ordered phase is a result of the interplay between diverging intrachain fluctuations and interchain couplings, and a reasonable estimate is to expect the transition at about a quarter of the mean-field value.

Note that charge-density waves have been discovered not only in quasione-dimensional systems. Several quasi-two-dimensional compounds as well as different polytypes of the layered transition-metal dichalcogenides of composition MX_2 with M = Nb, Ta, V and X = S, Se have a CDW ground state. Their Fermi surfaces have flat portions and the nesting property induces an instability against the formation of CDW.

33.5.2 Nonlinear and Oscillation Phenomena

Most of the electrons of the valence band are condensed into the density wave in these materials at low temperatures. Since impurities pin locally the phase, the density wave cannot slide freely. An external electric field induces only a weak current arising from normal electrons. If the pinning force can be overcome by a strong enough electric field, the density wave can start to slide. This occurs when the electric field exceeds a threshold value $E_{\rm T}$, and a highly nonlinear conductivity is measured, as displayed in Fig. 33.28. Similar non-ohmic behavior can be observed in SDW materials as well.



Fig. 33.28. (a) Normalized differential resistance of NbSe₃ as a function of the electric field at two temperatures [Reprinted with permission from R. M. Fleming, *Phys. Rev. B* 22, 5606 (1980). © (1980) by the American Physical Society]. (b) Normalized conductivity of several quasi-one-dimensional CDW materials vs. electric field normalized by the threshold field [P. Monceau, in *Electronic Properties of Inorganic Quasi-One-Dimensional Materials*, D. Reidel Publishing Company, Vol. II. p. 139 (1985)]

As the CDW is depinned above the threshold, the electric field drags it over a random arrangement of impurities, over a random (bumpy) potential. A fluctuating voltage called *broad-band noise* is expected to appear. However, the CDW itself is periodic, and it returns to the same position relative to the impurities whenever the CDW is shifted by one wavelength. This happens regularly in time with period $t_0 = \lambda/v_{\rm dr}$, where $v_{\rm dr}$ is the drift velocity of the density wave. Hence a characteristic frequency

$$\nu_0 = 1/t_0 = v_{\rm dr}/\lambda = v_{\rm dr}k_{\rm F}/\pi \tag{33.5.1}$$

and its harmonics appear in the motion of the CDW. This gives the so-called *narrow-band noise* in the Fourier spectrum of the voltage, which is superimposed on the broad-band noise. Such characteristic frequencies can indeed be observed experimentally as shown in Fig. 33.29.



Fig. 33.29. Fourier spectrum of the time-dependent voltage in NbSe₃ for increasing currents from zero to $I = 270 \,\mu\text{A}$. The frequency increases with current and a second frequency appears at higher currents [Reprinted with permission from R. M. Fleming and C. C. Grimes, *Phys. Rev. Lett.* 42, 1423 (1979). \bigcirc (1979) by the American Physical Society]

Since the current per chain is

$$j = -en_{\rm e}v_{\rm dr}\,,\qquad(33.5.2)$$

the ratio of the current density and the characteristic frequency is given by

$$\frac{j}{\nu_0} = -en_{\rm e}\lambda\,.\tag{33.5.3}$$

The particle density is related to the Fermi wave number via (33.4.56) at low temperatures, where all particles are assumed to be condensed into the CDW, and $\lambda = \pi/k_{\rm F}$. Hence

$$\frac{j}{\nu_0} = -2e\,. \tag{33.5.4}$$

It is independent of the current driven through the sample, in agreement with experiments. The number of electrons condensed into the CDW decreases with increasing temperature, and this ratio decreases accordingly, but remains independent of the current.

An interesting phenomenon can be observed if the current–voltage characteristics are measured on samples exposed to a radio-frequency field. As seen in Fig. 33.30, steps appear in the characteristics at integer multiples of the current where the internal characteristic frequency ν_0 is equal to the frequency of the radio-frequency field, $\nu_{\rm rf}$, that is for all harmonics of the external field, when

$$\nu_0 = p\nu_{\rm rf} \,. \tag{33.5.5}$$



Fig. 33.30. Current–voltage characteristics of NbSe₃ at 42 K when a radiofrequency field of amplitude V_{ac} is applied at frequency 100 MHz [Reprinted with permission from A. Zettl and G. Grüner, *Phys. Rev. B* 29, 755 (1984). \bigcirc (1984) by the American Physical Society]

These steps are the analogs of the Shapiro steps exhibited in Fig. 26.29, since the equations describing the motion of the CDW are formally similar to the equations describing the behavior of Josephson junctions.¹⁴

A new feature appears in the current–voltage characteristics of CDW materials compared to similar measurement in Josephson junctions due to the internal structure of the CDW. As seen in Fig. 33.31, sharp peaks in the differential resistance (steps in the current–voltage characteristics) appear not only at higher harmonics of the frequency of the radio-frequency field, but at subharmonics as well, where

$$q\nu_0 = p\nu_{\rm rf},$$
 (33.5.6)

that is when any harmonic of the internal frequency is equal to any harmonic of the external field. The values p/q are also indicated in the figure.



Fig. 33.31. Differential resistance of NbSe₃ with and without an applied radiofrequency voltage at 25 MHz. The numbers indicate the various subharmonic steps [Reprinted with permission from S. E. Brown, G. Mozurkewich, and G. Grüner, *Phys. Rev. Lett.* **52**, 2277 (1984). \bigcirc (1984) by the American Physical Society]

¹⁴ The electric field plays the role in the motion of the CDW that is played by the current in a Josephson junction. Current oscillations in the current-carrying CDW with $j/\nu_0 = 2e$ per chain corresponds to the AC Josephson effect with voltage–current relation $\nu/V = 2e/h$ [see (26.5.26)].

Further Reading

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Microscopic Theory of Superconductivity

Superconductivity was introduced in Chapter 26 of the previous volume. It was shown there that the unusual electrodynamic properties of superconductors are accompanied by anomalous thermodynamic behavior. After the presentation of some experimental results a phenomenological description was given using the London equations and the Ginzburg–Landau equations. Now that we have acquainted ourselves with the microscopic theory of some broken-symmetry phases, we return to the theory of superconductivity and attempt to give a microscopic description of this particular state of matter.

Usually, superconductivity is observed at low temperatures, at much lower temperatures than the typical critical temperature of magnetic ordering or the typical transition temperature to density-wave states. A thermal energy on the order of a few millielectron volts can destroy it. This indicates that the interaction responsible for this phenomenon is much weaker than the Coulomb repulsion or the exchange which are the dominant interactions in electronic systems. Such considerations independently led H. FRÖHLICH and J. BARDEEN in 1950 to the idea that electron-phonon interactions may be responsible for superconductivity. The discovery of the isotope effect in the same year made clear that the ions and their vibrations play a nonnegligible role. In fact, the direct interaction between electrons is irrelevant in a large class of superconductors. Nonetheless, we treat the microscopic theory of superconductivity in this volume, after the broken-symmetry phases caused by the electronelectron interaction, since their theoretical descriptions are formally rather similar, and many of the calculational procedures and results learned there can be taken over once we know how to characterize the superconducting order.

34.1 Instability Against Pair Formation

We have seen in Chapter 23 that the process in which a phonon is emitted by an electron and the same phonon absorbed by another electron can be interpreted as an effective interaction between the two electrons. We have also shown that this phonon-mediated interaction is attractive when both electrons are near the Fermi surface, within a range of width $2\hbar\omega_{\rm D}$ determined by the phonon spectrum. Pictorially we could say that the first electron deforms and polarizes the lattice, and this polarization attracts the other electron. If this attraction is strong enough, it can overcome the Coulomb repulsion between the electrons. The effects of electrons far from the Fermi energy, outside the range of width $2\hbar\omega_{\rm D}$, where the interaction is repulsive, can be eliminated by a renormalization transformation. We will therefore assume in what follows that the interaction between electrons lying near the Fermi energy is attractive, and the contributions coming from electrons lying further away can be neglected.

These considerations are valid for conventional superconductors. Attraction between electrons can, however, be generated by other mechanisms as well, e.g., by interactions of magnetic origin. Superconductivity seems to compete with magnetic ordering in high-temperature superconductors and the "normal" state above the critical temperature often does not exhibit normal Fermi-liquid behavior. Since magnetic ordering is due to exchange and thus due to the Coulomb interaction between electrons, it is conceivable that the anomalous properties of high- $T_{\rm c}$ materials are caused by interactions acting within the electron system. The theoretical treatment of this competition is made extremely difficult by the complicated band structure. Although the origin of the superconductivity and the nature of the interactions responsible for it in these materials is still a subject of intensive research since the discovery of high-temperature superconductors, we cannot go into these details. In what follows, an effective attraction between the electrons will be simply assumed without specifying its origin. Nevertheless, many of our subsequent results can be applied not only to the case when the interaction is mediated by phonons, but in part more generally, for other mechanisms as well.

34.1.1 Cooper Pairs

An important step toward the microscopic theory of superconductivity was made by L. N. COOPER in 1956, when he demonstrated that a bound state is formed between a pair of electrons moving through the background of a filled Fermi sea if the pair potential between them is attractive. The bound electron pair is called a *Cooper pair*. The presence of the Fermi sea is essential and the electrons filling it play an active role in the formation of the bound state.

Consider a Fermi sea in its ground state and add two electrons to it. Neglecting the interaction between the electrons for the moment the Hamiltonian of the system is

$$\mathcal{H}_{0} = \mathcal{H}_{\rm FS} + \frac{1}{2m_{\rm e}} \left[\left(\frac{\hbar}{\rm i} \boldsymbol{\nabla}_{1}\right)^{2} + \left(\frac{\hbar}{\rm i} \boldsymbol{\nabla}_{2}\right)^{2} \right], \qquad (34.1.1)$$

where \mathcal{H}_{FS} contains the kinetic energy of the electrons in the Fermi sea. If the extra electrons are in plane-wave states with wave vectors k_1 and k_2 , the wavefunction of the full system is

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{V} \mathrm{e}^{\mathrm{i}\boldsymbol{k}_1 \cdot \boldsymbol{r}_1} \mathrm{e}^{\mathrm{i}\boldsymbol{k}_2 \cdot \boldsymbol{r}_2} \Psi_{\mathrm{FS}}, \qquad (34.1.2)$$

where $\Phi_{\rm FS}$ denotes the filled Fermi sea. This form does not satisfy the antisymmetry requirement. It is expected that the lowest energy state be symmetric in the spatial variables, because then the wavefunctions of the electrons can overlap and the particles can take advantage of the attraction to lower their energy. The spin part of the wavefunction is then antisymmetric and the spins of the two electrons form a spin singlet.¹ The appropriate wavefunction is

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2} \left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2 \right] \frac{1}{V} \left(e^{i\boldsymbol{k}_1 \cdot \boldsymbol{r}_1} e^{i\boldsymbol{k}_2 \cdot \boldsymbol{r}_2} + e^{i\boldsymbol{k}_2 \cdot \boldsymbol{r}_1} e^{i\boldsymbol{k}_1 \cdot \boldsymbol{r}_2} \right) \Psi_{\rm FS} \,.$$
(34.1.3)

The unperturbed energy of this state is $E_{\rm FS} + \varepsilon_{k_1} + \varepsilon_{k_2}$.

When the interaction between the electrons is switched on, the two extra electrons can be scattered to states with wave vectors $\mathbf{k}_1 + \mathbf{q}$ and $\mathbf{k}_2 - \mathbf{q}$. The wavefunction of the perturbed state could be looked for as a linear combination of such states. Instead of trying to solve this problem in this general form, we will consider a state with total momentum zero, that is $\mathbf{k}_1 = -\mathbf{k}_2 \equiv \mathbf{k}$, as this is expected to have lower energy than states with finite momentum. The wavefunction is then chosen in the form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2} \left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2 \right] \frac{1}{V} \sum_{\boldsymbol{k}} \alpha_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{r}_1 - \boldsymbol{r}_2)} \Psi_{\mathrm{FS}} \qquad (34.1.4)$$

with $\alpha_{\mathbf{k}} = \alpha_{-\mathbf{k}}^*$ to satisfy the symmetry requirement, and the summation over the wave vector runs over $|\mathbf{k}| > k_{\rm F}$, since all states inside the Fermi sphere are filled. The coefficients $\alpha_{\mathbf{k}}$ and the energy have to be determined from the Schrödinger equation in the presence of a two-particle potential $U(\mathbf{r}_1 - \mathbf{r}_2)$ between the electrons.

The problem is easier to solve if reformulated in second quantization. The wavefunction is written in the form

$$|\Psi\rangle = \sum_{\mathbf{k}'} \alpha_{\mathbf{k}'} c^{\dagger}_{\mathbf{k}'\uparrow} c^{\dagger}_{-\mathbf{k}'\downarrow} |\Psi_{\rm FS}\rangle, \qquad (34.1.5)$$

and the Schrödinger equation to be solved is

$$\left[\mathcal{H}_{0} + \frac{1}{2V} \sum_{\boldsymbol{q}} \sum_{\boldsymbol{k}_{1} \boldsymbol{k}_{2} \sigma \sigma'} U(\boldsymbol{k}_{1}, \boldsymbol{k}_{2}, \boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}_{1} + \boldsymbol{q} \sigma} c^{\dagger}_{\boldsymbol{k}_{2} - \boldsymbol{q} \sigma'} c_{\boldsymbol{k}_{2} \sigma'} c_{\boldsymbol{k}_{1} \sigma}\right] |\Psi\rangle = (E_{\mathrm{FS}} + \varepsilon) |\Psi\rangle,$$

$$(34.1.6)$$

where ε is the change in the energy of the Fermi system owing to the two extra particles. Multiplying this equation by the adjoint of $c^{\dagger}_{\mathbf{k}\uparrow}c^{\dagger}_{-\mathbf{k}\downarrow}|\Psi_{\rm FS}\rangle$ from the left we get

¹ A pair with different symmetry should be found in the superfluid phase of ³He. Since the helium atoms cannot overlap, the spatial part of the wavefunction has to be antisymmetric and the spin part is a symmetric triplet.

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$$(2\varepsilon_{\boldsymbol{k}} - \varepsilon)\alpha_{\boldsymbol{k}} + \frac{1}{V}\sum_{\boldsymbol{k}'} U(\boldsymbol{k}', -\boldsymbol{k}', \boldsymbol{k} - \boldsymbol{k}')\alpha_{\boldsymbol{k}'} = 0.$$
(34.1.7)

To comply with the convention in the superconductivity literature, the pair potential will be denoted by V and the volume of the sample by Ω . In what follows the notation $V_{kk'}$ will be used for the potential when a singlet pair with momenta k' and -k' is scattered into a pair state with momenta k and -k.

For the sake of simplicity we assume, as was mentioned already, that the interaction matrix element is negative and constant for electrons lying in a range of width $2\hbar\omega_{\rm D}$ about the Fermi energy and vanishes otherwise, that is for

$$V_{\boldsymbol{k}\boldsymbol{k}'} = \begin{cases} -V_0 & \text{for } \varepsilon_{\rm F} - \hbar\omega_{\rm D} < \varepsilon_{\boldsymbol{k}}, \, \varepsilon_{\boldsymbol{k}'} < \varepsilon_{\rm F} + \hbar\omega_{\rm D}, \\ 0 & \text{otherwise.} \end{cases}$$
(34.1.8)

With this assumption, taking into account that the extra electrons are initially above the Fermi energy and therefore they can be scattered only into states above the Fermi energy, the equation for the coefficients α_k takes the form

$$\alpha_{\mathbf{k}} = \frac{V_0}{2\varepsilon_{\mathbf{k}} - \varepsilon} \frac{1}{\Omega} \sum_{\mathbf{k}'} \alpha_{\mathbf{k}'}$$
(34.1.9)

with \mathbf{k}' restricted to the range $\varepsilon_{\rm F} < \varepsilon_{\mathbf{k}'} < \varepsilon_{\rm F} + \hbar \omega_{\rm D}$.

Summing both sides over k a solution with nonvanishing α_k exists if the self-consistency condition

$$1 = \frac{1}{\Omega} \sum_{\boldsymbol{k}} \frac{V_0}{2\varepsilon_{\boldsymbol{k}} - \varepsilon}, \qquad \varepsilon_{\rm F} < \varepsilon_{\boldsymbol{k}} < \varepsilon_{\rm F} + \hbar\omega_{\rm D} \qquad (34.1.10)$$

is satisfied. The energy eigenvalues can be obtained from the graphical solution used several times already, e.g., in Chapter 20, where the energy of impurity levels was calculated, or in the previous chapter, when the spectrum of collective excitations was determined. When the interaction is attractive, $V_0 > 0$, there is a solution with energy below $2\varepsilon_{\rm F}$, which means that there is a bound state of the two electrons for arbitrarily weak attractive interaction. The two electrons form a bound Cooper pair.

When the sum over k in (34.1.10) is replaced by an integral over energy, this equation is transformed into

$$1 = V_0 \int_{\varepsilon_{\rm F}}^{\varepsilon_{\rm F} + \hbar\omega_{\rm D}} \frac{1}{2} \rho(\varepsilon') \frac{1}{2\varepsilon' - \varepsilon} \,\mathrm{d}\varepsilon' \,. \tag{34.1.11}$$

The factor 1/2 appeared since $\rho(\varepsilon)$ is the full density of states whereas the density of states for one spin orientation is needed. An analytic expression can

be obtained for the binding energy if the density of states can be approximated by a constant in the energy range of the integration. Taking the density of states at the Fermi energy we get

$$\frac{2}{V_0\rho(\varepsilon_{\rm F})} = \int_{\varepsilon_{\rm F}}^{\varepsilon_{\rm F}+\hbar\omega_{\rm D}} \frac{1}{2\varepsilon'-\varepsilon} \,\mathrm{d}\varepsilon' = \frac{1}{2}\ln\frac{2\varepsilon_{\rm F}+2\hbar\omega_{\rm D}-\varepsilon}{2\varepsilon_{\rm F}-\varepsilon} \,. \tag{34.1.12}$$

The lowest energy the two extra free particles could have is $2\varepsilon_{\rm F}$. The binding energy Δ is therefore defined via $\varepsilon = 2\varepsilon_{\rm F} - \Delta$. Assuming that it is much smaller than the relevant bandwidth $2\hbar\omega_{\rm D}$ – this will be checked afterwards – we have

$$\frac{2}{V_0\rho(\varepsilon_{\rm F})} = \frac{1}{2}\ln\frac{2\hbar\omega_{\rm D}}{\Delta},\qquad(34.1.13)$$

from which

$$\Delta = 2\hbar\omega_{\rm D} \mathrm{e}^{-4/V_0\rho(\varepsilon_{\rm F})}.$$
(34.1.14)

Owing to the exponential factor this binding energy is indeed much smaller than $2\hbar\omega_{\rm D}$ in the weak-coupling limit, when $V_0\rho(\varepsilon_{\rm F}) \ll 1$.

Note that the approximation to replace $V_{kk'}$ by a constant is not always admissible. The dependence on the angle ξ between k and k' might be relevant. The dependence on the length of k and k' is much less important since the wave vectors of the electrons participating in the scattering processes have to be in the neighborhood of the Fermi surface. The ξ dependence of the potential can be expanded in Legendre polynomials or – if the polar and azimuthal angles θ, φ and θ', φ' of the unit vectors in the directions of k and k' are used – in terms of the spherical harmonics applying (C.4.36):

$$V_{\boldsymbol{k}\boldsymbol{k}'} = \sum_{l=0}^{\infty} V_l \sum_{m=-l}^{l} Y_l^m(\theta,\varphi) Y_l^{m*}(\theta',\varphi') . \qquad (34.1.15)$$

With this form for $V_{kk'}$ the coefficients α_k satisfy the equation

$$(2\varepsilon_{\boldsymbol{k}} - \varepsilon)\alpha_{\boldsymbol{k}} - \frac{1}{\Omega}\sum_{\boldsymbol{k}'}\sum_{l=0}^{\infty} V_l \sum_{m=-l}^{l} Y_l^m(\theta, \varphi) Y_l^{m*}(\theta', \varphi')\alpha_{\boldsymbol{k}'} = 0.$$
(34.1.16)

It is readily seen by expanding α_{k} in spherical harmonics in the form

$$\alpha_{k} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \alpha_{lm}(k) Y_{l}^{m}(\theta, \varphi)$$
(34.1.17)

and using the orthogonality relations that the amplitudes V_l do not mix for different l values, and a self-consistency condition analogous to (34.1.11) is obtained for each l: 398 34 Microscopic Theory of Superconductivity

$$1 = V_l \int_{\varepsilon_{\rm F}}^{\varepsilon_{\rm F} + \hbar\omega_{\rm D}} \frac{1}{2} \rho(\varepsilon') \frac{1}{2\varepsilon' - \varepsilon} \,\mathrm{d}\varepsilon' \,. \tag{34.1.18}$$

The binding energy of the pairs in channel l is given by

$$\Delta_l = 2\hbar\omega_{\rm D} \mathrm{e}^{-4/V_l\rho(\varepsilon_{\rm F})} \,. \tag{34.1.19}$$

The Cooper pairs with l = 0, 1, 2, ... have *s*-, *p*-, *d*-wave symmetries. The l dependence of the binding energy implies that pairs of different symmetry appear at different temperatures. According to the experimental findings, Cooper pairs with *s*-wave symmetry are found in the vast majority of superconductors, perhaps exclusively in the superconductors known before the 80s of the last century. For this reason and for the sake of simplicity, pairs with *s*-wave symmetry will be assumed in the bulk of this chapter. We will return to unconventional superconductors at the end of the chapter.

In the previous calculation we considered the formation of a single Cooper pair and determined its binding energy. For obtaining the bound state it was necessary to have a filled Fermi sea which constrained the possible final states of the scattered electrons. In fact, if the interaction is attractive between the electrons, the pairs are formed not individually, but the entire Fermi sea becomes unstable against their formation below a critical temperature T_c . The electron states are rearranged and a completely novel state appears with properties that differ drastically from the "normal-state" properties of the Fermi system. The nonanalyticity of the binding energy of the Cooper pairs as a function of the interaction potential indicates that this state, the superconducting state, cannot be obtained from the noninteracting Fermi sea in perturbation theory.

34.1.2 Instability at Finite Temperatures

Before going on to the problem of the superconducting ground state, where all electrons are bound into pairs, we consider now the interacting electron gas at finite temperatures, in the normal phase. Adding two electrons to the Fermi gas right on the Fermi surface with opposite momenta and spins, we will calculate the temperature where the bound state first appears.

Assuming that the Fermi system is in the state $|\Psi_n\rangle$ which occurs with probability p_n in thermodynamic equilibrium we take the state with two extra electrons,

$$|\Psi_{\boldsymbol{k}}\rangle = c^{\dagger}_{\boldsymbol{k}\uparrow}c^{\dagger}_{-\boldsymbol{k}\downarrow}|\Psi_{n}\rangle, \qquad (34.1.20)$$

as the initial state. The energy of this state is $E_{\mathbf{k}} = E_n + 2\varepsilon_{\mathrm{F}}$. It can be scattered owing to the interaction into the state

$$|\Psi_{\boldsymbol{k}'}\rangle = c^{\dagger}_{\boldsymbol{k}'\uparrow}c^{\dagger}_{-\boldsymbol{k}'\downarrow}|\Psi_n\rangle, \qquad (34.1.21)$$

where the wave vectors of the two electrons are changed from \mathbf{k} and $-\mathbf{k}$ to \mathbf{k}' and $-\mathbf{k}'$. The scattered electrons have to be on the Fermi surface to conserve energy. To calculate the strength of this scattering process we consider the matrix elements of the scattering matrix defined via

$$T(z) = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{int}} \frac{1}{z - \mathcal{H}_0} T(z), \qquad (34.1.22)$$

where \mathcal{H}_{int} is the interaction Hamiltonian. If this equation is iterated,

$$T(z) = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{int}} \frac{1}{z - \mathcal{H}_0} \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{int}} \frac{1}{z - \mathcal{H}_0} \mathcal{H}_{\text{int}} \frac{1}{z - \mathcal{H}_0} \mathcal{H}_{\text{int}} + \cdots$$
(34.1.23)

Since we are considering the scattering of electrons with opposite spins, the most important processes are expected to be those in which electrons of opposite spins are scattered in every elementary process. We will therefore assume that the interaction Hamiltonian can be written in second quantization in the form

$$\mathcal{H}_{\text{int}} = -\frac{V_0}{\Omega} \sum_{\boldsymbol{k}_1 \boldsymbol{k}_2 \boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}_1 + \boldsymbol{q}\uparrow} c^{\dagger}_{\boldsymbol{k}_2 - \boldsymbol{q}\downarrow} c_{\boldsymbol{k}_2 \downarrow} c_{\boldsymbol{k}_1\uparrow}, \qquad (34.1.24)$$

where a constant amplitude is taken for the potential according to (34.1.8).

To first order in the interaction we find

$$\langle \Psi_{\boldsymbol{k}'} | \mathcal{H}_{\text{int}} | \Psi_{\boldsymbol{k}} \rangle = \langle \Psi_n | c_{-\boldsymbol{k}' \downarrow} c_{\boldsymbol{k}' \uparrow} \mathcal{H}_{\text{int}} c_{\boldsymbol{k} \uparrow}^{\dagger} c_{-\boldsymbol{k} \downarrow}^{\dagger} | \Psi_n \rangle = -V_0 / \Omega , \qquad (34.1.25)$$

since the only nonvanishing contribution is given by the term where $k_1 = k$, $k_2 = -k$, and q = k' - k.

The second-order matrix element is

$$\begin{split} \langle \Psi_{\mathbf{k}'} | \mathcal{H}_{\text{int}} \frac{1}{z - \mathcal{H}_{0}} \mathcal{H}_{\text{int}} | \Psi_{\mathbf{k}} \rangle \\ &= \langle \Psi_{n} | c_{-\mathbf{k}' \downarrow} c_{\mathbf{k}' \uparrow} \mathcal{H}_{\text{int}} \frac{1}{z - \mathcal{H}_{0}} \mathcal{H}_{\text{int}} c_{\mathbf{k} \uparrow}^{\dagger} c_{-\mathbf{k} \downarrow}^{\dagger} | \Psi_{n} \rangle \qquad (34.1.26) \\ &= \langle \Psi_{n} | c_{-\mathbf{k}' \downarrow} c_{\mathbf{k}' \uparrow} \left(-\frac{V_{0}}{\Omega} \right) \sum_{\mathbf{k}_{1} \mathbf{k}_{2} \mathbf{q}} c_{\mathbf{k}_{1} + \mathbf{q} \uparrow}^{\dagger} c_{\mathbf{k}_{2} - \mathbf{q} \downarrow}^{\dagger} c_{\mathbf{k}_{2} \downarrow} c_{\mathbf{k}_{1} \uparrow} \frac{1}{z - \mathcal{H}_{0}} \\ &\times \left(-\frac{V_{0}}{\Omega} \right) \sum_{\mathbf{k}_{3} \mathbf{k}_{4} \mathbf{q}'} c_{\mathbf{k}_{3} + \mathbf{q}' \uparrow}^{\dagger} c_{\mathbf{k}_{4} - \mathbf{q}' \downarrow}^{\dagger} c_{\mathbf{k}_{4} \downarrow} c_{\mathbf{k}_{3} \uparrow} c_{\mathbf{k} \uparrow}^{\dagger} c_{-\mathbf{k} \downarrow}^{\dagger} | \Psi_{n} \rangle. \end{split}$$

The scattering processes contributing to this matrix element can be visualized by diagrams. The two lines entering the diagram from the right represent the two electrons added to the system and the scattering processes are drawn from right to left as they stand in the matrix element. The two lines arriving at the left represent the two electrons in the final state. There are two second-order processes displayed in Fig. 34.1.

In one possible process the two electrons with $\mathbf{k} \uparrow$ and $-\mathbf{k} \downarrow$ are scattered into an intermediate state containing the pair $(\mathbf{k}'' \uparrow, -\mathbf{k}'' \downarrow)$. This happens



Fig. 34.1. Second-order scattering processes with electron pair and hole pair intermediate states

when $\mathbf{k}_3 = \mathbf{k}$, $\mathbf{k}_4 = -\mathbf{k}$, and $\mathbf{q}' = \mathbf{k}'' - \mathbf{k}_3 = \mathbf{k}'' - \mathbf{k}$. The energy of the intermediate state is $E_n + 2\varepsilon_{\mathbf{k}''}$. This pair is then scattered in the next step into the pair state $(\mathbf{k}'\uparrow, -\mathbf{k}'\downarrow)$. For this to happen, the wave vectors of the electrons in the second process have to satisfy the relations $\mathbf{k}_1 = \mathbf{k}'', \mathbf{k}_2 = -\mathbf{k}''$, and $\mathbf{q} = \mathbf{k}' - \mathbf{k}''$. The role of the Fermi sea is to restrict the possible intermediate states, as this scattering process can take place only if the pair with $(\mathbf{k}''\uparrow, -\mathbf{k}''\downarrow)$ is not present initially in the state $|\Psi_n\rangle$. Since the electron system is assumed to be in thermal equilibrium, a thermal average of the matrix elements between the states $|\Psi_n\rangle$ has to be taken. This condition gives a factor $[1 - f_0(\varepsilon_{\mathbf{k}''})][1 - f_0(\varepsilon_{-\mathbf{k}''})]$ as the weight of this process.

If the energy variable z is identified with the energy of the initial state, $E_{\mathbf{k}}$, the energy difference $-(2\varepsilon_{\mathbf{k}''} - 2\varepsilon_{\mathrm{F}})$ appears in the denominator of the *T*-matrix and the contribution of this process is

$$\left(\frac{V_0}{\Omega}\right)^2 \sum_{\boldsymbol{k}''} \frac{\left[1 - f_0(\varepsilon_{\boldsymbol{k}''})\right]^2}{2\varepsilon_{\rm F} - 2\varepsilon_{\boldsymbol{k}''}} \,. \tag{34.1.27}$$

Looking now at the other scattering process, nothing happens with the two extra electrons in the first interaction. Two electrons with $\mathbf{k}''\uparrow$ and $-\mathbf{k}''\downarrow$ are scattered from the Fermi sea into the final states $\mathbf{k}'\uparrow$ and $-\mathbf{k}'\downarrow$ leaving two holes behind. The intermediate state has four electrons and two holes in addition to the Fermi sea. The energy of this state is

$$E_n + \varepsilon_{\mathbf{k}} + \varepsilon_{-\mathbf{k}} + \varepsilon_{\mathbf{k}'} + \varepsilon_{-\mathbf{k}'} - \varepsilon_{\mathbf{k}''} - \varepsilon_{-\mathbf{k}''} = E_n + 4\varepsilon_{\mathrm{F}} - 2\varepsilon_{\mathbf{k}''}, \quad (34.1.28)$$

and the energy denominator is $2\varepsilon_{\mathbf{k}''} - 2\varepsilon_{\rm F}$. Creation of holes is possible in the intermediate state if the states $\mathbf{k}''\uparrow$ and $-\mathbf{k}''\downarrow$ were initially occupied, which gives a factor $[f_0(\varepsilon_{\mathbf{k}''})]^2$. These holes are then filled in the next step when the initial extra electrons are scattered into these states. The contribution of this process is

$$\left(\frac{V_0}{\Omega}\right)^2 \sum_{\mathbf{k}''} \frac{\left[f_0(\varepsilon_{\mathbf{k}''})\right]^2}{2\varepsilon_{\mathbf{k}''} - 2\varepsilon_{\rm F}}.$$
(34.1.29)

Adding up the contributions of the second-order processes we have

$$-\left(\frac{V_0}{\Omega}\right)^2 \sum_{\boldsymbol{k}''} \frac{1-2f_0(\varepsilon_{\boldsymbol{k}''})}{2\varepsilon_{\boldsymbol{k}''}-2\varepsilon_{\rm F}},\qquad(34.1.30)$$

which together with the first-order contribution gives

$$\langle T \rangle = -\frac{V_0}{\Omega} - \left(\frac{V_0}{\Omega}\right)^2 \sum_{\boldsymbol{k}''} \frac{1 - 2f_0(\varepsilon_{\boldsymbol{k}''})}{2\varepsilon_{\boldsymbol{k}''} - 2\varepsilon_{\rm F}}.$$
 (34.1.31)

The pair $(\mathbf{k}''\uparrow, -\mathbf{k}''\downarrow)$ is present in the intermediate state either as an electron pair or as a hole pair. We will see below that the sum appearing in the second-order contribution is logarithmically singular, proportional to $\ln T$, at low temperatures.² We expect that the most important contributions to the *T*-matrix in higher orders of perturbation theory come from similar processes, in which electron pairs and hole pairs are present in the intermediate states. Such third-order processes are depicted in Fig. 34.2.



Fig. 34.2. Third-order scattering processes of two electrons with electron pair and hole pair intermediate states

The contributions of these processes form a geometric progression which can be summed up to yield

$$\langle T \rangle = \frac{-V_0/\Omega}{1 - \frac{V_0}{\Omega} \sum_{\mathbf{k}''} \frac{1 - 2f_0(\varepsilon_{\mathbf{k}''})}{2\varepsilon_{\mathbf{k}''} - 2\varepsilon_{\rm F}}} \,. \tag{34.1.32}$$

The denominator is always less than unity in the attractive $(V_0 > 0)$ case; the higher order corrections enhance the strength of the *T*-matrix compared to the bare potential. Similar enhancement is found when the temperature is lowered

² At zero temperature electrons with energy $\xi_{k} = \varepsilon_{k} - \varepsilon_{F}$ contribute a term to the *T*-matrix which is proportional to $\ln \xi_{k}$. It diverges logarithmically as the energy of the scattered electrons approaches the Fermi energy.

starting from high temperatures. Since the sum diverges at zero temperature, the thermal average of the scattering matrix over the configurations of the Fermi sea becomes infinitely large at the temperature where

$$1 = \frac{V_0}{\Omega} \sum_{\boldsymbol{k}''} \frac{1 - 2f_0(\varepsilon_{\boldsymbol{k}''})}{2\varepsilon_{\boldsymbol{k}''} - 2\varepsilon_{\rm F}}, \qquad (34.1.33)$$

and the electron system becomes unstable against the formation of pairs.

To calculate the critical temperature of this instability we rewrite the right-hand side in terms of the quantity $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \varepsilon_{\mathrm{F}}$ using the relation

$$1 - 2f_0(\xi_k) = 1 - \frac{2}{e^{\xi_k/k_B T} + 1} = \tanh \frac{\xi_k}{2k_B T}.$$
 (34.1.34)

The equation determining the critical temperature is then

$$1 = \frac{V_0}{\Omega} \sum_{k} \frac{1}{2\xi_k} \tanh \frac{\xi_k}{2k_{\rm B}T_{\rm c}} \,. \tag{34.1.35}$$

Replacing the sum by an integral and using the fact that the electrons are assumed to interact in an energy range of width $2\hbar\omega_{\rm D}$ we have

$$1 = \frac{1}{2} V_0 \int_{-\hbar\omega_{\rm D}}^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{2\xi} \,\rho(\xi) \,\tanh\frac{\xi}{2k_{\rm B}T_{\rm c}} \,.$$
(34.1.36)

If the density of states is approximated by its value at the Fermi energy, $\rho(\varepsilon_{\rm F})$, the even parity of the integrand allows us to transform this equation into

$$1 = \frac{1}{2} V_0 \rho(\varepsilon_{\rm F}) \int_0^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{\xi} \tanh \frac{\xi}{2k_{\rm B}T_{\rm c}} \,. \tag{34.1.37}$$

Introducing the variable $x = \frac{\xi}{2k_{\rm B}T_{\rm c}}$ gives

$$1 = \frac{1}{2} V_0 \rho(\varepsilon_{\rm F}) \int_{0}^{\frac{\hbar\omega_{\rm D}}{2k_{\rm B}T_{\rm c}}} \frac{\mathrm{d}x}{x} \tanh x \,. \tag{34.1.38}$$

This integral has been evaluated in the previous chapter when the critical temperature of the spin-density-wave state was determined. We can use the result derived there, since $k_{\rm B}T_{\rm c} \ll \hbar\omega_{\rm D}$, and we have

$$1 = \frac{1}{2} V_0 \rho(\varepsilon_{\rm F}) \left(\ln \frac{\hbar \omega_{\rm D}}{2k_{\rm B}T_{\rm c}} - \int_0^{\frac{\hbar \omega_{\rm D}}{2k_{\rm B}T_{\rm c}}} \frac{\ln x}{\cosh^2 x} \,\mathrm{d}x \right)$$

$$= \frac{1}{2} V_0 \rho(\varepsilon_{\rm F}) \left(\ln \frac{\hbar \omega_{\rm D}}{2k_{\rm B}T_{\rm c}} + \ln \frac{4\mathrm{e}^{\gamma}}{\pi} \right).$$
(34.1.39)

Algebraic manipulations lead to

$$k_{\rm B}T_{\rm c} = \frac{{\rm e}^{\gamma}}{\pi} 2\hbar\omega_{\rm D} \exp\left(-\frac{2}{V_0\rho(\varepsilon_{\rm F})}\right)$$
(34.1.40)

for the instability temperature of the electron system. Formally it is similar to the expression obtained for density-wave systems in the mean-field approximation. There is, however, an important difference concerning its accuracy, as will be shown below.

Thus far we considered a special class of processes in which an electron pair of total momentum zero is scattered into another pair state with total momentum zero in each intermediate step, although the momenta of the electrons in the pair are different before and after the scattering. We neglected those higher order processes in which only one member of the pair is scattered at a given time. Such scattering events are displayed in Fig. 34.3.



Fig. 34.3. Second-order scattering processes with electron-hole pairs in the intermediate state

The energy denominators and the probability of finding empty or occupied states can easily be given. The contribution of the first process to the T-matrix is

$$-\left(\frac{V_0}{\Omega}\right)^2 \sum_{\mathbf{k}^{\prime\prime}} \frac{\left[1 - f_0(\varepsilon_{\mathbf{k}+\mathbf{k}^{\prime}+\mathbf{k}^{\prime\prime}})\right] f_0(\varepsilon_{\mathbf{k}^{\prime\prime}})}{\varepsilon_{\mathbf{k}^{\prime\prime}} - \varepsilon_{\mathbf{k}+\mathbf{k}^{\prime}+\mathbf{k}^{\prime\prime}}},$$
(34.1.41)

and the second process gives

$$-\left(\frac{V_0}{\Omega}\right)^2 \sum_{\mathbf{k}^{\prime\prime}} \frac{\left[1 - f_0(\varepsilon_{\mathbf{k}^{\prime\prime}})\right] f_0(\varepsilon_{\mathbf{k}+\mathbf{k}^{\prime}+\mathbf{k}^{\prime\prime}})}{\varepsilon_{\mathbf{k}+\mathbf{k}^{\prime}+\mathbf{k}^{\prime\prime}} - \varepsilon_{\mathbf{k}^{\prime\prime}}}.$$
(34.1.42)

Adding up the two contributions we can recognize in

$$-\left(\frac{V_0}{\Omega}\right)^2 \sum_{\boldsymbol{k}^{\prime\prime}} \frac{f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{k}^{\prime}+\boldsymbol{k}^{\prime\prime}}) - f_0(\varepsilon_{\boldsymbol{k}^{\prime\prime}})}{\varepsilon_{\boldsymbol{k}+\boldsymbol{k}^{\prime}+\boldsymbol{k}^{\prime\prime}} - \varepsilon_{\boldsymbol{k}^{\prime\prime}}}$$
(34.1.43)

the expression appearing in the Lindhard form of the dielectric function. This is not surprising since an electron–hole pair is present in the intermediate state just as in the polarization bubble. The contribution of these processes is a smooth function of $\mathbf{k} + \mathbf{k}'$ contrary to the logarithmically singular contribution of the processes discussed earlier. That is the reason why it suffices to consider only the processes with electron pair intermediate states.

The situation is different in one-dimensional systems. The instability against the formation of density waves is caused by the logarithmic singularity of the propagation of an electron-hole pair with total momentum $2k_{\rm F}$. The polarization bubble and the susceptibility display precisely the same type of logarithmic singularity at $q = 2k_{\rm F}$ as the Cooper channel does for total momentum zero. Note that the singularity in the Cooper channel is in fact independent of the dimension, while the electron-hole channel is singular only in one dimension. That is why it was not sufficient to treat the density waves of one-dimensional systems in the RPA, and that is why the role of fluctuations had to be considered. Similarly, a mean-field treatment of superconductivity would give unsatisfactory results in one dimension.

34.2 The Bardeen–Cooper–Schrieffer Theory

The discovery of the instability of the electron gas against the formation of Cooper pairs was an important ingredient that allowed J. BARDEEN, L. N. COOPER, and J. R. SCHRIEFFER³ to elaborate the microscopic theory of superconductivity by 1957. From the initials of their names, it is known as the BCS theory.

34.2.1 BCS Hamiltonian and BCS Ground State

The effective electron–electron interaction mediated by phonons was given in (23.3.51). The BCS theory uses a simplified form for this attractive interaction. Assuming that singlet Cooper pairs play the dominant role, we consider only those processes in which singlet pairs with total momentum zero are scattered into singlet pairs. The reduced BCS Hamiltonian acting in this restricted Hilbert space of the q = 0 singlet pair states has the form

$$\mathcal{H}_{BCS} = \sum_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}} \left(c_{\boldsymbol{k}\uparrow}^{\dagger} c_{\boldsymbol{k}\uparrow} + c_{-\boldsymbol{k}\downarrow}^{\dagger} c_{-\boldsymbol{k}\downarrow} \right) + \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} c_{\boldsymbol{k}\uparrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger} c_{\boldsymbol{k}\uparrow\uparrow}^{\dagger} . \quad (34.2.1)$$

The restriction to singlet pairs is not admissible in the superfluid phase of 3 He. Moreover, there are experimental indications that some unconventional superconductors have triplet pairs. We will return to their theoretical treatment later on.

As mentioned earlier, the interaction $V_{kk'}$ depends weakly on the length of k and k', since only electrons near the Fermi surface participate in the

³ See page 4 in Volume 1.

formation of Cooper pairs. On the other hand, the dependence on the angle ξ between \mathbf{k} and \mathbf{k}' can be appreciable. Expanding the potential in Legendre polynomials the interaction can be characterized by the amplitudes V_l . It is usual to take a contact potential in real space, which corresponds to a momentum-independent interaction for electrons near the Fermi energy as given in (34.1.8). Only the l = 0 component of the potential is nonvanishing, and the wavefunction of the pair has s-wave symmetry. This leads to the BCS theory of conventional superconductors. There are, however, materials, where this simplification cannot be justified, and a more general treatment is needed. We will therefore keep the momentum dependence of $V_{\mathbf{kk'}}$ in most of the calculations. It will be dropped when explicit expressions for the critical temperature or the gap are given for conventional superconductors. A separate section will be devoted to unconventional superconductors.

Another important assumption of the BCS theory is that all electrons are condensed into Cooper pairs in the ground state of superconductors. If a state with wave vector \mathbf{k} and spin \uparrow is occupied, the state with wave vector $-\mathbf{k}$ and spin \downarrow is also occupied. The ground state of the noninteracting Fermi gas satisfies this requirement. This is best seen if it is written in the form

$$|\Psi_{\rm FS}\rangle = \prod_{|\mathbf{k}| < k_{\rm F}} c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow} |0\rangle , \qquad (34.2.2)$$

where $|0\rangle$ is the vacuum of electrons. Electrons cannot take advantage of the attraction between them since there are no available empty states into which they could be scattered elastically. If the discontinuity in the momentum distribution function is smeared out, that is if there are empty states below the chemical potential and then necessarily filled states above the chemical potential, the kinetic energy is increased compared to the free electron ground state, but this increase could be compensated by the binding energy of the Cooper pairs. It could be energetically favorable for the system to undergo a transition to a new state in which the smearing of the distribution function extends to a finite energy range, but all electrons present are dynamically bound into pairs by the attractive effective interaction.

The BCS theory assumes that the superconducting ground state is a coherent linear combination of states involving products of Cooper pairs with all possible values of k. A natural choice for $N_{\rm e}$ electrons would be

$$|\Psi_{N_{\mathrm{e}}}\rangle = \sum_{\boldsymbol{k}_{1}} \cdots \sum_{\boldsymbol{k}_{N_{\mathrm{e}}/2}} \alpha_{\boldsymbol{k}_{1}} \dots \alpha_{\boldsymbol{k}_{N_{\mathrm{e}}/2}} c^{\dagger}_{\boldsymbol{k}_{1}\uparrow} c^{\dagger}_{-\boldsymbol{k}_{1}\downarrow} \dots c^{\dagger}_{\boldsymbol{k}_{N_{\mathrm{e}}/2}\uparrow} c^{\dagger}_{-\boldsymbol{k}_{N_{\mathrm{e}}/2}\downarrow} |0\rangle. \quad (34.2.3)$$

Further calculations with this wavefunction would be rather tedious. BARDEEN, COOPER, and SCHRIEFFER proposed a different form

$$|\Psi_{\rm BCS}\rangle = \prod_{\boldsymbol{k}} \left(u_{\boldsymbol{k}} + v_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \right) |0\rangle , \qquad (34.2.4)$$

where all possible values of \boldsymbol{k} appear in the product. This is the BCS wave-function.

According to the probabilistic interpretation of the wavefunction, $|v_{k}|^{2}$ is the probability of finding the pair in the system and $|u_{k}|^{2}$ gives the probability of its absence. The relation

$$|u_{k}|^{2} + |v_{k}|^{2} = 1 \tag{34.2.5}$$

has to be satisfied, which is at the same time the normalization condition of the wavefunction. The factor u_k can be chosen real without restricting the generality; the factor v_k should, however, be allowed to take complex values. We will see that the superconducting order parameter has a complex phase and the same phase appears in v_k independently of k. This phase which appears in the wavefunction in the form

$$|\Psi_{\rm BCS}\rangle = \prod_{\boldsymbol{k}} \left(u_{\boldsymbol{k}} + |v_{\boldsymbol{k}}| e^{i\phi} c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \right) |0\rangle \tag{34.2.6}$$

gives rise to macroscopic quantum phenomena.

An essential difference compared to the wavefunction given in (34.2.3) is that the number of pairs is not fixed in the BCS state; it is a linear combination of states with $0, 2, 4, \ldots, N, \ldots$ electrons

$$|\Psi_{\rm BCS}\rangle = \sum_{N} \lambda_N |\Psi_N\rangle,$$
 (34.2.7)

with the normalization condition

$$\sum_{N} |\lambda_N|^2 = 1.$$
 (34.2.8)

The probability amplitude λ_N of the state with N particles (N/2 Cooper pairs) contains a phase factor $\exp(iN\phi/2)$. The state with N particles can be recovered from the BCS state by multiplying it with the inverse of the phase factor and integrating over ϕ :

$$|\Psi_N\rangle = \int_{0}^{2\pi} \mathrm{d}\phi \,\mathrm{e}^{-\mathrm{i}\frac{N}{2}\phi} \prod_{\boldsymbol{k}} \left(u_{\boldsymbol{k}} + |v_{\boldsymbol{k}}| \mathrm{e}^{\mathrm{i}\phi} c_{\boldsymbol{k}\uparrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger} \right) |0\rangle \,. \tag{34.2.9}$$

The particle number N and the phase ϕ are conjugate variables; they cannot take sharp values at the same time. The uncertainty relation

$$\delta N \delta \phi \ge 1 \tag{34.2.10}$$

has to be satisfied.

The BCS wavefunction is a natural choice when tunneling phenomena are studied, where the number of electrons is not conserved on the left and right sides of the junction. In other cases a wavefunction with fixed number of particles corresponds to the physical situation. Nevertheless, the physical quantities are obtained correctly, when we work with the BCS wavefunction with a fixed phase, since the probability amplitude λ_N is strongly peaked around the mean number of particles in a macroscopic system. In order to show that we calculate the mean number of particles and the root-meansquare fluctuations in the number of particles. The expectation value of the number of particles,

$$N = \sum_{\boldsymbol{k},\sigma} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} = \sum_{\boldsymbol{k}} \left(c^{\dagger}_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}\uparrow} + c^{\dagger}_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}\downarrow} \right), \qquad (34.2.11)$$

is

$$\langle N \rangle = \langle \Psi_{\rm BCS} | N | \Psi_{\rm BCS} \rangle = \sum_{k} 2 |v_k|^2$$
 (34.2.12)

in the BCS state and the mean-square deviation from the average number is

$$\left\langle (\delta N)^2 \right\rangle = \left\langle \Psi_{\rm BCS} | N^2 | \Psi_{\rm BCS} \right\rangle - \left\langle \Psi_{\rm BCS} | N | \Psi_{\rm BCS} \right\rangle^2 = \sum_{\boldsymbol{k}} 4u_{\boldsymbol{k}}^2 |v_{\boldsymbol{k}}|^2 \,. \quad (34.2.13)$$

The summation over the wave vectors gives values proportional to the volume for both quantities, which means that

$$\frac{\sqrt{\langle (\delta N)^2 \rangle}}{\langle N \rangle} \propto \Omega^{-1/2} \propto \langle N \rangle^{-1/2} \,. \tag{34.2.14}$$

The width in the distribution of the probability amplitude is proportional to the square root of the average number of particles, which indicates, as displayed in Fig. 34.4, that the probability amplitude is indeed strongly peaked. The relative difference between the results calculated with fixed number of particles or with the BCS wavefunction should therefore be extremely small, on the order of 10^{-11} , for a macroscopic sample with 10^{23} electrons.



Fig. 34.4. The probability amplitude λ_N of finding a configuration with N particles in the BCS ground state

Since the particle number is not fixed in the BCS theory, we work with a grand canonical ensemble and the Hamiltonian

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$$\mathcal{H}_{\rm BCS}' = \mathcal{H}_{\rm BCS} - \mu N \tag{34.2.15}$$

has to be considered instead of \mathcal{H}_{BCS} . In what follows we drop the prime from \mathcal{H}'_{BCS} and will use

$$\frac{\mathcal{H}_{BCS} = \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} \left(c^{\dagger}_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}\uparrow} + c^{\dagger}_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}\downarrow} \right) + \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow},}{(34.2.16)}$$

where $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu$ is the energy of the electrons measured from the chemical potential. This reduced Hamiltonian contains explicitly only the interaction between the Cooper pairs. The effects of other processes can partially be incorporated into the energy $\xi_{\mathbf{k}}$ by assuming that the operator $c_{\mathbf{k}\sigma}^{\dagger}$ is the creation operator of a Landau quasiparticle with effective mass m^* .

Our next task is to determine the coefficients u_k and v_k in the BCS state and to calculate the ground-state energy.

34.2.2 Variational Calculation of the Coherence Factors

The restriction to consider the reduced Hamiltonian was based on physical considerations. Further approximations are needed to determine the ground state and the excited states. One usual approach is to treat the interaction between the pairs in mean-field theory. We will apply this method when the finite-temperature properties will be considered. Here we follow the original ideas of BARDEEN, COOPER, and SCHRIEFFER and calculate the ground state and its energy from the variational principle, minimizing the expectation value of the BCS Hamiltonian,

$$E_{\rm BCS}^0 = \langle \Psi_{\rm BCS} | \mathcal{H}_{\rm BCS} | \Psi_{\rm BCS} \rangle, \qquad (34.2.17)$$

with respect to the free parameters of the trial wavefunction.

We introduce the creation and annihilation operators of pairs via

$$b_{\boldsymbol{k}} = c_{-\boldsymbol{k}\downarrow} c_{\boldsymbol{k}\uparrow} , \qquad b_{\boldsymbol{k}}^{\dagger} = c_{\boldsymbol{k}\uparrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger} . \qquad (34.2.18)$$

These operators are not truly bosonic; their commutation relation is

$$\left[b_{\boldsymbol{k}}, b_{\boldsymbol{k}'}^{\dagger}\right]_{-} = \delta_{\boldsymbol{k}\boldsymbol{k}'} \left(1 - n_{\boldsymbol{k}\uparrow} - n_{-\boldsymbol{k}\downarrow}\right), \qquad (34.2.19)$$

nevertheless, the superconducting state is sometimes interpreted as the Bose condensate of bosonic Cooper pairs. The kinetic energy can be rewritten using

$$n_{\boldsymbol{k}\uparrow} + n_{-\boldsymbol{k}\downarrow} = 1 - b_{\boldsymbol{k}} b_{\boldsymbol{k}}^{\dagger} + b_{\boldsymbol{k}}^{\dagger} b_{\boldsymbol{k}} \,. \tag{34.2.20}$$

The interaction can also be given in terms of $b_{\mathbf{k}}$ and $b_{\mathbf{k}}^{\dagger}$ since pairs are scattered into pairs in the reduced BCS Hamiltonian. Finally, we get an expression that is bilinear in the operators,

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$$\mathcal{H}_{BCS} = \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} \left(1 - b_{\boldsymbol{k}} b_{\boldsymbol{k}}^{\dagger} + b_{\boldsymbol{k}}^{\dagger} b_{\boldsymbol{k}} \right) + \frac{1}{\Omega} \sum_{\boldsymbol{k} \boldsymbol{k}'} V_{\boldsymbol{k} \boldsymbol{k}'} b_{\boldsymbol{k}}^{\dagger} b_{\boldsymbol{k}'} , \qquad (34.2.21)$$

and the BCS wavefunction takes the form

$$|\Psi_{\rm BCS}\rangle = \prod_{\boldsymbol{k}} \left(u_{\boldsymbol{k}} + v_{\boldsymbol{k}} b_{\boldsymbol{k}}^{\dagger} \right) |0\rangle \,. \tag{34.2.22}$$

It is readily seen that

$$E_{\rm BCS}^0 = \sum_{\mathbf{k}} \xi_{\mathbf{k}} \left(1 - |u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 \right) + \frac{1}{\Omega} \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}}^* u_{\mathbf{k}'}^* u_{\mathbf{k}} v_{\mathbf{k}'}^* , \qquad (34.2.23)$$

since the pair $(\mathbf{k}^{\prime}\uparrow, -\mathbf{k}^{\prime}\downarrow)$ can be scattered into the pair state $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ if the pair $(\mathbf{k}^{\prime}\uparrow, -\mathbf{k}^{\prime}\downarrow)$ is initially present in $|\Psi_{\text{BCS}}\rangle$ and the other pair is absent, and the reverse is true after the interaction.

The total energy has to be minimized with the constraint $|u_k|^2 + |v_k|^2 = 1$, which can be taken into account by a Lagrange multiplier. The values of the coherence factors that provide the energy minimum are to be determined from the equations

$$-\xi_{\mathbf{k}}u_{\mathbf{k}}^{*} + \frac{1}{\Omega}\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}v_{\mathbf{k}}^{*}u_{\mathbf{k}'}^{*}v_{\mathbf{k}'} - \lambda u_{\mathbf{k}}^{*} = 0,$$

$$-\xi_{\mathbf{k}}u_{\mathbf{k}} + \frac{1}{\Omega}\sum_{\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}}v_{\mathbf{k}'}^{*}u_{\mathbf{k}'}v_{\mathbf{k}} - \lambda u_{\mathbf{k}} = 0,$$

$$\xi_{\mathbf{k}}v_{\mathbf{k}}^{*} + \frac{1}{\Omega}\sum_{\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}}v_{\mathbf{k}'}^{*}u_{\mathbf{k}'}u_{\mathbf{k}}^{*} - \lambda v_{\mathbf{k}}^{*} = 0,$$

$$\xi_{\mathbf{k}}v_{\mathbf{k}} + \frac{1}{\Omega}\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}u_{\mathbf{k}}u_{\mathbf{k}'}^{*}v_{\mathbf{k}'} - \lambda v_{\mathbf{k}} = 0.$$

(34.2.24)

Introducing the quantity

$$\Delta_{\boldsymbol{k}} = -\frac{1}{\Omega} \sum_{\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} u_{\boldsymbol{k}'}^* v_{\boldsymbol{k}'}$$
(34.2.25)

and using the relation

$$V_{kk'} = V_{k'k}^*$$
(34.2.26)

that follows from the properties of the Fourier components, the system of equations for the coherence factors takes the form

$$-\xi_{\mathbf{k}}u_{\mathbf{k}}^{*} - \Delta_{\mathbf{k}}v_{\mathbf{k}}^{*} - \lambda u_{\mathbf{k}}^{*} = 0,$$

$$-\xi_{\mathbf{k}}u_{\mathbf{k}} - \Delta_{\mathbf{k}}^{*}v_{\mathbf{k}} - \lambda u_{\mathbf{k}} = 0,$$

$$\xi_{\mathbf{k}}v_{\mathbf{k}}^{*} - \Delta_{\mathbf{k}}^{*}u_{\mathbf{k}}^{*} - \lambda v_{\mathbf{k}}^{*} = 0,$$

$$\xi_{\mathbf{k}}v_{\mathbf{k}} - \Delta_{\mathbf{k}}u_{\mathbf{k}} - \lambda v_{\mathbf{k}} = 0.$$

(34.2.27)

If u_k is real, the complex phase of v_k should be independent of k and is equal to the phase of Δ_k . This was anticipated when the wavefunction was written in the form given in (34.2.6). Since the pairs occur with the same phase in the total wavefunction, the wavefunction has a macroscopic phase. This explains the macroscopic quantum phenomena such as the Josephson effects. The fixed phase implies that the superconducting state is not gauge invariant; the continuous gauge symmetry is broken in superconductors, as already mentioned in Chapter 26. The phase can be arbitrary, but a fixed phase is realized in nature, just as the magnetization points in a fixed direction in a ferromagnet, although this direction can be arbitrary in an isotropic system.

The Lagrange multiplier λ can be eliminated if the first equation is multiplied by v_k , the fourth is multiplied by u_k^* , and the two equations are subtracted. We find

$$2\xi_{k}u_{k}^{*}v_{k} = \Delta_{k}\left(|u_{k}|^{2} - |v_{k}|^{2}\right).$$
(34.2.28)

The solution of this equation satisfying the auxiliary condition as well is

$$|u_{\mathbf{k}}|^{2} = \frac{1}{2} \left[1 + \frac{\xi_{\mathbf{k}}}{\sqrt{\xi_{\mathbf{k}}^{2} + |\Delta_{\mathbf{k}}|^{2}}} \right], \quad |v_{\mathbf{k}}|^{2} = \frac{1}{2} \left[1 - \frac{\xi_{\mathbf{k}}}{\sqrt{\xi_{\mathbf{k}}^{2} + |\Delta_{\mathbf{k}}|^{2}}} \right], \quad (34.2.29)$$

and

$$u_{k}^{*}v_{k} = \frac{\Delta_{k}}{2\sqrt{\xi_{k}^{2} + |\Delta_{k}|^{2}}}.$$
 (34.2.30)

The energy dependence of the coherence factors u_k and v_k is displayed in Fig. 34.5.



Fig. 34.5. Energy dependence of the coherence factors $|u_k|^2$ and $|v_k|^2$ giving the probability of absence and presence of Cooper pairs in the BCS ground state

It follows from the BCS form of the wavefunction that $|v_k|^2$ is the probability that the state with wave vector k is occupied,

$$\langle n_{\boldsymbol{k}\sigma} \rangle = \langle \Psi_{\rm BCS} | c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} | \Psi_{\rm BCS} \rangle = | v_{\boldsymbol{k}} |^2 .$$
 (34.2.31)

This probability is nearly unity, $|v_k|^2 \approx 1$, well below the chemical potential and $|v_k|^2 \approx 0$ far above the chemical potential. High-energy pairs are practically not present in the system. Compared to the sharp discontinuity in the
distribution function, $|v_{\mathbf{k}}|^2$ is a smooth function of $\xi_{\mathbf{k}}$ and the occupation probability is smeared over a range of width 2Δ about the Fermi energy. The Fermi edge is absent in superconductors.

Substitution of (34.2.30) into (34.2.25) gives a self-consistency condition for Δ_k :

$$\Delta_{k} = -\frac{1}{\Omega} \sum_{k'} \frac{V_{kk'} \Delta_{k'}}{2\sqrt{\xi_{k'}^{2} + |\Delta_{k'}|^{2}}} \,. \tag{34.2.32}$$

The quantity Δ_k itself becomes independent of the wave vector for a structureless attractive potential given in (34.1.8). Denoting it by Δ_0 we get

$$\frac{1}{V_0} = \frac{1}{\Omega} \sum_{\mathbf{k}'} \frac{1}{2\sqrt{\xi_{\mathbf{k}'}^2 + \Delta_0^2}} \,. \tag{34.2.33}$$

Transforming the sum over wave vector to an integral over energy, the integration can be carried out if the density of states is approximated by a constant in the range of width $2\hbar\omega_{\rm D}$. Since there is no summation over the spin, only half of the density of states $\rho(\varepsilon_{\rm F})$ should be taken and we have

$$\frac{2}{V_0\rho(\varepsilon_{\rm F})} = \int_{-\hbar\omega_{\rm D}}^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{2\sqrt{\xi^2 + \Delta_0^2}} = \ln\left(\frac{\hbar\omega_{\rm D}}{\Delta_0} + \sqrt{\left(\frac{\hbar\omega_{\rm D}}{\Delta_0}\right)^2 + 1}\right), \quad (34.2.34)$$

from which

$$\Delta_0 = \hbar \omega_{\rm D} \, \sinh^{-1} \left(\frac{2}{V_0 \rho(\varepsilon_{\rm F})} \right). \tag{34.2.35}$$

In the weak-coupling limit, when $V_0\rho(\varepsilon_{\rm F}) \ll 1$ and also $\Delta_0 \ll \hbar\omega_{\rm D}$,

$$\Delta_0 = 2\hbar\omega_{\rm D} \exp\left(-\frac{2}{V_0\rho(\varepsilon_{\rm F})}\right). \tag{34.2.36}$$

This expression is analogous to (34.1.14) obtained for the binding energy of a Cooper pair. Note, however, the factor of 2 in the exponent.

34.2.3 Coherence Length

The Cooper pairs as bound states of pairs of electrons are formed in momentum space, not in real space. They are in fact wave packets formed from electrons with quantum numbers $\mathbf{k} \uparrow$ and $-\mathbf{k} \downarrow$, in which states from the neighborhood of the Fermi energy, from a region of width Δ_0 , are mixed. This region corresponds to a range of width

$$\hbar |\Delta k| \approx \frac{\Delta_0}{v_{\rm F}} \tag{34.2.37}$$

in momentum space. The linear extension of the wave packet is then

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$$\xi_0 \approx \frac{\hbar v_{\rm F}}{\Delta_0} \,. \tag{34.2.38}$$

The same characteristic length is obtained if the root-mean-square distance of the two elements of the pair is calculated using (34.1.4) for the wavefunction of the Cooper pair. Substituting this form into

$$\langle r^2 \rangle = \frac{\int |\Psi(\mathbf{r})|^2 \mathbf{r}^2 \,\mathrm{d}\mathbf{r}}{\int |\Psi(\mathbf{r})|^2 \,\mathrm{d}\mathbf{r}}, \qquad (34.2.39)$$

where $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$, simple algebra gives

$$\langle r^2 \rangle = \frac{\sum_{\boldsymbol{k}} |\nabla_{\boldsymbol{k}} \alpha_{\boldsymbol{k}}|^2}{\sum_{\boldsymbol{k}} |\alpha_{\boldsymbol{k}}|^2} \,. \tag{34.2.40}$$

Using (34.1.9) for α_k we get

$$\langle r^2 \rangle = \frac{4}{3} \left(\frac{\hbar v_{\rm F}}{\Delta_0} \right)^2. \tag{34.2.41}$$

Since electrons are correlated up to this distance in the superconducting state, this characteristic distance is called the *coherence length* and is denoted by ξ_0 . Since Δ_0 is much smaller than the Fermi energy, ξ_0 can be as large as $10^{-6} - 10^{-7}$ m, that is, it is typically much longer than the atomic dimensions.

A better picture can be obtained about correlations between electrons in the BCS state if the pair distribution function of opposite-spin electrons defined in (28.4.47) and (28.4.50) is considered. We have seen in Chapter 28 that there are no correlations between electrons of opposite spins in the Hartree– Fock approximation. Such correlations occur, however, in the superconducting state. The pair distribution function can be evaluated if the electron operators are expressed in terms of the operators of the quasiparticles to be introduced later, in Section 34.2.6. We get

$$g_{\uparrow\downarrow}(\boldsymbol{r}-\boldsymbol{r}') = \left[1 - \left(\frac{1}{N_{\rm e}}\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}\frac{\Delta_0}{E_{\boldsymbol{k}}}\right)^2\right]$$
(34.2.42)

instead of (28.4.57). Replacing the sum by an integral, its value can be estimated. Correlations are appreciable only up to a distance ξ_0 defined in (34.2.38). The pair distribution function $g_{\uparrow\downarrow}(\boldsymbol{r} - \boldsymbol{r}')$ takes practically unit value beyond that, that is correlations vanish for $|\boldsymbol{r} - \boldsymbol{r}'| > \xi_0$.

34.2.4 Energy of the Superconducting State

We now return to the problem of calculating explicitly the ground-state energy given in (34.2.23) and we prove that it is lower than the energy

$$E_{\rm FS}^0 = 2 \sum_{|\mathbf{k}| < k_{\rm F}} \xi_{\mathbf{k}}$$
(34.2.43)

of the completely filled Fermi sea with a sharp Fermi edge. Their difference is

$$E_{BCS}^{0} - E_{FS}^{0} = \sum_{\mathbf{k}} \xi_{\mathbf{k}} \left(1 - |u_{\mathbf{k}}|^{2} + |v_{\mathbf{k}}|^{2} \right) + \frac{1}{\Omega} \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}}^{*} u_{\mathbf{k}} u_{\mathbf{k}'}^{*} v_{\mathbf{k}'} - 2 \sum_{|\mathbf{k}| < k_{F}} \xi_{\mathbf{k}} .$$
(34.2.44)

The sum in the first term is divided into two parts, into the contributions coming from the regions $|\mathbf{k}| < k_{\rm F}$ and $|\mathbf{k}| > k_{\rm F}$. Using the normalization condition $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$ we have

$$E_{BCS}^{0} - E_{FS}^{0} = -2 \sum_{|\mathbf{k}| < k_{F}} \xi_{\mathbf{k}} |u_{\mathbf{k}}|^{2} + 2 \sum_{|\mathbf{k}| > k_{F}} \xi_{\mathbf{k}} |v_{\mathbf{k}}|^{2} + \frac{1}{\Omega} \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}}^{*} u_{\mathbf{k}} u_{\mathbf{k}'}^{*} v_{\mathbf{k}'} .$$
(34.2.45)

With the change of variables $\xi_k \rightarrow -\xi_k$ in the first term and using (34.2.29) and (34.2.30) for the coherence factors we find

$$E_{\rm BCS}^{0} - E_{\rm FS}^{0} = 4 \sum_{|\mathbf{k}| > k_{\rm F}} \xi_{\mathbf{k}} |v_{\mathbf{k}}|^{2} + \frac{1}{\Omega} \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}}^{*} u_{\mathbf{k}} u_{\mathbf{k}'}^{*} v_{\mathbf{k}'}$$
(34.2.46)
$$= 2 \sum_{|\mathbf{k}| > k_{\rm F}} \xi_{\mathbf{k}} \left(1 - \frac{\xi_{\mathbf{k}}}{\sqrt{\xi_{\mathbf{k}}^{2} + |\Delta_{\mathbf{k}}|^{2}}} \right) - \sum_{\mathbf{k}} \frac{|\Delta_{\mathbf{k}}|^{2}}{2\sqrt{\xi_{\mathbf{k}}^{2} + |\Delta_{\mathbf{k}}|^{2}}}$$
$$= 2 \sum_{|\mathbf{k}| > k_{\rm F}} \left(\xi_{\mathbf{k}} - \frac{\xi_{\mathbf{k}}^{2}}{\sqrt{\xi_{\mathbf{k}}^{2} + |\Delta_{\mathbf{k}}|^{2}}} - \frac{|\Delta_{\mathbf{k}}|^{2}}{2\sqrt{\xi_{\mathbf{k}}^{2} + |\Delta_{\mathbf{k}}|^{2}}} \right).$$

The explicit calculation will be done for s-wave superconductors. Simple algebra gives

$$E_{\rm BCS}^{0} - E_{\rm FS}^{0} = 2 \sum_{|\mathbf{k}| > k_{\rm F}} \left[\xi_{\mathbf{k}} \frac{\Delta_{0}^{2}}{\sqrt{\xi_{\mathbf{k}}^{2} + \Delta_{0}^{2}} \left(\sqrt{\xi_{\mathbf{k}}^{2} + \Delta_{0}^{2}} + \xi_{\mathbf{k}} \right)} - \frac{\Delta_{0}^{2}}{2\sqrt{\xi_{\mathbf{k}}^{2} + \Delta_{0}^{2}}} \right]$$
$$= -2\Delta_{0}^{2} \sum_{|\mathbf{k}| > k_{\rm F}} \frac{1}{2\sqrt{\xi_{\mathbf{k}}^{2} + \Delta_{0}^{2}}} \frac{\Delta_{0}^{2}}{\left(\sqrt{\xi_{\mathbf{k}}^{2} + \Delta_{0}^{2}} + \xi_{\mathbf{k}}\right)^{2}} . \quad (34.2.47)$$

Converting the sum over k to an integral over ξ using a constant density of states we get

$$E_{\rm BCS}^0 - E_{\rm FS}^0 = -\Omega \Delta_0^2 \rho(\varepsilon_{\rm F}) \int_0^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{2\sqrt{\xi^2 + \Delta_0^2}} \frac{\Delta_0^2}{\left(\sqrt{\xi^2 + \Delta_0^2} + \xi\right)^2} \,. \quad (34.2.48)$$

With a change of variables from ξ to x defined via $\sinh x = \xi/\Delta_0$ and using (34.2.35) we get

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$$E_{\rm BCS}^0 - E_{\rm FS}^0 = -\frac{1}{2} \Omega \Delta_0^2 \rho(\varepsilon_{\rm F}) \int_0^{2/V_0 \rho(\varepsilon_{\rm F})} \frac{\mathrm{d}x}{(\sinh x + \cosh x)^2} , \qquad (34.2.49)$$

from which

$$E_{\rm BCS}^{0} - E_{\rm FS}^{0} = -\frac{1}{4} \Omega \Delta_{0}^{2} \rho(\varepsilon_{\rm F}) \Big[1 - e^{-4/V_{0}\rho(\varepsilon_{\rm F})} \Big]$$

$$= -\Omega \rho(\varepsilon_{\rm F}) \left(\hbar\omega_{\rm D}\right)^{2} \frac{1}{e^{4/V_{0}\rho(\varepsilon_{\rm F})} - 1} .$$
(34.2.50)

The lowering of the energy in the weak-coupling limit is given by

$$E_{\rm BCS}^0 - E_{\rm FS}^0 = -\Omega \rho(\varepsilon_{\rm F}) \left(\hbar\omega_{\rm D}\right)^2 e^{-4/V_0 \rho(\varepsilon_{\rm F})} = -\Omega \frac{1}{4} \rho(\varepsilon_{\rm F}) \Delta_0^2.$$
(34.2.51)

This can be easily understood if we recall that those electrons can form bound Cooper pairs which are in a range of width $\hbar\omega_{\rm D}$ below the Fermi energy (the density of states can be approximated by $\rho(\varepsilon_{\rm F})$ in this range) and the binding energy per particle is $\hbar\omega_{\rm D}e^{-4/V_0\rho(\varepsilon_{\rm F})}$.

We know that the transition from the superconducting state to the normal state occurs at the critical magnetic field H_c where the energy of the magnetic field is equal to the energy lowering due to the condensation energy of the Cooper pairs, that is when

$$\frac{1}{4}\rho(\varepsilon_{\rm F})\Delta_0^2 = \frac{1}{2}\mu_0 H_{\rm c}^2\,,\tag{34.2.52}$$

from which we get

$$H_{\rm c}(0) = \left[\frac{1}{2\mu_0}\rho(\varepsilon_{\rm F})\right]^{1/2} \Delta_0 \qquad (34.2.53)$$

for the critical field at T = 0.

34.2.5 Excited States of Superconductors

Excited states can be obtained when one or more Cooper pairs are removed from the condensate ground-state configuration. As the simplest example we assume that all pairs are in the configuration $u_{\mathbf{k}} + v_{\mathbf{k}} b_{\mathbf{k}}^{\dagger}$ corresponding to the BCS state except for the pair $(\mathbf{k}_1 \uparrow, -\mathbf{k}_1 \downarrow)$ which is in an orthogonal configuration. Such a state can easily be constructed:

$$|\Psi_{\text{exc}}^{(1)}\rangle = \left(u_{\boldsymbol{k}_{1}}^{*}b_{\boldsymbol{k}_{1}}^{\dagger} - v_{\boldsymbol{k}_{1}}^{*}\right)\prod_{\boldsymbol{k}\neq\boldsymbol{k}_{1}}\left(u_{\boldsymbol{k}} + v_{\boldsymbol{k}}b_{\boldsymbol{k}}^{\dagger}\right)|0\rangle.$$
(34.2.54)

It is indeed true that $\langle \Psi_{\rm BCS} | \Psi_{\rm exc}^{(1)} \rangle = 0.$

To calculate the energy of this state we first consider the energy needed to remove the pair $(\mathbf{k}_1\uparrow, -\mathbf{k}_1\downarrow)$ from the ground state and then add the change in energy when the electrons are put back into a different configuration. The

change in energy when a pair is removed is readily obtained from (34.2.23) by picking the terms from the sum in which the wave vector k_1 occurs. We find

$$\xi_{\boldsymbol{k}_{1}} \left(1 - |u_{\boldsymbol{k}_{1}}|^{2} + |v_{\boldsymbol{k}_{1}}|^{2} \right) + \frac{1}{\Omega} \sum_{\boldsymbol{k}'} \left[V_{\boldsymbol{k}_{1}\boldsymbol{k}'} v_{\boldsymbol{k}_{1}}^{*} u_{\boldsymbol{k}_{1}} u_{\boldsymbol{k}'}^{*} v_{\boldsymbol{k}'} + V_{\boldsymbol{k}'\boldsymbol{k}_{1}} v_{\boldsymbol{k}'}^{*} u_{\boldsymbol{k}'} u_{\boldsymbol{k}'}^{*} u_{\boldsymbol{k}_{1}}^{*} v_{\boldsymbol{k}_{1}} \right] = 2\xi_{\boldsymbol{k}_{1}} |v_{\boldsymbol{k}_{1}}|^{2} - \Delta_{\boldsymbol{k}_{1}} v_{\boldsymbol{k}_{1}}^{*} u_{\boldsymbol{k}_{1}} - \Delta_{\boldsymbol{k}_{1}}^{*} u_{\boldsymbol{k}_{1}}^{*} v_{\boldsymbol{k}_{1}} .$$
(34.2.55)

It is instructive to look back at the ground-state energy of the superconductor given in (34.2.23). It can be rewritten in the alternative forms

$$E_{BCS}^{0} = 2 \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^{2} - \sum_{\boldsymbol{k}} \Delta_{\boldsymbol{k}} v_{\boldsymbol{k}}^{*} u_{\boldsymbol{k}}$$
$$= 2 \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^{2} - \sum_{\boldsymbol{k'}} \Delta_{\boldsymbol{k'}}^{*} u_{\boldsymbol{k'}}^{*} v_{\boldsymbol{k'}}$$
(34.2.56)

or

$$E_{\rm BCS}^{0} = 2\sum_{k} \xi_{k} |v_{k}|^{2} - \frac{1}{2} \sum_{k} \left(\Delta_{k} v_{k}^{*} u_{k} + \Delta_{k}^{*} u_{k}^{*} v_{k} \right).$$
(34.2.57)

Only half of the term coming from the interaction in (34.2.55) has to be summed when the total energy is calculated. This is natural, since only half of the energy correction has to be attributed to each electron to avoid double counting.

When the pair $(\mathbf{k}_1\uparrow, -\mathbf{k}_1\downarrow)$ is in state $u_{\mathbf{k}_1}^* b_{\mathbf{k}_1}^\dagger - v_{\mathbf{k}_1}^*$ instead of $u_{\mathbf{k}_1} + v_{\mathbf{k}_1} b_{\mathbf{k}_1}^\dagger$, its energy can be obtained from (34.2.55) by the replacements $u_{\mathbf{k}_1} \to -v_{\mathbf{k}_1}^*$, $v_{\mathbf{k}_1} \to u_{\mathbf{k}_1}^*$. The energy needed to add such a pair is then

$$\xi_{\boldsymbol{k}_{1}} \left(1 - |v_{\boldsymbol{k}_{1}}|^{2} + |u_{\boldsymbol{k}_{1}}|^{2}\right) - \frac{1}{\Omega} \sum_{\boldsymbol{k}'} \left[V_{\boldsymbol{k}_{1}\boldsymbol{k}'} u_{\boldsymbol{k}_{1}} v_{\boldsymbol{k}_{1}}^{*} u_{\boldsymbol{k}'}^{*} v_{\boldsymbol{k}'} + V_{\boldsymbol{k}'\boldsymbol{k}_{1}} v_{\boldsymbol{k}'}^{*} u_{\boldsymbol{k}'} v_{\boldsymbol{k}_{1}} u_{\boldsymbol{k}_{1}}^{*} \right]$$

= $2\xi_{\boldsymbol{k}_{1}} |u_{\boldsymbol{k}_{1}}|^{2} + \Delta_{\boldsymbol{k}_{1}} u_{\boldsymbol{k}_{1}} v_{\boldsymbol{k}_{1}}^{*} + \Delta_{\boldsymbol{k}_{1}}^{*} v_{\boldsymbol{k}_{1}} u_{\boldsymbol{k}_{1}}^{*}.$ (34.2.58)

The excitation energy is equal to the difference between (34.2.58) and (34.2.55):

$$E_{\text{exc}}^{(1)} - E_{\text{BCS}}^{0} = 2\xi_{\boldsymbol{k}_{1}} \left[|u_{\boldsymbol{k}_{1}}|^{2} - |v_{\boldsymbol{k}_{1}}|^{2} \right] + 2\Delta_{\boldsymbol{k}_{1}} u_{\boldsymbol{k}_{1}} v_{\boldsymbol{k}_{1}}^{*} + 2\Delta_{\boldsymbol{k}_{1}}^{*} u_{\boldsymbol{k}_{1}}^{*} v_{\boldsymbol{k}_{1}} = 2\sqrt{\xi_{\boldsymbol{k}_{1}}^{2} + |\Delta_{\boldsymbol{k}_{1}}|^{2}} .$$
(34.2.59)

In conventional superconductors, where $\Delta_{\mathbf{k}}$ takes the same finite value in all \mathbf{k} points of the Fermi surface of the normal state, the minimum excitation energy is $2\Delta_0$.

Another type of excited state is obtained when all electrons are in their ground-state pair configurations except for two which occupy the states $\mathbf{k}_1 \uparrow$ and $\mathbf{k}_2 \downarrow$ with $\mathbf{k}_2 \neq -\mathbf{k}_1$. Clearly the pairs with quantum numbers $(\mathbf{k}_1 \uparrow, -\mathbf{k}_1 \downarrow)$ and $(-\mathbf{k}_2 \uparrow, \mathbf{k}_2 \downarrow)$ may not be present and the wavefunction is

$$|\Psi_{\text{exc}}^{(2)}\rangle = c_{\boldsymbol{k}_{1}\uparrow}^{\dagger} c_{\boldsymbol{k}_{2}\downarrow}^{\dagger} \prod_{\boldsymbol{k}\neq\boldsymbol{k}_{1},\boldsymbol{k}_{2}} \left(u_{\boldsymbol{k}} + v_{\boldsymbol{k}} b_{\boldsymbol{k}}^{\dagger} \right) |0\rangle .$$
(34.2.60)

To get the energy of this excited state we take (34.2.55) which gives the change of energy due to the removal of the pair $(\mathbf{k}_1\uparrow, -\mathbf{k}_1\downarrow)$ and add $\xi_{\mathbf{k}_1}$ which is the energy needed to fill the state $\mathbf{k}_1\uparrow$. We get

$$E_{\mathbf{k}_{1}} = \xi_{\mathbf{k}_{1}} - \left(2\xi_{\mathbf{k}_{1}}|v_{\mathbf{k}_{1}}|^{2} - \Delta_{\mathbf{k}_{1}}v_{\mathbf{k}_{1}}^{*}u_{\mathbf{k}_{1}} - \Delta_{\mathbf{k}_{1}}^{*}u_{\mathbf{k}_{1}}^{*}v_{\mathbf{k}_{1}}\right)$$

$$= \frac{\xi_{\mathbf{k}_{1}}^{2}}{\sqrt{\xi_{\mathbf{k}_{1}}^{2} + |\Delta_{\mathbf{k}_{1}}|^{2}}} + \frac{\Delta_{\mathbf{k}_{1}}\Delta_{\mathbf{k}_{1}}^{*}}{\sqrt{\xi_{\mathbf{k}_{1}}^{2} + |\Delta_{\mathbf{k}_{1}}|^{2}}}$$

$$= \sqrt{\xi_{\mathbf{k}_{1}}^{2} + |\Delta_{\mathbf{k}_{1}}|^{2}}.$$
(34.2.61)

Similar expression is obtained for the particle with wave vector k_2 . The energy of this excited state is then

$$E_{\rm exc}^{(2)} - E_{\rm BCS}^0 = E_{\boldsymbol{k}_1} + E_{\boldsymbol{k}_2} = \sqrt{\xi_{\boldsymbol{k}_1}^2 + |\Delta_{\boldsymbol{k}_1}|^2} + \sqrt{\xi_{\boldsymbol{k}_2}^2 + |\Delta_{\boldsymbol{k}_2}|^2} \,. \quad (34.2.62)$$

The minimum energy is again $2\Delta_0$. This gap in the excitation spectrum explains the exponentially small heat capacity of superconductors at low temperatures, well below the critical temperature.

34.2.6 Quasiparticles in the Superconducting State

In order to get a better picture of the excited states we reformulate the BCS theory. We introduce new operators instead of the creation and annihilation operators of the electron states by a unitary transformation, which will turn out to be the creation and annihilation operators of the quasiparticles of the superconducting state.

The procedure is similar to the one used in the previous chapter to treat broken-symmetry phases; however, since the Cooper pairs, which play a dominant role now, are present in a macroscopic number, we will assume that the anomalous averages $\langle c^{\dagger}_{\boldsymbol{k}\uparrow}c^{\dagger}_{-\boldsymbol{k}\downarrow}\rangle$ and $\langle c_{-\boldsymbol{k}\downarrow}c_{\boldsymbol{k}\uparrow}\rangle$ containing the operators of the pairs take nonvanishing values. The mean-field theory of superconductivity corresponds to neglecting the terms

$$\left(c_{\boldsymbol{k}\uparrow}^{\dagger}c_{-\boldsymbol{k}\downarrow}^{\dagger}-\langle c_{\boldsymbol{k}\uparrow}^{\dagger}c_{-\boldsymbol{k}\downarrow}^{\dagger}\rangle\right)\left(c_{-\boldsymbol{k}'\downarrow}c_{\boldsymbol{k}'\uparrow}-\langle c_{-\boldsymbol{k}'\downarrow}c_{\boldsymbol{k}'\uparrow}\rangle\right)$$
(34.2.63)

in the BCS Hamiltonian. This leads to the expression

$$\mathcal{H}_{BCS} = \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} \left(c^{\dagger}_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}\uparrow} + c^{\dagger}_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}\downarrow} \right) + \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle$$

$$(34.2.64)$$

$$+ \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \langle c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \rangle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} - \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \langle c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \rangle \langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle.$$

Using the BCS wavefunction we readily find

$$\langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle = u_{\boldsymbol{k}'}^* v_{\boldsymbol{k}'} ,$$

$$\langle c_{\boldsymbol{k}'\uparrow}^{\dagger} c_{-\boldsymbol{k}'\downarrow}^{\dagger} \rangle = u_{\boldsymbol{k}'} v_{\boldsymbol{k}'}^* .$$

$$(34.2.65)$$

Comparison with (34.2.25) suggests that the order parameter should be defined via

$$\begin{aligned} \Delta_{\mathbf{k}} &= -\frac{1}{\Omega} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle ,\\ \Delta_{\mathbf{k}}^* &= -\frac{1}{\Omega} \sum_{\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}} \langle c_{\mathbf{k}'\uparrow}^{\dagger} c_{-\mathbf{k}'\downarrow}^{\dagger} \rangle . \end{aligned}$$
(34.2.66)

The Hamiltonian then becomes

$$\mathcal{H}_{BCS} = -\frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \langle c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \rangle \langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle + \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} \left(c^{\dagger}_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}\uparrow} + c^{\dagger}_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}\downarrow} \right) - \sum_{\boldsymbol{k}} \left(\Delta_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} + \Delta^{*}_{\boldsymbol{k}} c_{-\boldsymbol{k}\downarrow} c_{\boldsymbol{k}\uparrow} \right).$$
(34.2.67)

Being bilinear in the creation and annihilation operators this Hamiltonian can be diagonalized by a Bogoliubov transformation also known as Bogoliubov–Valatin transformation.⁴ For this we define new operators by a unitary transformation:

$$\begin{aligned} \alpha_{\boldsymbol{k}\uparrow} &= u_{\boldsymbol{k}} c_{\boldsymbol{k}\uparrow} - v_{\boldsymbol{k}} c_{-\boldsymbol{k}\downarrow}^{\dagger} , \qquad \alpha_{-\boldsymbol{k}\downarrow} = u_{\boldsymbol{k}} c_{-\boldsymbol{k}\downarrow} + v_{\boldsymbol{k}} c_{\boldsymbol{k}\uparrow}^{\dagger} , \\ \alpha_{\boldsymbol{k}\uparrow}^{\dagger} &= u_{\boldsymbol{k}}^{*} c_{\boldsymbol{k}\uparrow}^{\dagger} - v_{\boldsymbol{k}}^{*} c_{-\boldsymbol{k}\downarrow} , \qquad \alpha_{-\boldsymbol{k}\downarrow}^{\dagger} = u_{\boldsymbol{k}}^{*} c_{-\boldsymbol{k}\downarrow}^{\dagger} + v_{\boldsymbol{k}}^{*} c_{\boldsymbol{k}\uparrow} . \end{aligned}$$

$$(34.2.68)$$

Fermionic anticommutation relations are obeyed if $|u_{k}|^2+|v_{k}|^2=1.$ Inverting the transformation gives

$$c_{\mathbf{k}\uparrow} = u_{\mathbf{k}}^* \alpha_{\mathbf{k}\uparrow} + v_{\mathbf{k}} \alpha_{-\mathbf{k}\downarrow}^{\dagger}, \qquad c_{-\mathbf{k}\downarrow} = u_{\mathbf{k}}^* \alpha_{-\mathbf{k}\downarrow} - v_{\mathbf{k}} \alpha_{\mathbf{k}\uparrow}^{\dagger}, c_{\mathbf{k}\uparrow}^{\dagger} = u_{\mathbf{k}} \alpha_{\mathbf{k}\uparrow}^{\dagger} + v_{\mathbf{k}}^* \alpha_{-\mathbf{k}\downarrow}, \qquad c_{-\mathbf{k}\downarrow}^{\dagger} = u_{\mathbf{k}} \alpha_{-\mathbf{k}\downarrow}^{\dagger} - v_{\mathbf{k}}^* \alpha_{\mathbf{k}\uparrow}.$$
(34.2.69)

Substituting these expressions in the mean-field Hamiltonian we get

$$\mathcal{H}_{BCS} = \sum_{\mathbf{k}} \xi_{\mathbf{k}} \left(|u_{\mathbf{k}}|^{2} - |v_{\mathbf{k}}|^{2} \right) \left(\alpha_{\mathbf{k}\uparrow}^{\dagger} \alpha_{\mathbf{k}\uparrow} + \alpha_{-\mathbf{k}\downarrow}^{\dagger} \alpha_{-\mathbf{k}\downarrow} \right) + \sum_{\mathbf{k}} 2\xi_{\mathbf{k}} |v_{\mathbf{k}}|^{2} + \sum_{\mathbf{k}} \left(\Delta_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}}^{*} + \Delta_{\mathbf{k}}^{*} u_{\mathbf{k}}^{*} v_{\mathbf{k}} \right) \left(\alpha_{\mathbf{k}\uparrow}^{\dagger} \alpha_{\mathbf{k}\uparrow} + \alpha_{-\mathbf{k}\downarrow}^{\dagger} \alpha_{-\mathbf{k}\downarrow} - 1 \right) + \sum_{\mathbf{k}} 2\xi_{\mathbf{k}} \left(u_{\mathbf{k}} v_{\mathbf{k}} \alpha_{\mathbf{k}\uparrow}^{\dagger} \alpha_{-\mathbf{k}\downarrow}^{\dagger} + u_{\mathbf{k}}^{*} v_{\mathbf{k}}^{*} \alpha_{-\mathbf{k}\downarrow} \alpha_{\mathbf{k}\uparrow} \right)$$
(34.2.70)
$$+ \sum_{\mathbf{k}} \left[\left(\Delta_{\mathbf{k}} v_{\mathbf{k}}^{*2} - \Delta_{\mathbf{k}}^{*} u_{\mathbf{k}}^{*2} \right) \alpha_{-\mathbf{k}\downarrow} \alpha_{\mathbf{k}\uparrow} + \left(\Delta_{\mathbf{k}}^{*} v_{\mathbf{k}}^{2} - \Delta_{\mathbf{k}} u_{\mathbf{k}}^{2} \right) \alpha_{\mathbf{k}\uparrow}^{\dagger} \alpha_{-\mathbf{k}\downarrow}^{\dagger} \right] - \frac{1}{\Omega} \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \langle c_{\mathbf{k}\uparrow}^{\dagger} c_{-\mathbf{k}\downarrow}^{\dagger} \rangle \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle.$$

⁴ N. N. Bogoliubov, 1958, J. G. Valatin, 1958.

The off-diagonal terms vanish if

$$2\xi_{\boldsymbol{k}}u_{\boldsymbol{k}}v_{\boldsymbol{k}} + \Delta_{\boldsymbol{k}}^{*}v_{\boldsymbol{k}}^{2} - \Delta_{\boldsymbol{k}}u_{\boldsymbol{k}}^{2} = 0. \qquad (34.2.71)$$

It is readily seen that this equation is satisfied if the expressions given in (34.2.29) and (34.2.30) are used for the coherence factors and the diagonal Hamiltonian takes the form

$$\mathcal{H}_{\rm BCS} = E^0_{\rm BCS} + \sum_{\boldsymbol{k}} E_{\boldsymbol{k}} \left(\alpha^{\dagger}_{\boldsymbol{k}\uparrow} \alpha_{\boldsymbol{k}\uparrow} + \alpha^{\dagger}_{-\boldsymbol{k}\downarrow} \alpha_{-\boldsymbol{k}\downarrow} \right)$$
(34.2.72)

with

$$E_{BCS}^{0} = -\frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \langle c_{\boldsymbol{k}\uparrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger} \rangle \langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle + 2 \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^{2} - \sum_{\boldsymbol{k}} \left(\Delta_{\boldsymbol{k}} u_{\boldsymbol{k}} v_{\boldsymbol{k}}^{*} + \Delta_{\boldsymbol{k}}^{*} u_{\boldsymbol{k}}^{*} v_{\boldsymbol{k}} \right)$$
(34.2.73)

and

$$E_{k} = \xi_{k} \left(|u_{k}|^{2} - |v_{k}|^{2} \right) + \left(\Delta_{k} u_{k} v_{k}^{*} + \Delta_{k}^{*} u_{k}^{*} v_{k} \right)$$

$$= \xi_{k} \frac{\xi_{k}}{\sqrt{\xi_{k}^{2} + \Delta_{k}^{2}}} + \Delta_{k} \frac{\Delta_{k}^{*}}{\sqrt{\xi_{k}^{2} + |\Delta_{k}|^{2}}}$$

$$= \sqrt{\xi_{k}^{2} + |\Delta_{k}|^{2}}.$$
(34.2.74)

 E_{BCS}^0 is the ground-state energy of the superconductor and the operators $\alpha^{\dagger}_{\boldsymbol{k}\uparrow}$ and $\alpha^{\dagger}_{-\boldsymbol{k}\downarrow}$ generate excited states with energy

$$E_{k} = \sqrt{\xi_{k}^{2} + |\Delta_{k}|^{2}}.$$
 (34.2.75)

They can be considered as the creation operators of the quasiparticles of the superconducting state. These quasiparticles should be distinguished from the Landau quasiparticles of normal Fermi liquids and are known as *Bogoliubov quasiparticles*, or *bogolons*, or *bogoliubons*. They are electronlike above the Fermi energy and holelike below it. They correspond to particles whose pair is missing. A further justification of this quasiparticle picture is provided by the fact that the ground-state wavefunction of the BCS theory can be written, apart from a normalization factor, in the form

$$|\Psi_{\rm BCS}\rangle = \prod_{\boldsymbol{k}} \alpha_{-\boldsymbol{k}\downarrow} \alpha_{\boldsymbol{k}\uparrow} |0\rangle , \qquad (34.2.76)$$

which implies that $|\Psi_{\rm BCS}\rangle$ is the vacuum of bogolons,

$$\alpha_{\mathbf{k}\uparrow}|\Psi_{\rm BCS}\rangle = 0\,,\qquad \alpha_{-\mathbf{k}\downarrow}|\Psi_{\rm BCS}\rangle = 0\,. \tag{34.2.77}$$

Furthermore, the excited states considered previously can be written as

$$|\Psi_{\rm exc}^{(1)}\rangle = \alpha_{\boldsymbol{k}_1\uparrow}^{\dagger} \alpha_{-\boldsymbol{k}_1\downarrow}^{\dagger} |\Psi_{\rm BCS}\rangle \tag{34.2.78}$$

and

$$|\Psi_{\rm exc}^{(2)}\rangle = \alpha_{\boldsymbol{k}_1\uparrow}^{\dagger} \alpha_{\boldsymbol{k}_2\downarrow}^{\dagger} |\Psi_{\rm BCS}\rangle, \qquad (34.2.79)$$

that is they contain two Bogoliubov quasiparticles.

The number of quasiparticles may change by one in tunneling experiments when a pair is broken up into two quasiparticles and one of them tunnels to the other side of the junction. The state with one Bogoliubov quasiparticle on the superconducting side is

$$\begin{aligned} \alpha_{\mathbf{k}\uparrow}^{\dagger} |\Psi_{\mathrm{BCS}}\rangle &= \left(u_{\mathbf{k}}^{*} c_{\mathbf{k}\uparrow}^{\dagger} - v_{\mathbf{k}}^{*} c_{-\mathbf{k}\downarrow} \right) \prod_{\mathbf{k}'} \left(u_{\mathbf{k}'} + v_{\mathbf{k}'} c_{\mathbf{k}'\uparrow}^{\dagger} c_{-\mathbf{k}'\downarrow}^{\dagger} \right) |0\rangle \\ &= \left(|u_{\mathbf{k}}|^{2} c_{\mathbf{k}\uparrow}^{\dagger} + |v_{\mathbf{k}}|^{2} c_{\mathbf{k}\uparrow}^{\dagger} \right) \prod_{\mathbf{k}'\neq\mathbf{k}} \left(u_{\mathbf{k}'} + v_{\mathbf{k}'} c_{\mathbf{k}'\uparrow}^{\dagger} c_{-\mathbf{k}'\downarrow}^{\dagger} \right) |0\rangle \\ &= c_{\mathbf{k}\uparrow}^{\dagger} \prod_{\mathbf{k}'\neq\mathbf{k}} \left(u_{\mathbf{k}'} + v_{\mathbf{k}'} c_{\mathbf{k}'\uparrow}^{\dagger} c_{-\mathbf{k}'\downarrow}^{\dagger} \right) |0\rangle. \end{aligned}$$
(34.2.80)

The energy of this state is readily obtained from our earlier considerations. We find

$$E_{k} = \sqrt{\xi_{k}^{2} + |\Delta_{k}|^{2}}.$$
 (34.2.81)

Note that the same state is obtained if an electron with quantum numbers $\mathbf{k} \uparrow$ is added to the BCS state or if an electron with quantum numbers $-\mathbf{k} \downarrow$ is removed. The minimum energy of these excitations is Δ_0 . The spectrum of quasiparticles is displayed in Fig. 34.6.



Fig. 34.6. Spectrum and density of states of quasiparticles of the superconducting state

The density of states of the quasiparticles can be calculated from the relation

$$\rho_{\rm s}(E) \,\mathrm{d}E = \rho_{\rm n}(\xi) \,\mathrm{d}\xi,$$
(34.2.82)

where the subscripts s and n refer to the superconducting and the normal states, respectively. Assuming that the density of states is constant in the normal state we find

$$\rho_{\rm s}(E) = \begin{cases} \rho_{\rm n}(\varepsilon_{\rm F}) \frac{E}{\sqrt{E^2 - \Delta_0^2}} & E > \Delta, \\ 0 & E < \Delta. \end{cases}$$
(34.2.83)

This is also shown in Fig. 34.6. The states expelled from the gap give rise to an inverse-square-root singularity in the density of states. This will be used to interpret the tunneling characteristics.

34.2.7 BCS Theory at Finite Temperatures

Knowing the ground state and the low-lying excited states we can now turn to the problem of calculating the thermodynamic behavior of superconductors at finite temperatures. This can be achieved most simply in a mean-field approach by self-consistently calculating the nonvanishing anomalous averages $\langle c^{\dagger}_{\boldsymbol{k}\uparrow}c^{-}_{-\boldsymbol{k}\downarrow}\rangle$ and $\langle c_{-\boldsymbol{k}\downarrow}c_{\boldsymbol{k}\uparrow}\rangle$ at finite temperature as thermal averages, neglecting their fluctuations. The mean-field Hamiltonian takes the same form as in (34.2.67),

$$\mathcal{H}_{BCS} = -\frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \langle c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \rangle \langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle + \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} (c^{\dagger}_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}\uparrow} + c^{\dagger}_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{k}\downarrow}) - \sum_{\boldsymbol{k}} \left(\Delta_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} + \Delta^{*}_{\boldsymbol{k}} c_{-\boldsymbol{k}\downarrow} c_{\boldsymbol{k}\uparrow} \right)$$
(34.2.84)

with a temperature-dependent order parameter defined in analogy to (34.2.66) via

$$\Delta_{\mathbf{k}} = -\frac{1}{\Omega} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \langle c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} \rangle, \qquad \Delta_{\mathbf{k}}^* = -\frac{1}{\Omega} \sum_{\mathbf{k}'} V_{\mathbf{k}'\mathbf{k}} \langle c_{\mathbf{k}'\uparrow}^{\dagger} c_{-\mathbf{k}'\downarrow}^{\dagger} \rangle.$$
(34.2.85)

This Hamiltonian can be diagonalized by repeating formally the same steps that were made at T = 0. The creation and annihilation operators of the quasiparticles are defined in terms of the creation and annihilation operators of electron states by a unitary transformation similar to (34.2.68) with complex coefficients:

$$\begin{aligned} \alpha_{\boldsymbol{k}\uparrow} &= u_{\boldsymbol{k}} c_{\boldsymbol{k}\uparrow} - v_{\boldsymbol{k}} c_{-\boldsymbol{k}\downarrow}^{\dagger} , \qquad \alpha_{-\boldsymbol{k}\downarrow} = u_{\boldsymbol{k}} c_{-\boldsymbol{k}\downarrow} + v_{\boldsymbol{k}} c_{\boldsymbol{k}\uparrow}^{\dagger} , \\ \alpha_{\boldsymbol{k}\uparrow}^{\dagger} &= u_{\boldsymbol{k}}^{*} c_{\boldsymbol{k}\uparrow}^{\dagger} - v_{\boldsymbol{k}}^{*} c_{-\boldsymbol{k}\downarrow} , \qquad \alpha_{-\boldsymbol{k}\downarrow}^{\dagger} = u_{\boldsymbol{k}}^{*} c_{-\boldsymbol{k}\downarrow}^{\dagger} + v_{\boldsymbol{k}}^{*} c_{\boldsymbol{k}\uparrow} . \end{aligned}$$
(34.2.86)

The inverse transformation is

$$c_{\boldsymbol{k}\uparrow} = u_{\boldsymbol{k}}^* \alpha_{\boldsymbol{k}\uparrow} + v_{\boldsymbol{k}} \alpha_{-\boldsymbol{k}\downarrow}^{\dagger}, \qquad c_{-\boldsymbol{k}\downarrow} = u_{\boldsymbol{k}}^* \alpha_{-\boldsymbol{k}\downarrow} - v_{\boldsymbol{k}} \alpha_{\boldsymbol{k}\uparrow}^{\dagger}, c_{\boldsymbol{k}\uparrow}^{\dagger} = u_{\boldsymbol{k}} \alpha_{\boldsymbol{k}\uparrow}^{\dagger} + v_{\boldsymbol{k}}^* \alpha_{-\boldsymbol{k}\downarrow}, \qquad c_{-\boldsymbol{k}\downarrow}^{\dagger} = u_{\boldsymbol{k}} \alpha_{-\boldsymbol{k}\downarrow}^{\dagger} - v_{\boldsymbol{k}}^* \alpha_{\boldsymbol{k}\uparrow}.$$
(34.2.87)

The Hamiltonian takes the diagonal form

$$\mathcal{H} = E_{\text{cond}}(T) + \sum_{\boldsymbol{k}} E_{\boldsymbol{k}} \left(\alpha_{\boldsymbol{k}\uparrow}^{\dagger} \alpha_{\boldsymbol{k}\uparrow} + \alpha_{-\boldsymbol{k}\downarrow}^{\dagger} \alpha_{-\boldsymbol{k}\downarrow} \right)$$
(34.2.88)

with

$$E_{\boldsymbol{k}} = \sqrt{\xi_{\boldsymbol{k}}^2 + |\Delta_{\boldsymbol{k}}|^2} \tag{34.2.89}$$

and

$$E_{\text{cond}}(T) = -\frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \langle c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \rangle \langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle + 2 \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2 - \sum_{\boldsymbol{k}} \left(\Delta_{\boldsymbol{k}} u_{\boldsymbol{k}} v^*_{\boldsymbol{k}} + \Delta^*_{\boldsymbol{k}} u^*_{\boldsymbol{k}} v_{\boldsymbol{k}} \right), \qquad (34.2.90)$$

if the coherence factors u_{k} and v_{k} satisfy the relations

$$|u_{k}|^{2} = \frac{1}{2} \left[1 + \frac{\xi_{k}}{E_{k}} \right], \qquad |v_{k}|^{2} = \frac{1}{2} \left[1 - \frac{\xi_{k}}{E_{k}} \right],$$
(34.2.91)

$$u_{\boldsymbol{k}}^* v_{\boldsymbol{k}} = \frac{\Delta_{\boldsymbol{k}}}{2E_{\boldsymbol{k}}} \,. \tag{34.2.92}$$

The temperature dependence of the coherence factors and of the quasiparticle energy is due to the temperature dependence of Δ_k which has to be determined self-consistently. Combining (34.2.85) with (34.2.87) we have

$$\Delta_{\boldsymbol{k}} = -\frac{1}{\Omega} \sum_{\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \Big\langle \left(u_{\boldsymbol{k}'}^* \alpha_{-\boldsymbol{k}'\downarrow} - v_{\boldsymbol{k}'} \alpha_{\boldsymbol{k}'\uparrow}^\dagger \right) \left(u_{\boldsymbol{k}'}^* \alpha_{\boldsymbol{k}'\uparrow} + v_{\boldsymbol{k}'} \alpha_{-\boldsymbol{k}'\downarrow}^\dagger \right) \Big\rangle. \quad (34.2.93)$$

Assuming that only the usual, normal averages are finite for the quasiparticles we get

$$\Delta_{\boldsymbol{k}} = -\frac{1}{\Omega} \sum_{\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} u_{\boldsymbol{k}'}^* v_{\boldsymbol{k}'} \Big(\left\langle \alpha_{-\boldsymbol{k}'\downarrow} \alpha_{-\boldsymbol{k}'\downarrow}^{\dagger} \right\rangle - \left\langle \alpha_{\boldsymbol{k}'\uparrow}^{\dagger} \alpha_{\boldsymbol{k}'\uparrow} \right\rangle \Big).$$
(34.2.94)

The quasiparticles are fermions; their thermal occupation in thermodynamic equilibrium is given by the Fermi distribution function at the quasiparticle energy:

$$f_0(E_k) = \frac{1}{\mathrm{e}^{\beta E_k} + 1} \,. \tag{34.2.95}$$

The self-consistency condition then leads to

$$\Delta_{\mathbf{k}} = -\frac{1}{\Omega} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u_{\mathbf{k}'}^* v_{\mathbf{k}'} \left[1 - 2f_0(E_{\mathbf{k}'}) \right]$$

= $-\frac{1}{\Omega} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2\sqrt{\xi_{\mathbf{k}'}^2 + |\Delta_{\mathbf{k}'}|^2}} \tanh \frac{\sqrt{\xi_{\mathbf{k}'}^2 + |\Delta_{\mathbf{k}'}|^2}}{2k_{\mathrm{B}}T}.$ (34.2.96)

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In the case of conventional superconductors, where the potential $V_{kk'}$ can be approximated by a constant, the gap equation (34.2.33) is recovered in the limit $T \to 0$. Taking a real gap, the temperature dependence is obtained from the self-consistent solution of

$$1 = \frac{V_0}{\Omega} \sum_{\mathbf{k}'} \frac{1}{2\sqrt{\xi_{\mathbf{k}'}^2 + \Delta^2(T)}} \tanh \frac{\sqrt{\xi_{\mathbf{k}'}^2 + \Delta^2(T)}}{2k_{\rm B}T}.$$
 (34.2.97)

Combining it with the equation valid for T = 0 we have

$$\sum_{k} \frac{1}{2\sqrt{\xi_{k}^{2} + \Delta_{0}^{2}}} = \sum_{k} \frac{1}{2\sqrt{\xi_{k}^{2} + \Delta^{2}(T)}} \tanh \frac{\sqrt{\xi_{k}^{2} + \Delta^{2}(T)}}{2k_{\rm B}T}, \quad (34.2.98)$$

or if the function tanh x is expressed in terms of the Fermi function,

$$\sum_{k} \left[\frac{1}{2\sqrt{\xi_{k}^{2} + \Delta^{2}(T)}} - \frac{1}{2\sqrt{\xi_{k}^{2} + \Delta_{0}^{2}}} \right]$$

$$= \sum_{k} \frac{1}{\sqrt{\xi_{k}^{2} + \Delta^{2}(T)}} f_{0} \left(\sqrt{\xi_{k}^{2} + \Delta^{2}(T)} \right).$$
(34.2.99)

Converting the sums to integrals

$$\frac{1}{2}\rho(\varepsilon_{\rm F}) \int_{0}^{\hbar\omega_{\rm D}} \left[\frac{1}{\sqrt{\xi^2 + \Delta^2(T)}} - \frac{1}{\sqrt{\xi^2 + \Delta_0^2}} \right] d\xi$$

$$= \rho(\varepsilon_{\rm F}) \int_{0}^{\hbar\omega_{\rm D}} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2(T)}} f_0\left(\sqrt{\xi^2 + \Delta^2(T)}\right).$$
(34.2.100)

The integral on the right-hand side cuts off sharply at high energies owing to the Fermi function; hence the upper limit of integration can be shifted to infinity. Expanding the Fermi function in inverse powers of the exponential function we can recognize the integral representation of the modified Bessel function K_0 :

$$K_0(nz) = \int_0^\infty \frac{1}{\sqrt{t^2 + z^2}} \exp\left(-n\sqrt{t^2 + z^2}\right) \mathrm{d}t.$$
 (34.2.101)

The dominant contribution to the integral on the left-hand side comes from the lower limit and we find

$$\ln \frac{\Delta_0}{\Delta(T)} = 2 \sum_{n=1}^{\infty} (-1)^{n+1} K_0 \left(n \frac{\Delta(T)}{k_{\rm B} T} \right).$$
(34.2.102)

At low temperatures, where $k_{\rm B}T \ll \Delta(T)$, we can use the asymptotic form of the modified Bessel function given in (C.3.59). An exponentially small temperature correction is obtained:

$$\Delta(T) = \Delta_0 \left[1 - \sqrt{\frac{2\pi k_{\rm B} T}{\Delta_0}} e^{-\Delta_0 / k_{\rm B} T} \right].$$
(34.2.103)

 $\Delta(T)$ decreases faster at higher temperatures and vanishes at a T_c where the thermal energy is on the order of Δ_0 . The critical temperature is determined from the gap equation as the temperature where the self-consistency condition (34.2.97) is met with $\Delta(T_c) = 0$, that is when

$$1 = \frac{V_0}{\Omega} \sum_{k} \frac{1}{2\xi_k} \tanh \frac{\xi_k}{2k_{\rm B}T_{\rm c}}.$$
 (34.2.104)

This is the same equation as (34.1.35) which was obtained for the instability temperature against pair formation. Its solution is known to give

$$k_{\rm B}T_{\rm c} = \frac{{\rm e}^{\gamma}}{\pi} 2\hbar\omega_{\rm D} \exp\left(-\frac{2}{V_0\rho(\varepsilon_{\rm F})}\right). \tag{34.2.105}$$

We thus find, just as for density waves, that the same temperature is obtained irrespective of whether the instability of the disordered phase is studied on approaching the transition from the high-temperature phase or by the vanishing of the order parameter in the low-temperature phase.

Close to the critical temperature, where the gap and hence also the argument of the modified Bessel function in (34.2.102) is small, it is no longer sufficient to take the leading term given in (C.3.59), but we must take into account the quadratic corrections. A more convenient procedure is to rewrite the integral form of (34.2.97),

$$1 = \frac{1}{2} V_0 \rho(\varepsilon_{\rm F}) \int_0^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{\sqrt{\xi^2 + \Delta^2(T)}} \tanh \frac{\sqrt{\xi^2 + \Delta^2(T)}}{2k_{\rm B}T}, \qquad (34.2.106)$$

in the equivalent form

$$\frac{2}{V_0\rho(\varepsilon_{\rm F})} = 2k_{\rm B}T \sum_{n=-\infty}^{\infty} \int_0^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{(\hbar\omega_n)^2 + \xi^2 + \Delta^2(T)}, \qquad (34.2.107)$$

where the summation goes over the frequencies $\hbar\omega_n = (2n+1)\pi k_{\rm B}T$. The equivalence of the two expressions can be readily verified by recalling that $\tanh z$ has simple poles at $z = i(n+\frac{1}{2})\pi$ for integer n and hence

$$\tanh z = \sum_{n=-\infty}^{\infty} \frac{1}{z + i(n + \frac{1}{2})\pi} = \frac{1}{2} \sum_{n=-\infty}^{\infty} \left[\frac{1}{z + i(n + \frac{1}{2})\pi} + \frac{1}{z - i(n + \frac{1}{2})\pi} \right]$$
$$= \sum_{n=-\infty}^{\infty} \frac{z}{z^2 + (n + \frac{1}{2})^2 \pi^2} \,. \tag{34.2.108}$$

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With the variable $z/2k_{\rm B}T$ we have

$$\tanh \frac{z}{2k_{\rm B}T} = 2k_{\rm B}T \sum_{n=-\infty}^{\infty} \frac{z}{z^2 + (\hbar\omega_n)^2} \,. \tag{34.2.109}$$

Alternatively we can make use of (K.2.63) on the right-hand side of (34.2.107) and then take into account that the integrand has poles at $\hbar\omega = \pm\sqrt{\xi^2 + \Delta^2}$.

Expanding the right-hand side of (34.2.107) for small values of $\Delta(T)$, the zeroth-order terms can be summed up to yield an integral containing $\tanh(\xi/2k_{\rm B}T)$ and we get

$$\frac{2}{V_0\rho(\varepsilon_{\rm F})} = \int_0^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{\xi} \tanh\frac{\xi}{2k_{\rm B}T} - 2k_{\rm B}T\Delta^2(T) \sum_{n=-\infty}^{\infty} \int_0^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{\left[(\hbar\omega_n)^2 + \xi^2\right]^2} \,. \tag{34.2.110}$$

The expression on the left-hand side can be written according to (34.1.39) as

$$\frac{2}{V_0\rho(\varepsilon_{\rm F})} = \ln\frac{\hbar\omega_{\rm D}}{2k_{\rm B}T_{\rm c}} + \ln\frac{4\mathrm{e}^{\gamma}}{\pi}.$$
(34.2.111)

The integral in the first term on the right-hand side of (34.2.110) was evaluated in (33.3.14):

$$\int_{0}^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{\xi} \tanh \frac{\xi}{2k_{\rm B}T} = \ln \frac{\hbar\omega_{\rm D}}{2k_{\rm B}T} + \ln \frac{4\mathrm{e}^{\gamma}}{\pi} \,. \tag{34.2.112}$$

The integration over ξ in the second term can be extended to infinity since $\hbar\omega_{\rm D} \gg k_{\rm B}T$, and we find

$$\sum_{n=-\infty}^{\infty} \int_{0}^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{\left[(\hbar\omega_{n})^{2} + \xi^{2}\right]^{2}} = \frac{\pi}{4} \sum_{n=-\infty}^{\infty} \frac{1}{|\hbar\omega_{n}|^{3}} = \frac{\pi}{2} \frac{1}{(\pi k_{\rm B}T)^{3}} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^{3}}.$$
(34.2.113)

Combining these expressions gives

$$\ln \frac{T}{T_{\rm c}} = -\frac{7\zeta(3)}{8\pi^2} \frac{\Delta^2(T)}{(k_{\rm B}T)^2}, \qquad (34.2.114)$$

that is

$$\Delta^2(T) = -\frac{8\pi^2}{7\zeta(3)} (k_{\rm B}T)^2 \ln \frac{T}{T_{\rm c}} \,. \tag{34.2.115}$$

Expansion in the neighborhood of $T_{\rm c}$ yields

$$\Delta(T) = \sqrt{\frac{8\pi^2}{7\zeta(3)}} k_{\rm B} T_{\rm c} \sqrt{1 - \frac{T}{T_{\rm c}}} \approx 3.06 \, k_{\rm B} T_{\rm c} \sqrt{1 - \frac{T}{T_{\rm c}}} \,. \tag{34.2.116}$$

Figure 34.7 compares the theoretically calculated temperature dependence of the gap with experimental data in the full $T < T_c$ range. The measured temperature dependence is in good agreement with the predictions of the BCS theory for type I elemental superconductors.



Fig. 34.7. Measured values of the reduced superconducting gap for some elemental superconductors as a function of reduced temperature, compared to the curve calculated in BCS theory [Reprinted with permission from P. Townsend and J. Sutton, *Phys. Rev.* 128, 591 (1962). © (1962) by the American Physical Society]

34.2.8 Critical Temperature and the Gap

The quantity Δ_{k} appearing in the coherence factors has a direct physical meaning: it gives the width of the forbidden region in the excitation spectrum. In conventional superconductors, where the gap is independent of k, it is very simply related to the critical temperature. Comparison of (34.2.36) with (34.2.105) gives

$$k_{\rm B}T_{\rm c} = \frac{{\rm e}^{\gamma}}{\pi} \Delta_0 = 0.567 \,\Delta_0 \,, \qquad (34.2.117)$$

which is conventionally written in the form

$$\frac{2\Delta_0}{k_{\rm B}T_{\rm c}} = 3.528\dots$$
 (34.2.118)

The ratio of the gap and the critical temperature takes the same value that was found for density waves. It was pointed out there that this ratio is universal, independent of material properties. The same is true in the BCS theory, which is essentially a mean-field theory. There is, however, an important difference compared to quasi-one-dimensional density-wave materials. Fluctuation effects, which are neglected in mean-field theory, become nonnegligible near the critical point, where the correlation length starts to diverge. The Ginzburg criterion (also known as the Levanyuk–Ginzburg criterion⁵) gives an estimate for the width of this range by comparing the root-mean-square fluctuations of the order parameter to the order parameter itself. Fluctuations

⁵ A. P. LEVANYUK, 1959, V. L. GINZBURG, 1960.

are so prevalent in quasi-one-dimensional systems that the transition temperature is drastically lowered compared to the mean-field value. In contrast to that, the BCS theory is a very good approximation for conventional superconductors because of the large coherence length, much larger than atomic dimensions. Taking a sphere with a radius on the order of the distance between the two electrons in a Cooper pair, there might be about 10^6 other pairs in that volume and fluctuations are averaged out. Critical phenomena, deviations from mean-field behavior, could be observed in an extremely narrow, experimentally inaccessible temperature range of order 10^{-6} K on both sides of T_c . We therefore expect good agreement between the BCS theory and experiments in conventional superconductors. In high-temperature superconductors, where – as seen in Table 26.12 – the coherence length can be as small as the lattice constant, the applicability of a mean-field theory is questionable.

There are several methods of measuring the gap. The most direct and most reliable value is obtained from the tunneling experiments discussed at the end of the chapter, but also ultrasound- or phonon-absorption experiments can be used. Even though the measured gap values are somewhat uncertain, the ratios of the experimental values are rather close to the theoretically predicted one for elemental superconductors. They vary between 3 and 4.5 as seen in Table 34.1. There are, however, materials where this ratio is appreciably different. This points up the limitations of the BCS theory.

Material	$2\Delta_0/k_{\rm B}T_{\rm c}$	Material	$2\Delta_0/k_{ m B}T_{ m c}$
Al	3.53	Hg	4.6
Cd	3.44	Pb	4.3
In	3.65	Os	4.8
Nb	3.65	Ir	5.6
Sn	3.59	$YBa_2Cu_3O_{7-\delta}$	4.0
Та	3.63	$\mathrm{Bi}_2\mathrm{Sr}_2\mathrm{Ca}_2\mathrm{Cu}_3\mathrm{O}_{10}$	5.7

Table 34.1. The ratio $2\Delta_0/k_{\rm B}T_{\rm c}$ for some superconductors

34.3 Thermodynamics and Electrodynamics of Superconductors

The thermodynamics and electrodynamics of superconductors were discussed in Chapter 26 using the London equations and in the framework of the phenomenological Ginzburg–Landau theory. These properties will now be considered in the BCS theory. In particular we will calculate the temperature dependence of the heat capacity, will explain the vanishing of the resistivity, and will show that the magnetic field is indeed expelled from the bulk of homogeneous superconductors.

34.3.1 Thermodynamic Properties

The energy of superconductors at finite temperatures is the sum of the condensation energy given in (34.2.90) and the thermal energy of the fermionic bogolons:

$$E_{\rm s} = E_{\rm cond}(T) + 2\sum_{k} E_{k} f_{0}(E_{k})$$
 (34.3.1)

with

$$E_{\text{cond}}(T) = -\frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \langle c^{\dagger}_{\boldsymbol{k}\uparrow} c^{\dagger}_{-\boldsymbol{k}\downarrow} \rangle \langle c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \rangle + 2 \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} |v_{\boldsymbol{k}}|^2 - \sum_{\boldsymbol{k}} \left(\Delta_{\boldsymbol{k}} u_{\boldsymbol{k}} v^*_{\boldsymbol{k}} + \Delta^*_{\boldsymbol{k}} u^*_{\boldsymbol{k}} v_{\boldsymbol{k}} \right).$$
(34.3.2)

Expressing the anomalous averages as well as the order parameter in terms of the distribution function of quasiparticles, we have

$$\langle c_{\mathbf{k}\uparrow}^{\dagger} c_{-\mathbf{k}\downarrow}^{\dagger} \rangle = u_{\mathbf{k}} v_{\mathbf{k}}^{*} [1 - 2f_{0}(E_{\mathbf{k}})] ,$$

$$\langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle = u_{\mathbf{k}}^{*} v_{\mathbf{k}} [1 - 2f_{0}(E_{\mathbf{k}})] ,$$

$$\Delta_{\mathbf{k}} = -\frac{1}{\Omega} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u_{\mathbf{k}'}^{*} v_{\mathbf{k}'} [1 - 2f_{0}(E_{\mathbf{k}'})] .$$

$$(34.3.3)$$

Then, making use of

$$E_{k} = \xi_{k} \left(|u_{k}|^{2} - |v_{k}|^{2} \right) + \left(\Delta_{k} u_{k} v_{k}^{*} + \Delta_{k}^{*} u_{k}^{*} v_{k} \right), \qquad (34.3.4)$$

the energy can be written as

$$E_{s} = 2 \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} \left[|v_{\boldsymbol{k}}|^{2} + (u_{\boldsymbol{k}}^{2} - |v_{\boldsymbol{k}}|^{2}) f_{0}(E_{\boldsymbol{k}}) \right] + \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} u_{\boldsymbol{k}} v_{\boldsymbol{k}}^{*} u_{\boldsymbol{k}'}^{*} v_{\boldsymbol{k}'} \left[1 - 2f_{0}(E_{\boldsymbol{k}}) \right] \left[1 - 2f_{0}(E_{\boldsymbol{k}'}) \right].$$
(34.3.5)

This form could have been derived directly by taking the expectation value of the BCS Hamiltonian, in which the electron operators are expressed in terms of the quasiparticle operators using the Bogoliubov transformation.

Since the BCS Hamiltonian is diagonal in terms of the bogolon operators, the entropy of superconductors can be written in a form analogous to that of free fermion systems,

$$S_{\rm s} = -2k_{\rm B} \sum_{k} \left\{ f_0(E_k) \ln f_0(E_k) + \left[1 - f_0(E_k) \right] \ln \left[1 - f_0(E_k) \right] \right\}$$

= $\frac{2}{T} \sum_{k} E_k f_0(E_k) + 2k_{\rm B} \sum_{k} \ln \left(1 + e^{-\beta E_k} \right),$ (34.3.6)

and the free energy takes the form

$$F_{\rm s} = E_{\rm cond}(T) - 2k_{\rm B}T \sum_{k} \ln\left(1 + e^{-\beta E_{k}}\right).$$
(34.3.7)

Alternatively we can proceed from a formula given in Chapter 30. We have seen that the change in the free energy caused by the interaction can be given according to (30.1.49) via

$$F(\lambda) = F(\lambda = 0) + \int_{0}^{\lambda} \frac{\mathrm{d}\lambda'}{\lambda'} \langle \mathcal{H}_{\mathrm{int}}(\lambda') \rangle, \qquad (34.3.8)$$

where λ is the coupling constant of the interaction. Using the Hamiltonian of the BCS theory for s-wave superconductors, we have

$$F_{\rm s} = F_{\rm n} - \int_{0}^{V_0} \frac{\mathrm{d}V_0'}{V_0'} \left\langle \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'} V_0' c_{\boldsymbol{k}\uparrow}^{\dagger} c_{-\boldsymbol{k}\downarrow}^{\dagger} c_{-\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}'\uparrow} \right\rangle.$$
(34.3.9)

The mean value of the product of the four operators can be decoupled, in the spirit of mean-field theory, into the product of the expectation values of two operators. The relevant two-operator terms are related to the order parameter Δ , hence

$$F_{\rm s} = F_{\rm n} - \Omega \int_{0}^{V_0} \frac{\mathrm{d}V_0'}{{V_0'}^2} |\Delta(V_0')|^2 = F_{\rm n} + \Omega \int_{0}^{V_0} \mathrm{d}(1/V_0') |\Delta(V_0')|^2, \qquad (34.3.10)$$

where we denoted explicitly that the order parameter belonging to the potential V'_0 has to be used. Changing to the variable $\Delta' \equiv \Delta(V'_0)$ from V'_0 we get

$$F_{\rm s} = F_{\rm n} + \Omega \int_{0}^{\Delta} \mathrm{d}\Delta' \frac{\mathrm{d}(1/V_0')}{\mathrm{d}\Delta'} |\Delta'|^2 \,. \tag{34.3.11}$$

The relationship between $1/V_0$ and Δ given in (34.2.97) can be rewritten as

$$\frac{1}{V_0} = \frac{1}{\Omega} \sum_{\mathbf{k}'} \frac{1}{2\sqrt{\xi_{\mathbf{k}'}^2 + |\Delta|^2}} \tanh \frac{\sqrt{\xi_{\mathbf{k}'}^2 + |\Delta|^2}}{2k_{\rm B}T}$$
(34.3.12)
$$= \frac{1}{\Omega} \sum_{\mathbf{k}'} \frac{1}{2\sqrt{\xi_{\mathbf{k}'}^2 + |\Delta|^2}} - \frac{1}{\Omega} \sum_{\mathbf{k}'} \frac{1}{\sqrt{\xi_{\mathbf{k}'}^2 + |\Delta|^2}} f_0\left(\sqrt{\xi_{\mathbf{k}'}^2 + |\Delta|^2}\right).$$

Replacing the summation by integration, the integrals can be expressed in terms of the modified Bessel function K_0 . At low temperatures, where the asymptotic form of K_0 can be used, we find

$$\frac{F_{\rm s} - F_{\rm n}}{\Omega} = \frac{1}{6}\pi^2 \rho(\varepsilon_{\rm F}) (k_{\rm B}T)^2 \qquad (34.3.13)$$
$$-\frac{1}{4}\rho(\varepsilon_{\rm F}) \left[\Delta_0^2 + \sqrt{8\pi\Delta_0^3 k_{\rm B}T} \left(1 + \frac{15}{8} \frac{k_{\rm B}T}{\Delta_0} \right) e^{-\Delta_0/k_{\rm B}T} \right].$$

The first term is the negative of the leading thermal correction to the free energy of normal metals. It gives the well-known linear specific heat. The term proportional to Δ_0^2 is the lowering of the free energy due to the condensation of electrons into pairs. The thermal corrections are exponentially small owing to the gap in the excitation spectrum. The low-temperature form of the entropy and of the heat capacity are

$$\frac{S_{\rm s}}{\Omega} = \rho(\varepsilon_{\rm F})\Delta_0 \sqrt{2\pi} \left(\frac{\Delta_0}{k_{\rm B}T}\right)^{1/2} e^{-\Delta_0/k_{\rm B}T},$$

$$\frac{C_{\rm s}}{\Omega} = \rho(\varepsilon_{\rm F})\Delta_0 k_{\rm B} \sqrt{2\pi} \left(\frac{\Delta_0}{k_{\rm B}T}\right)^{3/2} e^{-\Delta_0/k_{\rm B}T}.$$
(34.3.14)

Near $T_{\rm c},$ where the gap is small compared to the thermal energy, we start from the relationship

$$\frac{1}{V_0} = k_{\rm B} T \rho(\varepsilon_{\rm F}) \sum_{n=-\infty}^{\infty} \int_0^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{(\hbar\omega_n)^2 + \xi^2 + \Delta^2(T)}, \qquad (34.3.15)$$

which follows from (34.2.107), and expand the right-hand side for small values of the gap. We find

$$\frac{F_{\rm s} - F_{\rm n}}{\Omega} = -\frac{1}{2}k_{\rm B}T\rho(\varepsilon_{\rm F})\Delta^4(T)\sum_{n=-\infty}^{\infty}\int_{0}^{\hbar\omega_{\rm D}} \frac{\mathrm{d}\xi}{\left[(\hbar\omega_n)^2 + \xi^2\right]^2}.$$
 (34.3.16)

Since $\hbar\omega_{\rm D} \gg k_{\rm B}T$, the integration may be extended to infinity and we get

$$\frac{F_{\rm s} - F_{\rm n}}{\Omega} = -\frac{1}{2}k_{\rm B}T\rho(\varepsilon_{\rm F})\Delta^4(T)\frac{\pi}{4}\sum_{n=-\infty}^{\infty}\frac{1}{|\hbar\omega_n|^3}$$

$$= -\frac{1}{2}\rho(\varepsilon_{\rm F})\frac{7\zeta(3)}{16\pi^2}\frac{\Delta^4(T)}{(k_{\rm B}T)^2}$$

$$= -\rho(\varepsilon_{\rm F})\frac{2\pi^2}{7\zeta(3)}(k_{\rm B}T_{\rm c})^2\left(1 - \frac{T}{T_{\rm c}}\right)^2.$$
(34.3.17)

This gives

$$\frac{S_{\rm s} - S_{\rm n}}{\Omega} = -\frac{4\pi^2}{7\zeta(3)}\rho(\varepsilon_{\rm F})k_{\rm B}^2 T_{\rm c}\left(1 - \frac{T}{T_{\rm c}}\right)$$
(34.3.18)

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for the entropy and

$$\frac{C_{\rm s} - C_{\rm n}}{\Omega} = \frac{4\pi^2}{7\zeta(3)}\rho(\varepsilon_{\rm F})k_{\rm B}^2 T \tag{34.3.19}$$

for the heat capacity. As was displayed in Fig. 26.13, the entropy of the superconducting state is lower than that of the normal state owing to the ordering of the electrons into pairs. The heat capacity is, however, larger in the superconducting state near T_c . Right at the transition

$$\frac{C_{\rm s}(T_{\rm c}) - C_{\rm n}(T_{\rm c})}{\Omega} = \frac{4\pi^2}{7\zeta(3)}\rho(\varepsilon_{\rm F})k_{\rm B}^2 T_{\rm c}\,.$$
(34.3.20)

Using the expression derived for the heat capacity of normal metals in the Sommerfeld model, the relative jump of the heat capacity is

$$\frac{C_{\rm s}(T_{\rm c}) - C_{\rm n}(T_{\rm c})}{C_{\rm n}(T_{\rm c})} = \frac{12}{7\zeta(3)} = 1.426.$$
(34.3.21)

This result was already given in (26.1.6). We pointed out there that the experimental results presented in Table 26.2 are often in good agreement with this theoretical prediction of the BCS theory.

Knowing the lowering of the free energy of the superconducting state with respect to the normal state we can calculate the temperature dependence of the thermodynamic critical magnetic field, which is defined as the field where this condensation energy is compensated by the energy of the magnetic field. At low temperatures, taking the leading terms from (34.3.13), we have

$$\frac{F_{\rm s} - F_{\rm n}}{\Omega} = -\frac{1}{4}\rho(\varepsilon_{\rm F})\Delta_0^2 + \frac{1}{6}\pi^2\rho(\varepsilon_{\rm F})(k_{\rm B}T)^2.$$
(34.3.22)

This gives

$$H_{\rm c}^2(T) = H_{\rm c}^2(0) \left[1 - \frac{2}{3} \pi^2 (k_{\rm B} T / \Delta_0)^2 \right], \qquad (34.3.23)$$

from which

$$H_{\rm c}(T) \approx H_{\rm c}(0) \left[1 - 1.07 (T/T_{\rm c})^2\right],$$
 (34.3.24)

where $H_{\rm c}(0) = \left[\frac{1}{2}\rho(\varepsilon_{\rm F})\Delta_0^2/\mu_0\right]^{1/2}$. On the other hand, near the critical point, where the change in the free energy is given by (34.3.17), we find

$$H_{\rm c}(T) = H_{\rm c}(0) {\rm e}^{\gamma} \left(\frac{8}{7\zeta(3)}\right)^{1/2} \left(1 - \frac{T}{T_{\rm c}}\right)$$

= 1.74 $H_{\rm c}(0) \left(1 - \frac{T}{T_{\rm c}}\right).$ (34.3.25)

Note that the experimental data can be well fit in almost the full temperature range $T < T_c$ by a parabolic temperature dependence.

34.3.2 Infinite Conductivity

The Cooper pairs of the BCS state are formed by electrons with wave vectors \mathbf{k} and $-\mathbf{k}$. Their total momentum is zero. Pairs with finite momentum $\hbar q$ are obtained if electrons with $\mathbf{k} + \mathbf{q}/2$ and $-\mathbf{k} + \mathbf{q}/2$ are bound together. If \mathbf{q} is the same for all pairs, this is equivalent to considering the original BCS state in a moving frame that is boosted with velocity $-\hbar \mathbf{q}/2m_{\rm e}$. Since the centers of mass of the pairs drift with velocity $\hbar \mathbf{q}/2m_{\rm e}$, a current flows in the sample with current density

$$\boldsymbol{j} = -en_{\rm e}\frac{\hbar\boldsymbol{q}}{2m_{\rm e}}\,.\tag{34.3.26}$$

The generation of the current is accompanied by an increase of the energy by the amount

$$\Delta E = N_{\rm e} \frac{\hbar^2 q^2}{8m_{\rm e}} \,. \tag{34.3.27}$$

We demonstrate that impurities or other defects, which contribute essentially to the destruction of current in normal metals, cannot efficiently break up the Cooper pairs.

The most important contribution to the resistivity of normal metals comes from backward scattering, when an electron is scattered to the opposite side of the Fermi sphere. The current decays even if the scattering is elastic. The interaction with defects can lead to a decay of the current in superconductors if Cooper pairs are broken up. Consider a pair $(\mathbf{k} + \mathbf{q}/2\uparrow, -\mathbf{k} + \mathbf{q}/2\downarrow)$. If this pair is broken and the electron with wave vector $\mathbf{k} + \mathbf{q}/2$ propagating in the direction of the current is scattered elastically into the state with wave vector $-\mathbf{k} + \mathbf{q}/2$, the conservation of energy can be met provided that

$$\frac{\hbar^2 (\boldsymbol{k} + \boldsymbol{q}/2)^2}{2m_{\rm e}} \ge \frac{\hbar^2 (-\boldsymbol{k} + \boldsymbol{q}/2)^2}{2m_{\rm e}} + 2\Delta_0, \qquad (34.3.28)$$

since the minimum energy needed to break up a pair is $2\Delta_0$. This leads to the condition

$$q \frac{\hbar^2 k_{\rm F}}{m_{\rm e}} \ge 2\Delta_0 \,.$$
 (34.3.29)

It can be satisfied only if q exceed a certain critical value, which gives the estimate

$$j_{\rm c} = -\frac{en_{\rm e}\Delta_0}{\hbar k_{\rm F}} \tag{34.3.30}$$

for the critical current density. Taking a value 1 meV for the gap at T = 0, our estimate for the critical current density is $10^7 \,\text{A/cm}^2$. The experimentally observed values are often a few orders of magnitude smaller than that, since we did not take into account that no current can flow inside a homogeneous superconductor from where the magnetic field is expelled. The critical current has to flow on the surface, within a distance on the order of the penetration depth.

Our considerations are valid for elastic potential scattering by nonmagnetic impurities. Breaking up of Cooper pairs occurs more easily when paramagnetic impurities are present, since the spin of the electron can be flipped by such impurities. The gap decreases fast with the concentration of magnetic impurities and superconductivity can be destroyed completely when the concentration exceeds a few percent. A particularly interesting feature of superconductors doped with paramagnetic impurities is that the vanishing of the gap does not coincide with the destruction of superconductivity. There is a narrow concentration range where the superconducting order parameter is finite, Cooper pairs are present, the electrical properties are those of superconductors, but there is no gap in the excitation spectrum of quasiparticles. This phenomenon is known as *gapless superconductivity*.

34.3.3 The Meissner–Ochsenfeld Effect

Consider now a superconductor in an external magnetic field. Since the kinetic energy contains the kinetic momentum, the Hamiltonian of the interaction with the field can be written as

$$\mathcal{H}' = \frac{1}{2m_{\rm e}} \left(\boldsymbol{p} + e\boldsymbol{A} \right)^2 - \frac{1}{2m_{\rm e}} \boldsymbol{p}^2 \approx \frac{e}{2m_{\rm e}} \left(\boldsymbol{p} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p} \right), \qquad (34.3.31)$$

if the effect of the field is treated up to first order in the vector potential. In second quantization

$$\mathcal{H}' = \frac{e\hbar}{2m_{\rm e}\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma} \int d\boldsymbol{r} \, \mathrm{e}^{\mathrm{i}(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}} \boldsymbol{A} \cdot (\boldsymbol{k}+\boldsymbol{k}') c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}'\sigma}$$

$$= \frac{e\hbar}{2m_{\rm e}\Omega} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} \boldsymbol{A}(-\boldsymbol{q}) \cdot (2\boldsymbol{k}+\boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma} , \qquad (34.3.32)$$

where A(-q) is the Fourier transform of the vector potential.

When the quantum mechanical current operator

$$\hat{\boldsymbol{j}} = \frac{\mathrm{i}e\hbar}{2m_{\mathrm{e}}} \left(\psi^* \nabla \psi - \psi \nabla \psi^* \right) - \frac{e^2}{m_{\mathrm{e}}} \boldsymbol{A} \psi^* \psi \qquad (34.3.33)$$

is written in second quantization in terms of the creation and annihilation operators,

$$\hat{\boldsymbol{j}} = \frac{1}{\Omega} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma} \left[-\frac{e\hbar}{2m_{\rm e}} (\boldsymbol{k} + \boldsymbol{k}') - \frac{e^2}{m_{\rm e}} \boldsymbol{A} \right] e^{i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}'\sigma}
= \frac{1}{\Omega} \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \sum_{\boldsymbol{k}\sigma} \left[-\frac{e\hbar}{2m_{\rm e}} (2\boldsymbol{k} + \boldsymbol{q}) - \frac{e^2}{m_{\rm e}} \boldsymbol{A} \right] c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma} .$$
(34.3.34)

As usual, the current is divided into two parts: $j = j_{p} + j_{d}$. The diamagnetic current, the expectation value of the second term, contains the vector potential

explicitly; hence, $\langle c^{\dagger}_{k\sigma}c_{k+q\sigma} \rangle$ is calculated in the absence of magnetic field. Only the q = 0 component is nonvanishing and we have

$$\boldsymbol{j}_{\rm d} = \langle \hat{\boldsymbol{j}}_{\rm d} \rangle = -\frac{e^2}{m_{\rm e}\Omega} \boldsymbol{A} \sum_{\boldsymbol{k}\sigma} \left\langle c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \right\rangle = -\frac{e^2 n_{\rm e}}{m_{\rm e}} \boldsymbol{A}.$$
(34.3.35)

This contribution remains unchanged at the transition from the normal to the superconducting state; it has to be compensated by the paramagnetic current in the superconducting state.

To calculate the paramagnetic contribution we have to determine the expectation value of

$$\hat{\boldsymbol{j}}_{\mathrm{p}}(\boldsymbol{q}) = -\frac{e\hbar}{2m_{\mathrm{e}}\Omega} \sum_{\boldsymbol{k}\sigma} (2\boldsymbol{k} + \boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}$$
(34.3.36)

in the presence of the magnetic field to first order in the vector potential. Comparison with (34.3.32) shows that the same expression appears in the interaction with the external field,

$$\mathcal{H}' = -\hat{\boldsymbol{j}}_{p}(\boldsymbol{q})\boldsymbol{A}(-\boldsymbol{q}). \qquad (34.3.37)$$

Hence, according to the linear response theory, the kernel K(q) that relates the Fourier components of the current to the vector potential in

$$\boldsymbol{j}(\boldsymbol{q}) = -K(\boldsymbol{q})\boldsymbol{A}(\boldsymbol{q}) \tag{34.3.38}$$

is the retarded current–current response function. Its full q dependence is needed to get the nonlocal relationship in real space in type I superconductors. Tedious, partly numerical calculations give in fact a spatial dependence, which is rather close to the form proposed by PIPPARD [see (26.3.50)], with an explicit expression

$$\xi_0 = \frac{\hbar v_{\rm F}}{\pi \Delta_0} \tag{34.3.39}$$

for the coherence length.

The full form of $K(\mathbf{q})$ is not needed if we are interested in the Meissner– Ochsenfeld effect, in the expulsion of the magnetic induction from the bulk of a superconductor. It is sufficient to show that $K(\mathbf{q})$ takes a finite positive value in the long-wavelength limit, when $\mathbf{q} \to 0$. In this limit we get

$$\boldsymbol{j}(\boldsymbol{q}) = -\frac{n_{\rm s}(T)e^2}{m_{\rm e}}\boldsymbol{A}(\boldsymbol{q}), \qquad (34.3.40)$$

which resembles the second London equation with $n_{\rm s}(T)$, the density of superconducting electrons, given by

$$n_{\rm s}(T) = n_{\rm e} - \frac{\hbar^2}{3\pi^2 m_{\rm e}} \int_0^\infty k^4 \left[-\frac{\partial f_0(E_k)}{\partial E_k} \right] \mathrm{d}k \,. \tag{34.3.41}$$

Evaluating it with the excitation energies of the BCS theory we find

$$\frac{n_{\rm s}(T)}{n_{\rm e}} = \begin{cases} 1 - \left(\frac{2\pi\Delta_0}{k_{\rm B}T}\right)^{1/2} {\rm e}^{-\Delta_0/k_{\rm B}T} & T \to 0, \\ \\ 2\left(1 - \frac{T}{T_{\rm c}}\right) & T \to T_{\rm c}. \end{cases}$$
(34.3.42)

In type II superconductors, where the kernel $K(\mathbf{q})$ is independent of \mathbf{q} and the second London equation expresses a local relationship between the current and the vector potential, the temperature-dependent prefactor in (34.3.40) gives a temperature-dependent penetration depth:

$$\left(\frac{\lambda(T)}{\lambda_{\rm L}}\right)^2 = \frac{n_{\rm e}}{n_{\rm s}(T)}\,.\tag{34.3.43}$$

It diverges at the critical temperature $T_{\rm c}$, where the density of superconducting electrons vanishes.

34.4 Inhomogeneous Superconductors and Retardation Effects

So far we have considered the uniform superconducting state. This is certainly not true in the Shubnikov phase of type II superconductors. Spatial nonuniformity may appear in type I superconductors as well, when the sample is doped with impurities or when the boundary effects of a finite sample cannot be neglected. The mean-field theory is in principle applicable also to the case when the order parameter is position dependent. Here we only write down the equations that the order parameter has to satisfy and show, using the Green functions of many-body theory, how the phenomenological Ginzburg–Landau equations discussed in Chapter 26 can be derived from the microscopic theory.

Another important element of the BCS theory is the assumption that the effective interaction mediated by phonons between electrons is instantaneous; there is no time delay between the emission and the absorption of the phonon. This is a reasonable approximation when the electron–phonon interaction is weak. Retardation effects become important for stronger couplings, and the frequency dependence of the effective interaction in Fourier representation cannot be neglected. The propagation of phonons and electrons can be treated simultaneously using Green functions and this allows us to discuss the effect of retardation on the superconducting state.

34.4.1 Bogoliubov Equations

Nonuniform superconductors are conveniently studied in real-space representation by writing the Hamiltonian in terms of the field operators. Assuming a spin-independent, local, attractive two-particle potential $-V_0\delta(\mathbf{r}-\mathbf{r'})$ between electrons, the interaction Hamiltonian takes the form

$$\mathcal{H}_{\text{int}} = -\frac{1}{2} \sum_{\sigma\sigma'} \int \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}) V_0 \hat{\psi}_{\sigma'}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) \,\mathrm{d}\boldsymbol{r} \,.$$
(34.4.1)

It will be treated in the mean-field approximation assuming a nonvanishing, position-dependent value for the anomalous average,

$$\Delta(\mathbf{r}) = -V_0 \langle \hat{\psi}_{\downarrow}(\mathbf{r}) \hat{\psi}_{\uparrow}(\mathbf{r}) \rangle = V_0 \langle \hat{\psi}_{\uparrow}(\mathbf{r}) \hat{\psi}_{\downarrow}(\mathbf{r}) \rangle, \Delta^*(\mathbf{r}) = -V_0 \langle \hat{\psi}_{\uparrow}^{\dagger}(\mathbf{r}) \hat{\psi}_{\downarrow}^{\dagger}(\mathbf{r}) \rangle = V_0 \langle \hat{\psi}_{\downarrow}^{\dagger}(\mathbf{r}) \hat{\psi}_{\uparrow}^{\dagger}(\mathbf{r}) \rangle,$$
(34.4.2)

in addition to the Hartree term. Dropping the $c\mbox{-number terms}$ the total Hamiltonian becomes

$$\mathcal{H} = \mathcal{H}_0 + \int \left[\Delta(\boldsymbol{r}) \hat{\psi}_{\uparrow}^{\dagger}(\boldsymbol{r}) \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r}) + \Delta^*(\boldsymbol{r}) \hat{\psi}_{\downarrow}(\boldsymbol{r}) \hat{\psi}_{\uparrow}(\boldsymbol{r}) \right] \, \mathrm{d}\boldsymbol{r} \,, \qquad (34.4.3)$$

where the unperturbed part,

$$\mathcal{H}_{0} = \sum_{\sigma} \int \mathrm{d}\boldsymbol{r} \, \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) \left[\frac{1}{2m_{\mathrm{e}}} \left(\frac{\hbar}{\mathrm{i}} \boldsymbol{\nabla} + e\boldsymbol{A} \right)^{2} + U(\boldsymbol{r}) - \mu \right] \hat{\psi}_{\sigma}(\boldsymbol{r}) \,, \quad (34.4.4)$$

contains the kinetic energy and a local one-particle potential

$$U(\boldsymbol{r}) = U_0(\boldsymbol{r}) - V_0 \left\langle \hat{\psi}_{\uparrow}^{\dagger}(\boldsymbol{r}) \hat{\psi}_{\uparrow}(\boldsymbol{r}) \right\rangle = U_0(\boldsymbol{r}) - V_0 \left\langle \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r}) \hat{\psi}_{\downarrow}(\boldsymbol{r}) \right\rangle, \quad (34.4.5)$$

which is the sum of the external potential $U_0(\mathbf{r})$ and the Hartree term. The nondiagonal part contains the pairing potential $\Delta(\mathbf{r})$.

It is convenient to introduce the row and column vectors,

$$\hat{\Psi}^{\dagger}(\boldsymbol{r}) = \left(\hat{\psi}^{\dagger}_{\uparrow}(\boldsymbol{r}) \ \hat{\psi}_{\downarrow}(\boldsymbol{r})\right), \qquad \hat{\Psi}(\boldsymbol{r}) = \begin{pmatrix}\hat{\psi}_{\uparrow}(\boldsymbol{r})\\ \hat{\psi}^{\dagger}_{\downarrow}(\boldsymbol{r})\end{pmatrix}, \qquad (34.4.6)$$

and the Hamiltonian matrix

$$\hat{\mathcal{H}}(\boldsymbol{r}) = \begin{pmatrix} \mathcal{H}_{e}(\boldsymbol{r}) & \Delta(\boldsymbol{r}) \\ \Delta^{*}(\boldsymbol{r}) & -\mathcal{H}_{e}(\boldsymbol{r}) \end{pmatrix}$$
(34.4.7)

with

$$\mathcal{H}_{e}(\boldsymbol{r}) = \frac{1}{2m_{e}} \left(\frac{\hbar}{i} \boldsymbol{\nabla} + e\boldsymbol{A}\right)^{2} + U(\boldsymbol{r}) - \mu. \qquad (34.4.8)$$

The Hamiltonian then takes the form

$$\mathcal{H} = \int \mathrm{d}\boldsymbol{r} \,\hat{\boldsymbol{\Psi}}^{\dagger}(\boldsymbol{r}) \hat{\mathcal{H}}(\boldsymbol{r}) \hat{\boldsymbol{\Psi}}(\boldsymbol{r}) \,. \tag{34.4.9}$$

We attempt to diagonalize it by a generalized Bogoliubov transformation by expanding the field operators in terms of a set of fermionic operators $\alpha_{n\sigma}$ and $\alpha^{\dagger}_{n\sigma}$ in the form

$$\hat{\psi}_{\uparrow}(\boldsymbol{r}) = \sum_{n} \left[u_{n}(\boldsymbol{r})\alpha_{n\uparrow} - v_{n}^{*}(\boldsymbol{r})\alpha_{n\downarrow}^{\dagger} \right],$$

$$\hat{\psi}_{\downarrow}(\boldsymbol{r}) = \sum_{n} \left[u_{n}(\boldsymbol{r})\alpha_{n\downarrow} + v_{n}^{*}(\boldsymbol{r})\alpha_{n\uparrow}^{\dagger} \right].$$
(34.4.10)

The corresponding Hermitian conjugate operators are

$$\hat{\psi}_{\uparrow}^{\dagger}(\boldsymbol{r}) = \sum_{n} \left[u_{n}^{*}(\boldsymbol{r})\alpha_{n\uparrow}^{\dagger} - v_{n}(\boldsymbol{r})\alpha_{n\downarrow} \right],$$

$$\hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r}) = \sum_{n} \left[u_{n}^{*}(\boldsymbol{r})\alpha_{n\downarrow}^{\dagger} + v_{n}(\boldsymbol{r})\alpha_{n\uparrow} \right].$$
(34.4.11)

Written in matrix form,

$$\hat{\Psi}^{\dagger}(\boldsymbol{r}) = \sum_{n} \hat{\alpha}_{n}^{\dagger} U_{n}^{\dagger}, \qquad \hat{\Psi}(\boldsymbol{r}) = \sum_{n} U_{n} \hat{\alpha}_{n} \qquad (34.4.12)$$

with

$$U_n = \begin{pmatrix} u_n(\mathbf{r}) & -v_n^*(\mathbf{r}) \\ v_n(\mathbf{r}) & u_n^*(\mathbf{r}) \end{pmatrix}, \qquad (34.4.13)$$

where the row and column vectors formed from the new operators are defined via

$$\hat{\alpha}_{n}^{\dagger} = \begin{pmatrix} \alpha_{n\uparrow}^{\dagger} & \alpha_{n\downarrow} \end{pmatrix}, \qquad \hat{\alpha}_{n} = \begin{pmatrix} \alpha_{n\uparrow} \\ \alpha_{n\downarrow}^{\dagger} \end{pmatrix}.$$
(34.4.14)

The anticommutation relations of the field operators are satisfied if

$$\sum_{n} \left[u_{n}^{*}(\boldsymbol{r})u_{n}(\boldsymbol{r}') + v_{n}(\boldsymbol{r})v_{n}^{*}(\boldsymbol{r}') \right] = \delta(\boldsymbol{r} - \boldsymbol{r}'),$$

$$\sum_{n} \left[u_{n}(\boldsymbol{r})v_{n}^{*}(\boldsymbol{r}') - v_{n}^{*}(\boldsymbol{r})u_{n}(\boldsymbol{r}') \right] = 0.$$
(34.4.15)

The inverse transformations are then given by

$$\begin{aligned} \alpha_{n\uparrow} &= \int \mathrm{d}\boldsymbol{r} \left[u_n(\boldsymbol{r}) \hat{\psi}_{\uparrow}(\boldsymbol{r}) - v_n(\boldsymbol{r}) \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r}) \right], \\ \alpha_{n\downarrow}^{\dagger} &= \int \mathrm{d}\boldsymbol{r} \left[u_n^*(\boldsymbol{r}) \hat{\psi}_{\downarrow}(\boldsymbol{r}) + v_n^*(\boldsymbol{r}) \hat{\psi}_{\uparrow}(\boldsymbol{r}) \right], \end{aligned} \tag{34.4.16}$$

and their fermionic anticommutation relations are satisfied if

$$\int \left[u_m^*(\boldsymbol{r}) u_n(\boldsymbol{r}) + v_m^*(\boldsymbol{r}) v_n(\boldsymbol{r}) \right] d\boldsymbol{r} = \delta_{mn} ,$$

$$\int \left[v_m(\boldsymbol{r}) u_n(\boldsymbol{r}) - u_m(\boldsymbol{r}) v_n(\boldsymbol{r}) \right] d\boldsymbol{r} = 0 .$$
(34.4.17)

The complex functions $u_n(\mathbf{r})$ and $v_n(\mathbf{r})$ are determined from the requirement that the full Hamiltonian assume the diagonal form

$$\mathcal{H} = E_{0s} + \sum_{n\sigma} \varepsilon_n \alpha_{n\sigma}^{\dagger} \alpha_{n\sigma} , \qquad (34.4.18)$$

which is equivalent to the commutators

$$\left[\mathcal{H}, \alpha_{n\sigma}\right]_{-} = -\varepsilon_n \alpha_{n\sigma}, \qquad \left[\mathcal{H}, \alpha_{n\sigma}^{\dagger}\right]_{-} = \varepsilon_n \alpha_{n\sigma}^{\dagger}. \tag{34.4.19}$$

The commutators of the Hamiltonian with the field operators are easily calculated to yield

$$\begin{bmatrix} \mathcal{H}, \hat{\psi}_{\uparrow}(\boldsymbol{r}) \end{bmatrix}_{-} = -\mathcal{H}_{e} \hat{\psi}_{\uparrow}(\boldsymbol{r}) - \Delta(\boldsymbol{r}) \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r}) , \\ \begin{bmatrix} \mathcal{H}, \hat{\psi}_{\downarrow}(\boldsymbol{r}) \end{bmatrix}_{-} = -\mathcal{H}_{e} \hat{\psi}_{\downarrow}(\boldsymbol{r}) + \Delta(\boldsymbol{r}) \hat{\psi}_{\uparrow}^{\dagger}(\boldsymbol{r}) .$$
 (34.4.20)

Substituting the expansion (34.4.10) into this equation the diagonalization conditions are satisfied if

$$\mathcal{H}_{e}u_{n}(\boldsymbol{r}) + \Delta(\boldsymbol{r})v_{n}(\boldsymbol{r}) = \varepsilon_{n}u_{n}(\boldsymbol{r}),$$

$$\Delta^{*}(\boldsymbol{r})u_{n}(\boldsymbol{r}) - \mathcal{H}_{e}v_{n}(\boldsymbol{r}) = \varepsilon_{n}v_{n}(\boldsymbol{r}).$$
(34.4.21)

These relations are equivalent to the statement that the column vector function

$$\begin{pmatrix} u_n(\boldsymbol{r}) \\ v_n(\boldsymbol{r}) \end{pmatrix}$$
(34.4.22)

is an eigenfunction of (34.4.7). This coupled set of differential equations for the coefficients $u_n(\mathbf{r})$ and $v_n(\mathbf{r})$ and for the eigenvalues ε_n are the *Bogoliubov* equations also known as the *Bogoliubov*-de Gennes (BdG) equations.⁶ The one-particle potential and the pairing potential have to be determined selfconsistently from the equations

$$U(\mathbf{r}) = U_0(\mathbf{r}) - V_0 \sum_n \left\{ |u_n(\mathbf{r})|^2 f_0(\varepsilon_n) + |v_n(\mathbf{r})|^2 [1 - f_0(\varepsilon_n)] \right\},$$

$$\Delta(\mathbf{r}) = V_0 \sum_n u_n(\mathbf{r}) v_n^*(\mathbf{r}) [1 - 2f_0(\varepsilon_n)].$$
(34.4.23)

The BdG equations are readily generalized to spin-dependent potentials, when the term containing the one-particle potential $U_0(\mathbf{r})$ is replaced in the Hamiltonian by

⁶ N. N. BOGOLIUBOV, 1958, P. G. DE GENNES, 1966. PIERRE-GILLES DE GENNES (1932–2007) was awarded the Nobel Prize in 1991 "for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers".

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$$\sum_{\sigma\sigma'} \int \mathrm{d}\boldsymbol{r} \, \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) U^{(0)}_{\sigma\sigma'}(\boldsymbol{r}) \hat{\psi}_{\sigma'}(\boldsymbol{r}) \,. \tag{34.4.24}$$

The off-diagonal terms correspond to spin-flip processes. The properties of inhomogeneous non-s-wave superconductors can also be treated using the Bogoliubov equations if the effective interaction between electrons is chosen in the most general form

$$\mathcal{H}_{\text{int}} = -\frac{1}{2} \sum_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} \iint \hat{\psi}^{\dagger}_{\sigma_1}(\boldsymbol{r}) \hat{\psi}^{\dagger}_{\sigma_2}(\boldsymbol{r}') V_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}(\boldsymbol{r}, \boldsymbol{r}') \hat{\psi}_{\sigma_3}(\boldsymbol{r}') \hat{\psi}_{\sigma_4}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' \,.$$
(34.4.25)

As mentioned above, the Bogoliubov equations allow us to study situations where the order parameter is position dependent, e.g., to determine the detailed structure of the vortex in a type II superconductor or to consider effects taking place at a normal-superconductor interface, such as the Andreev reflection.⁷ Near the critical point, where the order parameter is small, inhomogeneous superconductors are treated mostly in the framework of the phenomenological Ginzburg–Landau theory exposed in Chapter 26.

34.4.2 Derivation of the Ginzburg–Landau Equations

An equivalent set of equations can be derived for nonuniform superconductors by using the Green functions. Starting again with the Hamiltonian given in (34.4.3) and (34.4.4) we write the equation of motion for the Green function and treat it in the mean-field approximation. This will lead us to the Gorkov equations also known as Gorkov-Nambu equations⁸ from which the Ginzburg-Landau equations can be derived.

The causal Green function is defined in real space and time in the usual way via

$$G_{\sigma\sigma'}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \left\langle T\left\{\hat{\psi}_{\sigma}(\boldsymbol{r},t)\hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}',t')\right\}\right\rangle, \qquad (34.4.26)$$

where $\langle \cdots \rangle$ denotes the thermodynamic average. Since the interaction Hamiltonian is bilinear in the field operators, an anomalous Green function

$$F_{\sigma\sigma'}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \left\langle T\{\hat{\psi}_{\sigma}(\boldsymbol{r},t)\hat{\psi}_{\sigma'}(\boldsymbol{r}',t')\}\right\rangle$$
(34.4.27)

⁷ A. F. ANDREEV, 1964. An electron approaching the normal–superconductor interface from the normal side with wave vector \boldsymbol{k} is unable to penetrate deep into the superconductor if its energy measured from the chemical potential is smaller than the gap in the superconductor. It can be specularly reflected from the interface. Alternatively, the incident electron together with another electron of momentum -k can penetrate into the superconductor to form a Cooper pair there. The electron with -k missing from the normal side can be interpreted as a reflected hole with wave vector \boldsymbol{k} . It retraces the path of the incident electron.

⁸ L. P. Gorkov, 1959, Y. Nambu, 1960.

and its complex conjugate,

$$F^*_{\sigma\sigma'}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \left\langle T\left\{\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r},t)\hat{\psi}^{\dagger}_{\sigma'}(\boldsymbol{r}',t')\right\}\right\rangle, \qquad (34.4.28)$$

appear in the equation of motion. When the equation of motion is written for the anomalous Green function, no new functions appear, and a closed set of equations is obtained.

The Green function matrix $G_{\sigma\sigma'}$ can be given in terms of a single function in the unpolarized state,

$$G_{\sigma\sigma'}(\boldsymbol{r},t;\boldsymbol{r}',t') = \delta_{\sigma\sigma'}G(\boldsymbol{r},t;\boldsymbol{r}',t'). \qquad (34.4.29)$$

For singlet superconductors, where only the off-diagonal terms of the anomalous Green function are nonzero,

$$F_{\uparrow\downarrow}(\boldsymbol{r},t;\boldsymbol{r}',t') = -F_{\downarrow\uparrow}(\boldsymbol{r},t;\boldsymbol{r}',t') = F(\boldsymbol{r},t;\boldsymbol{r}',t')$$
(34.4.30)

and

$$F^*_{\uparrow\downarrow}(\mathbf{r},t;\mathbf{r}',t') = -F^*_{\downarrow\uparrow}(\mathbf{r},t;\mathbf{r}',t') = F^*(\mathbf{r},t;\mathbf{r}',t').$$
(34.4.31)

The order parameter defined earlier by

$$\Delta(\mathbf{r}) = -V_0 \langle \hat{\psi}_{\downarrow}(\mathbf{r}) \hat{\psi}_{\uparrow}(\mathbf{r}) \rangle, \quad \Delta^*(\mathbf{r}) = -V_0 \langle \hat{\psi}_{\uparrow}^{\dagger}(\mathbf{r}) \hat{\psi}_{\downarrow}^{\dagger}(\mathbf{r}) \rangle$$
(34.4.32)

is simply related to the anomalous Green function

$$\Delta(\mathbf{r}) = i\hbar V_0 F(\mathbf{r}, t+\delta; \mathbf{r}, t), \quad \Delta^*(\mathbf{r}) = -i\hbar V_0 F^*(\mathbf{r}, t+\delta; \mathbf{r}, t) \quad (34.4.33)$$

with a positive infinitesimal δ to ensure the correct order of the operators.

The equation of motion for the Green functions can readily be obtained from the time derivative of the field operators. Using (34.4.20) we find

$$-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial t}\hat{\psi}_{\uparrow}(\boldsymbol{r},t) = \mathcal{H}_{\mathrm{e}}\hat{\psi}_{\uparrow}(\boldsymbol{r},t) + \Delta(\boldsymbol{r})\hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},t)$$
(34.4.34)

and

$$-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial t}\hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},t) = -\mathcal{H}_{\mathrm{e}}^{*}\hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},t) + \Delta^{*}(\boldsymbol{r})\hat{\psi}_{\uparrow}(\boldsymbol{r},t). \qquad (34.4.35)$$

These equations lead to

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial t}-\mathcal{H}_{\mathrm{e}}\right)G(\boldsymbol{r},t;\boldsymbol{r}',t')+\Delta(\boldsymbol{r})F^{*}(\boldsymbol{r},t;\boldsymbol{r}',t')$$

$$=\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t')$$
(34.4.36)

and

$$\Delta^*(\boldsymbol{r})G(\boldsymbol{r},t;\boldsymbol{r}',t') + \left(-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial t} + \mathcal{H}_{\mathrm{e}}^*\right)F^*(\boldsymbol{r},t;\boldsymbol{r}',t') = 0.$$
(34.4.37)

These are the Gorkov equations. They form a closed set of equations if (34.4.33) is also taken into account.

The results of the BCS theory are recovered for a homogeneous, stationary system. The derivation of the gap equation (34.2.96) is shown in Appendix K. Here we only discuss the relationship to the Ginzburg–Landau theory near T_c , where the order parameter $\Delta(\mathbf{r})$ is small and the Gorkov equations can be expanded in powers of Δ keeping only the leading terms. The calculations outlined in the appendix lead to the result that the quantity

$$\Psi(\mathbf{r}) = \left[\frac{7\zeta(3)n_{\rm e}}{8(\pi k_{\rm B}T_{\rm c})^2}\right]^{1/2} \Delta(\mathbf{r})$$
(34.4.38)

satisfies the equation

$$\frac{1}{4m_{\rm e}} \left(\frac{\hbar}{\rm i} \boldsymbol{\nabla} + 2e\boldsymbol{A}(\boldsymbol{r})\right)^2 \boldsymbol{\Psi}(\boldsymbol{r}) \qquad (34.4.39) \\
+ \frac{6(\pi k_{\rm B} T_{\rm c})^2}{7\zeta(3)\varepsilon_{\rm F}} \left[-\left(1 - \frac{T}{T_{\rm c}}\right) \boldsymbol{\Psi}(\boldsymbol{r}) + \frac{1}{n_{\rm e}} \boldsymbol{\Psi}(\boldsymbol{r}) |\boldsymbol{\Psi}(\boldsymbol{r})|^2 \right] = 0,$$

which can be identified with the first Ginzburg–Landau equation if the parameters e^* and m^* are replaced with $e^* = 2e$, $m^* = 2m_e$. The microscopic expressions for the coefficients α and β of the Ginzburg–Landau expansion are given by

$$\alpha = -\frac{6(\pi k_{\rm B} T_{\rm c})^2}{7\zeta(3)\varepsilon_{\rm F}} \left(1 - \frac{T}{T_{\rm c}}\right), \qquad \beta = \frac{6(\pi k_{\rm B} T_{\rm c})^2}{7\zeta(3)\varepsilon_{\rm F} n_{\rm e}}.$$
 (34.4.40)

The second Ginzburg–Landau equation can be derived by writing the quantum mechanical expression for the current operator in terms of the field operators

$$\hat{\boldsymbol{j}}(\boldsymbol{r}) = -\lim_{\boldsymbol{r}' \to \boldsymbol{r}} \frac{e\hbar}{2m_{\rm e}i} \sum_{\sigma} \left[\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}') \boldsymbol{\nabla}_{\boldsymbol{r}} \hat{\psi}_{\sigma}(\boldsymbol{r}) - \boldsymbol{\nabla}_{\boldsymbol{r}'} \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}') \hat{\psi}_{\sigma}(\boldsymbol{r}) \right] - \frac{e^2}{m_{\rm e}} \boldsymbol{A}(\boldsymbol{r}) \sum_{\sigma} \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) .$$
(34.4.41)

Its expectation value can be expressed in terms of the one-particle Green function as

$$\boldsymbol{j}(\boldsymbol{r}) = \langle \hat{\boldsymbol{j}}(\boldsymbol{r}) \rangle = \lim_{\boldsymbol{r}' \to \boldsymbol{r}} \frac{e\hbar^2}{m_{\rm e}} \left[\boldsymbol{\nabla}_{\boldsymbol{r}} - \boldsymbol{\nabla}_{\boldsymbol{r}'} \right] G(\boldsymbol{r}, t; \boldsymbol{r}', t + \delta) - \frac{2e^2\hbar}{m_{\rm e}i} \boldsymbol{A}(\boldsymbol{r}) G(\boldsymbol{r}, t; \boldsymbol{r}, t + \delta) .$$
(34.4.42)

Inserting the solution of the Gorkov equations for the Green function keeping only the leading terms in powers of $\Delta(\mathbf{r})$ and expressing $\Delta(\mathbf{r})$ by $\Psi(\mathbf{r})$ according to (34.4.38), the current can be written after a lengthy but straightforward calculation as 34.4 Inhomogeneous Superconductors and Retardation Effects 441

$$\boldsymbol{j}(\boldsymbol{r}) = -\frac{2e}{4m_{\rm e}} \boldsymbol{\Psi}^*(\boldsymbol{r}) \left(\frac{\hbar}{\mathrm{i}} \boldsymbol{\nabla} + 2e\boldsymbol{A}(\boldsymbol{r})\right) \boldsymbol{\Psi}(\boldsymbol{r}) + \mathrm{c.c.}, \qquad (34.4.43)$$

which is precisely the second Ginzburg–Landau equation.

We have seen in the phenomenological description of superconductivity that the two characteristic lengths, the penetration depth and the coherence length, can be expressed in terms of the α and β parameters of the Ginzburg– Landau expansion. Using the result given above we have

$$\lambda^{2}(T) = -\frac{m^{*}\beta}{\mu_{0}e^{*2}\alpha} = \frac{m_{e}}{2\mu_{0}e^{2}n_{e}} \left(1 - \frac{T}{T_{c}}\right)^{-1},$$

$$\xi^{2}(T) = -\frac{\hbar^{2}}{2m^{*}\alpha} = \frac{7\zeta(3)\hbar^{2}\varepsilon_{F}}{24m_{e}(\pi k_{B}T_{c})^{2}} \left(1 - \frac{T}{T_{c}}\right)^{-1}.$$
(34.4.44)

Expressing them in terms of the London penetration depth $\lambda_{\rm L}(0)$ and the coherence length $\xi_0 = \hbar v_{\rm F} / \pi \Delta_0$ of the BCS theory we find

$$\lambda(T) = \frac{1}{\sqrt{2}} \lambda_{\rm L}(0) \left(1 - \frac{T}{T_{\rm c}}\right)^{-1/2},$$

$$\xi(T) = \xi_0 \pi e^{-\gamma} \left[\frac{7\zeta(3)}{48}\right]^{1/2} \left(1 - \frac{T}{T_{\rm c}}\right)^{-1/2}.$$
(34.4.45)

34.4.3 Eliashberg Equations

The use of Green functions allows us to consider the effects which are due to the retardation of the effective interaction mediated by phonons. For that, following G. M. ELIASHBERG (1960), we have to treat the electron and the phonon subsystems on equal footing. In addition to the normal Green function describing the propagation of electrons and the anomalous Green function related to the pairs we introduce the phonon propagator and study the coupled set of their equations of motion. Since we only consider homogeneous systems here, the Green functions will be given in momentum space.

The causal Green function of electrons is defined by the usual expression

$$G_{\sigma}(\boldsymbol{k}, t - t') = -\frac{\mathrm{i}}{\hbar} \left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}\sigma}^{\dagger}(t') \right\} \right\rangle.$$
(34.4.46)

For the sake of simplicity a single phonon branch is taken and the polarization index λ will be dropped. We will use the propagator of the Fourier transform of the phonon field, $\phi_{\boldsymbol{q}}(t) = a_{\boldsymbol{q}}(t) + a^{\dagger}_{-\boldsymbol{q}}(t)$, which is defined via

$$\mathcal{D}(\boldsymbol{q}, t - t') = -\frac{\mathrm{i}}{\hbar} \left\langle T \left\{ \phi_{\boldsymbol{q}}(t) \phi_{-\boldsymbol{q}}(t') \right\} \right\rangle.$$
(34.4.47)

Using (23.2.14) for the Hamiltonian of the electron-phonon interaction, the equation of motion of the electron Green function is

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$$\left[\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'} - \varepsilon_{\boldsymbol{k}\sigma}\right]G_{\sigma}(\boldsymbol{k}, t - t') = \delta(t - t') \qquad (34.4.48)$$
$$-\frac{\mathrm{i}}{\hbar}\sum_{\boldsymbol{q}}D_{\boldsymbol{q}}\left\langle T\left\{c_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t')\phi_{\boldsymbol{q}}(t')\right\}\right\rangle.$$

A new, higher order Green function,

$$G_2(\boldsymbol{k}, \boldsymbol{q}, t, t_1, t') = -\frac{\mathrm{i}}{\hbar} \left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t_1) \phi_{\boldsymbol{q}}(t') \right\} \right\rangle, \qquad (34.4.49)$$

appeared on the right-hand side, containing both electron and phonon operators. The equation of motion for this new Green function gives

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'}G_2(\boldsymbol{k},\boldsymbol{q},t,t_1,t') = -\hbar\omega_{\boldsymbol{q}}\left(-\frac{\mathrm{i}}{\hbar}\right)\left\langle T\left\{c_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t_1)\pi_{\boldsymbol{q}}(t')\right\}\right\rangle,\tag{34.4.50}$$

where $\pi_{q}(t) = a_{q}(t) - a_{-q}^{\dagger}(t)$. Taking the time derivative once more we find

$$\left[\left(\frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t'} \right)^2 - (\hbar\omega_{\boldsymbol{q}})^2 \right] G_2(\boldsymbol{k}, \boldsymbol{q}, t, t_1, t') = 2\hbar\omega_{\boldsymbol{q}} D_{-\boldsymbol{q}} \qquad (34.4.51)$$
$$\times \left(-\frac{\mathrm{i}}{\hbar} \right) \sum_{\boldsymbol{k}'\sigma'} \left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t_1) c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}(t') c_{\boldsymbol{k}'\sigma'}(t') \right\} \right\rangle.$$

The Green function of free phonons satisfies the equation

$$\left[\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'}\right)^2 - (\hbar\omega_{\boldsymbol{q}})^2\right]\mathcal{D}_0(\boldsymbol{q}, t - t') = 2\hbar\omega_{\boldsymbol{q}}\delta(t - t').$$
(34.4.52)

Combining this equation with the previous one for G_2 it is readily seen that

$$G_{2}(\boldsymbol{k},\boldsymbol{q},t,t_{1},t') = \sum_{\boldsymbol{k}'\sigma'} \int \mathrm{d}t_{2} D_{-\boldsymbol{q}} \mathcal{D}_{0}(\boldsymbol{q},t_{2}-t') \qquad (34.4.53)$$
$$\times \left(-\frac{\mathrm{i}}{\hbar}\right) \left\langle T\left\{c_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t_{1})c_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}^{\dagger}(t_{2})c_{\boldsymbol{k}'\sigma'}(t_{2})\right\}\right\rangle.$$

Substitution of this expression in the equation for the electron propagator gives

$$\left[\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'} - \varepsilon_{\boldsymbol{k}\sigma}\right]G_{\sigma}(\boldsymbol{k}, t - t') = \delta(t - t') + \sum_{\boldsymbol{q}}|D_{\boldsymbol{q}}|^{2}\sum_{\boldsymbol{k}'\sigma'}\int\mathrm{d}t_{2}\mathcal{D}_{0}(\boldsymbol{q}, t_{2} - t')$$
$$\times \left(-\frac{\mathrm{i}}{\hbar}\right)\left\langle T\left\{c_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t')c_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}^{\dagger}(t_{2})c_{\boldsymbol{k}'\sigma'}(t_{2})\right\}\right\rangle. \quad (34.4.54)$$

At this point we can decouple the higher order Green function. As has been done repeatedly, the expectation value of the product of four operators is approximated by the product of the expectation values of two-operator terms. A natural choice for the decoupling in a normal system would be

$$\left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t') c_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}^{\dagger}(t_2) c_{\boldsymbol{k}'\sigma'}(t_2) \right\} \right\rangle \approx \delta_{\boldsymbol{k},\boldsymbol{k}'-\boldsymbol{q}} \delta_{\sigma\sigma'} \qquad (34.4.55) \\ \times \left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}\sigma}^{\dagger}(t_2) \right\} \right\rangle \left\langle T \left\{ c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t_2) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t') \right\} \right\rangle.$$

The resulting equation for the single-particle Green function can be integrated out formally by making use of the equation for the Green function of free particles. We get

$$G_{\sigma}(\mathbf{k}, t - t') = G_{\sigma}^{0}(\mathbf{k}, t - t') + \int dt_{1} G_{\sigma}^{0}(\mathbf{k}, t_{1} - t') \sum_{\mathbf{q}} |D_{\mathbf{q}}|^{2} \qquad (34.4.56)$$
$$\times \int dt_{2} \mathcal{D}_{0}(\mathbf{q}, t_{2} - t_{1}) \left(-\frac{\hbar}{i}\right) G_{\sigma}(\mathbf{k} + \mathbf{q}, t_{2} - t_{1}) G_{\sigma}(\mathbf{k}, t - t_{2}).$$

This equation is visualized diagrammatically by the first three diagrams in Fig. 34.8(a). Thin lines denote the free propagation of electrons while heavy lines stand for the full propagator, in which all self-energy corrections are taken into account. As the diagrams show, an electron propagates either freely or it can emit and then reabsorb a phonon. As for the emitted phonon, it is absorbed without participating in other scattering processes, since self-energy corrections in the phonon propagation and vertex correction to the electron–phonon interaction can be neglected in three-dimensional systems according to the *Migdal theorem.*⁹



Fig. 34.8. (a) Diagrammatic equation for the one-particle propagator showing the processes in which a phonon is emitted and then absorbed. (b) Diagrammatic equation for the anomalous Green function

We should, however, take into account in the decoupling procedure that the anomalous average $\langle c_{-k\downarrow}c_{k\uparrow}\rangle$ takes a nonvanishing value in a superconductor. An alternative decoupling of the four-operator term in (34.4.55) yields

$$-\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\sigma,-\sigma'}\Big\langle T\big\{c_{\boldsymbol{k}\sigma}(t)c_{-\boldsymbol{k},-\sigma}(t_2)\big\}\Big\rangle\Big\langle T\big\{c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t')c_{-\boldsymbol{k}-\boldsymbol{q},-\sigma}^{\dagger}(t_2)\big\}\Big\rangle, (34.4.57)$$

that is the anomalous Green function

⁹ A. B. MIGDAL, 1958.

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$$F(\boldsymbol{k},t) = -\frac{\mathrm{i}}{\hbar} \left\langle T \left\{ c_{\boldsymbol{k}\uparrow}(t) c_{-\boldsymbol{k}\downarrow}(0) \right\} \right\rangle$$
(34.4.58)

will also appear in the equation for the one-particle propagator. The term corresponding to this decoupling is represented by the last diagram in the diagrammatic equation in Fig. 34.8(a) for the one-particle Green function, where the lines with two incoming or two outgoing arrows denote the anomalous Green functions. The fact that the terms corresponding to both the normal and the anomalous decoupling schemes have to be taken into account simultaneously can be shown in a more rigorous treatment of this many-body problem, using the Wick theorem for the causal Green functions. To get a closed set of equations we write the equation of motion for the anomalous Green function as well, as was done in the derivation of the Gorkov equations. These are the *Eliashberg equations*. They are depicted in diagrammatic form in Fig. 34.8.

The excitation spectrum is rather similar to that obtained in the BCS theory. The excited states are separated from the ground state by a finite gap. The thermodynamic and electrodynamic properties are not essentially modified when retardation effects are included. However, the temperature dependence of the gap and the value of the critical temperature have to be determined from more complicated equations. Numerical solution of the Eliashberg equations taking a screened Coulomb interaction in addition to the electron–phonon coupling leads to the *McMillan formula*¹⁰ for the critical temperature,

$$k_{\rm B}T_{\rm c} = \frac{\hbar\omega_{\rm D}}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right],$$
 (34.4.59)

where the dimensionless parameter λ characterizes the electron–phonon interaction,

$$\lambda = 2 \int_{0}^{\omega_{\rm D}} \alpha^2 F(\omega) \frac{\mathrm{d}\omega}{\omega} , \qquad (34.4.60)$$

and the function $\alpha^2 F(\omega)$ can be calculated from

$$\alpha^2 F(\omega) = \rho(\varepsilon_{\rm F}) \int_{0}^{2k_{\rm F}} \frac{q \,\mathrm{d}q}{2\hbar k_{\rm F}^2} |D_q|^2 \delta(\omega - \omega_q)$$
(34.4.61)

if the phonon spectrum and the coupling constant of the electron–phonon interaction are known. The other dimensionless parameter, μ^* , is related to the strength of the electron–electron interaction

$$\mu^* = \frac{\rho(\varepsilon_{\rm F})U}{1 + \rho(\varepsilon_{\rm F})U\ln(\varepsilon_{\rm F}/\hbar\omega_{\rm D})}.$$
(34.4.62)

¹⁰ W. L. MCMILLAN, 1968.

Retardation of the effective interaction is not relevant in the weak-coupling limit where the results of the BCS theory are recovered. Deviations from the BCS theory occur for strong electron–phonon couplings. One remarkable result of this theory is that the critical temperature cannot increase arbitrarily up to the Debye temperature but saturates in the strong-coupling limit.

34.5 Unconventional Superconductors

A basic assumption of BCS theory is that superconductivity is due to singlet Cooper pairs formed by electrons in a certain energy range about the Fermi energy. The phonon-mediated attraction between electrons is approximated by a nonretarded, momentum-independent effective electron–electron interaction. A further assumption is that this interaction can be treated at the mean-field level owing to the large coherence length. This theory provides a good description of the thermodynamics and electrodynamics of type I elemental superconductors. It has become clear, however, recently that the BCS theory is not capable of explaining many of the unusual properties of high- $T_{\rm c}$ and heavy-fermion superconductors. These questions will be discussed in this section.

34.5.1 Non-s-Wave Superconductors

We assume that the pairs responsible for superconductivity have total momentum zero, but we allow for a spin-dependent effective electron–electron interaction and the pairs are not required to be in a spin-singlet state. The most general form of the reduced Hamiltonian is

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \frac{1}{2\Omega} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}} V_{\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}(\boldsymbol{k}, \boldsymbol{k}') c^{\dagger}_{\boldsymbol{k}\sigma_{1}} c^{\dagger}_{-\boldsymbol{k}\sigma_{2}} c_{-\boldsymbol{k}'\sigma_{3}} c_{\boldsymbol{k}'\sigma_{4}},$$
(34.5.1)

where the two-particle potential satisfies the usual symmetry requirements:

$$V_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}(\boldsymbol{k}, \boldsymbol{k}') = -V_{\sigma_2 \sigma_1 \sigma_3 \sigma_4}(-\boldsymbol{k}, \boldsymbol{k}')$$

= $-V_{\sigma_1 \sigma_2 \sigma_4 \sigma_3}(\boldsymbol{k}, -\boldsymbol{k}')$ (34.5.2)
= $V_{\sigma_4 \sigma_3 \sigma_2 \sigma_1}(\boldsymbol{k}', \boldsymbol{k})$.

The spin dependence and the momentum dependence of the potential can be separated if the spin–orbit coupling is negligible and we have

$$V_{\sigma_1\sigma_2\sigma_3\sigma_4}(\boldsymbol{k},\boldsymbol{k}') = V_{\boldsymbol{k}\boldsymbol{k}'}\Gamma_{\sigma_1\sigma_2\sigma_3\sigma_4}.$$
(34.5.3)

In the vicinity of the Fermi surface, where the dependence on the length of \mathbf{k} and \mathbf{k}' can be neglected, only the polar angles matter, $V_{\mathbf{k}\mathbf{k}'}$ can be

expanded according to (34.1.15) in spherical harmonics. The spin structure of the potential depends on l. The symmetry requirements given in (34.5.2) can be satisfied for even l – taking into account the symmetry properties of the spherical harmonics – if the spin factor is chosen in the form

$$\Gamma_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} = \frac{1}{2} (\mathrm{i}\sigma_y)_{\sigma_1 \sigma_2} (\mathrm{i}\sigma_y)_{\sigma_3 \sigma_4}^{\dagger} \,. \tag{34.5.4}$$

The Cooper pairs are spin singlets as in the l = 0 s-wave case. The spin state has to be triplet for odd l, which can be achieved by the spin factor

$$\Gamma_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} = \frac{1}{2} (i \boldsymbol{\sigma} \sigma_y)_{\sigma_1 \sigma_2} \cdot (i \boldsymbol{\sigma} \sigma_y)_{\sigma_3 \sigma_4}^{\dagger} .$$
(34.5.5)

Assuming that the anomalous average $\langle c^{\dagger}_{k\sigma_1}c^{\dagger}_{-k\sigma_2}\rangle$ takes a nonvanishing value in these superconductors, the mean-field approximation leads to

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{1}{2\Omega} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}} V_{\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}(\boldsymbol{k},\boldsymbol{k}') \langle c_{\boldsymbol{k}\sigma_{1}}^{\dagger} c_{-\boldsymbol{k}\sigma_{2}}^{\dagger} \rangle c_{-\boldsymbol{k}'\sigma_{3}} c_{\boldsymbol{k}'\sigma_{4}} + \frac{1}{2\Omega} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}} V_{\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}(\boldsymbol{k},\boldsymbol{k}') c_{\boldsymbol{k}\sigma_{1}}^{\dagger} c_{-\boldsymbol{k}\sigma_{2}}^{\dagger} \langle c_{-\boldsymbol{k}'\sigma_{3}} c_{\boldsymbol{k}'\sigma_{4}} \rangle \qquad (34.5.6)$$
$$-\frac{1}{2\Omega} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}} V_{\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}(\boldsymbol{k},\boldsymbol{k}') \langle c_{\boldsymbol{k}\sigma_{1}}^{\dagger} c_{-\boldsymbol{k}\sigma_{2}}^{\dagger} \rangle \langle c_{-\boldsymbol{k}'\sigma_{3}} c_{\boldsymbol{k}'\sigma_{4}} \rangle .$$

Introducing the notations

$$\Delta_{\boldsymbol{k}\sigma_{1}\sigma_{2}} = \frac{1}{\Omega} \sum_{\boldsymbol{k}'\sigma_{3}\sigma_{4}} V_{\sigma_{1}\sigma_{2}\sigma_{3}\sigma_{4}}(\boldsymbol{k},\boldsymbol{k}') \langle c_{-\boldsymbol{k}'\sigma_{3}}c_{\boldsymbol{k}'\sigma_{4}} \rangle,$$

$$\Delta^{*}_{-\boldsymbol{k}\sigma_{1}\sigma_{2}} = -\frac{1}{\Omega} \sum_{\boldsymbol{k}'\sigma_{3}\sigma_{4}} V_{\sigma_{3}\sigma_{4}\sigma_{1}\sigma_{2}}(\boldsymbol{k},\boldsymbol{k}') \langle c^{\dagger}_{\boldsymbol{k}'\sigma_{3}}c^{\dagger}_{-\boldsymbol{k}'\sigma_{4}} \rangle$$
(34.5.7)

and neglecting the constant terms in the Hamiltonian, we have

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{1}{2} \sum_{\boldsymbol{k}\sigma_{1}\sigma_{2}} \left[\varDelta_{\boldsymbol{k}\sigma_{1}\sigma_{2}} c_{\boldsymbol{k}\sigma_{1}}^{\dagger} c_{-\boldsymbol{k}\sigma_{2}}^{\dagger} - \varDelta_{-\boldsymbol{k}\sigma_{1}\sigma_{2}}^{*} c_{-\boldsymbol{k}\sigma_{1}} c_{\boldsymbol{k}\sigma_{2}} \right].$$
(34.5.8)

It is convenient to write the kinetic energy in a more symmetric form by measuring the electron energy from the chemical potential

$$\mathcal{H} = \frac{1}{2} \sum_{\boldsymbol{k}\sigma} \xi_{\boldsymbol{k}} \left[c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} - c_{-\boldsymbol{k}\sigma} c_{-\boldsymbol{k}\sigma}^{\dagger} \right] + \frac{1}{2} \sum_{\boldsymbol{k}\sigma_{1}\sigma_{2}} \left[\Delta_{\boldsymbol{k}\sigma_{1}\sigma_{2}} c_{\boldsymbol{k}\sigma_{1}}^{\dagger} c_{-\boldsymbol{k}\sigma_{2}}^{\dagger} - \Delta_{-\boldsymbol{k}\sigma_{1}\sigma_{2}}^{*} c_{-\boldsymbol{k}\sigma_{1}} c_{\boldsymbol{k}\sigma_{2}} \right].$$
(34.5.9)

This bilinear Hamiltonian can be written in a concise form,
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$$\mathcal{H} = \sum_{\boldsymbol{k}} \hat{\boldsymbol{c}}_{\boldsymbol{k}}^{\dagger} \hat{\boldsymbol{c}}_{\boldsymbol{k}} \hat{\boldsymbol{c}}_{\boldsymbol{k}} , \qquad (34.5.10)$$

in terms of the column and row vectors

$$\hat{\boldsymbol{c}}_{\boldsymbol{k}} = \begin{pmatrix} c_{\boldsymbol{k}\uparrow} \\ c_{\boldsymbol{k}\downarrow} \\ c^{\dagger}_{-\boldsymbol{k}\uparrow} \\ c^{\dagger}_{-\boldsymbol{k}\downarrow} \end{pmatrix}, \qquad \hat{\boldsymbol{c}}^{\dagger}_{\boldsymbol{k}} = \begin{pmatrix} c^{\dagger}_{\boldsymbol{k}\uparrow}, \ c^{\dagger}_{\boldsymbol{k}\downarrow}, \ c_{-\boldsymbol{k}\uparrow}, \ c_{-\boldsymbol{k}\downarrow} \end{pmatrix}, \qquad (34.5.11)$$

where

$$\hat{\boldsymbol{\varepsilon}}_{\boldsymbol{k}} = \begin{pmatrix} \xi_{\boldsymbol{k}} & 0 & \Delta_{\boldsymbol{k}\uparrow\uparrow} & \Delta_{\boldsymbol{k}\uparrow\downarrow} \\ 0 & \xi_{\boldsymbol{k}} & \Delta_{\boldsymbol{k}\downarrow\uparrow} & \Delta_{\boldsymbol{k}\downarrow\downarrow} \\ -\Delta_{-\boldsymbol{k}\uparrow\uparrow}^* & -\Delta_{-\boldsymbol{k}\uparrow\downarrow}^* & -\xi_{\boldsymbol{k}} & 0 \\ -\Delta_{-\boldsymbol{k}\downarrow\uparrow}^* & -\Delta_{-\boldsymbol{k}\downarrow\downarrow}^* & 0 & -\xi_{\boldsymbol{k}} \end{pmatrix}.$$
(34.5.12)

This Hamiltonian can be diagonalized by a generalized Bogoliubov transformation

$$c_{\boldsymbol{k}\sigma} = \sum_{\sigma'} \left(u_{\boldsymbol{k}\sigma\sigma'} \alpha_{\boldsymbol{k}\sigma'} + v_{\boldsymbol{k}\sigma\sigma'} \alpha^{\dagger}_{-\boldsymbol{k}\sigma'} \right),$$

$$c^{\dagger}_{\boldsymbol{k}\sigma} = \sum_{\sigma'} \left(u^{*}_{\boldsymbol{k}\sigma\sigma'} \alpha^{\dagger}_{\boldsymbol{k}\sigma'} + v^{*}_{\boldsymbol{k}\sigma\sigma'} \alpha_{-\boldsymbol{k}\sigma'} \right).$$
(34.5.13)

If written in terms of the column vector

$$\hat{\boldsymbol{\alpha}}_{\boldsymbol{k}} = \begin{pmatrix} \alpha_{\boldsymbol{k}\uparrow} \\ \alpha_{\boldsymbol{k}\downarrow} \\ \alpha^{\dagger}_{-\boldsymbol{k}\uparrow} \\ \alpha^{\dagger}_{-\boldsymbol{k}\downarrow} \end{pmatrix}$$
(34.5.14)

and its adjoint, the row vector

$$\hat{\boldsymbol{\alpha}}_{\boldsymbol{k}}^{\dagger} = \left(\alpha_{\boldsymbol{k}\uparrow}^{\dagger}, \ \alpha_{\boldsymbol{k}\downarrow}^{\dagger}, \ \alpha_{-\boldsymbol{k}\uparrow}, \ \alpha_{-\boldsymbol{k}\downarrow} \right), \qquad (34.5.15)$$

the Bogoliubov transformation takes the concise form

$$\hat{\boldsymbol{c}}_{\boldsymbol{k}} = \boldsymbol{U}_{\boldsymbol{k}} \hat{\boldsymbol{\alpha}}_{\boldsymbol{k}} \,, \tag{34.5.16}$$

with

$$\boldsymbol{U}_{\boldsymbol{k}} = \begin{pmatrix} u_{\boldsymbol{k}\uparrow\uparrow} & u_{\boldsymbol{k}\uparrow\downarrow} & v_{\boldsymbol{k}\uparrow\uparrow} & v_{\boldsymbol{k}\uparrow\downarrow} \\ u_{\boldsymbol{k}\downarrow\uparrow} & u_{\boldsymbol{k}\downarrow\downarrow} & v_{\boldsymbol{k}\downarrow\uparrow} & v_{\boldsymbol{k}\downarrow\downarrow} \\ v_{-\boldsymbol{k}\uparrow\uparrow}^{*} & v_{-\boldsymbol{k}\uparrow\downarrow}^{*} & u_{-\boldsymbol{k}\uparrow\uparrow}^{*} & u_{-\boldsymbol{k}\uparrow\downarrow}^{*} \\ v_{-\boldsymbol{k}\downarrow\uparrow}^{*} & v_{-\boldsymbol{k}\downarrow\downarrow}^{*} & u_{-\boldsymbol{k}\downarrow\uparrow}^{*} & u_{-\boldsymbol{k}\downarrow\downarrow}^{*} \end{pmatrix}.$$
(34.5.17)

It follows from the fermionic anticommutation rules of the α and c operators that

$$\sum_{\sigma''} \left(u_{\boldsymbol{k}\sigma\sigma''} u_{\boldsymbol{k}\sigma\sigma''}^* + v_{\boldsymbol{k}\sigma\sigma''} v_{\boldsymbol{k}\sigma'\sigma''}^* \right) = \delta_{\sigma\sigma'} ,$$

$$\sum_{\sigma''} \left(u_{\boldsymbol{k}\sigma\sigma''} v_{-\boldsymbol{k}\sigma'\sigma''} + v_{\boldsymbol{k}\sigma\sigma''} u_{-\boldsymbol{k}\sigma'\sigma''} \right) = 0 ,$$
(34.5.18)

which are equivalent to the condition that the matrix $\boldsymbol{U}_{\boldsymbol{k}}$ be unitary,

$$U_{k}U_{k}^{\dagger} = 1.$$
 (34.5.19)

Inserting this into (34.5.10) we get

$$\mathcal{H} = \sum_{k} \hat{c}_{k}^{\dagger} U_{k} U_{k}^{\dagger} \hat{c}_{k} U_{k} U_{k}^{\dagger} \hat{c}_{k} = \sum_{k} \hat{\alpha}_{k}^{\dagger} U_{k}^{\dagger} \hat{c}_{k} U_{k} \hat{\alpha}_{k}. \qquad (34.5.20)$$

The matrix elements of \boldsymbol{U}_{k} are determined from the diagonalization condition, that is the matrix

$$\hat{\boldsymbol{E}}_{\boldsymbol{k}} = \boldsymbol{U}_{\boldsymbol{k}}^{\dagger} \hat{\boldsymbol{\varepsilon}}_{\boldsymbol{k}} \boldsymbol{U}_{\boldsymbol{k}}$$
(34.5.21)

has to take the form

$$\boldsymbol{E}_{\boldsymbol{k}} = \begin{pmatrix} E_{\boldsymbol{k}\uparrow} & 0 & 0 & 0\\ 0 & E_{\boldsymbol{k}\downarrow} & 0 & 0\\ 0 & 0 & -E_{-\boldsymbol{k}\uparrow} & 0\\ 0 & 0 & 0 & -E_{-\boldsymbol{k}\downarrow} \end{pmatrix}.$$
 (34.5.22)

The diagonal Hamiltonian is then

$$\mathcal{H} = E_0 + \sum_{k\sigma} \left[E_{k\sigma} \alpha^{\dagger}_{k\sigma} \alpha_{k\sigma} - E_{-k\sigma} \alpha_{-k\sigma} \alpha^{\dagger}_{-k\sigma} \right].$$
(34.5.23)

It follows from the symmetry properties of the interaction and the fermionic anticommutation rule that $\Delta_{k\sigma_1\sigma_2}$, which is related to the wavefunction of the Cooper pairs, has the symmetry property

$$\begin{pmatrix} \Delta_{\boldsymbol{k}\uparrow\uparrow} & \Delta_{\boldsymbol{k}\uparrow\downarrow} \\ \Delta_{\boldsymbol{k}\downarrow\uparrow} & \Delta_{\boldsymbol{k}\downarrow\downarrow} \end{pmatrix} = - \begin{pmatrix} \Delta_{-\boldsymbol{k}\uparrow\uparrow} & \Delta_{-\boldsymbol{k}\downarrow\uparrow} \\ \Delta_{-\boldsymbol{k}\uparrow\downarrow} & \Delta_{-\boldsymbol{k}\downarrow\downarrow} \end{pmatrix}.$$
 (34.5.24)

This can be satisfied for spin-singlet pairs if the matrix is chosen as

$$\hat{\Delta}_{\boldsymbol{k}} = \Delta d_0(\boldsymbol{k}) \mathrm{i}\sigma_y = \Delta \begin{pmatrix} 0 & d_0(\boldsymbol{k}) \\ -d_0(\boldsymbol{k}) & 0 \end{pmatrix}, \qquad (34.5.25)$$

where $d_0(\mathbf{k})$ is an even function of \mathbf{k} . Since it is defined only in the vicinity of the Fermi surface, it is normalized by the condition

$$\int \frac{\mathrm{d}\Omega}{4\pi} |d_0(\mathbf{k})|^2 = 1, \qquad (34.5.26)$$

where $d\Omega$ is the elementary solid angle. The excitation energies are

$$E_{\boldsymbol{k}\sigma} = \left[\xi_{\boldsymbol{k}}^2 + |\Delta d_0(\boldsymbol{k})|^2\right]^{1/2}.$$
 (34.5.27)

Just as in conventional superconductors, a gap appears in the excitation spectrum at the Fermi energy. The width of this gap is given by $\Delta d_0(\mathbf{k})$, which means that the gap depends on the direction of \mathbf{k} . The angular dependence of $d_0(\mathbf{k})$ can be expanded in Legendre polynomials, where only even lcomponents appear due to the even parity. In the simplest case, for s-wave superconductors, the gap is independent of \mathbf{k} . When the angular dependence of the gap is described by the l = 2 Legendre polynomial, we are dealing with d-wave superconductivity. There are points in \mathbf{k} -space on the Fermi surface, where the gap vanishes. Since the density of states remains finite, although small, even at low energies, the thermodynamics of d-wave superconductors is different from that of conventional superconductors. The equations determining the critical temperature and the temperature dependence of the gap are similar to those derived earlier.

Before going on to present experimental results on unconventional superconductors we note that the Hamiltonian can be diagonalized for triplet superconductors as well. The gap function can be given in terms of a vector function d(k), which is odd in k, in the form

$$\hat{\Delta}_{\boldsymbol{k}} = \Delta \boldsymbol{d}(\boldsymbol{k}) \cdot \boldsymbol{\sigma} \mathrm{i}\sigma_{y} = \Delta \begin{pmatrix} -d_{x}(\boldsymbol{k}) + \mathrm{i}d_{y}(\boldsymbol{k}) & d_{z}(\boldsymbol{k}) \\ d_{z}(\boldsymbol{k}) & d_{x}(\boldsymbol{k}) + \mathrm{i}d_{y}(\boldsymbol{k}) \end{pmatrix}, \quad (34.5.28)$$

and the excitation energies can be written in the same form as for singlet superconductors. Such pairs are found in the superfluid phases of the fermionic ³He. There are also experimental indications for triplet superconductivity in Sr_2RuO_4 below $T_c = 1.5$ K.

34.5.2 High-Temperature Superconductors

We mentioned in Chapter 26, where the phenomenology of superconductivity was outlined, that although more and more superconducting materials were found over the decades following the discovery of superconductivity in 1912, the highest observed critical temperature increased only slowly, up to about 23 K, by the middle of the 1980s. The discovery of high-temperature superconductors (HTSC), revealing a sudden jump to much higher T_c in several classes of materials, was surprising and challenging because such high values were thought to be excluded by the theory in conventional, phonon-mediated superconductors. Although the critical temperature could be as high as the Debye temperature in the BCS theory for strong enough electron-phonon interaction, more precise calculations based on the Eliashberg equations do not support this result. Taking into account the retardation effect and also the screened Coulomb interaction between electrons, MCMILLAN derived the expression given in (34.4.59). Since the dimensionless coupling constant of the electron-phonon interaction appears in both the numerator and the denominator of the exponent, the critical temperature calculated from this formula saturates in the strong-coupling limit. On these grounds, superconductors with transition temperatures in excess of 30–40 K were thought not to be possible, a not wholly counterintuitive result because although increasing the strength of the electron-phonon interaction might at first sight be expected to increase the binding energy of Cooper pairs, and so the critical temperature, the stronger coupling to the lattice could result in a deformation where the electronic system lowers its energy more by adapting to the deformed lattice than by forming Cooper pairs.

The critical temperature of high-temperature superconductors is much higher than this upper limit. The high T_c is accompanied by unusual magnetic properties. As was shown in Fig. 26.25, the vortex lattice can melt into a vortex-liquid phase before H_{c2} is reached. Further complications arise from the strong anisotropy of their crystalline structure. As presented in Chapter 26, their structure exhibits a common feature, namely they contain CuO₂ planes or pairs of CuO₂ planes, which are relatively well separated by the other components. The conductivity is much higher in the planes than perpendicular to the planes, indicating that the electrons in the CuO₂ planes play a dominant role. The cores of the vortices appearing above H_{c1} are not rigid straight lines. Pancake vortices are formed in the planes moving almost independently owing to the weak interplane coupling.

Another interesting feature of these materials is the almost complete absence of the isotope effect. It is therefore thought that the mechanism responsible for superconductivity is not the electron–phonon-mediated coupling but some other interaction. This seems to be supported by the typical phase diagram of high- T_c superconductors depicted in Fig. 34.9.



Fig. 34.9. Typical phase diagram of high-temperature cuprate superconductors. The control parameter x is the concentration of a dopant or the pressure

High-temperature superconductors are typically nonstoichiometric compounds; they contain dopants in a certain concentration range. The ground state of the undoped or slightly doped samples would be antiferromagnetic. The Néel temperature decreases with dopant concentration and vanishes before the superconducting state appears at somewhat higher concentrations. The critical temperature itself varies nonmonotonically with concentration. A characteristic feature of these materials is that superconductivity appears close to a magnetically ordered phase. Another typical feature is the anomalous behavior in the "normal" state, above $T_{\rm c}$. The metallic behavior can be described by the Landau theory of normal Fermi liquids far from the magnetically ordered state. Two relatively well-defined regions, although without sharp boundaries, can be distinguished between the antiferromagnetic and normal Fermi-liquid phases. In the region marked as "anomalous metal" in Fig. 34.9, the resistivity increases linearly with temperature, but no quasiparticles are observed and the material behaves like a Luttinger liquid. Closer to the magnetic phase, below a not very well-defined crossover temperature T^* , the resistivity increases with decreasing temperature and the density of states decreases in the vicinity of the Fermi energy as if a gap were forming before the true superconducting gap appears. This part of the phase diagram is dubbed the *pseudogap* region.

The two types of anomalous behavior are well established experimentally, but there is as yet no consensus on their theoretical interpretation, despite various proposals.¹¹ Similarly, there is no consensus on the mechanism responsible for the superconductivity.¹² There is no doubt, however, that the superconductivity is unconventional in these materials and that the order parameter has *d*-wave symmetry, more precisely $d_{x^2-y^2}$ symmetry, which means that the angular dependence of the gap can be described by

$$d(\mathbf{k}) = \cos k_x - \cos k_y \,. \tag{34.5.29}$$

The best proof of this is provided by the results of the Josephson experiments shown in Fig. 34.10.

As was shown in Fig. 26.33, where the Josephson effect was studied, the field dependence of the current flowing through a junction placed in an external magnetic field displays a Fraunhofer-like interference pattern. If the junction is threaded by a magnetic flux Φ , the current is given by

$$I \propto \left| \frac{\sin(\pi \Phi/\Phi_0)}{\pi \Phi/\Phi_0} \right|. \tag{34.5.30}$$

The same pattern can be observed in s-wave superconductors, if the junction is at the corner of the sample. If, however, one of the superconductors is a

¹¹ Whether these materials behave as Luttinger liquids in the anomalous metallic phase could not be proved beyond doubt experimentally.

¹² We will see in Chapter 35 that the phase diagram of the two-dimensional Hubbard model has similar features to the phase diagram discussed here. This model is, however, too simplified to capture the physical reality of these systems.



Fig. 34.10. Left panels: (a) Fraunhofer diffraction pattern for current vs. magnetic flux in a single edge Josephson junction and (b) expected interference pattern for a corner junction for superconductors with s-wave and $d_{x^2-y^2}$ symmetry. The right panels show the experimental results on YBCO for (a) an edge junction and (b) a corner junction [Reprinted with permission from D. A. Wollman et al., *Phys. Rev. Lett.* **74**, 797 (1995). \bigcirc (1995) by the American Physical Society]

d-wave superconductor with symmetry $d_{x^2-y^2}$, the flux dependence of the current should be given by

$$I \propto \left| \frac{\sin^2(\pi \Phi/2\Phi_0)}{\pi \Phi/2\Phi_0} \right| \tag{34.5.31}$$

owing to the angular dependence of the gap. As seen in Fig. 34.10, the experiments are in good agreement with this expression. Further theoretical efforts are, however, needed to fully understand the mechanism responsible for superconductivity in these materials and to explain the anomalous behavior above the superconducting state.

34.5.3 Heavy-Fermion Superconductors

Another class of materials where unconventional superconductivity has been observed is heavy-fermion superconductors. In contrast to the strongly anisotropic, quasi-two-dimensional structure of cuprate superconductors, heavyfermion superconductors are truly three dimensional. We mentioned in Chapter 16, when the heat capacity of metals was discussed, that there are materials where the Sommerfeld coefficient γ of the linear term is two or even three orders of magnitude larger at low temperatures than expected in normal metals. This huge increase of γ could originate from an anomalously large effective mass of the quasiparticles. Hence the name *heavy-fermion* materials.

We know that the effective mass of Bloch electrons differs from the electron mass owing to the periodic potential of the lattice. In addition to that, the interactions between quasiparticles in the Landau theory of Fermi liquids give a further renormalization of the effective mass, but these effects are not expected to produce such a huge mass increase. It rather arises from strong correlations, a point to which we will return when we discuss strongly correlated systems in Chapter 35. Here we only note that some of the heavy-fermion materials become superconductors at low temperatures. We list some of them in Table 34.2 with their critical temperatures and Sommerfeld coefficients.

Table 34.2. Critical temperature of the superconducting phase, the Sommerfeld coefficient, the effective mass, and the Néel temperature of the antiferromagnetic phase for some heavy-fermion materials

Material	$T_{\rm c}({\rm K})$	$\gamma({ m mJ/molK^2})$	$m^*/m_{ m e}$	$T_{\rm N}$ (K)
$CeCu_2Si_2$	0.65	1000	< 380	0.8
URu_2Si_2	1.2	65	140	17
$\mathrm{UPd}_2\mathrm{Al}_3$	1.9	145	66	14
$\mathrm{UNi}_2\mathrm{Al}_3$	1.0	120	48	4.6
UPt_3	0.55	450	180	5.0
UBe_{13}	0.85	1100	260	
${\rm CeCoIn_5}$	2.3	290	121	
$CeIrIn_5$	0.4	720	100	
$\mathrm{PrOs}_4\mathrm{Sb}_{12}$	1.85	310	44	

As shown in the table, some of these materials exhibit a transition to an antiferromagnetically ordered state with $T_{\rm N} > T_{\rm c}$. The coexistence of superconducting and antiferromagnetic orders supports the assumption that, as in high-temperature superconductors, magnetic fluctuations may be responsible for superconductivity. This is probably the case in other materials as well, such as CeIn₃, CePd₂Si₂, CeRh₂Si₂, CeCu₂Ge₂, or CeRhIn₅, which become superconductors under high pressure and are antiferromagnets at ambient pressure. As seen in the phase diagrams of CeIn₃ and CePd₂Si₂ displayed in Fig. 34.11, superconductivity appears in both cases near the quantum critical point where the Néel temperature would go to zero and quantum fluctuations become important. The quantum criticality may also explain the anomalous temperature dependence of the resistivity in the "normal" phase.

Unconventional pairing may exist with different symmetries giving rise to several different superconducting phases for the same material, just as ³He has



Fig. 34.11. Phase diagram of (a) CeIn₃ and (b) CePd₂Si₂. The insets show the temperature dependence of the resistivity [N. D. Mathur et al., *Nature* 394, 39 (1998)]

two superfluid phases. This might be the case in UPt₃ whose phase diagram shown in Fig. 34.12 can be described as having a tetracritical point between superconducting phases with different symmetries. The lower critical field H_{c1} is so small that the boundary of the homogeneous phase cannot be seen.



Fig. 34.12. Phase diagram of UPt₃ for two different orientations of the magnetic field with respect to the crystalline axes. The three superconducting phases meet at a tetracritical point [Reprinted with permission from S. Adenwalla et al., *Phys. Rev. Lett.* 65, 2298 (1990). \bigcirc (1990) by the American Physical Society]

The theory of heavy-fermion superconductors is made difficult by the fact that the characteristic energy scale of the superconducting state, the gap, is not much smaller than the bandwidth of the electronic states, since the heavy electrons responsible for superconductivity form a very narrow band. Moreover, these materials are extreme type II superconductors with $\kappa \gg 1$. The penetration depth may be larger than 1000 Å owing to the heavy mass and the coherence length is only on the order of 100 Å.

34.5.4 Organic Superconductors

Organic superconductors constitute another special class. Superconductivity was first observed in 1979 in (TMTSF)₂PF₆, which was known to have an insulating spin-density-wave ground state at ambient pressure. It becomes superconducting under a pressure of about 6.5 kbar, but the highest transition temperature is only 1.2 K. Several related compounds, where PF_6^- is replaced by other ions, become superconducting under pressure. The compound (TMTSF)₂ClO₄ is superconducting already at ambient pressure below $T_c = 1.4$ K. Several other families of organic superconductors have also been discovered since then. T_c may be as high as 10 K in the quasi-two-dimensional compounds containing BEDT-TTF.



Fig. 34.13. Phase diagram of $(TMTSF)_2PF_6$ [Reprinted with permission from N. Doiron-Leyrand et al., *Phys. Rev. B* **80**, 214531 (2009). \bigcirc (2009) by the American Physical Society]

There is an obvious similarity between the phase diagram shown in Fig. 34.13 and the phase diagram of heavy-fermion superconductors or that of high-temperature superconductors. The control parameter, which is the concentration in high- T_c materials, is now the pressure. The same effect, the modification of the lattice parameters, can be achieved by changing the concentration of a component of the compound. The fact that superconductivity

appears close to the quantum critical point of the antiferromagnetic state in all these cases is a strong indication that magnetic fluctuations may indeed play a more or less decisive role in the formation of Cooper pairs. This is supported by experimental indications that the superconducting order parameter has perhaps p-wave symmetry with triplet pairs in (TMTSF)₂PF₆.

34.5.5 Coexistence of Superconductivity and Ferromagnetism

In some of the materials discussed so far superconductivity appeared next to an antiferromagnetic phase or these phases even coexisted. It is readily seen that conventional superconductivity cannot coexist with ferromagnetic order. The ferromagnetic polarization of the conduction electron band forbids the singlet pairing of Cooper pairs.¹³ Recently, several materials have been discovered in which superconductivity appears within the ferromagnetic phase with very low critical temperature. Figure 34.14 shows two examples.



Fig. 34.14. The temperature–pressure phase diagrams of (a) UGe₂ and (b) ZrZn₂. $T_{\rm C}$ and $T_{\rm FM}$ denote the Curie temperatures and $T_{\rm SC}$ is the superconducting transition temperature magnified by a factor of 10 [S. S. Saxena et al., *Nature* 406, 587 (2000) and C. Pfleiderer et al., *Nature* 412, 58 (2001)]

The superconducting state disappears in both cases exactly at the same hydrostatic pressure where the ferromagnetic Curie temperature vanishes, indicating that superconducting order can only exist in the presence of magnetic order. A somewhat different situation occurs in URhGe, where superconductivity and ferromagnetism coexist at ambient pressure below $T_{\rm c} = 0.25 \,\mathrm{K}$ (the Curie temperature is $T_{\rm C} = 9.5 \,\mathrm{K}$), but the Curie temperature and the critical temperature have opposite pressure dependence. $T_{\rm C}$ increases with pressure,

¹³ The coexistence of antiferromagnetism and superconductivity is not excluded, since the coherence length, the spatial extension of the Cooper pairs, is typically much larger than the spatial periodicity of the antiferromagnetic order or the wavelength of the spin-density wave.

while T_c decreases. Since the magnetic interactions prefer a parallel alignment of the spins, triplet Cooper pairs are formed. The order parameter has to have odd parity; it may be of *p*-wave symmetry.

34.6 Tunneling Phenomena

The most direct experimental evidence for the gap in the energy spectrum of superconductors is provided by tunneling measurements. First, we discuss the single-particle effects¹⁴ in junctions where one or both sides are superconductors and then give a microscopic description of the tunneling current.

34.6.1 General Description of Tunneling

The two electrodes of the tunneling junction are separated by a thin insulating layer. The electronic wavefunctions decay exponentially in the insulator, but their overlap establishes a weak coupling between the two sides, and electrons can be transferred from one side to the other. This process can be described by a simple, phenomenologically introduced Hamiltonian. Denoting the creation operator of electrons on the left side by $c_{k\sigma}^{\dagger}$ and the creation operator on the right side by $d_{d\sigma}^{\dagger}$, the tunneling Hamiltonian is chosen in the form

$$\mathcal{H}_{\mathrm{T}} = \sum_{\boldsymbol{q}\boldsymbol{k}\sigma} \left(T_{\boldsymbol{k}\boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}\sigma} d_{\boldsymbol{q}\sigma} + \mathrm{h.c.} \right), \qquad (34.6.1)$$

where T_{kq} is related to the overlap of the wavefunctions. Its absolute square gives the transition probability. In addition to this term, the total Hamiltonian contains the Hamiltonians \mathcal{H}_{L} and \mathcal{H}_{R} of the electrons in the left and right electrodes, respectively.

Since the bias normally applied in tunneling experiments is on the order of millivolts, only electrons in the vicinity of the chemical potential can participate. The coupling T_{kq} can be approximated by a constant in the relevant energy range. We note that practically only electrons which arrive perpendicularly to the interface can go across the insulating layer. That is why the anisotropy of the gap in non-s-wave superconductors can be studied by choosing interfaces with different crystallographic orientations.

The application of the tunneling Hamiltonian is not always satisfactory. Although the energy is conserved in normal tunneling, inelastic processes may occur when the electron emits or absorbs a phonon in the insulating layer. This process, which opens a new channel for electron transfer, is known as phononassisted tunneling. The tunneling electron can flip its spin if it is scattered by magnetic impurities. The Kondo effect gives rise to zero-bias anomalies in

¹⁴ The Josephson effect related to the supercurrent between superconducting electrodes was discussed in Chapter 26.

the tunneling characteristics. The description of these phenomena is beyond the scope of this brief presentation of tunneling effects, where we concentrate more on how the tunneling current is modified when one or both sides are superconducting.

In experiments we usually measure the current I flowing across the junction when a voltage V is applied between the two sides,¹⁵ that is the current– voltage characteristic. The junction is in thermal equilibrium without applied voltage; the chemical potentials are identical on the two sides. When the junction is biased, the voltage drop occurs entirely in the insulating layer, if the coupling between the two sides is weak. The electrodes can be thought to be in local thermodynamic equilibrium and the distribution of electrons can be described by the Fermi distribution function with, however, different chemical potentials on the two sides. The difference of the chemical potentials is equal to the energy of electrons in the applied voltage. If the left side is chosen as the positive electrode, the chemical potential is higher by -eV owing to the negative charge of the electrons,

$$\mu_{\rm R} - \mu_{\rm L} = eV. \tag{34.6.2}$$

The filling of states at T = 0 and at a finite temperature when both electrodes are normal metals are shown in Fig. 34.15.



Fig. 34.15. Filling of the electron states on the two sides of a tunnel junction between normal metals (a) at T = 0 and (b) at finite temperature. The horizontal arrows indicate the allowed elastic tunneling processes

Electrons can tunnel elastically from right to left for V > 0, if their energy is below the chemical potential $\mu_{\rm R}$, but above $\mu_{\rm L}$. At finite temperatures tunneling is allowed in both directions with finite probability. The total current is the difference between the current components flowing in the two directions:

$$I = -e \left(P_{\rm L-R} - P_{\rm R-L} \right), \tag{34.6.3}$$

 $^{^{15}}$ The effective two-particle interaction V does not occur in the rest of this chapter, V denotes the voltage.

where $P_{\text{L-R}}$ is the probability of transition from left to right. It can be calculated using the standard rules of quantum mechanics. Denoting the wave vector of electrons on the left side by \boldsymbol{q} and the wave vector of electrons on the right side by \boldsymbol{k} , tunneling from left to right can take place if the state with \boldsymbol{q} is occupied and the state with \boldsymbol{k} , into which the electron tunnels, is empty. We thus find

$$P_{\rm L-R} = 2\frac{2\pi}{\hbar} \sum_{\boldsymbol{k}\boldsymbol{q}} |T|^2 f_{\rm L}^0(\varepsilon_{\boldsymbol{q}}) \left[1 - f_{\rm R}^0(\varepsilon_{\boldsymbol{k}})\right] \delta(\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{q}}).$$
(34.6.4)

The extra factor 2 comes from the spin which is assumed to be conserved during tunneling.¹⁶ From now on we will measure the electron energies from the respective chemical potential, that is we will use the quantity

$$\xi_{\boldsymbol{q}} = \varepsilon_{\boldsymbol{q}} - \mu_{\mathrm{L}} \tag{34.6.5}$$

on the left side and

$$\xi_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}} - \mu_{\mathrm{R}} \tag{34.6.6}$$

on the right side. Using (34.6.2) we have

$$P_{\rm L-R} = 2\frac{2\pi}{\hbar} \sum_{kq} |T|^2 f_0(\xi_q) \left[1 - f_0(\xi_k)\right] \delta(\xi_k - \xi_q + eV), \qquad (34.6.7)$$

where the indices L and R are dropped from the Fermi functions, since the argument shows unequivocally which side they refer to.

The transition probability for tunneling from right to left is expressed analogously,

$$P_{\rm R-L} = 2\frac{2\pi}{\hbar} \sum_{kq} |T|^2 f_0(\xi_k) \left[1 - f_0(\xi_q)\right] \delta(\xi_k - \xi_q + eV), \qquad (34.6.8)$$

and the total tunneling current is given by

$$I = 2\frac{2\pi e}{\hbar} \sum_{kq} |T|^2 \left[f_0(\xi_k) - f_0(\xi_q) \right] \delta(\xi_k - \xi_q + eV) \,. \tag{34.6.9}$$

Converting the sum over wave vectors to an integral over energy, we find

$$I = \frac{\pi e}{\hbar} \iint d\xi_{\rm R} d\xi_{\rm L} |T|^2 \left[f_0(\xi_{\rm R}) - f_0(\xi_{\rm L}) \right] \rho_{\rm R}(\xi_{\rm R}) \rho_{\rm L}(\xi_{\rm L}) \delta(\xi_{\rm R} - \xi_{\rm L} + eV) = \frac{\pi e}{\hbar} \int d\xi |T|^2 \left[f_0(\xi) - f_0(\xi + eV) \right] \rho_{\rm R}(\xi) \rho_{\rm L}(\xi + eV) , \qquad (34.6.10)$$

where $\rho_{\rm L}(\xi)$ and $\rho_{\rm R}(\xi)$ are the full densities of states on the two sides. The current–voltage characteristic is determined mostly by the densities of states.

¹⁶ As mentioned before, we are not considering the case when magnetic impurities are present in the insulating layer.

When both electrodes are normal metals (MIM junction¹⁷), the densities of states can be approximated by constants for small voltages, when $eV \ll \varepsilon_{\rm F}$. The remaining integral can be done, the current is proportional to V, and the junction exhibits usual ohmic behavior,

$$I = \frac{\pi e^2}{\hbar} \left| T \right|^2 \rho_{\rm R}(\varepsilon_{\rm F}) \rho_{\rm L}(\varepsilon_{\rm F}) V \qquad (34.6.11)$$

with the normal-state conductance given by

$$G_{\rm n} = \frac{\pi e^2}{\hbar} \left| T \right|^2 \rho_{\rm R}(\varepsilon_{\rm F}) \rho_{\rm L}(\varepsilon_{\rm F}) \,. \tag{34.6.12}$$

34.6.2 Tunneling in SIN Junctions

As shown already in Fig. 26.14, the current–voltage characteristics are drastically different when one or both electrodes are superconducting. To understand this, we consider the electron transfer processes that contribute to the tunneling current. We consider first the case when the left side is a normal metal and the right side is superconducting. Such an arrangement is known as a SIN or NIS junction. The densities of states and the filled and empty states at T = 0 are depicted in Fig. 34.16.



Fig. 34.16. Filled and empty states in a SIN junction at T = 0 for (a) V = 0, (b) V < 0, and (c) V > 0. Arrows depict allowed electron transfer processes

Electrons can tunnel from the normal side to empty states on the superconducting side at T = 0 if a large enough negative voltage is applied to the normal electrode, raising the chemical potential above the bottom of the quasiparticle continuum in the superconductor. This happens if $V \leq -V_c = -\Delta/e$. The derivative of the current with respect to voltage is singularly large at the threshold owing to the inverse-square-root singularity in the density of states.

When a positive voltage is applied, the chemical potential of the superconductor lies higher than the Fermi energy on the normal side. Since all

¹⁷ MIM stands for metal-insulator-metal. The notation NIN for normal(metal)insulator-normal(metal) is also used.

electrons are bound into Cooper pairs in the superconductor, electrons can tunnel to the normal side only if some of the Cooper pairs are broken up. If one of the electrons is transferred to the normal side, it loses an energy eV. This energy is taken up by the other electron to occupy a quasiparticle state in the single-particle continuum. The minimum energy the quasiparticle has to gain is Δ ; hence, quasiparticle current starts to flow only if the voltage exceeds a threshold value $V_{\rm c} = \Delta/e$.

These considerations show that the same threshold is found for V < 0and V > 0, although the physical processes are different. Since electrons of the normal metal tunnel directly into the single-particle continuum of the superconductor in the first case, the description of the tunneling current in terms of the density of states of the single-particle excitations seem to be justified, provided the strongly energy dependent

$$\rho_{\rm s}(E) = \rho(\varepsilon_{\rm F}) \frac{E}{\sqrt{E^2 - \Delta^2}} \tag{34.6.13}$$

is used for the density of states of quasiparticles in the superconductor. For V > 0, when a Cooper pair has to be broken, we still have to understand why the coherence factors u_k and v_k , which are related to the probability of finding an electron with a given k in the BCS state, do not show up in the tunneling current. We recall that a Bogoliubov quasiparticle with energy E_k can be constructed in two ways. It follows from the expression

$$E_{\boldsymbol{k}} = \sqrt{\xi_{\boldsymbol{k}}^2 + \Delta^2} \tag{34.6.14}$$

for the quasiparticle energy that breaking up the pair $(\mathbf{k}\uparrow,-\mathbf{k}\downarrow)$ formed by electrons above the normal-state Fermi energy costs the same energy as breaking up the pair $(\mathbf{k}'\uparrow,-\mathbf{k}'\downarrow)$ formed by electrons below the normalstate Fermi energy, if $\xi_{\mathbf{k}} = -\xi_{\mathbf{k}'}$. Since the pair $(\mathbf{k}\uparrow,-\mathbf{k}\downarrow)$ is present with probability $v_{\mathbf{k}}^2$ in the BCS ground state, and the pair $(\mathbf{k}\uparrow,-\mathbf{k}\downarrow)$ is present with probability $v_{\mathbf{k}'}^2$, the factor $v_{\mathbf{k}}^2 + v_{\mathbf{k}'}^2$ should appear in the expression for the tunneling current when both processes are taken into account. Using (34.2.29) for the coherence factors we readily see that

$$v_{\mathbf{k}}^2 + v_{\mathbf{k}'}^2 = v_{\mathbf{k}}^2 + u_{\mathbf{k}}^2 = 1, \qquad (34.6.15)$$

if $\xi_{k} = -\xi_{k'}$, that is the coherence factors drop out from the total current.

At finite temperatures, where there are thermally excited electrons above the Fermi energy in the normal metal and there are thermally broken pairs in the superconductor, there is no threshold voltage in the current–voltage characteristic. Current can flow at arbitrarily small voltage, although the characteristic is strongly nonlinear at temperatures below the critical temperature of the superconducting electrode. An exponentially weak current flows for voltages less than V_c . The theoretical prediction for the current–voltage characteristic is shown schematically in Fig. 34.17(*a*). It is in good agreement with the experimental results.



Fig. 34.17. (a) Current–voltage characteristics of a normal metal–insulator–superconductor junction. (b) Differential conductance of the SIN junction

We still can use (34.6.10) for describing the current in terms of the density of states of single-particle excitations, but only the density of states of the normal electrode can be approximated by a constant. This yields

$$I = \frac{\pi e}{\hbar} |T|^2 \rho_{\rm L}(\varepsilon_{\rm F}) \int d\xi \, \rho_{\rm R}(\xi) \big[f_0(\xi) - f_0(\xi + eV) \big].$$
(34.6.16)

Changing the integration variable from ξ to the energy E of the Bogoliubov quasiparticles we find the expression

$$G = \frac{\mathrm{d}I}{\mathrm{d}V} = \frac{\pi e^2}{\hbar} |T|^2 \rho_{\mathrm{L}}(\varepsilon_{\mathrm{F}}) \int \mathrm{d}E \,\rho_{\mathrm{s}}(E) \left(-\frac{\partial f_0(E+eV)}{\partial(eV)}\right) \qquad (34.6.17)$$

for the differential conductance. At T = 0, where the only contribution to the integral comes from E + eV = 0 we have

$$G = \frac{2\pi e^2}{\hbar} \left| T \right|^2 \rho_{\rm L}(\varepsilon_{\rm F}) \rho_{\rm s}(-eV) \,. \tag{34.6.18}$$

The same result is obtained for positive V since the current is an odd function of the voltage. The differential conductance measures directly the density of states of the single-particle excitations in the superconductor. The conductance at finite temperatures can only be calculated numerically since the Sommerfeld expansion cannot be used owing to the singularity in the density of states. The differential conductance is shown schematically in Fig. 34.17(b).

Since the coherence factors dropped out from the expression of the current, the tunneling characteristics can be obtained in a semiconductor model, where the superconductor is represented by an ordinary semiconductor with a gap of width 2Δ and the singularity in the density of states characteristic for superconductors [see (34.2.83)] appears both at the top of the "valence band" and at the bottom of the "conduction band." The chemical potential lies in the middle of the gap. As can be seen from Fig. 34.18, current starts to flow at the threshold voltages $\pm \Delta/e$ and the characteristics are identical to that found in SIN junctions.



Fig. 34.18. Semiconductor model of tunneling in a SIN junction. Horizontal arrows depict the allowed tunneling processes

34.6.3 Tunneling in SIS Junctions

The tunneling current flowing between two superconducting electrodes can be obtained similarly. The electron states and the allowed tunneling processes are shown in Fig. 34.19.



Fig. 34.19. (a) Cooper pairs at the chemical potential and the empty bands of single-particle excitations at T = 0 in an SIS junction for V = 0. Pair-breaking processes with single-particle tunneling for (b) V < 0 and (c) V > 0

Current starts to flow at T = 0, irrespective of whether the voltage difference is positive or negative, only above a critical voltage. A Cooper pair is broken up on the side with higher chemical potential and one of the electrons is transferred to the other side, into a lower lying state of the single-particle continuum, giving enough energy to the other electron to be excited to the quasiparticle continuum. Such a process can take place if $V \ge V_c = (\Delta_L + \Delta_R)/e$ or $V \le -V_c = -(\Delta_L + \Delta_R)/e$. Since the densities of states are singular at the gap on both sides, the current, which vanishes below the threshold, appears with a discontinuous jump, 464 34 Microscopic Theory of Superconductivity

$$I(V_{\rm c}) = \frac{\pi}{4} G_{\rm n} V \,, \tag{34.6.19}$$

where G_n is the conductance of the junction in its normal state, that is the current above threshold is a fraction $\pi/4$ of the value of the normal current at the same voltage.

Nonvanishing current is observed already for smaller voltage differences at finite temperatures with a reduced discontinuous jump at $V = \pm (\Delta_{\rm L} + \Delta_{\rm R})/e$ and a weak logarithmic singularity at $V = \pm (\Delta_{\rm L} - \Delta_{\rm R})/e$. To understand its origin we consider the tunneling events displayed in Fig. 34.20 for the case when the gap is larger on the right side.



Fig. 34.20. Single-particle tunneling processes in an SIS junction at finite temperature contributing to the anomaly at $V = \pm (\Delta_{\rm L} - \Delta_{\rm R})/e$

A singular contribution occurs for V < 0, when the bottoms of the quasiparticle continua are at the same height [see Fig. 34.20(a)]. Although the densities of states are singularly large on both sides, only a small number of quasiparticles are excited thermally. That is why only a weak singularity is found in the current. For V > 0 [see Fig. 34.20(b)], a Cooper pair is broken up on the side where the chemical potential lies higher. One electron is excited to the quasiparticle continuum on the same side, and the other electron tunnels to the other side. Such a process alone is forbidden by energy conservation. It becomes allowed when a thermally excited quasiparticle forms a Cooper pair with the electron coming from the other side. When $V = |\Delta_{\rm L} - \Delta_{\rm R}|/e$, an electron can be excited into the bottom of the quasiparticle continuum on the right side while a quasiparticle is deexcited from the bottom of the continuum on the left side. The singularity in the current is again due to the singularities in the density of states at the bottom, and the weakness of the singularity is due to the small number of thermally excited quasiparticles. The differential resistivity is negative above this singular point. The theoretical prediction for the current–voltage characteristics is shown in Fig. 34.21.

The semiconductor model can be used for SIS junctions as well. This is shown in Fig. 34.22. The densities of states have gaps of width $2\Delta_{\rm L}$ and $2\Delta_{\rm R}$, respectively, with the chemical potential lying in the middle of the gap. Current starts to flow at T = 0 above a threshold $V = (\Delta_{\rm L} + \Delta_{\rm R})/e$, when electrons from the "valence" band can tunnel into states of the "conduction" band on the other side. Weak singularity appears at $V = |\Delta_{\rm L} - \Delta_{\rm R}|/e$, when



Fig. 34.21. I-V curve of superconductor-insulator-superconductor junctions

thermally excited electrons can tunnel from the bottom of the "conduction" band to states of the bottom of the "conduction" band on the other side or thermally excited holes from the top of the "valence" band can tunnel to the states at the top of the "valence" band on the other side.



Fig. 34.22. Semiconductor model of tunneling in an SIS junction. Horizontal arrows depict the tunneling processes

34.6.4 Microscopic Calculation of the Current

The physical picture used to explain tunneling phenomena, when one or both electrodes of the junction are superconductors, gives a qualitatively correct description. A microscopic, quantitatively correct theory can be worked out when the current is calculated from linear response theory.

The Hamiltonian of the junction can be divided into three parts:

$$\mathcal{H} = \mathcal{H}_{\mathrm{R}} + \mathcal{H}_{\mathrm{L}} + \mathcal{H}_{\mathrm{T}}.$$
 (34.6.20)

The terms \mathcal{H}_{R} and \mathcal{H}_{L} describe the electrons in the right and left sides of the junction, respectively, which can be either normal metals or superconductors. The term \mathcal{H}_{T} is the tunneling Hamiltonian given in (34.6.1). It describes the tunneling of electrons between the two sides. The entire system is not in thermodynamic equilibrium; the difference between the chemical potentials is proportional to the applied voltage according to (34.6.2), but the two sides of the junction are in separate thermodynamic equilibrium. Moreover, apart from the weak tunneling coupling, the two sides are independent, their Hamiltonians commute,

$$[\mathcal{H}_{\rm R}, \mathcal{H}_{\rm L}]_{-} = 0. \qquad (34.6.21)$$

The current, which is assumed to flow from left to right for positive voltage, can be calculated as the negative of the expectation value of the change in the number of particles on the left side multiplied by the electron charge:

$$I(t) = e \left\langle \dot{\mathcal{N}}_{\mathrm{L}}(t) \right\rangle, \qquad (34.6.22)$$

where

$$\mathcal{N}_{\rm L} = \sum_{q\sigma} d^{\dagger}_{q\sigma} d_{q\sigma} \,. \tag{34.6.23}$$

If the tunnel coupling \mathcal{H}_{T} is a weak perturbation, the time derivative of $\mathcal{N}_{\mathrm{L}}(t)$ can be calculated in linear response theory. According to the formulas given in Appendix J, the thermal average of $\dot{\mathcal{N}}_{\mathrm{L}}(t)$ in the presence of \mathcal{H}_{T} is

$$\left\langle \dot{\mathcal{N}}_{\mathrm{L}}(t) \right\rangle = -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{t} \left\langle \left[\dot{\mathcal{N}}_{\mathrm{L}}(t), \mathcal{H}_{\mathrm{T}}(t') \right]_{-} \right\rangle \,\mathrm{d}t' \,, \tag{34.6.24}$$

where the time dependence of the operators is governed by the unperturbed Hamiltonian $\mathcal{H}_0 = \mathcal{H}_R + \mathcal{H}_L$ via

$$\dot{\mathcal{N}}_{\mathrm{L}}(t) = \mathrm{e}^{\mathrm{i}\mathcal{H}_{0}t/\hbar} \dot{\mathcal{N}}_{\mathrm{L}} \mathrm{e}^{-\mathrm{i}\mathcal{H}_{0}t/\hbar},
\mathcal{H}_{\mathrm{T}}(t') = \mathrm{e}^{\mathrm{i}\mathcal{H}_{0}t'/\hbar} \mathcal{H}_{\mathrm{T}} \mathrm{e}^{-\mathrm{i}\mathcal{H}_{0}t'/\hbar}.$$
(34.6.25)

The time derivative of the particle-number operator is obtained from the usual quantum mechanical relation

$$\dot{\mathcal{N}}_{\mathrm{L}}(t) = \frac{\mathrm{i}}{\hbar} \big[\mathcal{H}, \mathcal{N}_{\mathrm{L}}(t) \big]_{-} \,. \tag{34.6.26}$$

Since the number of particles is conserved by both \mathcal{H}_R and \mathcal{H}_L irrespective of the form of the interaction between electrons, only the commutator with \mathcal{H}_T is left which gives

$$\dot{\mathcal{N}}_{\mathrm{L}}(t) = \frac{\mathrm{i}}{\hbar} \left[\mathcal{H}_{\mathrm{T}}, \mathcal{N}_{\mathrm{L}}(t) \right]_{-}$$
$$= \frac{\mathrm{i}}{\hbar} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} \left[T_{\boldsymbol{k}\boldsymbol{q}} c^{\dagger}_{\boldsymbol{k}\sigma}(t) d_{\boldsymbol{q}\sigma}(t) - T^{*}_{\boldsymbol{k}\boldsymbol{q}} d^{\dagger}_{\boldsymbol{q}\sigma}(t) c_{\boldsymbol{k}\sigma}(t) \right].$$
(34.6.27)

Introducing the quantity

$$A(t) = \sum_{kq\sigma} T_{kq} c^{\dagger}_{k\sigma}(t) d_{q\sigma}(t)$$
(34.6.28)

both the time derivative of the particle number and the tunneling Hamiltonian can be expressed through it. We have

$$\dot{\mathcal{N}}_{\mathrm{L}}(t) = \frac{\mathrm{i}}{\hbar} \left[A(t) - A^{\dagger}(t) \right]$$
(34.6.29)

and

$$\mathcal{H}_{\rm T}(t') = A(t') + A^{\dagger}(t').$$
 (34.6.30)

Combining these expressions with (34.6.24) and (34.6.22) the current takes the form

$$I(t) = \frac{e}{\hbar^2} \int_{-\infty}^{t} \mathrm{d}t' \left\langle \left[\left(A(t) - A^{\dagger}(t) \right), \left(A(t') + A^{\dagger}(t') \right) \right]_{-} \right\rangle.$$
(34.6.31)

Since the number of particles is not fixed in the BCS theory, the Hamiltonian

$$\mathcal{H}' = \mathcal{H} - \mu \mathcal{N} \tag{34.6.32}$$

was used throughout the calculation dropping the prime for convenience. The time-dependent operators, where the time evolution is calculated with either \mathcal{H}_0 or $\mathcal{H}'_0 = \mathcal{H}_0 - \mu_L \mathcal{N}_L - \mu_R \mathcal{N}_R$, are simply related:

$$A(t) = e^{i(\mu_{\rm R} - \mu_{\rm L})t/\hbar} \tilde{A}(t) = e^{ieVt/\hbar} \tilde{A}(t), \qquad (34.6.33)$$

where

$$\tilde{A}(t) = e^{i\mathcal{H}_0't/\hbar} A e^{-i\mathcal{H}_0't/\hbar} . \qquad (34.6.34)$$

The total current can be written as the sum of two terms:

$$I = I_{\rm qp} + I_{\rm J},$$
 (34.6.35)

where

$$I_{\rm qp} = \frac{e}{\hbar^2} \int_{-\infty}^{\infty} dt' \,\theta(t-t') \left\{ e^{ieV(t-t')/\hbar} \left\langle \left[\tilde{A}(t), \tilde{A}^{\dagger}(t') \right]_{-} \right\rangle - e^{-ieV(t-t')/\hbar} \left\langle \left[\tilde{A}^{\dagger}(t), \tilde{A}(t') \right]_{-} \right\rangle \right\}$$
(34.6.36)

and

 \sim

$$I_{\rm J} = \frac{e}{\hbar^2} \int_{-\infty}^{\infty} dt' \,\theta(t-t') \bigg\{ e^{ieV(t+t')/\hbar} \Big\langle \big[\tilde{A}(t), \tilde{A}(t')\big]_{-} \Big\rangle - e^{-ieV(t+t')/\hbar} \Big\langle \big[\tilde{A}^{\dagger}(t), \tilde{A}^{\dagger}(t')\big]_{-} \Big\rangle \bigg\}.$$
(34.6.37)

The first term describes the quasiparticle tunneling and the second is the supercurrent associated with the Josephson effect.

The quasiparticle current is readily calculated between normal metals in the free electron approximation. The time dependence of the creation and annihilation operators is a simple exponential function, and the commutators are nonvanishing only if $\mathbf{k} = \mathbf{k}'$, $\mathbf{q} = \mathbf{q}'$, and $\sigma = \sigma'$. The expectation values can be given in terms of the Fermi distribution functions and we find

$$I_{\rm qp} = \frac{e}{\hbar^2} \int_{-\infty}^{\infty} dt' \,\theta(t-t') \sum_{\boldsymbol{kq\sigma}} |T_{\boldsymbol{kq}}|^2 \left\{ e^{ieV(t-t')/\hbar} e^{i(\varepsilon_{\boldsymbol{k}}-\varepsilon_{\boldsymbol{q}})(t-t')/\hbar} \right. \\ \left. \times \left[f_{\rm R}^0(\varepsilon_{\boldsymbol{k}})(1-f_{\rm L}^0(\varepsilon_{\boldsymbol{q}})) - f_{\rm L}^0(\varepsilon_{\boldsymbol{q}})(1-f_{\rm R}^0(\varepsilon_{\boldsymbol{k}})) \right] \right. \\ \left. - e^{-ieV(t-t')/\hbar} e^{-i(\varepsilon_{\boldsymbol{k}}-\varepsilon_{\boldsymbol{q}})(t-t')/\hbar} \right.$$
(34.6.38)
$$\left. \times \left[f_{\rm L}^0(\varepsilon_{\boldsymbol{q}})(1-f_{\rm R}^0(\varepsilon_{\boldsymbol{k}})) - f_{\rm R}^0(\varepsilon_{\boldsymbol{k}})(1-f_{\rm L}^0(\varepsilon_{\boldsymbol{q}})) \right] \right\}.$$

Performing the integration yields

$$I_{\rm qp}(t) = \frac{e}{\hbar^2} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} |T_{\boldsymbol{k}\boldsymbol{q}}|^2 \left[f_{\rm R}^0(\varepsilon_{\boldsymbol{k}}) - f_{\rm L}^0(\varepsilon_{\boldsymbol{q}}) \right] \\ \times \left\{ \frac{\mathrm{i}\hbar}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{q}} + eV + \mathrm{i}\delta} - \frac{\mathrm{i}\hbar}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{q}} + eV - \mathrm{i}\delta} \right\}.$$
(34.6.39)

It is readily seen, making use of (C.3.3), that the expression derived for the current is precisely the same as (34.6.9) if the energies measured from the respective chemical potentials given in (34.6.5) and (34.6.6) are used.

When the electrode is superconducting on one side or on both sides, the creation and annihilation operators of the electron states on the superconducting electrode could be expressed in terms of the Bogoliubov quasiparticles using transformation (34.2.68). This formulation has a drawback which was uninteresting until now. The quasiparticles have a well-defined momentum, but their charge is not well defined, since the creation operators of a bogolon adds an electron with charge -e to the system, but it can also remove a particle changing the charge by +e. This difficulty can be remedied by introducing the operator S, which removes a Cooper pair from the condensate, and its adjoint S^{\dagger} , which adds a Cooper pair to the condensate. The operators

$$\alpha_{\mathbf{e}\mathbf{k}\uparrow}^{\dagger} = u_{\mathbf{k}}^{*}c_{\mathbf{k}\uparrow}^{\dagger} - v_{\mathbf{k}}^{*}S^{\dagger}c_{-\mathbf{k}\downarrow}, \qquad \alpha_{\mathbf{e}\mathbf{k}\downarrow}^{\dagger} = u_{\mathbf{k}}^{*}c_{-\mathbf{k}\downarrow}^{\dagger} + v_{\mathbf{k}}^{*}S^{\dagger}c_{\mathbf{k}\uparrow} \qquad (34.6.40)$$

add an electron to the system; they are the creation operators of an excited state with extra charge -e. Similarly the operators

$$\alpha_{\mathrm{h}\boldsymbol{k}\uparrow}^{\dagger} = u_{\boldsymbol{k}}^{*}Sc_{\boldsymbol{k}\uparrow}^{\dagger} - v_{\boldsymbol{k}}^{*}c_{-\boldsymbol{k}\downarrow}, \qquad \alpha_{\mathrm{h}\boldsymbol{k}\downarrow}^{\dagger} = u_{\boldsymbol{k}}^{*}Sc_{-\boldsymbol{k}\downarrow}^{\dagger} + v_{\boldsymbol{k}}^{*}c_{\boldsymbol{k}\uparrow} \qquad (34.6.41)$$

add a hole to the system; they create excited states where the charge is changed by +e. Note that

$$\alpha^{\dagger}_{\mathbf{h}\,\boldsymbol{k}\uparrow} = S\alpha^{\dagger}_{\mathbf{e}\,\boldsymbol{k}\uparrow}, \qquad \alpha^{\dagger}_{\mathbf{h}\,\boldsymbol{k}\downarrow} = S\alpha^{\dagger}_{\mathbf{e}\,\boldsymbol{k}\downarrow}, \qquad (34.6.42)$$

that is creating a holelike excitation is equivalent to creating an electronlike excitation and annihilating a pair. This transformation should be used for both the left and the right superconductors, taking into account that the phases in the coherence factors are different on the two sides.

Straightforward but tedious calculations lead to the result that the coherence factors as well as the pair-creation and pair-annihilation operators drop out, and the single-particle current can be described in terms of the density of states of the Bogoliubov quasiparticles. When one of the electrodes is superconducting, we find

$$I_{\rm qp} = \left(\frac{G_{\rm n}}{e}\right) \theta(eV - \Delta) \left[(eV)^2 - \Delta^2\right]^{1/2}$$
(34.6.43)

at T = 0 in agreement with the behavior shown in Fig. 34.17(*a*). Similarly, when both electrodes are superconducting, the same expression is derived as in the naive calculation. For superconductors with gap $\Delta_{\rm L}$ and $\Delta_{\rm R}$ on the two sides we find

$$I_{\rm qp} = \left(\frac{G_{\rm n}}{e}\right) \int_{-\infty}^{\infty} \mathrm{d}E \frac{|E|}{\left[E^2 - \Delta_{\rm L}^2\right]^{1/2}} \frac{|E + eV|}{\left[(E + eV)^2 - \Delta_{\rm R}^2\right]^{1/2}} \left[f_0(E) - f_0(E + eV)\right],$$
(34.6.44)

where the ranges $|E| < |\Delta_{\rm L}|$ and $|E + eV| < |\Delta_{\rm R}|$ have to be excluded from the integration. The current can be calculated only numerically to yield the characteristics displayed in Fig. 34.21.

The term I_J , which was neglected until now, contributes to the current in SIS junctions. The coherence factors and the creation and annihilation operators, S^{\dagger} and S, of the pairs do not drop out. There will be terms that contain the products $S_L S_R^{\dagger}$ or $S_L^{\dagger} S_R$, which describe the tunneling of Cooper pairs from one side to the other. Since the electrons are bound into pair states on both sides, their energy is unchanged during the transition. Such a process can take place at zero external potential, if the current is driven by a current generator. This is the DC Josephson effect discussed phenomenologically in Chapter 26. The microscopic treatment of the Josephson effect allows us to derive its most important feature, the dependence of the current on the difference between the phases of the two superconductors

$$I_{\rm J}(t) = I_0(eV)\sin(\omega t + \phi)$$
 (34.6.45)

with $\omega = 2eV/\hbar$. One can also derive (26.5.18), according to which the maximum supercurrent that can be driven through the junction without any voltage drop is given by

$$I_0(eV = 0) = \frac{\pi\Delta}{2e}G_n, \qquad (34.6.46)$$

and the Ambegaokar–Baratoff formula¹⁸ (26.5.19)

$$I_0(eV = 0, T) = \frac{\pi \Delta}{2e} G_n \tanh \frac{\Delta}{2k_B T}$$
(34.6.47)

that gives the temperature dependence of the maximum supercurrent.

34.6.5 Green-Function Theory of Tunneling

These results can be derived much more simply by using Green-function techniques. The single-particle current was expressed in (34.6.36) as a retarded Green function of the quantity A(t), which has to be evaluated in the absence of direct coupling between the two sides. The tunneling coupling was already taken into account in the derivation of the current formula from linear response theory and the voltage appears in the time-dependent exponential factor. One can show that the quasiparticle tunneling current can be expressed in terms of the spectral functions of the one-particle Green functions of the two sides in the form

$$I_{\rm qp} = \frac{e}{\hbar^2} \sum_{\boldsymbol{k}\boldsymbol{q}\sigma} |T_{\boldsymbol{k}\boldsymbol{q}}|^2 \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} A_{\rm R}(\boldsymbol{k},\omega) A_{\rm L}(\boldsymbol{q},\omega + eV/\hbar) \left[f_0(\hbar\omega) - f_0(\hbar\omega + eV) \right],$$
(34.6.48)

where the spectral function is

$$A(\mathbf{k},\omega) = 2\pi\hbar\delta(\hbar\omega - \xi_{\mathbf{k}}) \tag{34.6.49}$$

for normal metals if lifetime effects are neglected, and

$$A(\mathbf{k},\omega) = 2\pi\hbar \left[u_{\mathbf{k}}^2 \delta(\hbar\omega - E_{\mathbf{k}}) + v_{\mathbf{k}}^2 \delta(\hbar\omega + E_{\mathbf{k}}) \right]$$
(34.6.50)

for superconductors. Since the spectral function is related to the density of states, the results derived earlier for the quasiparticle current are recovered.

Green functions can be used in evaluating the Josephson current (34.6.37) as well, but now the Fourier transform, $F(\mathbf{k}, \omega)$, of the anomalous Green function and its complex conjugate appear in the current formula. We recover the results mentioned earlier.

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Strongly Correlated Systems

Electron–electron interactions were mostly treated at the mean-field level in the previous chapters. Restricting ourselves to the Hartree–Fock approach or the RPA seems to be justified if the interaction term is small compared to the kinetic energy or, more precisely, when the Coulomb repulsion U resulting from the intra-atomic interaction is small compared to the bandwidth W. The band structure and the spectrum of single-particle states can then be determined using a one-particle potential which includes exchange. As we have seen in Chapter 28, there are no correlations between electrons of opposite spin in the Hartree–Fock approximation. The Fermi hole (exchange hole), the dip in the pair distribution function of parallel-spin electrons, is due to the Pauli principle. The corrections beyond the Hartree–Fock approximation are known as the correlation contributions. They can be treated as weak perturbations when $U \ll W$. This is not always the case in physically realistic systems. Often the two energy scales set by the bandwidth and the Coulomb repulsion are quite comparable or the relation is even inverted. Such systems are known as strongly correlated systems. This is the case in particular in compounds containing lanthanoid (rare-earth) ions¹ with localized 4f electrons or actinoids with incomplete 5f shells.²

We saw in Chapter 33 that magnetically ordered phases may appear in interacting electron systems if the Coulomb repulsion is strong enough. It was emphasized there that the single-particle picture with spin-split bands is too simplistic to describe the symmetry-broken ferromagnetic state. This would lead to an overly high critical temperature and would not be able to account

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¹ Although lanthanoid means "like lanthanum" and so should not include lanthanum, the lanthanoid series comprises the 15 elements with atomic numbers 57–71, from lanthanum to lutetium. Following common usage in the solid-state physics literature rare earth and lanthanoid (previously lanthanide) are used synonymously, though the name "rare earth" is used in chemistry to describe the lanthanoids together with scandium and yttrium.

 $^{^2}$ The *f*-block elements, from cerium to lutetium and from thorium to lawrencium are also known as inner transition metals.

for the thermal spin fluctuations which destroy magnetism as the temperature is increased.

Similar difficulties are encountered in the theoretical description of the antiferromagnetic state of itinerant electron systems with a half-filled band. A simple-minded band structure calculation might be quite misleading for these materials. They turn out to be insulators in many cases where metallic behavior would be expected for a half-filled situation. An even more challenging theoretical problem is the appearance of a nonmetallic phase without magnetic ordering as a result of the strong correlations between electrons. This metal–insulator transition (MIT) is one of the subjects of this chapter.

The Kondo effect was touched upon briefly when the transport properties of metals were discussed. The scattering of conduction electrons by paramagnetic impurities gives rise to a logarithmic temperature-dependent correction to the resistivity and other observables. This singularity indicates that perturbation theory breaks down at low temperatures. Although the leading and next-to-leading logarithmic corrections can be summed up by a scaling procedure, this is not sufficient to get the true low-temperature behavior. Nonperturbative approaches are needed to describe the screening of the magnetic moment and the asymptotic behavior as $T \rightarrow 0$.

As a preliminary to the Kondo problem, we will study the formation of localized magnetic moments on impurity atoms in dilute alloys with the help of the Anderson model. A generalization of these models will lead us to a description of mixed-valence compounds and heavy-fermion materials, where the atoms with incomplete d or f shells form a regular lattice. We will have to consider the effects of the interactions of conduction electrons with the magnetically active electrons in the narrow d or f bands.

35.1 The Mott Metal–Insulator Transition

The transition between metallic and insulating phases can be interpreted in some cases in the usual band picture. Consider a simple metal with an even number of electrons per atom. Since the number of states in any band is twice the number of elementary cells, materials possessing an even number of electrons per atom and which crystallize in a structure with a monatomic unit cell should have completely filled or empty bands unless the bands overlap in energy. It is precisely due to the overlap of the bands that the divalent elements of the second group of the periodic table are metals. When the distance between the atoms is increased, the overlap of the wavefunctions of neighboring atoms decreases and the bands narrow. The atomic energy levels are recovered in the large-distance limit, when the atoms become independent. This narrowing of the bands is displayed in Fig. 35.1.

The overlap between the bands vanishes at a critical value of the interatomic distance. If the lower band is completely filled and the upper band is empty, the system becomes insulating. For smaller lattice parameters the



Fig. 35.1. Variation of the bandwidth with the distance between the atoms

material is metallic. This type of metal-nonmetal transition occurring as the lattice parameter is changed (it can be achieved, e.g., by applying pressure) is known as the *band-overlap* or *Wilson transition.*³ The insulating state is a *band insulator* or *Bloch-Wilson insulator*. The interaction with the periodic one-particle potential plays the dominant role in the formation of bands and this transition can be interpreted in the one-particle picture without having to take the electron-electron interaction into account.

By the same token, systems with an odd number of electrons per atom should always be metals in the one-particle band picture. This, however, is not the case in reality. We have already seen in Chapter 33 that the electron– phonon interaction may induce charge-density waves in quasi-one-dimensional solids and the formation of the CDW is accompanied by a displacive distortion of the regular array of atoms. The unit-cell size of the superstructure is increased, usually by period doubling (dimerization). This Peierls transition is a metal-insulator transition, since the folding of the Brillouin zone leads to a completely filled lower band. The decrease in the electronic energy due to the opening of a gap at the boundary of the new Brillouin zone outweighs the increase in elastic energy. A similar metal-insulator transition, owing to the folding of the Brillouin zone in the ordered phase, was suggested by SLATER [see Section 33.2.1] for repulsive electron–electron interaction, when itinerant electrons order antiferromagnetically and a spin-density wave is formed. Hartree–Fock theory predicts a continuous transition from the normal Fermiliquid to the magnetic insulator state.

Such a continuous transition from metallic to antiferromagnetic insulating state produced by the doubling of the unit cell at the Néel temperature has been observed recently in Cd₂Os₂O₇ at $T_{\rm N} = 226$ K. There are, however, several counter examples.⁴ The classical example is NiO. The 3*d* level of the nickel atom splits into two with symmetries e_g and t_{2g} which can accommodate four and six electrons, respectively. These levels broaden into bands in NiO.

³ A. H. WILSON, 1931.

⁴ We only consider here metal–insulator transitions due to electronic correlations. As will be shown in the next chapter, a similar transition can take place – although for completely different reasons – when the number of carriers is modified by varying the dopant concentration in a disordered system.

The Ni²⁺ ion has eight 3d electrons outside the [Ar] core. Although the band states cannot be filled by the eight electrons to form a full and an empty band, NiO is not metallic but a good insulator. This contradiction cannot be resolved by attributing the insulating behavior to antiferromagnetic ordering, since NiO is insulating even in the paramagnetic phase. The magnetically ordered state is not a Slater insulator. A similar transition from paramagnetic insulator to antiferromagnetic insulator sobserved in CoO with an odd number of d electrons.

Another example is V_2O_3 . The low-temperature antiferromagnetic insulating state undergoes a first-order phase transition into a metallic state where the conductivity changes discontinuously by several orders of magnitude. An even richer phase diagram is found when the pressure is changed or – in a certain sense equivalently – the lattice constants are varied by varying the composition. Three phases are seen in Fig. 35.2, a paramagnetic metallic, a paramagnetic insulating, and an antiferromagnetic insulating phase.



Fig. 35.2. The phase diagram of V_2O_3 doped with Cr and Ti under pressure [Reprinted with permission from D. B. McWhan et al., *Phys. Rev. B* **7**, 1920 (1973). \bigcirc (1973) by the American Physical Society]

These findings indicate that the intra-atomic correlations responsible for the appearance or disappearance of magnetic moments may play an important role in the nonmagnetic insulating state. N. F. MOTT suggested already in 1949 that if the band in the vicinity of the Fermi energy is not filled completely and is narrow enough, the interaction between electrons opens up a gap in the spectrum of charge excitations and this leads to an insulating state. If the bands are widened as the distance between atoms is decreased, a sharp, discontinuous (first-order) transition from insulating, strongly correlated to metallic, weakly correlated behavior is expected. This *Mott transition* occurs as the ratio U/W is altered by temperature or pressure variations or by changing the dopant concentration. In this chapter we first present the physical picture proposed by MOTT and then we treat the present status of the metal–nonmetal transition in the framework of the Hubbard model, pointing out the unsolved questions.

A different, well-known example of a metal-insulator transition that will not be discussed in what follows is the Verwey transition⁵ in magnetite, $Fe^{3+}[Fe^{3+}Fe^{2+}]O_4$, where a spontaneous, intercorrelated change of both lattice symmetry and electrical conductivity is observed below $T_V = 125$ K, well inside the ferrimagnetic regime. As explained in Section 14.1.4, the tetrahedral A sites of the inverse spinel structure are occupied by Fe^{3+} ions, while the octahedral B sites are occupied by an equal mixture of Fe^{3+} and Fe^{2+} ions. They are randomly distributed on the B sites above T_V permitting valency exchange by means of thermally activated electron hopping. The rapid increase of the resistivity below T_V is due to charge ordering within the sublattice of the octahedral sites.

35.1.1 Physical Picture for the Mott Transition

In order to form a physical picture for the Mott transition consider a crystal built of monovalent atoms. The electrons outside the closed shell form a halffilled band and the system is metallic even if the distance between atoms is so large that the overlap of the wavefunctions is exponentially small and the probability for an electron to hop to neighboring sites is almost negligible. This is because electron–electron interactions are neglected in the band structure calculations. If the wavefunction of the half-filled band described in terms of extended Bloch functions is expressed in terms of localized Wannier states, configurations with two electrons on some atoms and no electrons on others occur with high probability. These configurations have much higher energy than the configurations with one electron sitting on each atom when the intraatomic Coulomb repulsion is taken into account. Therefore, when the band is sufficiently narrow, the relatively high-energy charge fluctuations are expected to be blocked and the electrons become localized.

To make an estimate when this happens, MOTT suggested that the dominant factor determining whether an electron system is metallic or nonmetallic is the competition between the kinetic energy and the Coulomb energy that tends to bind electrons to the atoms. A simple estimate can be given by assuming that the system is metallic if the Fermi energy $\varepsilon_{\rm F}$, which characterizes

⁵ E. J. W. VERWEY, 1939, 1947.

the kinetic motion of electrons, is larger than the Coulomb energy. For electrons with an effective mass m^* moving in a medium with dielectric constant ϵ_r , the Coulomb energy can be estimated via

$$\frac{e^2}{4\pi\epsilon_0\epsilon_r a_0^*},\qquad(35.1.1)$$

where $a_0^* = a_0 \epsilon_r m_e/m^*$ is the effective Bohr radius of the medium with $a_0 = 4\pi\epsilon_0 \hbar^2/e^2 m_e$ the true Bohr radius. This energy can also be written as

$$\frac{\hbar^2}{\epsilon_{\rm r}m_{\rm e}} \frac{1}{a_0 a_0^*} = \frac{\hbar^2}{m^*} \frac{1}{a_0^{*2}}.$$
(35.1.2)

Expressing the Fermi energy in terms of the electron density,

$$\varepsilon_{\rm F} = (3\pi^2)^{2/3} \frac{\hbar^2}{2m^*} n_{\rm e}^{2/3} \,.$$
 (35.1.3)

Comparison of the two expressions gives

$$a_0^* n_{\rm e}^{1/3} > C \tag{35.1.4}$$

as the condition for the metallic phase with C of order unity. The system is insulating for smaller densities.

A somewhat different consideration leads to the same result. When the atoms are far apart, the electrons are bound to the positive ions by the Coulomb potential. The radius of the lowest energy state is the Bohr radius, the electrons are localized, and the system is insulating. When the atoms are closer and the density of mobile electrons is $n_{\rm e}$, a detached electron is attracted by the positive ion left behind via a potential screened by the other electrons. The screening length can be estimated as the inverse of the Thomas–Fermi wave number given according to (29.2.13) via

$$q_{\rm TF}^2 = 4\pi \tilde{e}^2 \rho(\varepsilon_{\rm F}) = (3\pi^2)^{1/3} \frac{4\tilde{e}^2 m_{\rm e}}{\hbar^2 \pi} n_{\rm e}^{1/3} = \left(\frac{3}{\pi}\right)^{1/3} \frac{4}{a_0} n_{\rm e}^{1/3} \,. \tag{35.1.5}$$

When the screening length $1/q_{\rm TF}$ is less than the Bohr radius, the screened potential cannot bind the electron any more, the electrons are free to move, and the system becomes metallic. Comparing $1/q_{\rm TF}$ with a_0 leads to condition (35.1.4) for the existence of a metallic state.

Although these considerations do not say anything about it, MOTT emphasized that the localized electrons will have localized magnetic moments in the insulating state, and these moments will persist in the correlated metallic state. The insulating nature of the state is not due to magnetism, but due to the on-site Coulomb repulsion, which operates in the paramagnetic state as well. The moments disappear at higher electron densities. J. HUBBARD (1963) proposed a model now known as the Hubbard model which incorporates electron–electron interactions and accomodates the eventual magnetic

properties of the electron system.⁶ In its simplest form the model assumes that there is a single nondegenerate Wannier state at each lattice site with energy ε_0 . Electrons can freely hop to neighboring sites if that site is empty. However, when two electrons with opposite spin share the same site, they repel each other. This repulsion is characterized by the Hubbard U.⁷

$$\mathcal{H} = \sum_{i,\sigma} \varepsilon_0 c_{i,\sigma}^{\dagger} c_{i,\sigma} + \sum_{\langle ij \rangle \sigma} t c_{i,\sigma}^{\dagger} c_{j,\sigma} + U \sum_i n_{i,\uparrow} n_{i,\downarrow} \,. \tag{35.1.6}$$

To understand the physics of the model we consider first the case where the number of electrons is equal to the number of lattice sites and treat the interaction between electrons in the mean-field approximation, an approximation which might be reasonable for weak couplings, when U is smaller than the bandwidth determined by the hopping amplitude. The electrons fill half of a band in the one-particle picture and the system is metallic.

On the other hand, in the opposite limit, when $U \gg t$, the half-filled Hubbard model is equivalent to an antiferromagnetic Heisenberg model with exchange coupling $J = -2t^2/U$, as was shown in Chapter 33. The spins can be exchanged but the electrons do not carry current; the system is insulating. If an electron hops to a neighboring site, double occupancy lasts only for a very short time due to the strong on-site repulsion and one of the electrons has to hop back to the temporarily empty site. The electron energies are around ε_0 and $\varepsilon_0 + U$, around meaning that the atomic energy levels are broadened into bands of width W = 2zt owing to the finite hopping probability, z being the number of nearest neighbors. The number of allowed states is equal to the number of sites in both bands, even if the spin quantum number is taken into account. The bands are well separated when W is small compared to U. They are the so-called lower and upper Hubbard bands. For one electron per site, which would give a half-filled band in the usual electronic band structure, the lower Hubbard band is completely filled and the upper is empty. The system behaves as an insulator.

Thus, as a consequence of the competition between the Coulomb repulsion and the hopping to neighboring sites, the system behaves differently in the limits $U \ll t$ and $U \gg t$. We may expect that separated bands exist above a certain critical value of the dimensionless coupling U/t. The gap between them disappears at $(U/t)_c$ and the two bands merge into one. The expected density of states is depicted in Fig. 35.3.

Whether the system is metallic or insulating is determined by the ratio of the energy scales, U/t. We know, however, that the exchange coupling $J \propto -t^2/U$ between the localized moments introduces another energy scale into the problem which is typically smaller than the band splitting and is related to the formation of localized moments. Mott insulators, where the

⁶ That is why this type of insulating state is also known as Mott–Hubbard insulator.

 $^{^7\,}$ The on-site Coulomb repulsion of the Hubbard model will be denoted by U instead of $U_{\rm H}$ in this chapter.



Fig. 35.3. The expected density of states of the Hubbard model in the limits $t \ll U$, $t \gg U$, and at the critical value of the coupling

moments are ordered antiferromagnetically by this exchange coupling, are sometimes denoted as *Mott–Heisenberg insulators*, restricting the name *Mott–Hubbard insulator* to materials in which the localized magnetic moments do not display long-range order.

35.1.2 Simple Treatment of the Hubbard Model

As suggested above the Mott metal–insulator transition can be most simply discussed in terms of the Hubbard model. We consider first the atomic limit, where hopping between neighboring sites is neglected. The Hamiltonian will be written in the form

$$\mathcal{H}_0 = \varepsilon_0 \sum_{i\sigma} n_{i,\sigma} + \frac{1}{2}U \sum_{i\sigma} n_{i,\sigma} n_{i,-\sigma} , \qquad (35.1.7)$$

where ε_0 is the energy of the atomic level. This model can be solved exactly. For this we introduce the retarded Green function

$$G_{ij,\sigma}(t) = -\frac{\mathrm{i}}{\hbar}\theta(t) \left\langle \left[c_{i\sigma}(t), c_{j\sigma}^{\dagger}(0) \right]_{+} \right\rangle$$
(35.1.8)

and write down its equation of motion:

$$-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}G_{ij,\sigma}(t) = \delta(t) \left[c_{i\sigma}, c_{j\sigma}^{\dagger}\right]_{+} + \frac{\mathrm{i}}{\hbar}\theta(t) \left\langle \left[\left[\mathcal{H}_{0}, c_{i\sigma}(t)\right]_{-}, c_{j\sigma}^{\dagger}(0)\right]_{+} \right\rangle.$$
(35.1.9)

Using the anticommutation rules of fermions, the commutator with the Hamiltonian yields

$$[\mathcal{H}_0, c_{i\sigma}]_{-} = -\varepsilon_0 c_{i\sigma} - U c_{i\sigma} n_{i,-\sigma} , \qquad (35.1.10)$$

and the Fourier transform of the Green function satisfies the equation

$$\hbar\omega G_{ij,\sigma}(\omega) = \delta_{ij} + \varepsilon_0 G_{ij,\sigma}(\omega) + U\Gamma_{ij,\sigma}(\omega), \qquad (35.1.11)$$

where the last term contains the Fourier transform of a higher order Green function,

$$\Gamma_{ij,\sigma}(t) = -\frac{\mathrm{i}}{\hbar} \theta(t) \left\langle \left[c_{i\sigma}(t) n_{i,-\sigma}(t), c_{j\sigma}^{\dagger}(0) \right]_{+} \right\rangle.$$
(35.1.12)

The equation of motion is easily derived for this Green function as well. Making use of $n_{i\sigma}^2 = n_{i\sigma}$,

$$\left[\mathcal{H}_{0}, c_{i\sigma} n_{i,-\sigma}\right]_{-} = -(\varepsilon_{0} + U)c_{i\sigma} n_{i,-\sigma}$$
(35.1.13)

and

$$\left[c_{i\sigma}n_{i,-\sigma},c_{j\sigma}^{\dagger}\right]_{+} = \delta_{ij}n_{i,-\sigma}, \qquad (35.1.14)$$

which lead to

$$\hbar\omega\Gamma_{ij,\sigma}(\omega) = \delta_{ij}\langle n_{i,-\sigma}\rangle + \varepsilon_0\Gamma_{ij,\sigma}(\omega) + U\Gamma_{ij,\sigma}(\omega).$$
(35.1.15)

The hierarchy of Green functions closes at this level and no new functions appear. The formal solution is

$$\Gamma_{ij,\sigma}(\omega) = \delta_{ij} \frac{\langle n_{i,-\sigma} \rangle}{\hbar \omega - \varepsilon_0 - U}$$
(35.1.16)

and

$$G_{ij,\sigma}(\omega) = \delta_{ij} \left[\frac{1 - \langle n_{i,-\sigma} \rangle}{\hbar \omega - \varepsilon_0} + \frac{\langle n_{i,-\sigma} \rangle}{\hbar \omega - \varepsilon_0 - U} \right].$$
(35.1.17)

This solution is not unique. Imaginary parts with Dirac deltas are also solutions and they are needed to ensure the correct analytic properties of the retarded Green functions. We find

$$G_{ij,\sigma}(\omega) = \delta_{ij} \left[\frac{1 - \langle n_{i,-\sigma} \rangle}{\hbar\omega - \varepsilon_0 + \mathrm{i}\delta} + \frac{\langle n_{i,-\sigma} \rangle}{\hbar\omega - \varepsilon_0 - U + \mathrm{i}\delta} \right].$$
(35.1.18)

The density of states is obtained from the imaginary part of the Green function. It has two Dirac delta peaks, one at ε_0 , the other at $\varepsilon_0 + U$:

$$\rho_{\sigma}(E) = \left(1 - \langle n_{-\sigma} \rangle\right) \delta(E - \varepsilon_0) + \langle n_{-\sigma} \rangle \delta(E - \varepsilon_0 - U) \,. \tag{35.1.19}$$

The first term is associated with the energy of adding an electron to an empty atom. When the atomic level is filled by one electron, the energy needed to add another electron with opposite spin is $\varepsilon_0 + U$ owing to the Coulomb repulsion.

When the overlap between the atomic wavefunctions of neighboring sites is taken into account, the two sharp peaks broaden and their width is proportional to the hopping amplitude. We again apply the equation of motion but now to the system described by the Hamiltonian

$$\mathcal{H} = \sum_{ij,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{1}{2} U \sum_{i\sigma} n_{i,\sigma} n_{i,-\sigma}$$
(35.1.20)

with $t_{ii} = \varepsilon_0$. The new terms in the equation of motion contain the singleparticle Green function and we find 482 35 Strongly Correlated Systems

$$\hbar\omega G_{ij,\sigma}(\omega) = \delta_{ij} + \sum_{l} t_{il} G_{lj,\sigma}(\omega) + U \Gamma_{ij,\sigma}(\omega) \,. \tag{35.1.21}$$

The equation for the higher order Green function is more complicated. A new function appears on the right-hand side which involves four operators on three lattice sites. In Fourier representation with respect to time we have

$$\hbar\omega\Gamma_{ij,\sigma}(\omega) = \delta_{ij}\langle n_{i,-\sigma}\rangle + \varepsilon_0\Gamma_{ij,\sigma}(\omega) + \sum_l t_{il}\Gamma_{liij,\sigma}^{(2)}(\omega) + \sum_l t_{li}\Gamma_{ilij,\sigma}^{(2)}(\omega) - \sum_l t_{il}\Gamma_{iilj,\sigma}^{(2)}(\omega) + U\Gamma_{ij,\sigma}(\omega), \qquad (35.1.22)$$

where

$$\Gamma_{iklj,\sigma}^{(2)}(t) = -\frac{\mathrm{i}}{\hbar}\theta(t) \left\langle \left[c_{i\sigma}(t)c_{k,-\sigma}^{\dagger}(t)c_{l,-\sigma}(t), c_{j\sigma}^{\dagger}(0) \right]_{+} \right\rangle.$$
(35.1.23)

Writing the equation of motion for this Green function, the system of equations does not close. New higher order Green functions appear. As an approximation, we can apply the decoupling procedure by writing $\Gamma^{(2)}$ in terms of lower order Green functions and mean values of operator products. With the decoupling

$$\Gamma_{liij,\sigma}^{(2)}(t) = -\frac{i}{\hbar}\theta(t) \left\langle \left[c_{l\sigma}(t)c_{i,-\sigma}^{\dagger}(t)c_{i,-\sigma}(t), c_{j\sigma}^{\dagger}(0) \right]_{+} \right\rangle \\
\approx \left\langle c_{i,-\sigma}^{\dagger}c_{i,-\sigma} \right\rangle G_{lj,\sigma}(t),$$
(35.1.24)

the contributions coming from the terms $\Gamma_{ilij,\sigma}^{(2)}$ and $\Gamma_{iilj,\sigma}^{(2)}$ cancel and we get

$$\hbar\omega\Gamma_{ij,\sigma}(\omega) = \delta_{ij}\langle n_{i,-\sigma}\rangle + (\varepsilon_0 + U)\Gamma_{ij,\sigma}(\omega) + \langle n_{i,-\sigma}\rangle \sum_{l\neq i} t_{il}G_{lj,\sigma}(\omega) . \quad (35.1.25)$$

The solution of this equation is

$$\Gamma_{ij,\sigma}(\omega) = \frac{\langle n_{i,-\sigma} \rangle}{\hbar\omega - \varepsilon_0 - U} \left[\delta_{ij} + \sum_{l \neq i} t_{il} G_{lj,\sigma}(\omega) \right].$$
(35.1.26)

In a homogeneous system, where t_{ij} , $G_{ij,\sigma}$, and $\Gamma_{ij,\sigma}$ depend solely on the distance between the lattice sites *i* and *j*, and $\langle n_{i,-\sigma} \rangle \equiv \langle n_{-\sigma} \rangle$ is independent of the position, it is convenient to work in momentum space by taking the Fourier transform of these equations. The Fourier transform of t_{ij} is the dispersion relation $\varepsilon_{\mathbf{k}}$ of the tight-binding model and we have

$$\Gamma_{\sigma}(\boldsymbol{k},\omega) = \frac{\langle n_{-\sigma} \rangle}{\hbar\omega - \varepsilon_0 - U} \left[1 + (\varepsilon_{\boldsymbol{k}} - \varepsilon_0) G_{\sigma}(\boldsymbol{k},\omega) \right].$$
(35.1.27)

The Fourier transform of (35.1.21) gives

$$\hbar\omega G_{\sigma}(\boldsymbol{k},\omega) = 1 + \varepsilon_{\boldsymbol{k}} G_{\sigma}(\boldsymbol{k},\omega) + U \Gamma_{\sigma}(\boldsymbol{k},\omega) \,. \tag{35.1.28}$$

Combining the two equations we find

$$G_{\sigma}(\boldsymbol{k},\omega) = \frac{\hbar\omega - \varepsilon_0 - U(1 - \langle n_{-\sigma} \rangle)}{(\hbar\omega - \varepsilon_{\boldsymbol{k}})(\hbar\omega - \varepsilon_0 - U) + \langle n_{-\sigma} \rangle(\varepsilon_0 - \varepsilon_{\boldsymbol{k}})U} \,. \tag{35.1.29}$$

This expression can be rewritten in the form

$$G_{\sigma}(\boldsymbol{k},\omega) = \frac{Z_{\boldsymbol{k}\sigma}^{(+)}}{\hbar\omega - E_{\boldsymbol{k}\sigma}^{(+)}} + \frac{Z_{\boldsymbol{k}\sigma}^{(-)}}{\hbar\omega - E_{\boldsymbol{k}\sigma}^{(-)}},\qquad(35.1.30)$$

where $E_{k\sigma}^{(+)}$ and $E_{k\sigma}^{(-)}$ are the roots of the equation

$$(E - \varepsilon_{\mathbf{k}})(E - \varepsilon_0 - U) + \langle n_{-\sigma} \rangle (\varepsilon_0 - \varepsilon_{\mathbf{k}})U = 0$$
(35.1.31)

and

$$Z_{k\sigma}^{(+)} + Z_{k\sigma}^{(-)} = 1. \qquad (35.1.32)$$

We find

$$E_{\boldsymbol{k}\sigma}^{(\pm)} = \frac{1}{2} \left(\varepsilon_{\boldsymbol{k}} + \varepsilon_0 + U \right) \pm \frac{1}{2} \sqrt{(\varepsilon_{\boldsymbol{k}} - \varepsilon_0 - U)^2 + 4U \langle n_{-\sigma} \rangle (\varepsilon_{\boldsymbol{k}} - \varepsilon_0)} \quad (35.1.33)$$

and

$$Z_{\boldsymbol{k}\sigma}^{(\pm)} = \pm \frac{E_{\boldsymbol{k}\sigma}^{(\pm)} - \varepsilon_0 - U(1 - \langle n_{-\sigma} \rangle)}{E_{\boldsymbol{k}\sigma}^{(+)} - E_{\boldsymbol{k}\sigma}^{(-)}} \,. \tag{35.1.34}$$

As before, the correct analytical properties can be ensured by infinitesimal imaginary terms in the denominators

$$G_{\sigma}(\boldsymbol{k},\omega) = \frac{Z_{\boldsymbol{k}\sigma}^{(+)}}{\hbar\omega - E_{\boldsymbol{k}\sigma}^{(+)} + \mathrm{i}\delta} + \frac{Z_{\boldsymbol{k}\sigma}^{(-)}}{\hbar\omega - E_{\boldsymbol{k}\sigma}^{(-)} + \mathrm{i}\delta}.$$
 (35.1.35)

The Green function has poles at $E_{k\sigma}^{(+)}$ and $E_{k\sigma}^{(-)}$. As usual, they give the energies of the quasiparticles. Thus, in this approximation, there are two quasiparticle states for each k with infinite lifetime, but with reduced quasiparticle weights. Note also that the energies $E_{k\sigma}^{(+)}$ and $E_{k\sigma}^{(-)}$ depend on the number of electrons. That is why the energy eigenstates of the interacting system cannot be determined in the single-particle picture. Nevertheless, as a rough approximation we may think that the lower band is formed by the electronic states of electrons put on empty sites. The states associated with electrons that are put on an already singly occupied site form the upper band.

In the atomic limit, where $\varepsilon_{\mathbf{k}} = \varepsilon_0$, the earlier result is recovered. There are two levels, one at ε_0 and another at $\varepsilon_0 + U$. These levels broaden into subbands when the wavefunctions of neighboring sites overlap and the electrons can hop to nearest neighbors. In the large-U limit, when U is large compared to the
bandwidth W of the noninteracting electrons given by the energy spread of $\varepsilon_{\mathbf{k}} - \varepsilon_0$, we find

$$E_{\boldsymbol{k}\sigma}^{(+)} = \varepsilon_0 + U + \langle n_{-\sigma} \rangle (\varepsilon_{\boldsymbol{k}} - \varepsilon_0),$$

$$E_{\boldsymbol{k}\sigma}^{(-)} = \varepsilon_0 + (1 - \langle n_{-\sigma} \rangle) (\varepsilon_{\boldsymbol{k}} - \varepsilon_0).$$
(35.1.36)

The two well-separated bands formed by the energies $E_{k\sigma}^{(+)}$ and $E_{k\sigma}^{(-)}$ are the upper and lower Hubbard bands. The bandwidths are shrunk by factors $\langle n_{-\sigma} \rangle$ and $(1 - \langle n_{-\sigma} \rangle)$, respectively, but they are finite, indicating that the electrons are not localized on the lattice sites. The number of states available for the electrons in the bands depends on the Coulomb coupling and the electron density, showing that the Hubbard bands are not the usual one-particle bands. When the number of electrons is equal to the number of lattice sites, $n_{\uparrow} = n_{\downarrow} = 1/2$, the quasiparticle weights are $Z_{k\sigma}^{(\pm)} \approx 1/2$ for large U. The lower Hubbard band is completely filled, the upper band is empty, and the system is insulating, as expected.

This approximate solution gives a surprising result for weak Coulomb repulsion. It can be shown that

$$E_{\boldsymbol{k}\sigma}^{(-)} < \varepsilon_0 + U\left(1 - \langle n_{-\sigma} \rangle\right) < E_{\boldsymbol{k}\sigma}^{(+)}, \qquad (35.1.37)$$

showing that the upper and lower Hubbard bands do not overlap for arbitrary positive value of U. This is in contradiction with our physical expectations that the metallic state survives if the electrons are weakly correlated and the uncorrelated metallic band only splits into two at a finite critical $(U/W)_c$ as U increases. The insulating phase should appear at this interaction strength. This necessitates a better treatment of the Hubbard model. HUBBARD himself proposed an improved approximation scheme. The so-called Hubbard-III solution provides a finite $(U/W)_c$ for the metal–insulator transition. This solution still has some inadequacies in that antiferromagnetic correlations are missing in the insulating phase, and neither antiferromagnetic ordering nor a Curie-like susceptibility is obtained at low temperatures. More serious is the finding that the metallic state is not a Fermi liquid, since the quasiparticles acquire a finite lifetime even at the Fermi energy. The latter problem can be corrected by a different approach.

35.1.3 The Gutzwiller–Brinkman–Rice Approach

W. F. BRINKMAN and T. M. RICE (1970) proposed a different approach to the metal-insulator transition based on the Gutzwiller wavefunction,⁸ in which the on-site repulsion between opposite-spin electrons is taken into account by a single variational parameter. When the ground-state wavefunction of the noninteracting Fermi sea,

⁸ M. C. Gutzwiller, 1963.

$$|\Psi_{\rm FS}\rangle = \prod_{|\mathbf{k}| < k_{\rm F}} c^{\dagger}_{\mathbf{k}\uparrow} \prod_{|\mathbf{k}'| < k_{\rm F}} c^{\dagger}_{\mathbf{k}'\downarrow} |0\rangle, \qquad (35.1.38)$$

is written in a Wannier instead of k-space representation, it would be a linear combination of all possible configurations with empty, singly occupied and doubly occupied sites. All these configurations would appear with equal weight in a noninteracting system. When the on-site repulsion is switched on, the energy of two singly occupied sites is lower than the energy of the configuration in which one of the sites is doubly occupied and the other is empty. Hence this latter configuration has a lower thermodynamic weight and should occur with smaller probability in the wavefunction. As one of the simplest approaches GUTZWILLER suggested taking this diminished probability into account by a factor g for every doubly occupied site. The limit g = 0 corresponds to forbidding completely double occupancy, while electrons are uncorrelated for g = 1.

Such a state can formally be written as

$$|\Psi_{\rm G}\rangle = g^D |\Psi_{\rm FS}\rangle, \qquad (35.1.39)$$

where

$$D = \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{35.1.40}$$

is the number operator of doubly occupied states. It follows from the fermionic properties of the electron operators that this *Gutzwiller wavefunction* can be written in the form

$$|\Psi_{\rm G}\rangle = \prod_{i} \left[1 - (1 - g) n_{i\uparrow} n_{i\downarrow} \right] |\Psi_{\rm FS}\rangle.$$
(35.1.41)

To check it, we rewrite the prefactor in an exponential form

$$\prod_{i} \left[1 - (1 - g)n_{i\uparrow}n_{i\downarrow} \right] = \exp\left\{ \sum_{i} \ln\left[1 - (1 - g)n_{i\uparrow}n_{i\downarrow} \right] \right\}.$$
 (35.1.42)

Noting that

$$\ln\left[1 - (1 - g)n_{i\uparrow}n_{i\downarrow}\right] = \begin{cases} 0 & \text{for } n_{i\uparrow}n_{i\downarrow} = 0, \\ \ln g & \text{for } n_{i\uparrow}n_{i\downarrow} = 1, \end{cases}$$
(35.1.43)

we indeed recover (35.1.39). g is a free parameter whose value can be determined from the condition that the wavefunction provides the lowest energy for the ground state, that is

$$E_0 = \frac{\langle \Psi_{\rm G} | \mathcal{H} | \Psi_{\rm G} \rangle}{\langle \Psi_{\rm G} | \Psi_{\rm G} \rangle} \tag{35.1.44}$$

should be minimized with respect to g.

The contribution of the Coulomb repulsion is easily obtained. It gives $U\langle D\rangle$, where $\langle D\rangle$ is the average number of doubly occupied sites. The probability of double occupancy, $\langle D\rangle/N$, where N is the number of lattice sites, will be denoted by d. The evaluation of the expectation value of the kinetic energy necessitates further approximations. We denote the mean number of up- and down-spin electrons by $\langle N_{\uparrow} \rangle$ and $\langle N_{\downarrow} \rangle$, respectively. Their densities are $n_{\sigma} = \langle N_{\sigma} \rangle/N$, and $n = n_{\uparrow} + n_{\downarrow}$ stands for the electron density. The probability of finding an empty site is then $1 - n_{\uparrow} - n_{\downarrow} + d$. Lengthy calculation gives

$$\frac{E_0}{N} = \sum_{\sigma} q_{\sigma} \overline{\varepsilon}_{\sigma} + Ud , \qquad (35.1.45)$$

where

$$\overline{\varepsilon}_{\sigma} = \frac{1}{N} \sum_{|\mathbf{k}| < k_{\rm F}} \varepsilon_{\mathbf{k}\sigma} \tag{35.1.46}$$

is the average kinetic energy of electrons without correlations and the reduction factor q_σ is

$$q_{\sigma} = \frac{\left[\sqrt{(1-n+d)(n_{\sigma}-d)} + \sqrt{d(n_{-\sigma}-d)}\right]^2}{n_{\sigma}(1-n_{\sigma})}.$$
 (35.1.47)

For a nonmagnetic half-filled band, where $n_{\uparrow} = n_{\downarrow} = 1/2$, the energy per site is

$$\frac{E_0}{N} = 8d(1-2d)\overline{\varepsilon} + Ud. \qquad (35.1.48)$$

Note that $\overline{\varepsilon} < 0$ for a half-filled tight-binding band. Minimization with respect to d gives

$$d_{\min} = \frac{8\overline{\varepsilon} + U}{32\overline{\varepsilon}} \equiv \frac{1}{4}(1 - U/U_{\rm c}), \qquad (35.1.49)$$

where $U_{\rm c} = 8|\overline{\varepsilon}|$, and the minimum energy per site is

$$\frac{E_{0\min}}{N} = \overline{\varepsilon} (1 - U/U_c)^2 \,. \tag{35.1.50}$$

These expressions are meaningful for $U \leq U_c$, since d_{\min} must be positive. As U increases from U = 0 toward U_c , the density of doubly occupied sites decreases from the uncorrelated value 1/4 and vanishes at U_c . This state persists for larger values of U. All sites are singly occupied; the electrons are localized and frozen on the sites in the ground state. Excitations involve hopping to an already occupied site. Since this requires overcoming the large Coulomb energy, a gap appears in the spectrum of charge excitations. The system that was metallic for small U becomes insulating at U_c .

We thus have the following picture of the metal-insulator transition in the Brinkman-Rice approach. Electrons move somewhat freely but correlated when $U < U_c$. The possible hops are restricted not only by the Pauli exclusion principle but also by the Coulomb repulsion. Hopping to a site occupied by another electron with the same spin is forbidden, whereas hopping to a site occupied by another electron with opposite spin is allowed, but with a smaller probability than to an empty site. This latter restriction becomes more and more stringent as U increases. The effective mass of quasiparticles increases and the bandwidth narrows. The density of states of the quasiparticles is displayed in Fig. 35.4. The bandwidth shrinks to zero at the transition and the effective mass diverges as

$$m^* = m_{\rm e} \left[1 - (U/U_{\rm c})^2 \right]^{-1}$$
. (35.1.51)

The susceptibility exhibits a similar divergence.



Fig. 35.4. Density of states of quasiparticles in the Brinkman-Rice model of the metal-insulator transition (a) for $U < U_c$ and (b) for $U \approx U_c$

A somewhat different physical picture is obtained when the number of electrons is varied at a fixed $U > U_c$. For electron concentration $n_{\uparrow} = n_{\downarrow} = 1/2 - \delta$, the system is metallic. As the band filling increases, a metal–insulator transition takes place at $\delta = 0$, where the number of free carriers vanishes. In contrast to the "bandwidth-controlled" MIT occurring at $U = U_c$ in the half-filled system, the quasiparticle mass does not diverge in the "filling-controlled" MIT.

The merit of this variational approach is that it takes into account the suppression of charge fluctuations by the on-site Coulomb repulsion, but it fails to include spin-spin correlations between sites.

35.1.4 Numerical Results

The two approaches, the equation-of-motion method and the Brinkman–Rice model based on the Gutzwiller wavefunction, give different physical pictures for the metal–nonmetal transition. The existence of narrow bands above and below the Fermi energy in the insulating state, as predicted in the first method, seems to be a correct feature. On the other hand, the second approach gives a better description of the quasiparticles near the Fermi energy, but says nothing about the states farther away. Calculations for infinite-dimensional models indicate that the correct theory should probably unify these features. Consider a *d*-dimensional hypercubic lattice, where each atom has 2*d* nearest neighbors. The kinetic energy is comparable with the energy correction coming from the electron–electron interaction in the limit $d \to \infty$, if the hopping matrix element t_{ij} , which is restricted to nearest neighbors, is scaled as $t/\sqrt{2d}$. The unperturbed density of states is a Gaussian,

$$\rho(\varepsilon) = \frac{1}{t\sqrt{2\pi}} \exp\left(-\frac{\varepsilon^2}{2t^2}\right). \tag{35.1.52}$$

The dynamical mean-field theory is exact owing to the large coordination number and the transition can be studied with both analytic and numerical methods.

The results for the infinite-dimensional model are displayed in Fig. 35.5. Starting from the metallic state in the weak-U limit, the weight of the states far from the Fermi energy increases gradually as U increases. Two additional peaks appear in the density of states. They are the precursors of the Hubbard bands. The central peak at the Fermi energy narrows, the quasiparticle weight decreases, and the effective mass increases. The density of states gradually diminishes between the quasiparticle peak and the side peaks, and a pseudogap develops. Finally, the central peak becomes infinitely narrow at a critical value of the Coulomb interaction, the effective mass of the quasiparticles diverges, and the upper and lower Hubbard bands are separated by a true gap of finite



Fig. 35.5. Density of states of the infinite-dimensional half-filled Hubbard model for several values of U/t. The ratio U/t increase from top to bottom [Reprinted with permission from A. Georges et al., *Rev. Mod. Phys.* **68**, 13 (1996). \bigcirc (1996) by the American Physical Society]

width. The transition from the metallic phase with quasiparticles near the Fermi energy to the insulating phase with a completely filled lower Hubbard band and an empty upper band is of first order.

The first-order nature of the transition is supported by finite-temperature calculations, which at the same time provide a somewhat different picture for the appearance of the gap. The spectral function, which is closely related to the density of states, has a narrow central peak at high temperatures for small U. The weight of this peak diminishes gradually, as displayed in Fig. 35.6(a), when U increases. The metalliclike behavior changes into insulatorlike with no sharp transition at these temperatures.



Fig. 35.6. Frequency dependence of the spectral function of the infinite-dimensional half-filled Hubbard model for several values of U/W, where W is the bandwidth, at temperatures (a) T = 0.0276W and (b) T = 0.0103W [Reprinted with permission from R. Bulla, T. A. Costi, and D. Vollhardt, *Phys. Rev. B* **64**, 045103 (2001). \bigcirc (2001) by the American Physical Society]

A true metal-insulator transition takes place at lower temperatures. As U increases, the density of states at the Fermi energy jumps from a finite value to zero at some U_{c1} . As expected for first-order transitions and displayed in Fig. 35.6(b), the transition takes place at a somewhat different U_{c2} when U decreases.

Numerical calculations for the two-dimensional half-filled Hubbard model give a somewhat different picture for the metal-insulator transition. The two Hubbard bands are separated by a finite gap for arbitrary positive U in the ground state. The density of states is finite and the gap is gradually filled in as the temperature is increased. As seen in Fig. 35.7, the gap turns into a pseudogap. A broad peak emerges at the Fermi energy at higher temperatures. The quasiparticles in this peak are responsible for the metallic behavior.



Fig. 35.7. The density of states of the two-dimensional half-filled Hubbard model for two values of U/t at different temperatures [S. Onoda and M. Imada, J. Phys. Soc. Japan, 70, 3398 (2001)]

It is not yet clear which of these scenarios describes better the metalinsulator transition in three-dimensional models. It is clear, however, that these mechanisms can explain the transition only in half-filled systems. Different mechanisms, such as the Anderson localization due to disorder, should also be taken into account if we want to explain the occurrence of the insulating phase for electron concentrations away from half filling.

35.1.5 Other Phases of the Hubbard Model

It was assumed in the foregoing discussion that the uncorrelated band is half filled. In that case the Coulomb repulsion may localize the electrons to the lattice sites. Since doubly occupied sites tend to be forbidden, all sites are singly occupied and the motion of electrons is frozen out. It may be more interesting to ask what happens if the number of carriers is varied by changing the dopant concentration and the band filling deviates slightly from half filling. When the number of electrons is somewhat less than the number of sites, the empty sites allow the propagation of electrons even if U is large and doubly occupied sites are forbidden. Electrons on singly occupied sites can exchange their spins and the effective Hamiltonian can be written in the form

$$\mathcal{H} = t \sum_{i,j,\sigma} c_{i,\sigma}^{\dagger} c_{j,\sigma} - J \sum_{\langle i,j \rangle} \boldsymbol{s}_i \cdot \boldsymbol{s}_j \,. \tag{35.1.53}$$

This model, known as the t-J model, should be solved with the condition that only empty and singly occupied sites are permitted. Doubly occupied sites are forbidden. The propagation of empty sites (holes) gives a metallic character to the otherwise magnetic system. This can be of particular interest in two-dimensional materials, where the metallic phase might become superconducting.

We consider first the case when the band is almost half filled. There are just a few empty sites, holes. An electron can hop to an empty site from a neighboring singly occupied site. Formulating differently, the holes propagate. This has two consequences. The system gains in kinetic energy, but at the same time the antiferromagnetic order of the spins created by the antiferromagnetic coupling J is partially destroyed and the exchange energy increases. For large U, where $J \propto t^2/U$ is small, the gain in kinetic energy may compensate this loss and the ferromagnetic or paramagnetic state may be energetically more favorable than the antiferromagnetic state. This is indeed the result in a mean-field approximation. The phase diagrams determined for the two- and three-dimensional Hubbard models in MFA are displayed in Fig. 35.8.



Fig. 35.8. Mean-field phase diagram of the Hubbard model as a function of U/t and the band filling in two and three dimensions. P, AF, and F represent paramagnetic, antiferromagnetic, and ferromagnetic phases, respectively. The spiral phases are not marked for simplicity. Solid lines indicate second-order transitions and dashed lines indicate first-order transitions [Reprinted with permission from J. E. Hirsch, *Phys. Rev. B* **31**, 4403 (1985) and D. R. Penn, *Phys. Rev.* **142**, 350 (1966). © by the American Physical Society]

The antiferromagnetic phase is only stable at and near half-band filling. The critical coupling for antiferromagnetic ordering is $U_c = 0$, since bipartite lattices were considered, where the Fermi surface of the half-filled model has the perfect nesting property. The electron system is metallic except for n = 1. The antiferromagnetic region near half filling may become insulating when Anderson localization due to disorder is taken into account. As the electron density is increased or decreased, the paramagnetic state has lower energy in the weakly correlated phase, while a transition to a ferromagnetic state occurs for large U values, as predicted by the Stoner condition. The paramagnetic phase is stable for large concentrations of holes.

Although mean-field theory usually provides a good approximation for three-dimensional system, it is not necessarily so for the Hubbard model with nearest-neighbor hopping on a bipartite lattice. The Fermi surface of the tight-binding model may have the nesting property and anomalies characteristic of quasi-one-dimensional systems may appear. An additional difficulty arises in the two-dimensional model from the Van Hove singularities of the density of states, all of which may lead to the appearance of new phases. Such a possible new phase is the unconventional *d*-wave superconducting state with $d_{x^2-y^2}$ symmetry.

There are strong indications from numerical calculations that the electrons do indeed form Cooper pairs with d-wave symmetry, even though the only interaction taken into account is the Coulomb repulsion. The superconducting state may be the stable phase close to half filling if U is not too large compared to the bandwidth. The numerically determined phase diagram of the two-dimensional Hubbard model is shown in Fig. 35.9 for fixed U as a function of temperature and band filling.



Fig. 35.9. Numerically determined temperature–doping phase diagram of the twodimensional Hubbard model [M. Jarrell et al., *Europhys. Lett.* 56, 563 (2001)]

d-wave superconductivity can be further stabilized when hopping to nextto-nearest neighbors is also allowed. To what extent these results on the twodimensional Hubbard model are relevant in understanding the experimentally observed unconventional superconductivity in a variety of materials is still an open question.

35.2 Magnetic Impurities in Metals

We have learned from the Hubbard model that new features may show up compared to the noninteracting electron gas if the intra-atomic Coulomb repulsion is comparable to the bandwidth. It is even more so when we are dealing not with one type of electrons, but with two bands of different symmetry, when an s and a d band or an s and an f band, are close to the Fermi energy and both affect the behavior of the system. Before turning to this problem we discuss a simpler situation when a single transition metal or rare-earth atom with an incomplete d or f shell is embedded in a metallic host with a single s band. In what follows, for the sake of simplicity, we will talk about a d level, but the results are valid for rare-earth impurities as well.

First, we consider the Anderson model and study the condition for the formation of a localized magnetic moment. We then turn to the Kondo problem and try to answer the question about what happens around the paramagnetic impurity as conduction electrons scattered off it. This problem is of interest not only on its own right. The methods worked out for solving the Kondo problem can be used in many other fields of physics. We will use the renormalization group and scaling arguments to describe the behavior down to the Kondo temperature, and then the local-Fermi-liquid theory and the numerical renormalization-group method to get the ground state and the lowtemperature properties.

35.2.1 The Anderson Model

For the sake of simplicity we will forget about the degeneracy of the d and f shells of the transition metal and rare-earth ions, respectively, and assume that the impurity atom has a single nondegenerate level. It will be called a d level and its energy is denoted by ε_d . This level can be at most doubly occupied. Because of the Coulomb repulsion, the energy of the doubly occupied state is not simply $2\varepsilon_d$ but $2\varepsilon_d + U$. Moreover, since the wavefunction of the d level is not orthogonal to the states of the conduction band, they may be hybridized. P. W. ANDERSON (1961) proposed the Hamiltonian

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \sum_{\sigma} \varepsilon_{d} d_{\sigma}^{\dagger} d_{\sigma} + U n_{d\uparrow} n_{d\downarrow} + \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}\sigma} \left(V_{d\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} d_{\sigma} + V_{\boldsymbol{k}d} d_{\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \right)$$
(35.2.1)

to describe the system of conduction electrons interacting with a single impurity. This is the nondegenerate single-impurity *Anderson model*. It could be extended to the degenerate case by taking into account the intra-atomic exchange processes mentioned in Chapter 28 when the Hubbard model was introduced.

Consider first a free ion. It has four possible states. The d level is empty in state $|d^0\rangle$, it is occupied by an electron with spin σ in state $|d^1_{\sigma}\rangle$, and it is doubly occupied by electrons with opposite spins in state $|d^2\rangle$. The energies of these states are

$$\varepsilon(d^0) = 0, \qquad \varepsilon(d^1_{\sigma}) = \varepsilon_d, \qquad \varepsilon(d^2) = 2\varepsilon_d + U.$$
 (35.2.2)

The ground state of the ions has a magnetic moment if the magnetic doublet is the lowest energy state, that is if 494 35 Strongly Correlated Systems

$$\varepsilon(d^2) - \varepsilon(d^1_{\sigma}) = \varepsilon_d + U > 0,$$

$$\varepsilon(d^0) - \varepsilon(d^1_{\sigma}) = -\varepsilon_d > 0.$$
(35.2.3)

Written in a different form,

$$-\frac{1}{2}U < \varepsilon_d + \frac{1}{2}U < \frac{1}{2}U.$$
 (35.2.4)

When this ion is an impurity atom in a metal, the filling of the level depends on its position relative to the chemical potential. If hybridization is weak, conduction electrons can be distinguished from d electrons, and the states of both subsystems are filled up to the Fermi energy. The relevant one-particle energies, $\varepsilon_{\mathbf{k}}$ and ε_d , are measured from the Fermi energy and the notation $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu$ will be used. We expect that the situations when both ε_d and $\varepsilon_d + U$ are well below or well above the Fermi energy are physically not very interesting. The d level is practically filled with two electrons in the first case and the impurity atom has no magnetic moment. On the other hand, the d level is practically always empty in the other case; it is unavailable for conduction electrons near the Fermi energy. These states do not participate in the interesting scattering processes.

The interaction between the impurity atom and the conduction electrons will strongly influence the properties of the metallic host in two special cases. First, when ε_d or $\varepsilon_d + U$ is close to the Fermi energy. Hybridization with the conduction electrons broadens the sharp d levels of the ion. The empty, singly occupied, and doubly occupied states occur with nonvanishing probability and the fluctuating magnetic moment may disappear. It is dissolved in the metal. Charge fluctuations are then more important than spin fluctuations, and the number of electrons on the d level is not an integer. The impurity atom has an *intermediate valence* or *mixed valence*. We encounter this situation in rareearth compounds where the paramagnetic ions constitute a regular sublattice and the f levels form a narrow band. We will return to the physics of such systems later on.

Another interesting situation occurs when ε_d is well below the Fermi energy and $\varepsilon_d + U$ lies well above. The impurity is then practically always singly occupied notwithstanding the hybridization. It has a localized magnetic moment, although the orientation of the moment is not fixed rigidly. The interaction of the conduction electrons with this rapidly fluctuating magnetic moment opens a new channel for the scattering of electrons. The fundamental questions the Anderson model has to answer are as follows: when will a fluctuating localized magnetic moment appear, how will conduction electrons scattering off them influence the properties of the metal, and if charge fluctuations are more important than spin fluctuations, what is their role.

35.2.2 Formation of the Localized Moment

We will neglect the Coulomb repulsion in the first step and study the effect of hybridization on the atomic level when ε_d is below the Fermi energy but within the conduction band. Since hybridization is described by a bilinear operator, the Hamiltonian

$$\mathcal{H} = \sum_{k\sigma} \xi_{k\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} + \varepsilon_{d} d_{\sigma}^{\dagger} d_{\sigma} + \frac{1}{\sqrt{V}} \sum_{k} \left(V_{dk} c_{k\sigma}^{\dagger} d_{\sigma} + V_{kd} d_{\sigma}^{\dagger} c_{k\sigma} \right) \quad (35.2.5)$$

can readily be diagonalized by the unitary transformation

$$\alpha_{n\sigma}^{\dagger} = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \phi_{n\boldsymbol{k}\sigma}^{*} c_{\boldsymbol{k}\sigma}^{\dagger} + \phi_{nd\sigma}^{*} d_{\sigma}^{\dagger}, \quad \alpha_{n\sigma} = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \phi_{n\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \phi_{nd\sigma} d_{\sigma}.$$
(35.2.6)

If these operators are the creation and annihilation operators of new particles with energies $E_{n\sigma}$, and the Hamiltonian is diagonal in terms of them, they should satisfy the relations

$$\left[\mathcal{H}, \alpha_{n\sigma}^{\dagger}\right]_{-} = E_{n\sigma} \alpha_{n\sigma}^{\dagger}, \qquad \left[\mathcal{H}, \alpha_{n\sigma}\right]_{-} = -E_{n\sigma} \alpha_{n\sigma}. \qquad (35.2.7)$$

The unknown coefficients of the transformation and the eigenvalues can be calculated from these equations using the relations

$$\begin{bmatrix} \mathcal{H}, c_{\boldsymbol{k}\sigma}^{\dagger} \end{bmatrix}_{-} = \xi_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} + \frac{1}{\sqrt{V}} V_{\boldsymbol{k}d} d_{\sigma}^{\dagger} , \\ \begin{bmatrix} \mathcal{H}, d_{\sigma}^{\dagger} \end{bmatrix}_{-} = \varepsilon_{d} d_{\sigma}^{\dagger} + \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} V_{d\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} .$$
 (35.2.8)

We find

$$E_{n\sigma}\phi_{nk\sigma} = \xi_{k}\phi_{nk\sigma} + V_{kd}\phi_{nd\sigma} ,$$

$$E_{n\sigma}\phi_{nd\sigma} = \varepsilon_{d}\phi_{nd\sigma} + \frac{1}{V}\sum_{k}V_{dk}\phi_{nk\sigma} .$$
(35.2.9)

Expressing $\phi_{nk\sigma}$ from the first equation and inserting it into the second one give a self-consistency condition:

$$E_{n\sigma} = \varepsilon_d + \frac{1}{V} \sum_{\boldsymbol{k}} \frac{|V_{\boldsymbol{k}d}|^2}{E_{n\sigma} - \xi_{\boldsymbol{k}}} \,. \tag{35.2.10}$$

The solutions of this equation can be found numerically in the usual way. They lie inside the conduction band, slightly shifted from the unperturbed energies. They get somewhat closer to each other near ε_d , which results in an increase in the density of states. This increase can be interpreted as the broadened density of states of the *d* level. It can be calculated from the Green function of *d* electrons via

$$\rho_{d\sigma}(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} G_{d\sigma}(\varepsilon/\hbar) , \qquad (35.2.11)$$

where $G_{d\sigma}(\omega)$ is the Fourier transform of the retarded Green function

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$$G_{d\sigma}(t) = -\frac{\mathrm{i}}{\hbar}\theta(t) \left\langle \left[d_{\sigma}(t), d_{\sigma}^{\dagger}(0) \right]_{+} \right\rangle.$$
(35.2.12)

Solving the equation of motion of the Green function we readily find in the limit U = 0 that the density of states of the *d* level is a Lorentzian,

$$\rho_{d\sigma}(\varepsilon) = \frac{1}{\pi} \frac{\Delta}{(\varepsilon - \varepsilon_d)^2 + \Delta^2}$$
(35.2.13)

with width

$$\Delta = \pi \frac{1}{V} \sum_{\boldsymbol{k}} |V_{\boldsymbol{k}d}|^2 \delta(\varepsilon - \xi_{\boldsymbol{k}}) = \frac{1}{2} \pi \langle |V_{\boldsymbol{k}d}|^2 \rangle \rho(\varepsilon_{\rm F}) , \qquad (35.2.14)$$

where $\rho(\varepsilon_{\rm F})$ is the density of states of conduction electrons at the Fermi energy. If the interaction with the impurity is treated as a scattering problem, this peak in the density of states can be viewed as a consequence of the phase shift suffered by the conduction electrons when they are scattered by the impurity. The two are related according to scattering theory via

$$\rho_{d\sigma}(\varepsilon) = \frac{1}{\pi} \frac{\mathrm{d}\delta(\varepsilon)}{\mathrm{d}\varepsilon} \,. \tag{35.2.15}$$

For scattering by d electrons, the phase shift of the l = 2 partial wave is the relevant quantity, but the factor 2l + 1 in (16.4.53) is neglected since we consider a nondegenerate level.

The narrow peak in the density of states is then interpreted as a resonance occurring at the position of the d level owing to the hybridization. The phase shift

$$\delta(\varepsilon) = \frac{\pi}{2} + \operatorname{arccot} \frac{\varepsilon - \varepsilon_d}{\Delta}$$
(35.2.16)

is 0 or π for energies far from ε_d and it is $\pi/2$ at ε_d . We know that the scattering cross section and the resistivity contain the square of sin δ taken at the Fermi energy. Thus scattering by the impurity gives an important contribution to the resistivity only if the resonance is close to the Fermi energy.

Returning now to the question of the formation of the localized magnetic moment, we will consider the effect of the Coulomb term in a mean-field approximation. If, as usual, the four-operator term is decoupled by replacing products of two operators with their mean values, the effective Hamiltonian for spin σ electrons is

$$\mathcal{H}_{\sigma} = \sum_{k} \xi_{k} c_{k\sigma}^{\dagger} c_{k\sigma} + \varepsilon_{d} d_{\sigma}^{\dagger} d_{\sigma} + U \langle n_{d,-\sigma} \rangle n_{d\sigma} + \frac{1}{\sqrt{V}} \sum_{k} \left(V_{dk} c_{k\sigma}^{\dagger} d_{\sigma} + V_{kd} d_{\sigma}^{\dagger} c_{k\sigma} \right).$$
(35.2.17)

It is similar to the Hamiltonian discussed for U = 0 if ε_d is replaced with $\varepsilon_d + U \langle n_{d,-\sigma} \rangle$. Repeating the same steps as above, the energy eigenvalues are obtained from the solution of the equation

$$E_{n\sigma} = \varepsilon_d + U\langle n_{d,-\sigma} \rangle + \frac{1}{V} \sum_{\boldsymbol{k}} \frac{|V_{\boldsymbol{k}d}|^2}{E_{n\sigma} - \xi_{\boldsymbol{k}}} \,. \tag{35.2.18}$$

Comparison with (35.2.10) shows that the Coulomb repulsion yields a spindependent energy shift. The density of states is given by

$$\rho_{d\sigma}(\varepsilon) = \frac{1}{\pi} \frac{\Delta}{\left[\varepsilon - (\varepsilon_d + U\langle n_{d, -\sigma} \rangle)\right]^2 + \Delta^2}, \qquad (35.2.19)$$

that is a resonance of width Δ appears at $\varepsilon_d + U\langle n_{d,-\sigma} \rangle$. The actual filling of the *d* level at T = 0 is given by the integral of the density of states up to the Fermi energy, which – since the one-particle energies are measured from the Fermi energy – is at $\varepsilon = 0$. We find

$$\langle n_{d\sigma} \rangle = \frac{1}{\pi} \int_{-\infty}^{0} \frac{\Delta}{\left[\varepsilon - (\varepsilon_d + U \langle n_{d, -\sigma} \rangle)\right]^2 + \Delta^2} d\varepsilon$$

$$= \frac{1}{\pi} \operatorname{arccot} \frac{\varepsilon_d + U \langle n_{d, -\sigma} \rangle}{\Delta} .$$

$$(35.2.20)$$

When the equations for the two spin orientations are solved self-consistently, one possible solution is an unpolarized state: $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle = \frac{1}{2}n_d$. The solution is especially simple in the symmetric case, when $\varepsilon_d + \frac{1}{2}U = 0$, which means that the empty and doubly occupied levels lie symmetrically with respect to the Fermi energy. If the *d* level is half filled, $n_d = 1$, $\langle n_{d\sigma} \rangle = \frac{1}{2}$, and the resonance is right at the Fermi energy for both spin orientations, as shown in Fig. 35.11(*a*). Note that the resonance is not exactly at the Fermi energy in the nonsymmetric case. The filling of the *d* level is such that $\varepsilon_d + \frac{1}{2}Un_d$; the position of the resonance peak should be close to the Fermi energy.

This nonmagnetic solution is stable for weak Coulomb repulsion. It becomes unstable for large values of U/Δ . The states for the two spin orientations are unequally populated in the stable solution and the *d* level has a paramagnetic moment. The critical U_c above which this happens can be calculated from the equations derived above. For this we assume that

$$\langle n_{d\sigma} \rangle = \frac{1}{2}n_d + \sigma \delta n_d \tag{35.2.21}$$

and substitute it into (35.2.20). The zeroth-order terms in δn_d on the two sides of the equation yield

$$n_d = \frac{2}{\pi} \operatorname{arccot} \frac{\varepsilon_d + \frac{1}{2} U_c n_d}{\Delta}, \qquad (35.2.22)$$

and the first-order terms give

$$1 = \frac{U_{\rm c}}{\pi \Delta} \frac{1}{1 + \left[(\varepsilon_d + \frac{1}{2} U_{\rm c} n_d) / \Delta \right]^2} \,. \tag{35.2.23}$$

This system of equations can be solved self-consistently at a fixed value of ε_d/Δ for U_c/Δ . Localized magnetic moment appears for U/Δ larger than this critical value. Figure 35.10 displays the region where this happens compared to the region where the s = 1/2 doublet is the energetically favored solution for a free atom.



Fig. 35.10. The domain in the space $\varepsilon_d + U/2$ vs. U where (a) the doublet is energetically favored in the free atom and (b) localized paramagnetic moment is predicted by the Anderson model

Hybridization with the conduction electrons makes the formation of magnetic moment more difficult, since hybridization broadens the *d* level. The spin splitting which might arise from the Coulomb repulsion does not occur unless the splitting is larger than the level broadening. The critical coupling for the appearance of the localized moment is $U_c = \pi \Delta$ in the symmetric case. When *U* exceeds this critical value, two resonances are found, one below, the other above the Fermi energy. Their widths are identical and their positions shift gradually toward ε_d and $\varepsilon_d + U$. This situation is shown in Fig. 35.11(*b*). Practically only one of the resonances is filled.



Fig. 35.11. Mean-field result for the *d*-level density of states: (*a*) in the unpolarized state, for $U < \pi \Delta$ and (*b*) in the polarized state, for $U > \pi \Delta$

35.2.3 Better Treatment of the Anderson Model

The localized magnetic moment appears at a well-defined critical value of the Coulomb repulsion in the Hartree–Fock treatment of the Anderson model. The impurity being a zero-dimensional object, one can ask how quantum fluctuations, which are strongly enhanced in low dimensions, modify this result.

Consider the Anderson model in the parameter range where the Hartree– Fock approach predicts a localized moment. We know that even if U is large and the singly occupied site is energetically more favorable than the empty or doubly occupied site, the d electron can hop into the conduction band or a conduction electron can hop onto a singly occupied site for a short period. Although the impurity is singly occupied most of the time, the orientation of the magnetic moment may fluctuate with a characteristic time τ via these hopping processes. This time defines a characteristic temperature by the relation

$$k_{\rm B}T_{\rm K} = \frac{\hbar}{\tau} \,. \tag{35.2.24}$$

We expect that at temperatures above $T_{\rm K}$ the impurity behaves as if it had a well-defined paramagnetic moment, exhibiting a Curie-like temperature dependence of the susceptibility. Correlations between the *d* electrons responsible for the magnetic moment and the conduction electrons become important at temperatures below $T_{\rm K}$, and the model has to be treated in a better approximation than mean-field theory.

The scaling theory and the numerical renormalization group to be discussed later in connection with the Kondo problem can be applied to the Anderson model as well. As shown in Fig. 35.12, three distinct types of behavior are found in the symmetric model.



Fig. 35.12. Schematic phase diagram for the symmetric Anderson model in the space spanned by the temperature T, the Coulomb energy U, and the *d*-level width Δ [Reprinted with permission from H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, *Phys. Rev. B* 21, 1003 (1980). \bigcirc (1980) by the American Physical Society]

One possibility is that the impurity is decoupled from the conduction electrons. We are then dealing with a free electron system plus a free impurity. This free orbital limit, where the empty, singly occupied, and doubly occupied impurity states occur with equal probability, is realized at high temperatures. Localized magnetic moment is formed at lower temperatures, for $k_{\rm B}T < U/10$, if $U > \pi \Delta$, that is in the parameter range where mean-field theory predicts the appearance of a localized moment. The impurity atom is singly occupied and gives a Curie-like 1/T contribution to the susceptibility, as expected for a paramagnetic impurity. The susceptibility does not diverge, however, when $T \rightarrow 0$. At very low temperatures, below a characteristic $T_{\rm K}$, the localized moment is frozen out as if the correlation between the conduction electrons and the electron sitting on the impurity was screening the magnetic moment, and the susceptibility saturates at a finite value at zero temperature. In the limit when the conduction electron bandwidth is larger than U, the characteristic temperature is given by

$$k_{\rm B}T_{\rm K} = \left(\frac{2U\Delta}{\pi^2}\right)^{1/2} \exp\left(\frac{\pi\varepsilon_d(\varepsilon_d+U)}{2U\Delta}\right). \tag{35.2.25}$$

The electron system behaves as a normal Fermi liquid in this strong-coupling regime. The free orbital regime directly crosses over to Fermi-liquid behavior as the temperature is decreased for $U < \pi \Delta$.

An interesting new feature of the asymmetric Anderson model is the appearance of a fourth régime in which the energy difference between the empty and singly occupied levels is comparable with the thermal energy and the doubly occupied state lies much higher. The impurity then fluctuates between the d^0 and the d^1 configurations. This is the valence-fluctuation regime. Localized moment may be formed at lower temperatures but will eventually be quenched below $T_{\rm K}$.

These results on the behavior in the various regimes were confirmed analytically when it was discovered that the Anderson model, if reformulated somewhat without changing its physical content, can be solved exactly by the Bethe ansatz.

The density of states and the correlation functions, however, are not accessible from the exact solution. Detailed numerical and analytical studies, which cannot be repeated here, have shown that an extra, resonancelike peak appears in the density of states at low temperatures near the Fermi energy in addition to the two peaks corresponding to the spin-split d level. The extra peak, which arises from the interaction of the conduction electrons with the d electrons, is exactly at the Fermi energy in the symmetric model. This is displayed in Fig. 35.13.

It can be shown that the peak at the Fermi energy exists for arbitrary values of U/Δ and its height is exactly

$$\rho_{d\sigma}(0) = \frac{1}{\pi\Delta} \tag{35.2.26}$$

in the symmetric case. This peak is known as the Abrikosov-Suhl resonance⁹ or Kondo peak. Its existence is important in understanding the low-

⁹ A. A. ABRIKOSOV, 1965, and H. SUHL, 1965.



Fig. 35.13. (a) Density of states of the Anderson model for several values of U/Δ [T. A. Costi and A. C. Hewson, *Phil. Mag. B* **65**, 1165 (1992)]. (b) Broadening of the central Abrikosov–Suhl resonance as the temperature is increased [Reprinted with permission from B. Horvatić et al., *Phys. Rev. B* **36**, 675 (1987). \bigcirc (1987) by the American Physical Society]

temperature behavior of localized magnetic moments. We shall return to it when the Kondo model is studied, where the configurations d^0 and d^2 of the impurity can be neglected and only the dynamics of the localized moment is considered.

35.2.4 Kondo Model

We have learned above that when the energy of the d level is below the Fermi energy and U is large, the impurity is in the local-moment regime. The d level is singly occupied in the physically relevant states and its filling is practically unity. The empty and doubly occupied states can be neglected. J. R. SCHRIEFFER and P. A. WOLFF (1966) have shown that if only the spin-doublet state of the impurity is kept, the Hamiltonian of the Anderson model can be mapped by a canonical transformation to the s-d exchange model,

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \xi_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} - \frac{1}{V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\alpha\beta}} J_{\boldsymbol{k}\boldsymbol{k}'} \boldsymbol{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} c^{\dagger}_{\boldsymbol{k}'\alpha} c_{\boldsymbol{k}\beta} , \qquad (35.2.27)$$

where $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu$ is the electron energy measured from the chemical potential and, as shown in Appendix I, the strength of the exchange coupling is given by

$$J_{\boldsymbol{k}\boldsymbol{k}'} = -\frac{1}{2}V_{\boldsymbol{k}d}V_{d\boldsymbol{k}'} \left[\frac{1}{\varepsilon_d + U - \xi_{\boldsymbol{k}}} + \frac{1}{\varepsilon_d + U - \xi_{\boldsymbol{k}'}} + \frac{1}{\xi_{\boldsymbol{k}} - \varepsilon_d} + \frac{1}{\xi_{\boldsymbol{k}'} - \varepsilon_d} \right].$$
(35.2.28)

In addition to this term a spin-independent scattering potential also appears, though its effect can be neglected in most of the calculations.

Since $\varepsilon_d < 0$ and $\varepsilon_d + U > 0$ in the local-moment regime, the exchange coupling is antiferromagnetic, $J_{kk'} < 0$, for electrons in the vicinity of the Fermi energy where

$$|\xi_{\mathbf{k}}|, |\xi_{\mathbf{k}'}| \ll |\varepsilon_d|$$
 and $|\xi_{\mathbf{k}}|, |\xi_{\mathbf{k}'}| \ll |\varepsilon_d + U|$. (35.2.29)

In what follows, we will neglect the momentum dependence of this coupling, and – following the literature – the interaction is chosen in the form

$$\mathcal{H}_{\rm int} = \frac{J}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'} \left[S^+ c^{\dagger}_{\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}\uparrow} + S^- c^{\dagger}_{\boldsymbol{k}'\uparrow} c_{\boldsymbol{k}\downarrow} + S^z \left(c^{\dagger}_{\boldsymbol{k}'\uparrow} c_{\boldsymbol{k}\uparrow} - c^{\dagger}_{\boldsymbol{k}'\downarrow} c_{\boldsymbol{k}\downarrow} \right) \right], \quad (35.2.30)$$

where J > 0 corresponds to the antiferromagnetic case.

This interaction was used by KONDO in his celebrated paper in 1964 to explain the resistivity minimum in metals (see Section 24.4.3) at low temperatures. The s-d interaction is therefore often referred to as the Kondo Hamiltonian and the problem of a single magnetic impurity embedded in a metal as the Kondo problem.

35.2.5 Perturbative Treatment of the Kondo Problem

We have seen in our study of the transport properties in Chapter 24 that scattering by paramagnetic impurities gives rise to a strongly temperatureand energy-dependent cross section. Perturbation theory gives a logarithmically singular cross section at T = 0 for electrons on the Fermi surface and a logarithmically increasing contribution was found in the resistivity:

$$R_{\rm imp} \sim N_{\rm i} \left[J + J^2 \rho \ln \frac{D}{k_{\rm B}T} + \cdots \right]^2.$$
 (35.2.31)

A band of width 2D symmetric about the Fermi energy with a constant density of states ρ was assumed in this calculation. This infrared divergence is the consequence of an internal degree of freedom, the spin, of the paramagnetic impurity, which can be flipped without cost of energy.

Similar logarithmic corrections appear in perturbation theory for other physical quantities as well. The first logarithmic correction to the susceptibility of the paramagnetic atom appears in second order in J. When calculating the magnetization and the change in the susceptibility, we also have to take into account the contributions of the conduction electrons. For simplicity we assume that the g factor of the localized spin is the same g_e as for free electrons. The magnetization is then

$$M_{\rm imp}(H,T) = g_{\rm e}\mu_{\rm B} \left(\langle S^z + \sigma_{\rm cond}^z \rangle - \langle \sigma_{\rm cond}^z \rangle_0 \right), \qquad (35.2.32)$$

where σ_{cond}^{z} is the component of the total spin of conduction electrons in the direction of the external field. The term to be subtracted is the value for a noninteracting electron system. The perturbative result is

$$\chi_{\rm imp} = \frac{S(S+1)}{3k_{\rm B}T} (g_{\rm e}\mu_{\rm B})^2 \mu_0 \left(1 - J\rho - J^2\rho^2 \ln \frac{D}{k_{\rm B}T} + \cdots\right).$$
(35.2.33)

At T = 0, where a small magnetic field can saturate the magnetic moment, logarithmic corrections are found in the field dependence of the magnetization:

$$M_{\rm imp}(H) = g_{\rm e}\mu_{\rm B}S\left(1 - J\rho - J^2\rho^2 \ln \frac{D}{\mu_{\rm B}\mu_0 H} + \cdots\right).$$
 (35.2.34)

In contrast to the temperature-dependent corrections, which can be observed above a characteristic temperature $T_{\rm K}$, this logarithmic field dependence cannot be observed. As will be seen, the impurity spin will not be aligned at low temperatures in the direction of the field owing to a screening cloud.

The first logarithmic corrections to the entropy and the heat capacity appear in the fourth and fifth powers of J,

$$S_{\rm imp}(T) = k_{\rm B} \ln(2S+1) - \frac{\pi^2}{3} k_{\rm B} S(S+1) (J\rho)^3 \\ \times \left(1 + 3J\rho \ln \frac{D}{k_{\rm B}T} + 6J^2 \rho^2 \ln^2 \frac{D}{k_{\rm B}T} + \cdots\right),$$
(35.2.35)

and

$$C_{\rm imp}(T) = T \frac{\partial S_{\rm imp}}{\partial T} = k_{\rm B} \pi^2 S(S+1) (J\rho)^4 \left(1 + 4J\rho \ln \frac{D}{k_{\rm B}T} + \cdots \right). \quad (35.2.36)$$

It was pointed out already in Chapter 24 that the higher order corrections involve higher powers of the logarithmic temperature-dependent factor. In the resistivity or susceptibility, for example, the most singular contributions are of the type

$$J^{n} \ln^{n-1} \frac{D}{k_{\rm B}T} \tag{35.2.37}$$

in *n*th order of perturbation theory. When self-energy corrections to conduction electrons are considered at T = 0, corrections of the type

$$J^n \ln^{n-1} \frac{D}{\varepsilon} \tag{35.2.38}$$

appear. These are the so-called leading logarithmic corrections. When the properties of the impurity spin or the conduction electron system are studied at low temperatures, at $k_{\rm B}T \ll D$, or close to the Fermi energy, for $\varepsilon \ll D$, all these corrections have to be collected and summed up to infinity. This can be achieved if we notice that the coefficients of the leading logarithmic corrections for the resistivity, susceptibility, entropy, and heat capacity are

simply related. The terms form geometric progressions which can be summed up to yield

$$R_{\rm imp} \sim N_{\rm i} \frac{J^2}{\left[1 - J\rho \ln(D/k_{\rm B}T)\right]^2},$$

$$\chi_{\rm imp} = \frac{S(S+1)}{3k_{\rm B}T} (g_{\rm e}\mu_{\rm B})^2 \mu_0 \left[1 - \frac{J\rho}{1 - J\rho \ln(D/k_{\rm B}T)}\right],$$

$$S_{\rm imp}(T) = k_{\rm B} \ln(2S+1) - \frac{\pi^2}{3} \frac{k_{\rm B}S(S+1)(J\rho)^3}{\left[1 - J\rho \ln(D/k_{\rm B}T)\right]^3},$$

$$C_{\rm imp}(T) = \frac{\pi^2 k_{\rm B}S(S+1)(J\rho)^4}{\left[1 - J\rho \ln(D/k_{\rm B}T)\right]^4}.$$

(35.2.39)

Introducing the Kondo temperature defined by

$$k_{\rm B}T_{\rm K} = D {\rm e}^{-1/J\rho}$$
, (35.2.40)

the previous results take very simple concise forms:

$$R_{\rm imp} \sim N_{\rm i} \frac{1}{\ln^2(T/T_{\rm K})},$$

$$\chi_{\rm imp} = \frac{S(S+1)}{3k_{\rm B}T} (g\mu_{\rm B})^2 \mu_0 \left[1 - \frac{1}{\ln(T/T_{\rm K})}\right],$$

$$S_{\rm imp}(T) = k_{\rm B} \ln(2S+1) - \frac{\pi^2}{3} \frac{k_{\rm B}S(S+1)}{\ln^3(T/T_{\rm K})},$$

$$C_{\rm imp}(T) = \frac{\pi^2 k_{\rm B}S(S+1)}{\ln^4(T/T_{\rm K})}.$$
(35.2.41)

These expressions demonstrate that the physical quantities have a universal temperature dependence through $\ln(T/T_{\rm K})$. Everything that is specific to the host (bandwidth, density of states) or that characterizes the interaction (the coupling constant J) is incorporated into $T_{\rm K}$.

35.2.6 Scaling Theory of the Kondo Problem

Note that lower powers of the logarithmic factor $\ln(D/k_{\rm B}T)$ may also appear in perturbation theory. These subleading corrections should also be collected if we wish to correctly describe the physical properties at low temperatures. The summation of the leading and next-to-leading logarithmic corrections can be achieved and the universal behavior of the Kondo problem can be demonstrated more simply in the scaling theory. For this we take a more general model, in which the coupling constant of the spin-flip processes differs from that of the spin-conserving processes. Instead of using (35.2.30), we write the interaction Hamiltonian in the form

$$\mathcal{H}_{\rm int} = \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'\alpha\beta} \left[J_{\pm} \left(S^+ \sigma_{\alpha\beta}^- + S^- \sigma_{\alpha\beta}^+ \right) + J_z S^z \sigma_{\alpha\beta}^z \right] c_{\boldsymbol{k}'\alpha}^\dagger c_{\boldsymbol{k}\beta} \qquad (35.2.42)$$

and apply the "poor man's" scaling procedure described in Appendix M. We eliminate the states near the band edges by reducing the cutoff D to $D - \delta D$. The contribution of these degrees of freedom should be compensated by a change of the coupling constants to describe the same physics. The invariance of the physical properties is enforced in this procedure by requiring invariance of the matrix elements of the scattering matrix T for states in the vicinity of the Fermi energy.

The first correction to the effective interaction is

$$\delta \mathcal{H}_{\text{int}} = \left(\frac{1}{V}\right)^2 \sum_{\boldsymbol{k}_1 \boldsymbol{k}_2 \alpha \beta} \left[J_{\pm} \left(S^+ \sigma_{\alpha\beta}^- + S^- \sigma_{\alpha\beta}^+ \right) + J_z S^z \sigma_{\alpha\beta}^z \right] c_{\boldsymbol{k}_1 \alpha}^{\dagger} c_{\boldsymbol{k}_2 \beta}$$

$$(35.2.43)$$

$$\times P \frac{1}{z - \mathcal{H}_0} \sum_{\boldsymbol{k}_3 \boldsymbol{k}_4 \gamma \delta} \left[J_{\pm} \left(S^+ \sigma_{\gamma\delta}^- + S^- \sigma_{\gamma\delta}^+ \right) + J_z S^z \sigma_{\gamma\delta}^z \right] c_{\boldsymbol{k}_3 \gamma}^{\dagger} c_{\boldsymbol{k}_4 \delta}$$

according to (M.1.30), where z is the energy of the initial state, and P is a projection operator. It projects onto the subspace in which the intermediate state contains at least one particle near the upper band edge in the range of width δD , or at least one hole near the lower band edge, in the range of width δD . In our specific example the electron created by the operator $c_{k_1\delta}^{\dagger}$ has to be near the upper band edge and the hole created by the annihilation operator $c_{k_1\delta}$ has to be near the lower band edge.

The correction to the Hamiltonian, $\delta \mathcal{H}_{int}$, describes an effective impurityscattering process of an electron lying near the Fermi surface if the electron created near the upper band edge in the first interaction is destroyed in the second interaction, or if the hole created near the lower band edge in the first scattering process is filled by an electron in the second step. This means that $\mathbf{k}_2 = \mathbf{k}_3$, $\beta = \gamma$ in the first case and $\mathbf{k}_1 = \mathbf{k}_4$, $\alpha = \delta$ in the second case. These processes are displayed in Fig. 35.14.



Fig. 35.14. Effective single-particle scattering processes in the lowest order of renormalization

The details of the calculations are given in Appendix M. Here we only list the result. Neglecting the terms which yield a potential scattering, since they are irrelevant for the physics of the Kondo problem, the same types of spin-flip and spin-conserving terms are obtained that exist in the bare Hamiltonian. After a change of the summation variables we get

$$\delta \mathcal{H}_{\rm int} = \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'\alpha\beta} \left[\delta J_{\pm} \left(S^+ \sigma_{\alpha\beta}^- + S^- \sigma_{\alpha\beta}^+ \right) + \delta J_z S^z \sigma_{\alpha\beta}^z \right] c_{\boldsymbol{k}'\alpha}^\dagger c_{\boldsymbol{k}\beta} \,, \quad (35.2.44)$$

where

$$\delta J_{\pm} = -\frac{\rho \,\delta D}{z - D} J_{\pm} J_z \,, \qquad \delta J_z = -\frac{\rho \,\delta D}{z - D} J_{\pm}^2 \,. \tag{35.2.45}$$

When the scattering of particles in the vicinity of the Fermi energy is considered, their energy can be neglected compared to the cutoff and we find

$$\delta J_{\pm} = \frac{\rho \, \delta D}{D} J_{\pm} J_z \,, \qquad \delta J_z = \frac{\rho \, \delta D}{D} J_{\pm}^2 \,. \tag{35.2.46}$$

These equations can be written in a differential form for an infinitesimal change of the cutoff. Since the bandwidth was decreased by δD (the cutoff D was changed by $-\delta D$), a minus sign appears in the differential equation:

$$\frac{\mathrm{d}J_{\pm}}{\mathrm{d}D} = -\frac{\rho}{D}J_{\pm}J_z\,,\qquad \frac{\mathrm{d}J_z}{\mathrm{d}D} = -\frac{\rho}{D}J_{\pm}^2\,.\tag{35.2.47}$$

Integration of these equations gives the renormalized value of the coupling for a given cutoff. Figure 35.15 shows the flow diagram of the renormalized couplings. Arrows indicate the variations of the couplings as the cutoff is decreased.



Fig. 35.15. Flow diagram of the renormalized couplings of the anisotropic Kondo model

The renormalized coupling weakens and vanishes at the fixed point for an isotropic ferromagnetic $(J_{\pm} = -J_z)$ model. A potential-scattering term may survive, but the amplitude of the spin-flip processes is scaled out. This indicates that a ferromagnetic *s*-*d* coupling is irrelevant. In contrast to this behavior, the antiferromagnetic exchange $(J_{\pm} = J_z > 0)$ is relevant.¹⁰ The

¹⁰ It is only marginally relevant in a strict sense, since the renormalized coupling increases quadratically and not linearly for small bare couplings.

coupling constant of the effective model increases as the states near the band edge are gradually integrated out. The Kondo model scales toward strong coupling. Similar behavior is found in the anisotropic model when both J_{\pm} and J_z are positive, or when J_z is negative but $J_{\pm} > |J_z|$. The scaling equations have a fixed line, $J_{\pm} = 0$. This line is stable for $J_z < 0$ and unstable for $J_z > 0$.

When the couplings are relevant and scale to strong coupling, the higher order corrections to the flow equations cannot be neglected. The next, third-order corrections are determined in Appendix M. We then get the scaling equations given in (M.1.42):

$$\frac{\mathrm{d}J_{\pm}}{\mathrm{d}D} = -\frac{\rho}{D} \left[J_{\pm} J_z - \frac{1}{4} \left(J_{\pm} J_z^2 + J_{\pm}^3 \right) \rho + \cdots \right],$$

$$\frac{\mathrm{d}J_z}{\mathrm{d}D} = -\frac{\rho}{D} \left[J_{\pm}^2 - \frac{1}{2} J_{\pm}^2 J_z \rho + \cdots \right].$$
(35.2.48)

A new fixed point appears for antiferromagnetic couplings with a fixedpoint value of order unity. Since the further corrections are of equal importance, this fixed point is an artifact of the approximation. The third-order corrections to the scaling equations can only be used to sum up the next-toleading logarithmic corrections and to extend the validity of the perturbative expressions to somewhat lower temperatures, but they cannot predict the ground-state properties.

Introducing the dimensionless coupling $g = J\rho$ in the isotropic case, the scaling equations in (35.2.48) take the form

$$D\frac{\mathrm{d}g}{\mathrm{d}D} \equiv \frac{\mathrm{d}g}{\mathrm{d}\ln D} = -\left(g^2 - \frac{1}{2}g^3 + \cdots\right),\qquad(35.2.49)$$

or dividing both sides by g,

$$\frac{d\ln g}{d\ln D} = -\left(g - \frac{1}{2}g^2 + \cdots\right).$$
 (35.2.50)

Written in a more general form, the renormalized coupling satisfies a differential equation

$$\frac{\mathrm{d}\ln g}{\mathrm{d}\ln D} = \beta(g) \,. \tag{35.2.51}$$

The zeros of the β function give the fixed points of the renormalization transformation. The coupling remains unchanged when it reaches a fixed-point value. The sign of the β function near the fixed point determines whether the flow of the coupling is toward the fixed point (such a fixed point is stable, the deviation of the coupling from the fixed-point value is irrelevant) or away from the fixed point (such a fixed point is unstable, the coupling is relevant).

The solution of (35.2.51) yields the renormalized coupling when the bandwidth cutoff is scaled from D to D'. In an implicit form

$$\int_{g}^{g(D')} \frac{\mathrm{d}g'}{g'} \frac{1}{\beta(g')} = \int_{D}^{D'} \frac{\mathrm{d}D''}{D''} \,. \tag{35.2.52}$$

Only the first two terms of the power series of the β function are known for the Kondo problem. Taking the first term, the renormalized coupling is obtained from the solution of the equation

$$\int_{g}^{g(D')} \frac{\mathrm{d}g'}{{g'}^2} = -\int_{D}^{D'} \frac{\mathrm{d}D''}{D''} \,. \tag{35.2.53}$$

It is readily found that

$$g(D') = \frac{g}{1 + g \ln(D'/D)}.$$
 (35.2.54)

This expression can be used to sum up the leading logarithmic corrections in perturbation theory. Looking at the perturbative corrections for the Kondo problem we readily see that all logarithmic corrections vanish at a finite temperature T_D where the thermal energy $k_{\rm B}T_D$ is equal to the bandwidth D. The susceptibility, for example, for which the perturbation series is given in (35.2.33), takes the form

$$\chi_{\rm imp}(T_D) = \frac{S(S+1)}{3k_{\rm B}T_D} (g_{\rm e}\mu_{\rm B})^2 \mu_0 (1-g)$$
(35.2.55)

at $k_{\rm B}T_D = D$. It follows from the scaling theory that if this quantity is to be determined at a temperature T, this expression can be used by substituting g with the renormalized coupling calculated with the cutoff $D_T = k_{\rm B}T$, that is

$$\chi_{\rm imp}(T) = \frac{S(S+1)}{3k_{\rm B}T} (g_{\rm e}\mu_{\rm B})^2 \mu_0 [1 - g(D_T)] = \frac{S(S+1)}{3k_{\rm B}T} (g_{\rm e}\mu_{\rm B})^2 \mu_0 \left[1 - \frac{g}{1 + g\ln(k_{\rm B}T/D)}\right].$$
(35.2.56)

This is indeed identical with the expression given in (35.2.39), which was derived by summing up the leading logarithmic corrections. The perturbative expressions derived for the other physical quantities, e.g., for the entropy or heat capacity, can be obtained similarly. Thus the scaling hypothesis allows us to sum up the leading logarithmic terms if the first perturbative logarithmic correction is known.

The renormalized coupling of the Kondo problem increases as the cutoff decreases and diverges in our present approximation when a small but finite bandwidth D^* is reached, before all band states are scaled out. Although this scaling theory, which is based on perturbation theory, makes sense only until the renormalized coupling does not exceed unity, we might formally continue

using the scaling equations to D^* . Introducing the characteristic temperature T^* defined by $D^* = k_{\rm B}T^*$, we integrate the scaling equation up to this cutoff. We have

$$\int_{g}^{\infty} \frac{\mathrm{d}g'}{{g'}^2} = -\int_{D}^{k_{\rm B}T^*} \frac{\mathrm{d}D''}{D''} \,. \tag{35.2.57}$$

The solution of this equation gives

$$k_{\rm B}T^* = D\exp\left(-1/J\rho\right) \tag{35.2.58}$$

for the characteristic temperature. This temperature is the same as the Kondo temperature $T_{\rm K}$ introduced earlier. Expressing the renormalized coupling in terms of it we get

$$g(T) = \frac{1}{\ln(T/T_{\rm K})}$$
 (35.2.59)

This indicates that the physical quantities depend on the temperature only through $\ln(T/T_{\rm K})$, as has been seen earlier.

The expressions obtained by summing up the leading logarithmic corrections are valid for $T \gg T_{\rm K}$, where the scaled coupling is still weak. We can go beyond this approximation by taking into account the next-to-leading correction to the β function. For this we have to solve the equation

$$\int_{g}^{g(D')} \frac{\mathrm{d}g'}{{g'}^2 - \frac{1}{2}{g'}^3} = -\int_{D}^{D'} \frac{\mathrm{d}D''}{D''} \,. \tag{35.2.60}$$

Expanding the integrand on the left-hand side for g < 1 we get

$$\int_{g}^{g(D')} \mathrm{d}g' \left[\frac{1}{{g'}^2} + \frac{1}{2g'} \right] = -\int_{D}^{D'} \frac{\mathrm{d}D''}{D''} \,, \tag{35.2.61}$$

which yields

$$\frac{1}{g(D')} - \frac{1}{g} - \frac{1}{2}\ln\frac{g(D')}{g} = \ln\frac{D'}{D}.$$
(35.2.62)

The renormalized coupling does not diverge any more, but it can still be of order unity. We define a new Kondo temperature where this happens, and beyond which the perturbative approach is not applicable. For $g = J\rho \ll 1$, the solution of

$$-\frac{1}{g} + \frac{1}{2}\ln g = \ln \frac{k_{\rm B}T_{\rm K}}{D}$$
(35.2.63)

yields

$$k_{\rm B}T_{\rm K} = D \left(J\rho\right)^{1/2} \exp\left(-1/J\rho\right)$$
. (35.2.64)

The equation for the renormalized coupling can then be written as

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$$\frac{1}{g(D')} - \frac{1}{2}\ln g(D') = \ln \left(D'/k_{\rm B}T_{\rm K} \right)$$
(35.2.65)

and its solution is

$$g(D') = \frac{1}{\ln\left(D'/k_{\rm B}T_{\rm K}\right)} + \frac{\ln\left(\ln(D'/k_{\rm B}T_{\rm K})\right)}{2\ln^2(D'/k_{\rm B}T_{\rm K})} + \cdots$$
(35.2.66)

As we saw above, the physical quantities can be calculated at a temperature T from the perturbative expression valid at the cutoff, if the coupling is substituted by its renormalized value obtained by scaling the cutoff to $D_T = k_{\rm B}T$, e.g., for the susceptibility we have

$$\chi_{\rm imp} = \frac{S(S+1)}{3k_{\rm B}T} (g_{\rm e}\mu_{\rm B})^2 \mu_0 \left[1 - \frac{1}{\ln(T/T_{\rm K})} - \frac{\ln\left(\ln(T/T_{\rm K})\right)}{2\ln^2(T/T_{\rm K})} + \cdots \right].$$
(35.2.67)

Just as in the leading logarithmic approximation, in this improved theory as well, everything that is characteristic of the system or of the interaction with the impurity, e.g., the density of states at the Fermi energy, the bandwidth, and the bare coupling strength, is incorporated into a single parameter $T_{\rm K}$. It gives the energy or temperature scale on which all variations in the physical quantities take place. The temperature dependence is a universal function when expressed via the dimensionless ratio $T/T_{\rm K}$.

When we are interested in the field dependence of the magnetization at T = 0, we can scale down the cutoff until it reaches the magnetic energy of the impurity spin. We find

$$M_{\rm imp} = g_{\rm e}\mu_{\rm B}S \bigg[1 - \frac{1}{2\ln(\mu_{\rm B}\mu_0 H/k_{\rm B}T_{\rm K})} - \frac{\ln\big(\ln(\mu_{\rm B}\mu_0 H/k_{\rm B}T_{\rm K})\big)}{4\ln^2(\mu_{\rm B}\mu_0 H/k_{\rm B}T_{\rm K})} + \cdots \bigg],$$
(35.2.68)

which is a universal function of the dimensionless variable $\mu_0 H/k_{\rm B}T_{\rm K}$.

Taking realistic values for the density of states and the exchange coupling, the Kondo temperature may be on the order of a few kelvin. The logarithmic behavior can be observed above this temperature. At lower temperatures, especially in the study of the ground-state properties of the Kondo model, the summation of the leading and next-to-leading corrections is not sufficient. A completely different approach is needed.

35.2.7 Wilson's Solution of the Kondo Problem

We have learned from the perturbative treatment of the Kondo problem that the infrared divergences that show up in the form of logarithmic singularities are due to the fact that the electrons scattered by the impurity have an internal degree of freedom, the spin, which can be flipped without costing energy. Although the singularity appears at low temperatures at low energies, the bandwidth appears in the logarithmic expressions as a cutoff and the perturbative corrections would diverge in the limit $D \to \infty$. The entire band, in a wide range of energies from the upper and lower band edges to low energies (energies near the Fermi energy), has to be taken into account and every energy scale makes a contribution. Second, we have learned from the scaling theory of the Kondo problem that even if the coupling constant J is weak, it gets stronger and stronger during the renormalization procedure, though the scaling equations derived from perturbation theory did not allow us to determine unambiguously the fixed points of the renormalization-group transformation. Therefore, a nonperturbative approach is needed through which the contribution of the different energy scales can be equally treated. This can be achieved with the help of the numerical renormalization group (NRG) proposed by K. G. WILSON (1973).

The key idea of the NRG approach is that any quantum impurity problem can be mapped, after a series of transformations, to a hopping Hamiltonian on a semi-infinite chain. The impurity is sitting at one end and the hopping amplitude decreases exponentially far from the impurity. The energy spectrum is calculated by an iterative diagonalization starting at the impurity site. Here we only sketch the general strategy for the example of the Kondo model and list the results. Further details are given in Appendix M.

If the Kondo coupling $J_{kk'}$ is independent of k and k', the Kondo Hamiltonian for a single impurity at $R_i = 0$ can be written as

$$\mathcal{H}_{\mathrm{K}} = J \sum_{\alpha\beta} \boldsymbol{S} \cdot \hat{\psi}^{\dagger}_{\alpha}(0) \boldsymbol{\sigma}_{\alpha\beta} \hat{\psi}_{\beta}(0) , \qquad (35.2.69)$$

where $\hat{\psi}_{\alpha}(0)$ is the field operator of electrons with spin α at the position of the impurity. The interaction is local and the impurity spin couples to the spin density of conduction electrons. Since only *s* waves are scattered by a contact potential, it is convenient to use orbital-momentum eigenstates and to expand the field operator in terms of spherical waves, keeping only the l = 0 components. The wave number *k*, which could go from zero to infinity, is restricted in such a way that the energy should be in a band of width 2*D* around the Fermi energy. This continuous band is discretized by a logarithmic discretization procedure adapted to the logarithmic contribution of the various parts of the band. Leaving out the degrees of freedom that do not couple directly to the impurity, the on-site interaction takes the form

$$\mathcal{H}_{\mathrm{K}} = J\rho \sum_{\alpha\beta} \boldsymbol{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} f_{0,\alpha}^{\dagger} f_{0,\beta}, \qquad (35.2.70)$$

where $f_{0,\alpha}^{\dagger}$ is the creation operator of a fermionic state, which is the sum over a discrete set of states covering the entire band.

The kinetic energy can be transformed using the same procedure into a hopping Hamiltonian along a semi-infinite chain

$$\mathcal{H}_0 = \sum_{n=0}^{\infty} \sum_{\sigma} \left(t_n f_{n,\sigma}^{\dagger} f_{n+1,\sigma} + t_n^* f_{n+1,\sigma}^{\dagger} f_{n,\sigma} \right), \qquad (35.2.71)$$

with

$$t_n \approx \frac{1 + \Lambda^{-1}}{2\Lambda^{n/2}}$$
(35.2.72)

for large n, where $\Lambda > 1$ is a discretization parameter, and the operators $f_{n,\sigma}^{\dagger}(f_{n,\sigma})$ are fermionic creation (annihilation) operators. This is indeed the Hamiltonian of fermions hopping between nearest neighbors along a semi-infinite chain, if the index n is identified as the site index.

Taking into account the interaction with the impurity, the Kondo model is finally mapped onto a tight-binding model on a semi-infinite chain. The electrons hop between nearest-neighbor sites and interact with the impurity spin sitting at n = 0 only locally, when they hop to the impurity site. A spin exchange process can occur. Apart from an overall multiplicative factor we have

$$\mathcal{H} = \sum_{n,\sigma} \Lambda^{-n/2} \left(f_{n,\sigma}^{\dagger} f_{n+1,\sigma} + f_{n+1,\sigma}^{\dagger} f_{n,\sigma} \right) + \tilde{J} \sum_{\alpha\beta} \boldsymbol{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} f_{0,\alpha}^{\dagger} f_{0,\beta} \,, \quad (35.2.73)$$

where \tilde{J} is proportional to J.

WILSON calculated the physically interesting low-energy part of the spectrum by iterative diagonalization adding one extra site of the chain in each step of the iterative scheme. The number of states would increase exponentially as new sites are added. This problem is avoided and a numerically tractable scheme is obtained if the higher lying levels are truncated in each step by keeping a fixed number of low-lying levels (typically of order 10^3). The splitting of the levels is evaluated numerically and the flow of the low-lying part of the energy spectrum is studied as the chain length increases.

The Kondo model has two fixed points: the trivial fixed point $\tilde{J} = 0$ and a strong-coupling fixed point $J = \infty$. WILSON's numerical calculations have shown that the energy spectrum has the same structure in the $N \to \infty$ limit as the infinitely strong-coupling fixed point irrespective of the initial value of the coupling, provided that J > 0. An electron is trapped at the impurity site forming an infinitely strongly bound singlet with the impurity spin. The remaining $N_{\rm e} - 1$ electrons are free to move on the chain, except that they feel an infinitely high potential barrier at the impurity site. The phase of the electron states in the presence of this barrier is shifted by $\pi/2$ compared to the noninteracting case. This led to a simple physical picture for the Kondo problem, namely, the impurity is surrounded by an electron cloud which is polarized oppositely to the spin of the impurity. They form a tightly bound singlet in the ground state. In other words the polarized electron cloud completely screens the magnetic moment if the s-d coupling is antiferromagnetic. Since the magnetic moment of the impurity is frozen out, the system is expected to behave as a normal Fermi liquid. The susceptibility should be Pauli-like instead of Curie-like at low temperatures.

35.2.8 Low-Temperature Behavior of the Kondo Model

The low-temperature properties of the Kondo model are determined by the strong-coupling fixed point and the way the renormalized coupling scales to it. When the coupling is large but still finite, there are terms in the renormalized Hamiltonian which couple the n = 0 impurity site to neighboring sites. Since they are irrelevant perturbations, they can be treated in perturbation theory. WILSON found

$$\chi_{\rm imp} = \frac{(g_{\rm e}\mu_{\rm B})^2\mu_0}{4k_{\rm B}T_0} \tag{35.2.74}$$

for the susceptibility and

$$c_{\rm imp} = \frac{\pi^2 k_{\rm B}}{6T_0} T \tag{35.2.75}$$

for the heat capacity. The low-temperature value of the Wilson ratio,

$$R_{\rm W} = \frac{4\pi^2 k_{\rm B}^2 T}{3g_{\rm e}^2 \mu_{\rm B}^2 \mu_0} \frac{\chi_{\rm imp}}{c_{\rm imp}} = 2\,, \qquad (35.2.76)$$

is thus twice as big as for noninteracting electrons.

The characteristic temperature T_0 is not identical to $T_{\rm K}$, the characteristic temperature scale at higher temperatures. The relationship between them can be obtained from the NRG calculations. Their ratio,

$$w \equiv \frac{T_{\rm K}}{T_0} = 0.4128\,, \qquad (35.2.77)$$

is the so-called Wilson number.

The numerical solution was made possible by the assumption that the details of the dispersion relation of the conduction electrons are irrelevant in the sense that they do not influence the universal properties of the Kondo problem. Soon after the realization of this fact, P. WIEGMANN (1980) and N. ANDREI (1980) have shown independently that the model is exactly solvable by the Bethe ansatz if the dispersion relation is appropriately chosen. All the results obtained by WILSON could be reproduced in the exact solution. All physical quantities are universal functions of $\log T/T_{\rm K}$ at temperatures above $T_{\rm K}$. Conduction electrons start to screen the localized magnetic moment around $T_{\rm K}$. The density of states is deformed below $T_{\rm K}$ and a narrow resonance, the Abrikosov–Suhl resonance, of width $k_{\rm B}T_{\rm K}$ appears near the Fermi energy, just as in the Anderson model. At low temperatures, where the impurity is screened, the system is a Fermi liquid with a characteristic temperature T_0 . The screened impurity scatters the conduction electrons as would a nonmagnetic impurity and the contribution of the magnetic impurity to the resistivity saturates smoothly at T = 0 with a T^2 temperature dependence:

$$R_{\rm imp}(T) = R_0 \left[1 - \frac{\pi^4}{16} \left(\frac{T}{T_0} \right)^2 + \mathcal{O} \left(\frac{T}{T_0} \right)^4 \right], \qquad (35.2.78)$$

where R_0 is the resistivity corresponding to the unitarity limit of the scattering, that is to a phase shift $\delta_0 = \pi/2$ for the l = 0 partial wave (s wave). Knowing the relationship between the two characteristic temperatures the Bethe-ansatz solution allows us to study the crossover between the perturbative and the truly low-temperature regimes.

35.2.9 Nozières's Local-Fermi-Liquid Theory

The low-temperature properties of the Kondo problem can be described in a simple phenomenological model proposed by P. NOZIÈRES (1974). The starting point is the strong-coupling fixed point $J \to \infty$, where a singlet bound state is formed between the impurity and an electron on the n = 0 site. The rearrangement of the conduction electron states is confined to a range of width $k_{\rm B}T_{\rm K}$ in the vicinity of the Fermi energy. The singlet state is not an eigenstate of the z-component of the impurity spin and the spin fluctuates between the \uparrow and \downarrow states with a characteristic spin-flip relaxation time $\tau_{\rm s}$ determined by the binding energy $k_{\rm B}T_{\rm K}$ of the singlet,

$$\hbar/\tau_{\rm s} \sim k_{\rm B} T_{\rm K} \,. \tag{35.2.79}$$

Spin fluctuations are fast below $T_{\rm K}$ and the electrons propagating in the system see a vanishing average moment as if it were a nonmagnetic impurity. The spin relaxation time slows considerably above the Kondo temperature. Its temperature dependence is given by the Korringa relation

$$\hbar/\tau_{\rm s} \sim (J\rho)^2 k_{\rm B} T$$
. (35.2.80)

In this temperature range, the conduction electrons experience a well-defined impurity spin owing to the slow relaxation.

Although the impurity spin vanishes below $T_{\rm K}$, the electrons can polarize it, which induces a scattering of the conduction electrons by the singlet. NOZI-ÈRES assumed that the scattering is elastic and can be described by a spinand energy-dependent phase shift $\delta_{\sigma}(\varepsilon)$. The key element of the theory is the assumption that – in analogy with Landau's Fermi-liquid theory – the phase shift depends on the distribution of the other quasiparticles, and for electrons near the Fermi surface it can be expanded in the form

$$\delta_{0\sigma}(\varepsilon_{\boldsymbol{k}}) = \delta_0(\varepsilon_{\boldsymbol{k}}) + \sum_{\boldsymbol{k}'\sigma'} \phi_{\sigma\sigma'}(\varepsilon_{\boldsymbol{k}}, \varepsilon_{\boldsymbol{k}'}) \delta n_{\sigma'}(\varepsilon_{\boldsymbol{k}'}), \qquad (35.2.81)$$

where $\delta n_{\sigma'}(\varepsilon_{\mathbf{k}'})$ is the number of quasiparticles present in the system with energy $\varepsilon_{\mathbf{k}'}$. The parameters $\phi_{\sigma\sigma'}(\varepsilon_{\mathbf{k}}, \varepsilon_{\mathbf{k}'})$ can be taken independent of the energy for electrons near the Fermi energy. Approximating the energy dependence of $\delta_0(\varepsilon_{\mathbf{k}})$ by

$$\delta_0(\varepsilon_k) = \delta_0 + \alpha(\varepsilon_k - \mu) + \cdots, \qquad (35.2.82)$$

the behavior of the system is characterized by the parameters α and $\phi_{\sigma\sigma'}$. Since there is no interaction between electrons with identical spins owing to the Pauli principle, $\phi_{\sigma\sigma} = 0$. Introducing the symmetric and antisymmetric combinations by

$$\phi^{\rm s} = \frac{1}{2}(\phi_{\uparrow\uparrow} + \phi_{\uparrow\downarrow}), \qquad \phi^{\rm a} = \frac{1}{2}(\phi_{\uparrow\uparrow} - \phi_{\uparrow\downarrow}), \qquad (35.2.83)$$

we have the relation

$$\phi^{\rm s} + \phi^{\rm a} = 0. \qquad (35.2.84)$$

Moreover, since the singularity is tied to the Fermi energy in the Kondo problem, the phase shift $\delta_{0\sigma}(\varepsilon_k)$ remains unchanged if the energy and the chemical potential are shifted by the same amount $\delta \varepsilon$. However, the shift of the chemical potential increases the number of quasiparticles by an amount

$$\delta n_{\sigma} = \rho_{\sigma}(\varepsilon_{\rm F}) \delta \varepsilon \,. \tag{35.2.85}$$

The requirement of the invariance of the phase shift leads to

$$\alpha + 2\rho_{\sigma}(\varepsilon_{\rm F})\phi^{\rm s} = 0, \qquad (35.2.86)$$

hence the theory contains a single free parameter.

We know that the number of electrons accumulated around the impurity is simply related to the phase shift. Generalizing (16.4.52) and (16.4.53) to spin-dependent phase shifts the change in the number of states below the Fermi energy due to an impurity is given by

$$\delta N_{\sigma}(\varepsilon_{\rm F}) = \frac{1}{\pi} \sum_{l=0}^{\infty} (2l+1)\delta_{l\sigma}(\varepsilon_{\rm F}), \qquad (35.2.87)$$

and the change in the density of states is

$$\delta\rho_{\sigma}(\varepsilon_{\rm F}) = \frac{1}{\pi} \sum_{l=0}^{\infty} (2l+1) \frac{\mathrm{d}\delta_{\sigma l}(\varepsilon)}{\mathrm{d}\varepsilon} \Big|_{\varepsilon=\varepsilon_{\rm F}}.$$
(35.2.88)

Since only the l = 0 partial wave suffers phase shift, it follows from (35.2.81) and (35.2.82) that

$$\delta \rho_{\sigma}(\varepsilon_{\rm F}) = \frac{\alpha}{\pi} \,, \tag{35.2.89}$$

and the change in the total density of states is

$$\delta\rho(\varepsilon_{\rm F}) = 2\frac{\alpha}{\pi} \,. \tag{35.2.90}$$

This gives rise to a change in the heat capacity, which is known to be proportional to the density of states at the Fermi energy. The impurity contribution to the heat capacity is obtained by substituting the change of the density of states in (16.2.91). This gives

$$c_{\rm imp} = 2\frac{\alpha}{\pi} \frac{\pi^2}{3} k_{\rm B}^2 T$$
, (35.2.91)

and the relative change of the heat capacity is

$$c_{\rm imp}/c_{\rm el} = 2\frac{\alpha}{\pi} \frac{1}{\rho(\varepsilon_{\rm F})} = \frac{\delta\rho(\varepsilon_{\rm F})}{\rho(\varepsilon_{\rm F})}.$$
 (35.2.92)

The one-particle energies are shifted in an external magnetic field,

$$\varepsilon_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} - \frac{1}{2}\sigma g_{\mathrm{e}}\mu_{\mathrm{B}}B\,,\qquad(35.2.93)$$

which means that the electron states are filled up to

$$\varepsilon_{\mathrm{F}\sigma} = \varepsilon_{\mathrm{F}} + \frac{1}{2}\sigma g_{\mathrm{e}}\mu_{\mathrm{B}}B, \qquad (35.2.94)$$

where $\sigma = \pm 1$ is used for the spin orientations. The number of quasiparticles created by the field is given by

$$\delta n_{\sigma} = \sum_{k} \delta n_{\sigma}(\varepsilon_{k}) = \frac{1}{2} \sigma g_{e} \mu_{B} B \rho_{\sigma}(\varepsilon_{F}). \qquad (35.2.95)$$

Substituting this expression into the magnetization,

$$M = \frac{1}{2}g_{\rm e}\mu_{\rm B}(\delta n_{\uparrow} - \delta n_{\downarrow}), \qquad (35.2.96)$$

the Pauli susceptibility is recovered.

The scattering by the impurity gives rise to an additional contribution to the susceptibility. It follows from (35.2.87) that the number of particles accumulated around the impurity is related to the phase shift at the Fermi energy via

$$\delta n_{\sigma}^{\rm imp} = \frac{1}{\pi} \delta_{0\sigma}(\varepsilon_{\rm F\sigma}) \,. \tag{35.2.97}$$

Their contribution to the magnetization is

$$M_{\rm imp} = \frac{1}{2\pi} g_{\rm e} \mu_{\rm B} \left[\delta_{0\uparrow}(\varepsilon_{\rm F\sigma}) - \delta_{0\downarrow}(\varepsilon_{\rm F\sigma}) \right].$$
(35.2.98)

Using (35.2.95) for the number of quasiparticles created by the field and making use of (35.2.86) the phase shift can be written as

$$\delta_{0\sigma}(\varepsilon_{\mathrm{F}\sigma}) = \delta_0 + \alpha \frac{1}{2} \sigma g_{\mathrm{e}} \mu_{\mathrm{B}} B + 2\phi^{\mathrm{s}} \delta n_{-\sigma}$$

= $\delta_0 + \alpha \frac{1}{2} \sigma g_{\mathrm{e}} \mu_{\mathrm{B}} B - \phi^{\mathrm{s}} \sigma g_{\mathrm{e}} \mu_{\mathrm{B}} B \rho_{\sigma}(\varepsilon_{\mathrm{F}})$ (35.2.99)
= $\delta_0 + \alpha \sigma g_{\mathrm{e}} \mu_{\mathrm{B}} B$.

This gives

$$M_{\rm imp} = \frac{\alpha}{\pi} g_{\rm e}^2 \mu_{\rm B}^2 B$$
, $\chi_{\rm imp} = \frac{\alpha}{\pi} g_{\rm e}^2 \mu_{\rm B}^2 \mu_0$ (35.2.100)

for the impurity contribution to the magnetization and susceptibility. Comparing the latter with the Pauli susceptibility, we find 35.3 Mixed-Valence and Heavy-Fermion Compounds 517

$$\chi_{\rm imp}/\chi_{\rm P} = 4\frac{\alpha}{\pi} \frac{1}{\rho(\varepsilon_{\rm F})} = 2\frac{\delta\rho(\varepsilon_{\rm F})}{\rho(\varepsilon_{\rm F})} \,. \tag{35.2.101}$$

Thus the relative changes of the susceptibility and the heat capacity differ by a factor of 2:

$$\frac{\chi_{\rm imp}}{\chi_{\rm P}} = 2\frac{c_{\rm imp}}{c_{\rm el}} \,. \tag{35.2.102}$$

The Wilson ratio defined in (35.2.76)

$$R_{\rm W} = \frac{4\pi^2 k_{\rm B}^2 T}{3g_{\rm e}^2 \mu_{\rm B}^2 \mu_0} \frac{\chi_{\rm imp}}{c_{\rm imp}} = \frac{\chi_{\rm imp}/\chi_{\rm P}}{c_{\rm imp}/c_{\rm el}}$$
(35.2.103)

now has the value

$$R_{\rm W} = 2$$
 (35.2.104)

in agreement with the result obtained in the numerical renormalization group. The deviation from unity – the value for a noninteracting electron system – is the indication of strong correlations in the Kondo problem.

35.3 Mixed-Valence and Heavy-Fermion Compounds

We have discussed above the questions related to the behavior of a single magnetic impurity. In the rest of this section we will consider compounds containing a periodic array of paramagnetic rare-earth or actinoid ions. The feature that distinguishes the latter from compounds with 3d ions and makes their behavior particularly interesting is that the 4f or 5f band is much narrower than the 3d band. This is because the maximum of the f-electron density is closer to the nucleus than for the completely filled 5s-5p levels and the 4f (5f) wavefunctions hardly overlap between nearest neighbors.

The relevant part of the band structure of lanthanoid compounds is the broad, hybridized 5d-6s band containing two or three electrons and the flat 4f band. The spin and orbital momentum of the localized f electrons can be determined from Hund's rules taking into account the crystal field splitting. This system can be described by a generalized Anderson or Kondo model, where the paramagnetic ions are not situated far apart in the sea of conduction electrons, but are arranged in a regular, crystalline order. This may lead to a completely new type of behavior, such as the appearance of heavy quasiparticles.

A different type of behavior is found if the highest occupied f level is close to the Fermi energy. Even though the f band is narrow, part of it may lie above the Fermi energy due to the broadening caused by hybridization with the conduction electrons. The band is then only partially filled so that the occupancy of the f level may be noninteger. An especially interesting situation occurs if a lanthanoid atom has two different ionization states and the energy of both of them is close to the Fermi energy. Both states will occur with nonvanishing probability and the average valence will be an intermediate value between the two integers. This happens in the mixed-valence compounds.

A similar situation occurs in actinoids, where the narrow 5f band is filled in gradually and the broad conduction band is the 6d-7s band. In what follows, we will talk about lanthanoids and 4f states, but all the results can be naturally generalized to actinoids.

After a brief presentation of the properties of the mixed-valence and heavyfermion compounds we will consider the models proposed for their description: the generalization of the single-impurity Anderson and Kondo models to the case when the paramagnetic atoms form a regular lattice. These models are known as the periodic Anderson model and the Kondo lattice.

35.3.1 Mixed-Valence Compounds

We know that there are two electrons on the 6s shell outside the [Xe] core in the lanthanoids and the 4f shell is gradually filled in. Gadolinium is an exception where one electron sits on the 5d shell. One might therefore expect that the lanthanoid ions are divalent, except for gadolinium.¹¹ This is not the case in most rare-earth compounds. The rare-earth ions are usually in the trivalent state. That is why the 3+ ions were listed in Table 3.6 where the spin and orbital moments were given, and we could claim that these values are in good agreement with experiments. The reason for this is that rare-earth ions form a stronger bound in solids if one of the 4f electrons is excited into the broad hybridized 5d-6s band. Cerium, praseodymium, and terbium may even lose two 4f electrons to become tetravalent. Notable exceptions are europium and ytterbium, which are divalent in many of their compounds. Samarium and thulium, too, occur sometimes as 2+ ions.

The majority of rare-earth and actinoid compounds have localized magnetic moments: charge fluctuations are suppressed, the f orbitals are filled by an integral number of electrons, and the ions have an integral valence. This is, however, not always the case. We mentioned in connection with the problem of the formation of localized moment in the single-impurity Anderson model that a valence-fluctuation regime occurs when one of the impurity levels, ε_f or $\varepsilon_f + U$, is close to the Fermi energy, since the filling of the level will not be integer. Zero or one electron may be present on the impurity in the first case, while one or two in the other case. In a more realistic model, where the degeneracy of the f level is taken into account, the $4f^n$ and $4f^{n-1}5d$ configurations may have similar energies for a given n and may therefore coexist.

The typical fluctuation time of the ions between the two configurations is 10^{-12} s. In experiments with a shorter time scale we see a snapshot of the system, that is a random mixture of ions in the two ionic states. In X-ray photoelectron spectroscopy (XPS), for example, where the characteristic time

 $^{^{11}}$ The valence of rare-earth ions in a solid is defined as the number of electrons donated to the 5d--6s conduction band.

scale is 10^{-15} – 10^{-18} s, lines characteristic for both ionicities are observed. When the measurement is made on a longer timescale, e.g., in Mössbauer experiments, the fluctuations average out the individual properties of the ions and the result can be understood as if the valence of all the ions had an intermediate value. This state is known as the homogeneous *mixed-valence*, *intermediate-valence*, or *fluctuating-valence* state. The different names refer to the fact that one or the other aspect is dominant depending on the timescale on which the ion is studied.

Typical examples are $EuCu_2Si_2$, $EuPd_2Si_2$, $EuPd_3S_4$, $YbCu_2Si_2$, $YbPd_3S_4$, $YbAgCu_4$, $YbAl_2$, $CeBe_{13}$, $CeSn_3$, SmS, SmB_6 , TmSe. In $EuCu_2Si_2$, for example, the Eu^{2+} and Eu^{3+} states are only separated by $0.07 \, eV$.

It is worthwhile to recall that we have already met a material, the magnetite of composition Fe_3O_4 , in the context of ferrimagnetism in Chapter 14 where both divalent and trivalent iron atoms are simultaneously present. An important difference is, however, that the Fe^{2+} and Fe^{3+} ions are located on different sublattices, at inequivalent crystallographic positions, and their ionicities do not fluctuate in time.

The behavior of some samarium monochalcogenides is even more unusual. The ground state of the divalent Sm^{2+} ion with electron configuration $4f^6$ is the nonmagnetic ${}^7\mathrm{F}_0$ state according to Hund's rules. The compounds SmS, SmSe, and SmTe are nonmagnetic semiconductors at ambient pressure. The position of the *f* level is shifted relative to the conduction band under pressure and a 4f electron can be transferred to the conduction band above a critical pressure where the *f* level comes close enough to the Fermi energy. Trivalent Sm³⁺ ions appear suddenly with electron configuration $4f^5$. Since their radius is smaller than that of the divalent ions, the lattice parameter exhibits a jump at a certain pressure or decreases sharply with pressure. The lattice shrinks, the volume collapses, and the system reverts to a paramagnetic metallic phase.

35.3.2 Heavy-Fermion Materials

Since the 1980s more and more new materials have been discovered in which the electronic part of the low-temperature specific heat is linear, but the Sommerfeld coefficient is two to three orders of magnitude larger than in simple metals. The γ coefficient, which can be of the order of J/mol K², has been given for some of them in Table 16.7. We mentioned there that this behavior can be understood by assuming that the density of states is extremely large at the Fermi energy. A further interesting property of these materials is that the susceptibility shows Curie-like 1/T temperature dependence at high temperatures, indicating that localized magnetic moments are present in the system. The heavy-fermion materials contain rare-earth ions (such as cerium) or actinoids (such as uranium), and the 4f or 5f electrons might be responsible for the magnetic properties. The localized moments disappear, however, at low temperature owing to the interactions with the conduction electrons and with each other by a Kondo-like mechanism. A sharp Kondo peak appears in
the density of states near the Fermi energy. The system behaves on this very narrow energy scale as a Fermi liquid with large effective mass,¹² whence the name *heavy fermion*. "Classical" heavy-fermion systems are CeAl₃, CeCu₆, CeCu₂Si₂, UPt₃, UBe₁₃, and NpBe₁₃.

The anomalously large γ is accompanied by an anomalously large temperature-independent Pauli susceptibility, since the susceptibility, too, is proportional to the density of states at the Fermi energy. The Fermi-liquid behavior can be characterized by the Wilson ratio defined in this case as

$$R_{\rm W} = \frac{\chi}{\gamma} \frac{\pi^2 k_{\rm B}^2}{g_J^2 \mu_{\rm B}^2 J(J+1)}, \qquad (35.3.1)$$

where g_J is the Landé factor and J is the total angular momentum of the ions. Taking the experimentally measurable effective magnetic moment μ_{eff} from the high-temperature Curie-type behavior,

$$R_{\rm W} = \frac{\chi}{\gamma} \frac{\pi^2 k_{\rm B}^2}{\mu_{\rm eff}^2} \,. \tag{35.3.2}$$

As shown in Table 35.1, the Wilson ratio is relatively close to unity in most heavy-fermion systems.

Table 35.1. Wilson ratio for some heavy-fermion compounds

Compound	$R_{\rm W}$	Compound	$R_{\rm W}$	Compound	$R_{\rm W}$
CeAl ₃	0.7	UPt_3	0.6	UCd ₁₁	1.7
CeCu_6	0.6	UBe_{13}	0.5	$NpBe_{13}$	2.1
$CeCu_2Si_2$	0.2	$U_2 Zn_{17}$	0.8	YbBiPt	2.6

Further confirmation of the Fermi-liquid behavior of heavy-fermion systems is obtained when the Sommerfeld coefficient γ of the linear term of the specific heat is compared with the coefficient A of the T^2 term of the resistivity in $\rho = \rho_0 + AT^2$. The specific heat is proportional to m^* , while $A \propto (m^*)^2$ according to the Fermi-liquid theory; thus, the ratio A/γ^2 has to be universal. The Kadowaki–Woods relation,¹³

$$R_{\rm KW} = A/\gamma^2 \approx 1 \times 10^{-5} [\mu \Omega \,{\rm cm} \,({\rm mol} \,{\rm K/mJ})^2],$$
 (35.3.3)

is rather well satisfied at low temperatures in a large class of heavy-fermion systems that do not order antiferromagnetically even though strong magnetic fluctuations may be observed as, e.g., in CeAl₃.

¹² Also the cyclotron mass determined in the de Haas–van Alphen effect is one or two orders of magnitude larger than the electron mass.

¹³ K. KADOWAKI and S. B. WOODS, 1986.

The magnetic moments of the cerium or uranium atoms are ordered at low temperatures in many of the heavy-fermion systems. It was a great surprise that some of these materials become superconductors at a lower temperature. The most interesting parameters of these compounds were already given in Table 34.2. It was mentioned there that the origin of superconductivity may be related to magnetic fluctuations and these materials are probably unconventional superconductors. The compound $PrOs_4Sb_{12}$ is special, where indications for the dominant role of nonmagnetic quadrupolar interactions have been found experimentally. Table 35.2 contains the parameters for some heavy-fermion materials which order antiferromagnetically but are not superconductors at ambient pressure.

ically ordered neavy-termion compounds								
Compound	$T_{\rm N}$ (K)	$\gamma ({\rm mJ/mol}{\rm K}^2)$	Compound	$T_{\rm N}$ (K)	$\gamma ({\rm mJ/mol}{\rm K}^2)$			
$CeCu_2Ge_2$	4.1	100	UCd_{11}	5.0	840			
$CeNi_2Sn_2$	1.8	600	U_2Zn_{17}	9.7	500			
$CeRhIn_5$	3.8	420	$NpBe_{13}$	3.4	900			
Ce ₂ RhIn ₈	2.8	400	YbNiSi ₃	5.1	190			

 Table 35.2. Néel temperature and Sommerfeld coefficient of some antiferromagnetically ordered heavy-fermion compounds

A model that might describe the behavior of intermediate-valence or heavy-fermion compounds should have electrons in at least two bands, a broad s band and a narrow d or f band. The simplest such model is the periodic Anderson model, which might be capable of describing heavy-fermion, mixedvalence, and Kondo behavior depending on the values of the parameters.

35.3.3 Periodic Anderson Model

The periodic Anderson model (PAM) or Varma–Yafet model¹⁴ is a straightforward generalization of the single-impurity Anderson model given in (35.2.1). Instead of considering a single ion with a d or f level embedded in the sea of conduction electrons, we assume that the ions with partially filled f levels form a regular periodic lattice. There is no direct overlap between the wavefunctions of the rare-earth ions so that the f band is infinitely narrow, but the f electrons can hybridize with the conduction electrons. We write the Hamiltonian in the form

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \sum_{i\sigma} \varepsilon_{f} f^{\dagger}_{i\sigma} f_{i\sigma} + \sum_{i} U n^{f}_{i\uparrow} n^{f}_{i\downarrow} + \frac{1}{\sqrt{N}} \sum_{\boldsymbol{i}\boldsymbol{k}\sigma} \left(V_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_{i}} c^{\dagger}_{\boldsymbol{k}\sigma} f_{i\sigma} + V^{*}_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_{i}} f^{\dagger}_{i\sigma} c_{\boldsymbol{k}\sigma} \right),$$
(35.3.4)

¹⁴ C. M. VARMA and Y. YAFET, 1976.

where $n_{i\sigma}^f = f_{i\sigma}^{\dagger} f_{i\sigma}$ is the number of f electrons with spin σ on site i. The kinetic energy of f electrons and their hybridization with the conduction electrons could have been written equivalently in the Bloch representation as

$$\sum_{\boldsymbol{k}\sigma} \varepsilon_f f_{\boldsymbol{k}\sigma}^{\dagger} f_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k}\sigma} \left(V_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} f_{\boldsymbol{k}\sigma} + V_{\boldsymbol{k}}^* f_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \right), \qquad (35.3.5)$$

but the on-site Coulomb term is written most conveniently in the Wannier representation.

Neglecting for the moment the interaction between the f electrons, the bilinear Hamiltonian

$$\mathcal{H} = \sum_{k\sigma} \varepsilon_{k} c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k\sigma} \varepsilon_{f} f_{k\sigma}^{\dagger} f_{k\sigma} + \sum_{k\sigma} \left(V_{k} c_{k\sigma}^{\dagger} f_{k\sigma} + V_{k}^{*} f_{k\sigma}^{\dagger} c_{k\sigma} \right) \quad (35.3.6)$$

can be diagonalized by the unitary transformation

$$\alpha_{\boldsymbol{k}\sigma}^{(+)} = u_{\boldsymbol{k}}c_{\boldsymbol{k}\sigma} + v_{\boldsymbol{k}}f_{\boldsymbol{k}\sigma}, \qquad \alpha_{\boldsymbol{k}\sigma}^{(-)} = -v_{\boldsymbol{k}}c_{\boldsymbol{k}\sigma} + u_{\boldsymbol{k}}f_{\boldsymbol{k}\sigma}.$$
(35.3.7)

The diagonalization condition yields

$$|u_{\mathbf{k}}|^{2} = \frac{1}{2} \left[1 + \frac{\varepsilon_{\mathbf{k}} - \varepsilon_{f}}{\sqrt{(\varepsilon_{\mathbf{k}} - \varepsilon_{f})^{2} + 4|V_{\mathbf{k}}|^{2}}} \right],$$

$$|v_{\mathbf{k}}|^{2} = \frac{1}{2} \left[1 - \frac{\varepsilon_{\mathbf{k}} - \varepsilon_{f}}{\sqrt{(\varepsilon_{\mathbf{k}} - \varepsilon_{f})^{2} + 4|V_{\mathbf{k}}|^{2}}} \right]$$
(35.3.8)

with

$$u_{\boldsymbol{k}}v_{\boldsymbol{k}} = \frac{V_{\boldsymbol{k}}}{\sqrt{(\varepsilon_{\boldsymbol{k}} - \varepsilon_f)^2 + 4|V_{\boldsymbol{k}}|^2}}$$
(35.3.9)

for the parameters of the transformation and the eigenvalues are

$$E_{\boldsymbol{k}}^{\pm} = \frac{1}{2} \left(\varepsilon_{\boldsymbol{k}} + \varepsilon_f \pm \sqrt{(\varepsilon_{\boldsymbol{k}} - \varepsilon_f)^2 + 4|V_{\boldsymbol{k}}|^2} \right).$$
(35.3.10)

Two well-separated bands are obtained with a hybridization gap around ε_f if V_k is independent of k. The density of states is substantially increased on both sides of the gap compared to the density of states of the conduction band. The hybridized spectrum and the corresponding density of states is displayed schematically in Fig. 35.16. Note that if V_k vanishes at certain points of the Brillouin zone, no forbidden region appears, but the density of states has a deep minimum around ε_f with sharp peaks above and below this minimum.

In the ground state electrons fill the lowest energy states. The system is insulating for two electrons (one conduction electron and one f electron) per atom, since the lower band is completely filled, and this band is separated by a gap from the upper band. The system is metallic if extra electrons or holes are added to it.



Fig. 35.16. (a) Dispersion relation of hybridized s and f electrons. (b) Density of states of the hybridized bands

We assume for the sake of simplicity that the number of conduction electrons is equal to or less than the number of f electrons. The upper band is empty and the ground-state wavefunction takes the form

$$|\Psi_0\rangle = \prod_{\boldsymbol{k}\in\mathrm{FS}} \prod_{\sigma} \alpha_{\boldsymbol{k}\sigma}^{(-)\dagger} |0\rangle. \qquad (35.3.11)$$

The single-particle states have both s and f character according to the hybridization,

$$\begin{aligned}
|\Psi_0\rangle &= \prod_{\boldsymbol{k}\in\mathrm{FS}} \prod_{\sigma} \left(-v_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} + u_{\boldsymbol{k}} f^{\dagger}_{\boldsymbol{k}\sigma} \right) |0\rangle \\
&= \prod_{\boldsymbol{k}\in\mathrm{FS}} \prod_{\sigma} \left(1 + a^{(0)}_{\boldsymbol{k}} f^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \right) |\Psi_{\mathrm{FS}}\rangle
\end{aligned} \tag{35.3.12}$$

with

$$a_{\mathbf{k}}^{(0)} = \frac{2V_{\mathbf{k}}}{\varepsilon_f - \varepsilon_{\mathbf{k}} + \sqrt{(\varepsilon_{\mathbf{k}} - \varepsilon_f)^2 + 4|V_{\mathbf{k}}|^2}} \,. \tag{35.3.13}$$

Rewriting the creation operators of f-electron states in the Wannier representation, this state is obviously a linear combination of configurations in which the f level is empty, singly occupied, or doubly occupied. These configurations occur with roughly the same probability. This is because the on-site Coulomb interaction has been neglected so far. Its effect is to eliminate the configurations with double occupancy or at least to make them less probable. Different approximation schemes can be devised to cope with this problem. In the mixed-valent regime, the f^0 and f^1 configurations may be almost degenerate with the f-block ions fluctuating between the two ionicities. The energy of the f^2 configuration is much higher and the $U \to \infty$ limit may be taken. Double occupancy can be completely suppressed by a projection operator

$$P = \prod_{i} \left(1 - n_{i\uparrow}^f n_{i\downarrow}^f \right), \tag{35.3.14}$$

and a variational wavefunction can be chosen in the form

$$|\Psi\rangle = P \prod_{\boldsymbol{k}\in\mathrm{FS}} \prod_{\sigma} \left(1 + a_{\boldsymbol{k}} f_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \right) |\Psi_{\mathrm{FS}}\rangle$$
(35.3.15)

with a set of variational parameters $a_{\mathbf{k}}$, which may be different from $a_{\mathbf{k}}^{(0)}$. When ε_f is close to the Fermi energy and hybridization is relatively strong, a broad peak appears in the total density of states of s and f electrons. The average number of f electrons will be between 0 and 1, as it should in intermediate-valence compounds.

Alternatively, the Gutzwiller method can be used to take the effect of U into account. Following the prescription given in (35.1.41) the configurations are weighted by a factor g every time a site is doubly occupied. The trial wavefunction is then chosen in the form

$$|\Psi_{\rm G}\rangle = \prod_{i} \left[1 - (1-g)n^f_{i\uparrow}n^f_{i\downarrow} \right] |\Psi_0\rangle \,. \tag{35.3.16}$$

Since $|\Psi_0\rangle$ contains the hybridization parameters u_k and v_k , they can be taken as variational parameters together with g. The energy contribution coming from the Coulomb interaction can again be written as UdN, where d is the density of doubly occupied f orbitals. The expectation value of the remaining part of the Hamiltonian calculated with the Gutzwiller wavefunction turns out to be identical to the expectation value of an effective Hamiltonian evaluated with $|\Psi_0\rangle$,

$$E \equiv \left\langle \Psi_{\rm G} | \mathcal{H} | \Psi_{\rm G} \right\rangle = \left\langle \Psi_{0} | \mathcal{H}_{\rm eff} | \Psi_{0} \right\rangle + U dN \tag{35.3.17}$$

with

$$\mathcal{H}_{\text{eff}} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k}\sigma} \tilde{\varepsilon}_{f} f^{\dagger}_{\boldsymbol{k}\sigma} f_{\boldsymbol{k}\sigma} + V \sum_{\boldsymbol{k}\sigma} q(n^{f}_{\sigma}) \left(c^{\dagger}_{\boldsymbol{k}\sigma} f_{\boldsymbol{k}\sigma} + f^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \right).$$
(35.3.18)

This means that the Gutzwiller projection can be transformed out at the expense of renormalizing the hybridization terms by a factor $q(n_{\sigma}^{f})$ and shifting the energy of the f level. The mixed-valence compounds correspond to the situation where the f level broadened by the hybridization is near the Fermi energy and is only partially filled. On the other hand, heavy-fermion behavior is observed when ε_{f} is well below the Fermi energy and $\varepsilon_{f} + U$ lies well above it and the valence is close to unity. The renormalization of the hybridization is proportional to the probability that the f level is empty, $q^2 \propto 1 - n^{f}$ in the large-U limit. The hybridization is drastically suppressed resulting in a very narrow peak in the density of states with a narrow hybridization band around the renormalized $\tilde{\varepsilon}_{f}$.

To construct the wavefunction of the heavy-fermion state, we take a noninteracting Fermi sea with $N_{\rm e}$ conduction electrons and N_f f electrons. The state $|\Psi_{\rm FS}\rangle_{N_e+N_f}$ has much higher energy than the true ground state since the one-particle states fill a "large" Fermi sphere. The ground state can be obtained by removing high-energy electrons from the "large" Fermi sea and putting them on the localized f level with finite probability $|v_k|^2$. This can be achieved by introducing a factor

$$u_{\boldsymbol{k}} + v_{\boldsymbol{k}} f^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \tag{35.3.19}$$

in the wavefunction. To make sure that the f level is occupied by exactly one electron on each site, the wavefunction contains a projection operator

$$P = \prod_{i} \left[n_{i\uparrow}^{f} (1 - n_{i\downarrow}^{f}) + n_{i\downarrow}^{f} (1 - n_{i\uparrow}^{f}) \right].$$
(35.3.20)

The trial wavefunction is then

$$|\Psi\rangle = P \prod_{k\sigma} \left(u_{k} + v_{k} f_{k\sigma}^{\dagger} c_{k\sigma} \right) |\Psi_{\rm FS}\rangle_{N_{\rm e}+N_{f}} , \qquad (35.3.21)$$

where u_k and v_k are variational parameters. Lengthy calculation leads to the result that all electrons inside the "large" Fermi sphere containing $N_e + N_f$ electron states participate in the formation of a collective singlet state. The momentum distribution is displayed in Fig. 35.17.



Fig. 35.17. Momentum distribution in the collective singlet state

The Fermi edge is at the "large" Fermi surface. The k-space volume enclosed by it remains unchanged when the Coulomb interaction is switched on, in agreement with the Luttinger theorem, but the discontinuity, the quasiparticle weight, is much smaller than at U = 0, which is equivalent to an increase of the effective mass. The momentum distribution rises sharply at the k value corresponding to the "small" Fermi surface which encloses $N_{\rm e}$ conduction electron states. One might say that the interaction with magnetic electrons on the f level smears out the "small" Fermi surface, while states up to the "large" Fermi surface are partially filled, though with small probability. This increase in the kinetic energy is amply compensated by the gain in the exchange energy.

In the special case when the conduction band is half filled in the noninteracting model, the $N_e + N_f$ electrons fill the entire lower band and the system is a nonmagnetic insulator. One can prove exactly that if the lanthanoid (actinoid) ions occupy one sublattice of a bipartite lattice, the ground state is a nondegenerate singlet. These materials are called *Kondo insulators*. Typical examples are the cerium compounds: CeNiSn, CeRhSb, and Ce₃Bi₄Pt₃, or the compound YbB₁₂ which contains an element from the high end of the lanthanoid series. The width of the gap is only a few millielectron volts, so these compounds might be considered as narrow-gap semiconductors.

When the "large" Fermi surface is situated within the narrow peak around the hybridization gap, the density of states at the Fermi energy is large, as can be deduced from Fig. 35.16(b). The large effective mass in the heavy-fermion compounds is the consequence of the narrowness of the peak.

The existence of a sharp peak in the density of states and the hybridization gap are substantiated by calculations using the dynamical mean-field theory, which is exact when the dimensionality of the system tends to infinity, although the physical picture is somewhat different. The density of states of f electrons is displayed in Fig. 35.18 for the symmetric $(2\varepsilon_f + U = 0)$ and asymmetric periodic Anderson models.



Fig. 35.18. f density of states for the periodic Anderson model (full line) and the single impurity Anderson model (dashed line) (a) in the particle-hole symmetric case and (b) in the asymmetric case [Reprinted with permission from Th. Pruschke, R. Bulla, and M. Jarrell, *Phys. Rev. B* **61**, 12799 (2000). \bigcirc (2000) by the American Physical Society]

The peaks in the density of states at ε_f and $\varepsilon_f + U$ are quite similar in the single impurity and the periodic models. A narrow third peak signaling a coherent heavy-electron band corresponds to the Abrikosov–Suhl resonance of the single-impurity Anderson model. It appears at the Fermi energy below $T_{\rm K}$ in the periodic Anderson model as well. It is, however, split into two by the hybridization gap, which is a consequence of the periodicity of the structure.

35.3.4 Kondo Lattice

When ε_f is well below the Fermi energy and $\varepsilon_f + U$ is well above, the empty and doubly occupied configurations occur with negligible probability. They only appear virtually, for very short periods of time, as intermediate states. Because the occupancy of the f level is close to unity, the rare-earth ions have a localized moment, but its orientation fluctuates owing to the hybridization with the conduction electrons. The low-energy physics can be described by a model where the f-electron degrees of freedom are represented by a localized spin, just as in the Kondo problem. This model is the periodic Kondo lattice.

We assume that a spin S_i sits on every site R_i of a regular lattice and the spins interact with the conduction electrons via an s-d interaction of coupling J. The Hamiltonian of this Kondo lattice is chosen in the form

$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{J}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'} \sum_{\alpha\beta} \sum_{i} \boldsymbol{S}_{i} \cdot \boldsymbol{\sigma}_{\alpha\beta} c_{\boldsymbol{k}'\alpha}^{\dagger} c_{\boldsymbol{k}\beta} \mathrm{e}^{\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{R}_{i}} . \quad (35.3.22)$$

We know from the solution of the single-impurity Kondo problem that the conduction electrons screen the localized moment at low temperatures, below the characteristic Kondo temperature. The dominant role is played by electrons in a range of width $k_{\rm B}T_{\rm K}$ about the Fermi energy. It was thought for a long time that this screening cannot occur in a Kondo lattice, only in a dilute alloy, since there are not enough electrons in that range to screen all momenta. All electrons of the conduction band, even those lying quite far (at a few electron volts) from the Fermi energy, would be needed, but the thermal energy is not sufficient to rearrange these states. We might therefore expect a magnetically ordered ground state. As we have seen, magnetically ordered states do indeed occur in rare-earth and actinoid compounds with heavy quasiparticle mass in the normal state. There are quite a few heavy-fermion systems, however, where no magnetic ordering takes place. Their ground state is a collective singlet. Which of the two cases is found in a given material is determined by a delicate balance between two effects.

There is a single characteristic energy, $k_{\rm B}T_{\rm K}$, in the single-impurity problem, and the conduction electrons screen the localized moment below the Kondo temperature. When several localized moments are present, they interact through the intermediary of the conduction electrons. The RKKY interact through the intermediary of the conduction electrons. The RKKY interact through the intermediary of the conduction electrons. The RKKY interact through the magnetic atoms. The characteristic energy scale of the RKKY interaction is proportional to the square of the s-d exchange, $k_{\rm B}T_{\rm RKKY} \approx J^2 \rho(\varepsilon_{\rm F})$. S. DONIACH (1977) pointed out that two mechanisms, the Kondo screening of the magnetic moment and the ordering tendency due to the RKKY interaction, compete in a dense Kondo system. Whether the ground state is nonmagnetic or magnetically ordered depends on the outcome of this competition.

The Kondo temperature depends exponentially on the coupling J. The energy scale of the RKKY interaction is larger for small values of $J\rho(\varepsilon_{\rm F})$ and the magnetic moments order into a magnetic state before the Kondo screening becomes effective. The Kondo energy is also larger for larger values of J, and the ground state may then be nonmagnetic. A quantum critical point $[J\rho(\varepsilon_{\rm F})]_{\rm c}$, which is of order unity according to Monte Carlo calculations, separates the (anti)ferromagnetically ordered state from the Fermi-liquid state. The critical

temperature of the magnetically ordered state for small $J\rho(\varepsilon_{\rm F})$ should be on the order of $T_{\rm RKKY}$. This magnetic order is destroyed near the critical value of $J\rho(\varepsilon_{\rm F})$ when the critical temperature of the ordered state decreases to zero as shown in the schematic phase diagram in Fig. 35.19.



Fig. 35.19. Schematic phase diagram of the Kondo lattice

For stronger couplings and at high temperatures the spins are incoherent, the scattering is weak, and the system behaves as a normal metal, if the band is not half filled. The narrow Kondo peak in the density of states, which is related to the heavy mass of the quasiparticles, emerges gradually as the temperature is lowered and survives down to T = 0. The transition into the coherent singlet state at $T_{\rm K}$ is a crossover phenomenon, not a sharp phase transition. For a half-filled system the insulating nonmagnetic state is the Kondo spin-liquid state.

35.3.5 Open Problems

We have presented in the foregoing the simplest possible model of heavyfermion compounds in simplifying immensely the electronic structure of lanthanoids by considering a wide conduction band and a flat f band. While the solution of the single-impurity problem, a single f level, is known, the periodic model could only be solved, even for such a simplified band structure, after drastic approximations in the treatment of the effect of the on-site Coulomb repulsion between the f electrons.

The relevance of numerical results obtained in, e.g., the dynamical meanfield theory can also be questioned, since they are exact only for infinite dimensional models. Moreover, there are strong indications that the realistic electronic structure, the degeneracy of the f level, the crystal field splitting, etc., probably play a much more important role than assumed until now. We might expect, for example, that Yb³⁺ ions behave similar to Ce³⁺ ions owing to electron-hole symmetry, since Yb³⁺ has one hole in the f shell. The number of heavy-fermion ytterbium compounds is, however, much less than the number of cerium compounds. Thus much more refined models are needed to understand why cerium and uranium compounds play a special role. We should also bear in mind that heavy-fermion behavior is not restricted to them. It is observed in some compounds of the element next to cerium, praseodymium, as well. In fact, one of the heaviest mass (Sommerfeld coefficient $\gamma = 6.5 \,\text{J/mol}\,\text{K}^2$) was found in PrInAg₂, but the Pr³⁺ ions are probably in a nonmagnetic state owing to the crystal-field splitting and quadrupole interaction may be the dominant mechanism just as in the heavy-fermion superconductor PrOs₄Sb₁₂.

We did not discuss the problem of superconductivity of heavy-fermion materials, nor the role of the magnetic ions in forming the probably unconventional pairs. Spin fluctuations were also neglected although they can be strong as indicated by a $T^3 \ln T$ term in the specific heat, which appears in addition to the linear term due to the heavy quasiparticles and the T^3 term due to phonons.

A further open question is the role of quantum fluctuations at the quantum critical point separating the magnetically ordered phase from the heavyfermion Fermi liquid. They may destroy the normal metallic behavior at finite temperatures at the critical coupling just as in high-temperature superconductors. These problems are the subject of intensive ongoing research.

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Disordered Systems

It was pointed out at the very beginning of the presentation of the physics of solids that defects are inevitably present in macroscopic number even in crystalline materials. A fraction of them are thermally generated, but the majority of them are frozen in in the course of the crystal growth process. The structural aspects were discussed in Chapter 9. Every single property of the material is affected by the defects, though to different degrees. Nonetheless, the spectrum of electronic states and lattice vibrations were calculated for ideal crystal structures and the electronic and thermal properties of solids were explained in most of our previous considerations with the tacit assumption that the defect-related effects are negligible.

This is true for some properties of the solids. The thermodynamic or transport properties of metals are only weakly influenced by the defects, except for very low temperatures where the other scattering processes are frozen out and the impurities are responsible for the residual resistivity. Magnetic impurities play an even more spectacular role via the Kondo effect. The behavior of semiconductors cannot be understood at all if we forget about the donor and acceptor levels induced by the intentionally introduced impurities.

In studying these problems the dopants or impurities were assumed to be present in relatively low concentration and to act independently of each other. It was a legitimate approximation to consider the change in the electronic states around a single impurity. The impurity contribution to, e.g., the resistivity, the heat capacity, or the susceptibility is simply proportional to the number of impurities. A completely different treatment is needed when deviations from the regular arrangement of atoms are appreciable. When the positions of the atoms still form a regular crystalline lattice, but a fraction of the sites are randomly occupied by a different chemical substance, we are dealing with disordered alloys. The coherent potential approximation invented to tackle this problem will be briefly presented at the beginning of this chapter.

A different type of disorder is found in amorphous systems where the atoms do not form a regular lattice in the solid phase. As discussed in Chapter 10, the atomic arrangement is liquid like, as if the atoms were suddenly frozen at their positions in the liquid phase. Indeed, the easiest way to obtain amorphous materials is to quench them from the liquid state by rapid cooling. This type of disorder is found in glasses, too. That is why amorphous metals are also known as metallic glasses. The structural aspects of amorphous materials were touched upon briefly in Chapter 10. The ions are densely and randomly packed in metallic systems, while topological disorder is found when the ions are covalently bonded. As illustrated in Fig. 36.1, the covalent bonds may hold the ions together even when the ions are displaced from their crystalline positions. Whereas all bonds can be satisfied for slight displacements, dangling bonds occur for stronger disorder. Electrons that do not participate in the covalent bonding will strongly affect the physical properties of these materials. We will not go into such details, nor into the physics of metallic glasses. We restrict ourselves to one particularly interesting problem, namely to the question whether the electron states remain extended or become localized in a disordered system.



Fig. 36.1. (a) Distorted lattice where all covalent bonds are satisfied. (b) An amorphous structure with dangling bonds

We will consider a special problem at the end of the chapter. Disorder can be achieved by randomly placing atoms with magnetic moments into a nonmagnetic matrix. Depending on the distance between the magnetic ions the exchange coupling between them may be ferromagnetic or antiferromagnetic. Although the atomic moments are oriented in the direction of the local field at low temperatures, there is no global ordering, since the orientation of the local field generated by the randomly positioned neighbors is itself random. This static, randomly frozen-in, globally nonmagnetic state of the spin system is called a *spin glass*. We will present the most interesting properties of such systems and sketch the methods worked out to theoretically explain them.

36.1 Disordered Alloys

Alloys represent a simple class of disordered systems. Consider a binary alloy containing two types of atoms, A and B, with a fixed composition $A_x B_{1-x}$,

where the atoms randomly occupy the sites of a regular lattice.¹ A basic question concerning alloys is to what extent their electronic structure differs from that of the regular crystals composed exclusively of atoms of type A or atoms of type B. The theoretical description of disordered systems is more difficult than that of the crystalline state owing to the absence of an underlying lattice, owing to the absence of invariance under discrete translations. The states cannot be characterized by a wave vector for \mathbf{k} is not a good quantum number. The density of states remains, however, a physically meaningful quantity, and a series of observable physical quantities can be determined once the density of states is known. The density of states can be obtained from the one-particle Green function, so our primary aim is to show how the Green function of disordered alloys can be calculated.

For the sake of simplicity we consider a tight-binding model with a single electron state for each atom. Neglecting the spin and denoting the creation (annihilation) operator of the electron state at site i by $c_i^{\dagger}(c_i)$ the Hamiltonian of the model is

$$\mathcal{H} = \sum_{i} \varepsilon_{i} c_{i}^{\dagger} c_{i} + \sum_{i \neq j} t_{ij} c_{i}^{\dagger} c_{j} , \qquad (36.1.1)$$

where the energy ε_i in the diagonal part may take one of the two values: ε_A or ε_B . They appear with probability x and 1-x corresponding to the concentration of the atoms. The hopping integral between neighboring sites depends on whether the neighbors are of A–A, B–B, or A–B type. For simplicity the disorder in the overlap of the wavefunctions is usually neglected and a constant t is taken. This is a reasonable approximation when the potentials of the atoms do not differ significantly. The hopping integral t defines a bandwidth D = 2zt, where z is the coordination number (the number of nearest neighbors). The properties of the alloy depend on the parameter

$$\delta = (\varepsilon_{\rm A} - \varepsilon_{\rm B})/D \tag{36.1.2}$$

and on the concentrations $c_{\rm A} = x$ and $c_{\rm B} = 1 - x$.

The problem of the electronic structure will be considered as a scattering problem, how the electrons propagating in the system scatter on the random atomic potentials. We therefore write the Hamiltonian in the form

$$\mathcal{H} = \mathcal{H}_0 + V, \tag{36.1.3}$$

where \mathcal{H}_0 describes the homogeneous propagation and V is the sum of the atomic potentials. In what follows the atomic potentials will be denoted by $V_{\rm A}$ and $V_{\rm B}$, respectively.

36.1.1 Averaged T-Matrix Approximation

An alloy can most simply be described by considering an equivalent regular crystal with an effective average potential. The methods described in

¹ Even if the composition is stoichiometric and the atoms are ordered on two sublattices in the ground state, disordering may occur above a critical temperature.

Chapter 19 to calculate the electronic band structure of crystalline materials can then be used to get the electronic states. The simplest natural choice is a weighted average of the atomic potentials:

$$V_{\rm av} = c_{\rm A} V_{\rm A} + c_{\rm B} V_{\rm B} \,. \tag{36.1.4}$$

This is the *virtual-crystal approximation*. This might be a reasonable approximation when the potentials of the two types of atoms are not very different.

As mentioned before, the calculation of the electronic structure can be considered as a scattering problem. A natural generalization of the virtualcrystal approximation is then to use the scattering operator T and to average it instead of the potential. We recall some results of scattering theory. If the scattering potential is denoted by V, the scattering operator is defined via

$$T = V + VG_0T$$
 or $T = V + TG_0V$, (36.1.5)

where

$$G_0 = \frac{1}{\varepsilon - \mathcal{H}_0} \tag{36.1.6}$$

is the Green function operator of the noninteracting system. The formal solution is

$$T = \frac{V}{1 - G_0 V} \,. \tag{36.1.7}$$

The full Green operator in the presence of the potential,

$$G = \frac{1}{\varepsilon - \mathcal{H}_0 - V}, \qquad (36.1.8)$$

can be written formally as

$$\frac{1}{\varepsilon - \mathcal{H}_0 - V} = \frac{1}{\varepsilon - \mathcal{H}_0} \left(1 + V \frac{1}{\varepsilon - \mathcal{H}_0 - V} \right), \quad (36.1.9)$$

or in the concise form

$$G = G_0 + G_0 V G \,, \tag{36.1.10}$$

which is just the Dyson equation for the scattering problem. Iteration of this equation and comparison with (36.1.5) leads to the relationship

$$VG = TG_0$$
, (36.1.11)

and the full Green operator can be written as

$$G = G_0 + G_0 T G_0 \,. \tag{36.1.12}$$

The *T*-matrix for scattering by a single atom with potential V_i satisfies the equation

$$t_i = V_i + V_i G_0 t_i = \frac{V_i}{1 - G_0 V_i} \,. \tag{36.1.13}$$

For a collection of atoms with random potentials, the full potential is

$$V = \sum_{i} V_i \tag{36.1.14}$$

and the total T-matrix can also be written as a sum over lattice sites

$$T = \sum_{i} T_i \tag{36.1.15}$$

by introducing the quantity

$$T_i = V_i + T_i G_0 V = \frac{V_i}{1 - G_0 V}.$$
(36.1.16)

Using the relationship

$$T_i G_0 V = \frac{V_i}{1 - G_0 V} G_0 V = V_i G_0 T, \qquad (36.1.17)$$

we find

$$T_i = V_i + V_i G_0 T \,. \tag{36.1.18}$$

Separating from the total T-matrix the term belonging to site i and rearranging the terms give

$$(1 - V_i G_0)T_i = V_i + V_i G_0 \sum_{j \neq i} T_j, \qquad (36.1.19)$$

from which after division by $1 - V_i G_0$ and making use of (36.1.13) we get

$$T_i = t_i + t_i \sum_{j \neq i} G_0 T_j \,. \tag{36.1.20}$$

While t_i is the scattering operator of a single scattering center, the quantity T_i gives the contribution of the *i*th scattering center in the presence of other scatterers. Inserting this expression into the total *T*-matrix and then into the Green function, iteration leads to

$$G = G_0 + \sum_i G_0 t_i G_0 + \sum_i \sum_{j \neq i} G_0 t_i G_0 t_j G_0 + \cdots, \qquad (36.1.21)$$

which has a simple physical interpretation. The particle propagates freely until it first scatters at site i. After multiple scattering there described by t_i , it propagates to another site j, where it can again suffer multiple scattering before continuing. A succession of further multiple scatterings can occur.

The density of states can be obtained from the configurational average of the Green function. In the averaged T-matrix approximation the correlations between atoms are neglected and the approximation

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$$\langle G \rangle \approx G_0 + \sum_i G_0 \langle t_i \rangle G_0 + \sum_i \sum_{j \neq i} G_0 \langle t_i \rangle G_0 \langle t_j \rangle G_0 + \cdots$$
 (36.1.22)

is used. It is equivalent to

$$\langle T_i \rangle \approx \langle t_i \rangle + \langle t_i \rangle \sum_{j \neq i} G_0 \langle T_j \rangle.$$
 (36.1.23)

If the number of lattice sites N is large,

$$\langle T_i \rangle \approx \frac{\langle t_i \rangle}{1 - N \langle t_i \rangle G_0},$$
 (36.1.24)

and the expectation value of the total T-matrix is

$$\langle T \rangle \approx \frac{N \langle t_i \rangle}{1 - N \langle t_i \rangle G_0} \,.$$
 (36.1.25)

Substituting this expression into (36.1.12), the average of the Green function operator is

$$\langle G \rangle = G_0 + G_0 \langle T \rangle G_0 = \frac{G_0}{1 - N \langle t_i \rangle G_0} \,. \tag{36.1.26}$$

The Green function, the density of states, and other physical quantities are thus obtained from the average of the atomic t-matrix.

36.1.2 Coherent-Potential Approximation

The coherent-potential approximation (CPA)² goes one step further. To appreciate the underlying physical idea we recall that the KKR equations of the band structure calculation are equivalent to the self-consistency condition that the system is in a stationary state, when the wave incident on any muffin-tin sphere should be equal to the sum of the waves scattered from all other cells. We will therefore consider a homogeneous system with an as yet unknown coherent potential V_{CPA} which is chosen from the requirement that no scattering occurs on the average if this fictitious uniform potential is replaced by the true atomic potential at a single site with the appropriate probability.

The Green operator of the fictitious homogeneous system is

$$G_{\rm C}^{-1} = G_0^{-1} - V_{\rm CPA} \,.$$
 (36.1.27)

Taking now $\overline{V}_i = V_i - V_{\text{CPA}}$ as a perturbation, the scattering operator for scattering on site *i* alone is

$$\bar{t}_i = \overline{V}_i + \overline{V}_i G_{\text{CPA}} \bar{t}_i = \frac{\overline{V}_i}{1 - G_{\text{CPA}} \overline{V}_i}, \qquad (36.1.28)$$

² P. SOVEN, 1967.

and the total Green function satisfies the equation

$$G = G_{\text{CPA}} + \sum_{i} G_{\text{CPA}} \bar{t}_{i} G_{\text{CPA}} + \sum_{i} \sum_{j \neq i} G_{\text{CPA}} \bar{t}_{i} G_{\text{CPA}} \bar{t}_{j} G_{\text{CPA}} + \cdots$$
(36.1.29)

The total T-matrix can be written as

$$T = \sum_{i} \overline{T}_{i} , \qquad (36.1.30)$$

where

$$\overline{T}_i = \overline{t}_i + \overline{t}_i \sum_{j \neq i} G_{\text{CPA}} \overline{T}_j .$$
(36.1.31)

So far these transformations are exact. Since we require that deviations from $V_{\rm CPA}$ do not give rise to scattering on the average, CPA is equivalent to the condition

$$\left\langle \bar{t}_i \right\rangle = 0. \tag{36.1.32}$$

If short-range order in the spatial distribution of atoms is neglected, the configurational average of the Green function is equal in a good approximation (up to third order in \overline{V}_i) to the Green function of the regular crystal with the coherent potential

$$\langle G \rangle \approx G_{\rm CPA} \,. \tag{36.1.33}$$

Using (36.1.28) we readily find

$$V_{\rm CPA} = c_{\rm A} V_{\rm A} + c_{\rm B} V_{\rm B} + (V_{\rm CPA} - V_{\rm A}) G_{\rm CPA} (V_{\rm CPA} - V_{\rm B}).$$
(36.1.34)

Taking the first two terms on the right-hand side, the virtual-crystal approximation is recovered. Combining the CPA with the methods of the band structure calculation the electronic spectrum of disordered alloys can be described quite reasonably. A merit of this approach is that it can be extended to other disordered problems as well. It can be used, for example, to calculate the magnetic properties of metals in both the ferromagnetic and paramagnetic phases, where disorder is due to the fluctuating magnetic moment.

36.2 The Anderson Metal–Insulator Transition

The knowledge of the energy spectrum is not sufficient for describing the physical properties of disordered systems. It was pointed out by P. W. ANDERSON as early as in 1958 that the character of the electronic states may change in the presence of disorder. The extended Bloch-like wavefunctions with nonvanishing $|\psi(\mathbf{r})|^2$ in the entire sample may be transformed into localized states owing to multiple scattering by impurities. Taking the absolute square of the wavefunction at positions r and r', that is the probability density of finding the electrons there, the average of their product over the random configurations decays exponentially. The localization length ξ_{loc} is defined by the relation

$$\left[|\psi(\mathbf{r})|^2 |\psi(\mathbf{r}')|^2 \right]_{\rm av} \propto e^{-|\mathbf{r} - \mathbf{r}'|/\xi_{\rm loc}} \,. \tag{36.2.1}$$

It is a fundamental problem to know under what circumstances electrons in the vicinity of the Fermi surface become localized. If the localization conditions are met, the material, which is metallic in the absence of disorder, becomes insulating. We will only consider some of the aspects of this problem which have far-reaching consequences.

36.2.1 Anderson Localization

The problem can be formulated very simply in the tight-binding description of electron states. Neglecting the interaction between electrons and the spin variable, we will study the states of the Hamiltonian

$$\mathcal{H} = \sum_{i} \varepsilon_{i} c_{i}^{\dagger} c_{i} + \sum_{i \neq j} t_{ij} c_{i}^{\dagger} c_{j} \,. \tag{36.2.2}$$

Disorder might occur for two reasons. First, in contrast to alloys, where ε_i can take a few discrete values associated with the different types of atoms, the atomic energy ε_i may be distributed randomly over an energy range in amorphous systems. Second, the hopping amplitude between neighboring atoms may vary randomly. The former is called diagonal disorder, the latter offdiagonal disorder. ANDERSON assumed for the sake of simplicity that the off-diagonal disorder is negligible, each atom is surrounded by z nearest neighbors, and the amplitude of the hopping matrix element between them has the same value t. Disorder appears in the atomic energies which are distributed uniformly over a range of width W, that is, the probability distribution of the on-site energies is

$$P(\varepsilon_i) = \begin{cases} \frac{1}{W} & \text{for } |\varepsilon_i| \le \frac{W}{2}, \\ 0 & \text{otherwise.} \end{cases}$$
(36.2.3)

In an ordered system, where ε_i is identical for all sites, the tight-binding model would give extended Bloch states in a band of width D = 2zt. The product $|\psi(\mathbf{r})|^2 |\psi(\mathbf{r}')|^2$ would be independent of the distance between \mathbf{r} and \mathbf{r}' . P. W. ANDERSON raised the question in 1958 whether a particle can diffuse to arbitrary distance when impurities are present.

The answer is known for one-dimensional systems. The effect of disorder can be determined exactly in the Kronig–Penney model,³ where the atomic

³ R. de L. Kronig and W. G. Penney, 1931.

potential is approximated by a square potential well. All states are localized for arbitrarily weak randomness in the depth of the potential wells. The product $[|\psi(\mathbf{r})|^2|\psi(\mathbf{r}')|^2]_{av}$ decays exponentially as announced in (36.2.1). A disordered one-dimensional system cannot be metallic. The question is what happens in higher dimensions.

ANDERSON has shown that diffusion of electrons remains possible in threedimensional systems for electrons near the Fermi energy as long as the parameter W characterizing the disorder is weak compared to the bandwidth. Diffusion stops when W exceeds a critical value (an early estimate gave $W_c \approx 5D$) and all electron states become localized. This localization owing to the presence of disorder is known as Anderson localization.

MOTT⁴ pointed out that a so-called *mobility edge* lying inside the band separates the extended electron states from the localized ones for weak disorder. This is illustrated in Fig. 36.2. The density of states may be nonvanishing in a broader energy range than in the ordered system, the band develops tails both above and below the band, but the mobility $\mu(\varepsilon)$ defined in connection with the Kubo–Greenwood formula vanishes near the band edges. The states in the middle part of the band remain extended. The position of the mobility edge varies with the disorder.



Fig. 36.2. Electronic density of states of a disordered system with the mobility edge. Dashed line indicates the density of states in the absence of disorder

These observations have been followed by extensive numerical studies on the localized and delocalized nature of the electronic states. The results obtained for the three-dimensional model defined by (36.2.2) and (36.2.3) are displayed in Fig. 36.3. The bandwidth, which would have been 12t without disorder, is enhanced. The states in the tails are localized. For strong disorder, when W/t exceeds a critical value of $(W/t)_c = 16.5$ for the above model according to the numerical calculations, all states become localized.

Similar results are obtained for other distributions of the atomic energies. Taking a Gaussian probability distribution,

$$P(\varepsilon_i) = \frac{1}{\sqrt{2\pi W^2}} \exp\left(-\frac{\varepsilon_i^2}{2W^2}\right), \qquad (36.2.4)$$

⁴ N. F. Mott, 1966.



Fig. 36.3. Position of the mobility edge as a function of the diagonal disorder for a simple cubic lattice. States in the hashed region are localized [Reprinted with permission from A. D. Zdetsis et al., *Phys. Rev. B* **32**, 7811 (1985). © (1985) by the American Physical Society]

the critical disorder above which all state are localized is $(W/t)_c = 6.1$, while for a Lorentzian distribution

$$P(\varepsilon_i) = \frac{1}{\pi} \frac{W}{\varepsilon_i^2 + W^2} \tag{36.2.5}$$

we find $(W/t)_{c} = 4.3$.

The effect of disorder, either diagonal or off-diagonal, is drastically different in two-dimensional systems. We will return to this problem later on.

36.2.2 Continuous or Discontinuous Transition

It follows from the foregoing results that a three-dimensional metal becomes insulating if the mobility edge crosses the Fermi energy as disorder increases. This is the Anderson metal-insulator transition. An important difference compared to the Mott metal-insulator transition is the absence of gap in the energy spectrum. All band energies remain allowed. However, the states near the Fermi energy become localized with the result that they cannot conduct current at T = 0.

It seems plausible to assume that the Boltzmann equation based on the semiclassical approximation can be applied on the metallic side of the transition provided that the mean free path of electrons⁵ is longer than the Fermi wavelength (the distance over which the phase of electrons at the Fermi surface changes by 2π), that is, if $k_{\rm F}l > 1$. This is the *Ioffe-Regel criterion*⁶ for the existence of extended states. Electron states may exist in the opposite limit, when the mean free path is shorter than the Fermi wavelength, but they are localized. The transition from extended to localized states, from metallic

⁵ The statement will be refined later. It will be argued that the relevant distance is the phase-breaking length over which the electron wavefunction loses phase coherence.

⁶ A. F. IOFFE and A. R. REGEL, 1960.

to insulating behavior, occurs when the mean free path reaches the *Ioffe-Regel* limit, $k_{\rm F} l \approx 1$.

MOTT assumed that the transition is discontinuous, first order. It then follows that there exists a minimum metallic conductivity. To get an estimate we take the Drude form for the conductivity,

$$\sigma = \frac{n_{\rm e}e^2\tau}{m_{\rm e}} = \frac{n_{\rm e}e^2l}{\hbar k_{\rm F}}\,,\qquad(36.2.6)$$

where the relaxation time is expressed in terms of the mean free path using $\tau = l/v_{\rm F}$. In a three-dimensional system, where $n_{\rm e} = k_{\rm F}^3/3\pi^2$ and therefore

$$\sigma_{3\rm D} = \frac{1}{3\pi^2} \frac{e^2}{\hbar} k_{\rm F}(k_{\rm F}l) \,, \qquad (36.2.7)$$

the conductivity has to be larger than

$$\sigma_{3D}^{\min} \approx \frac{1}{3\pi^2} \frac{e^2}{\hbar} \frac{1}{a},$$
 (36.2.8)

where a is a microscopic length scale, since the inverse of $k_{\rm F}$ is on the order of atomic distances. The minimum metallic conductivity should then be of order $10^5 \,{\rm S/m}$. For two-dimensional systems, where $n_{\rm e} = k_{\rm F}^2/2\pi$, and consequently

$$\sigma_{2\rm D} = \frac{1}{2\pi} \frac{e^2}{\hbar} (k_{\rm F} l) \,, \tag{36.2.9}$$

the minimum metallic conductivity would have a universal value with no length scale in it,

$$\sigma_{\rm 2D}^{\rm min} \approx 0.1 \frac{e^2}{\hbar} \approx 3 \times 10^{-5} \,\Omega^{-1} \,.$$
 (36.2.10)

It corresponds to a maximum universal metallic sheet resistance⁷ of order $R_{\Box} \approx 30 \,\mathrm{k}\Omega/\Box$. The same minimum metallic conductivity has been predicted by MOTT for the metal-insulator transition due to electron-electron interactions.

It can be seen from Fig. 36.4, which shows the conductivity extrapolated to $T \rightarrow 0$ of silicon doped with phosphorus as a function of the dopant concentration, that the conductivity starts to decrease rather sharply when it comes close to the minimum metallic conductivity – the donor concentration, where this happens, corresponds to the Ioffe–Regel criterion – one can measure conductivities which are orders of magnitude smaller than the predicted minimum value. The metal–insulator transition is extremely sharp, but continuous, the conductivity vanishes as some power of the deviation from the critical concentration.

⁷ The sheet resistance R_{\Box} or $R_{\rm s}$ is the resistance of a thin film of thickness t if the length L and the width W of the film are equal and the current flows in the plane of the film. $R_{\rm s} = \rho/t$. The unit for sheet resistance is the ohm, but ohm per square (Ω/\Box) is also commonly used.



Fig. 36.4. Zero-temperature conductivity of metallic P-doped Si as a function of the donor density [Reprinted with permission from T. F. Rosenbaum, *Phys. Rev. Lett.*, **45**, 1723 (1980). © (1980) by the American Physical Society]

36.2.3 Phase Coherence and Interference of Electrons

To get a physical picture of the mechanism underlying localization, consider the propagation of a particle from r_1 to r_2 . A few possible diffusive trajectories are depicted in Fig. 36.5.



Fig. 36.5. Several paths for the diffusive propagation of a particle from r_1 to r_2

If the probability amplitude for the *i*th path is denoted by A_i , the probability of reaching the point r_2 is given by

$$W = \left|\sum_{i} A_{i}\right|^{2} = \sum_{i} \left|A_{i}\right|^{2} + \sum_{i \neq j} A_{i} A_{j}^{*}.$$
 (36.2.11)

The classical transport theory is based on the assumption that electrons lose their quantum mechanical phase during the scattering processes and when there is no phase coherence between particles following the different paths, the wavefunctions cannot interfere and the second term on the right-hand side is averaged out. The transition probability to get to r_2 is then equal to the sum of the probabilities of the individual trajectories.

The situation may change at low temperatures. The inelastic electronphonon processes, which are dominant at higher temperatures, and also the inelastic electron-electron interactions are gradually frozen out as the temperature decreases. The average time τ_{in} between inelastic scattering processes may become longer than the scattering time τ due to elastic processes. The distinction is important since the wave vector (or momentum) is changed in elastic potential scattering, but the phase of the wavefunction is conserved, while electrons lose their phase coherence in inelastic processes and also in spin-flip scattering by magnetic impurities. The inelastic scattering time $\tau_{\rm in}$ is also known as the phase-coherence time, phase-breaking time, or dephasing time and will be denoted by τ_{ϕ} . Classical transport theory can be applied when $\tau_{\phi} \ll \tau$. The inequality may be reversed at low temperatures, where inelastic processes become less frequent. Even though the electrons are frequently scattered elastically and propagate diffusively, not ballistically, between inelastic processes, phase coherence is maintained for a time $\tau_{\phi} \gg \tau$ and quantum interference can occur.

Along with the two characteristic timescales, we have to distinguish several length scales. $l = v_{\rm F}\tau$ is the mean free path for elastic scatterings and $l_{\phi} = v_{\rm F}\tau_{\phi}$ is the inelastic mean free path. At low temperatures, where $\tau_{\phi} \gg \tau$, the relevant distance over which the wave packet loses its phase coherence is the *phase-coherence length* or *phase-breaking length*, also known as the *Thouless length*,⁸ given by

$$L_{\phi} = \left(D\tau_{\phi}\right)^{1/2}, \qquad (36.2.12)$$

where D is the diffusion coefficient. The elastic scattering time and the mean free path being related to the diffusion coefficient via

$$D = v_{\rm F}^2 \tau / d = v_{\rm F} l / d \tag{36.2.13}$$

for a *d*-dimensional system, the phase-coherence length is the geometric mean of the elastic and inelastic mean free paths,

$$L_{\phi} \approx \left(l \, l_{\phi}\right)^{1/2}.\tag{36.2.14}$$

To see the effect of coherence consider a self-intersecting trajectory from r_1 to r_2 shown in Fig. 36.6(a) together with the path, where the electron travels along the closed loop in opposite direction.

The change of the phase along a path is given by the line integral

$$\Delta \phi = \frac{1}{\hbar} \int_{\boldsymbol{r}_1}^{\boldsymbol{r}_2} \boldsymbol{p} \cdot \mathrm{d} \boldsymbol{l} \,. \tag{36.2.15}$$

⁸ D. J. THOULESS, 1977.



Fig. 36.6. (a) Self-intersecting diffusive trajectory in real space. (b) The corresponding path in momentum space

When the electron traverses the closed loop in the opposite direction and all processes are elastic, the same phase difference is obtained; since the two paths are related by time reversal, they can be transformed into each other by reversing \boldsymbol{p} and $d\boldsymbol{l}$ simultaneously $(\boldsymbol{p} \rightarrow -\boldsymbol{p} \text{ and } d\boldsymbol{l} \rightarrow -d\boldsymbol{l})$. The contribution of these processes to the quantum mechanical probability of diffusion from \boldsymbol{r}_1 to \boldsymbol{r}_2 is

$$W_{\text{quant}} = 2|A|^2 + 2AA^* = 4|A|^2$$
 (36.2.16)

instead of the classical result

$$W_{\text{class}} = 2 |A|^2,$$
 (36.2.17)

since the interference term does not vanish. This shows that if phase coherence is maintained along the paths, the quantum mechanical interference enhances the return probability. The particle has a higher chance to return to the origin than a particle that diffuses incoherently. This implies that the probability to diffuse away from the origin decreases at low temperatures in a disordered system. Consequently the electron states become less extended and the conductivity decreases. Ultimately this may lead to the localization of electrons when the probability of return to an initial position is so overwhelming that the electron cannot escape. Since it is more likely to find self-intersecting paths in low dimensions, this effect manifests itself much more strongly in low-dimensional systems (films and wires).

It is worthwhile to show the two time-reversed paths in momentum representation. Assume that the electron undergoes a series of elastic scatterings with momentum transfers q_1, q_2, \ldots, q_n remaining always on the Fermi surface as shown in Fig. 36.6(b). The initial momentum k changes to -k at the end:

$$\mathbf{k} \rightarrow \mathbf{k}_1' = \mathbf{k} + \mathbf{q}_1 \rightarrow \mathbf{k}_2' = \mathbf{k}_1' + \mathbf{q}_2 \rightarrow \cdots \rightarrow -\mathbf{k} = \mathbf{k}_{n-1}' + \mathbf{q}_n.$$
 (36.2.18)

Consider now the process where the momentum transfer is q_n in the first step, q_{n-1} in the second step, and q_1 in the last step:

$$k \to k_1'' = k + q_n \to k_2'' = k_1'' + q_{n-1} \to \dots \to -k = k_{n-1}'' + q_1.$$
 (36.2.19)

The electron with momentum k is scattered into the state with -k at the end. The interference of these events gives rise to an increased probability of backward scattering, increasing the resistivity, i.e., decreasing the conductivity.

36.2.4 Oscillation Phenomena due to Phase Coherence

A direct consequence of the phase coherence is that oscillatory phenomena can be observed experimentally in normal metals at low temperatures. Y. AHARONOV and D. BOHM proposed a particular interference effect in 1959. If a beam of electrons of charge -e is split into two and the two beams propagate on opposite sides of a region traversed by a magnetic flux, the interference pattern of the beams depends on the strength of the magnetic field even if the electron beams do not penetrate into the region where $B \neq 0$. An analogous phenomenon has already been discussed in Chapter 26 in connection with the Josephson effect: the relative phase of two superconductors connected in parallel depends on the enclosed flux. Our considerations there concerned the macroscopic phase of superconductors. Here we consider the quantum mechanical phase of normal electrons.

If an electron propagates in a region where the vector potential is nonvanishing, the probability amplitude A_i associated with the trajectory is modified by a multiplicative factor,

$$A_i \to A_i \exp\left(\frac{\mathrm{i}e}{\hbar} \int \mathbf{A} \cdot \mathrm{d}l\right).$$
 (36.2.20)

The change in the phase as the particle travels from r_1 to r_2 is given by the line integral

$$\phi(\boldsymbol{r}_2) - \phi(\boldsymbol{r}_1) = \frac{e}{\hbar} \int_{\boldsymbol{r}_1}^{\boldsymbol{r}_2} \boldsymbol{A} \cdot d\boldsymbol{l} . \qquad (36.2.21)$$

If the beam is split into two and the two parts follow different paths, but come together at one point, the difference between the phase changes along the two trajectories is

$$\Delta \phi = \frac{e}{\hbar} \oint \mathbf{A} \cdot d\mathbf{l} = \frac{e}{\hbar} \int \operatorname{curl} \mathbf{A} \cdot d\mathbf{S} = \frac{e}{\hbar} \Phi = \pi \frac{\Phi}{\Phi_0}, \qquad (36.2.22)$$

where Φ is the flux going through the surface enclosed by the split beams and $\Phi_0 = h/2e$ is the SI unit of the magnetic flux quantum. An oscillation with period $\Delta \Phi = 2\Phi_0$ should be observed as the magnetic field is varied, if the phase coherence of the electron beams is not destroyed by scattering processes.

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Analogous oscillations can easily be observed in superconductors where the phase is a macroscopic quantity, but the oscillation period is $\Delta \Phi = \Phi_0$ and not $\Delta \Phi = 2\Phi_0$ since the carriers are Cooper pairs with charge -2e. It was thought for a long time that the Aharonov–Bohm effect cannot be observed in normal metals since electrons lose the phase coherence in the scattering processes over a relatively short distance, on a mesoscopic length scale. The developments in nanotechnology allowed us to fabricate samples where these quantum effects are observable. As shown in Fig. 36.7, the resistivity as a function of the magnetic field oscillates with period h/e at low temperatures in very small samples with linear extension smaller than the phase-coherence length.



Fig. 36.7. Aharonov–Bohm oscillations with period h/e measured in a normal gold ring with inner diameter less than 1 µm. The left panel shows the magnetoresistance at several temperatures and the right panel is the Fourier spectrum of the data on the left panel [Reprinted with permission from R. A. Webb et al., *Phys. Rev. Lett.* 54, 2696 (1985). \bigcirc (1985) by the American Physical Society]

A different oscillation was predicted by B. L. ALTSHULER, A. G. ARONOV, and B. Z. SPIVAK in 1981, a few years before the usual Aharonov–Bohm oscillations could be observed in normal metals. They pointed out that the conductance of a thin-walled cylinder is an oscillatory function of the magnetic flux inside the cylinder with period h/2e and not h/e, even if the sample is not superconducting. The experimental results are shown in Fig. 36.8.

The difference between the Aharonov–Bohm effect and the Altshuler– Aronov–Spivak effect can be best understood by looking at the schematic representation of the geometry of the measurements seen in Fig. 36.9. The electron wave propagates in the Aharonov–Bohm effect in the two arms of the interferometer. The phase difference given in (36.2.22) comes from the difference between the phases in the left and right arms. In contrast to this, the Altshuler–Aronov–Spivak effect arises from the interference of trajectories



Fig. 36.8. Resistivity oscillations with period h/2e for a narrow cylinder [D. Yu. Sharvin, Yu. V. Sharvin, *JETP Lett.*, 34, 272 (1981)]



Fig. 36.9. Trajectory of electrons (a) in the Aharonov–Bohm effect of period h/e and (b) in the Altshuler–Aronov–Spivak effect of period h/2e

going fully around the cylinder, but in opposite directions. The electron makes a full turn on both trajectories; its phase changes by

$$\delta\phi = \frac{e}{\hbar}\Phi = \pi\Phi/\Phi_0 \tag{36.2.23}$$

in one direction and by $-\pi \Phi/\Phi_0$ when it goes around the cylinder in the opposite direction. The contribution of the two paths to the return probability is

$$W(B) = \left[2A\cos\pi\Phi/\Phi_0\right]^2 = 2|A|^2 \left[1 + \cos 2\pi\Phi/\Phi_0\right].$$
 (36.2.24)

Hence the magnetoresistance oscillates with period $\Delta \Phi = h/2e$ in this geometry.

36.2.5 Quantum Corrections to Conductivity, Weak Localization

The constructive interference discussed above occurs on paths that are shorter than the phase-coherence length. In other words the trajectory should be traversed in less than the phase-coherence time τ_{ϕ} . As the dephasing time τ_{ϕ} exhibits a T^{-p} temperature dependence with p depending on the scattering mechanism (its value is typically between 1 and 2), interference effects may become relevant at low temperatures and may drastically change the conductivity of the sample.

To get an estimate of the effect we make use of the fact that the electron propagates ballistically for times shorter than the elastic relaxation time τ , and the propagation is diffusive for longer times. The probability P(r,t) that the particle gets to a distance r during time t can be obtained from solving Fick's second law⁹ for diffusion,

$$\frac{\partial P(r,t)}{\partial t} = D\boldsymbol{\nabla}^2 P(r,t), \qquad (36.2.25)$$

where $D \propto v_{\rm F}^2 \tau$ is the diffusion coefficient. The normalized solution for a *d*-dimensional system is

$$P(r,t) = (4\pi Dt)^{-d/2} e^{-r^2/4Dt}.$$
(36.2.26)

We will apply it to one-, two-, and three-dimensional systems. Note that we have in mind one- and two-dimensional systems in the physical sense. A sample can be considered as effectively one dimensional, if the linear extension is on the order of the Fermi wavelength in two directions and much longer in the third direction. Similarly, a sample is effectively two dimensional if the linear extension is small, on the order of the Fermi wavelength, in one direction only. The thickness of a film or the radius of a wire can in fact be even bigger. Since the most relevant timescale for seeing the quantum effects is the dephasing time, a film is two dimensional in its physical behavior if the time – on the order of a^2/D – needed for an electron to diffuse across the film of thickness *a* is much smaller than τ_{ϕ} . A similar limit can be set for the radius of a wire.

The diffusive range of an electron in time t is $(Dt)^{1/2}$, and the probability of return to the neighborhood of the origin after a time t is proportional to the inverse of the volume $(Dt)^{d/2}$ within which the electron has diffused. The probability of return to precisely the origin is of course zero for a pointlike object. However, the electron can be viewed as a wave packet with linear extension on the order of the Fermi wavelength $\lambda_{\rm F} \sim 1/k_{\rm F}$. It sweeps out a volume element $\lambda_{\rm F}^{d-1}v_{\rm F}dt$ in a time dt by ballistic motion. The wave packet can interfere with itself provided it returns to such a volume element about the origin at some time t. The probability for this to happen in the interval dt after time t is

$$P(\mathbf{r} = 0, t)\lambda_{\rm F}^{d-1}v_{\rm F} dt = \frac{\lambda_{\rm F}^{d-1}v_{\rm F}}{(4\pi D t)^{d/2}} dt.$$
(36.2.27)

The decrease of the conductivity is proportional to the return probability

⁹ A. E. FICK, 1855.

$$\frac{\delta\sigma}{\sigma_0} \sim -\int_{\tau}^{\tau_{\phi}} \frac{\lambda_{\rm F}^{d-1} v_{\rm F}}{(4\pi Dt)^{d/2}} \mathrm{d}t \,. \tag{36.2.28}$$

The lower and upper limits of integration are obtained from physical considerations. The diffusive motion sets in after the elastic mean free time. The propagation is ballistic for shorter times; there is no chance for return. As for the upper limit, phase coherence is lost for times longer than τ_{ϕ} , an electron returning after a longer time cannot interfere with itself. When $\tau_{\phi} \gg \tau$ we find

$$\frac{\delta\sigma}{\sigma_0} \sim \begin{cases} -\frac{1}{(k_{\rm F}l)^2} \left[1 - \left(\frac{\tau}{\tau_{\phi}}\right)^{1/2} \right] & d = 3, \\ -\frac{1}{k_{\rm F}l} \ln(\tau_{\phi}/\tau) & d = 2, \\ -(\tau_{\phi}/\tau)^{1/2} & d = 1. \end{cases}$$
(36.2.29)

Expressed in terms of the phase-coherence length,

$$\frac{\delta\sigma}{\sigma_0} \sim \begin{cases} -\frac{1}{(k_{\rm F}l)^2} \left[1 - \frac{l}{L_{\phi}} \right] & d = 3, \\ -\frac{1}{k_{\rm F}l} \ln(L_{\phi}/l) & d = 2, \\ -L_{\phi}/l & d = 1. \end{cases}$$
(36.2.30)

The prefactors can be determined using the methods of the many-body problem. We have seen in Chapter 29 that the conductivity can be calculated according to the Kubo formula from the current–current correlation function. The Drude result for scattering by impurities can be recovered by summing up to infinite order the contributions of a series of special processes depicted in Fig. 36.10(a). The dashed lines with a cross denote scattering by the impurity. The leading correction to the Drude result comes from another special class of diagrams, the so-called maximally crossed diagrams depicted in Fig. 36.10(b). These processes correspond to the self-intersecting trajectories with closed loops shown in Fig. 36.6.



Fig. 36.10. Diagrams representing the current–current correlation function. Dashed lines indicate the impurity scattering. (a) Typical diagram corresponding to the Drude result. (b) Example of maximally crossed diagrams contributing to the leading quantum corrections

The inelastic processes are frozen out at T = 0 and the propagation of electrons is limited by the size of the sample. Taking a *d*-dimensional hypercube of edge length L, the contributions of the maximally crossed diagrams give

$$\delta\sigma(L) = -c_d \left(\frac{e^2}{\hbar}\right) \frac{l^{2-d}}{d-2} \left[1 - \left(\frac{L}{l}\right)^{2-d}\right], \qquad (36.2.31)$$

where $c_d = (2/\pi)S_d/(2\pi)^d$ and S_d is the surface area of the *d*-dimensional unit sphere. For a three-dimensional system we have

$$\sigma_{3D}(L) = \sigma_0 - \frac{e^2}{\pi^3 \hbar} \left[\frac{1}{l} - \frac{1}{L} \right], \qquad (36.2.32)$$

whereas in two dimensions

$$\sigma_{2D}(L) = \sigma_0 - \frac{e^2}{\pi^2 \hbar} \ln \frac{L}{l}, \qquad (36.2.33)$$

while in one dimension

$$\sigma_{1D}(L) = \sigma_0 - \frac{e^2}{\pi\hbar} (L - l) \,. \tag{36.2.34}$$

In the regime where the first quantum corrections become observable, we speak of weak localization.

The inelastic processes and the loss of phase coherence caused by them on a length scale L_{ϕ} should be taken into account at finite temperatures. The conductivity can be obtained by replacing the size of the sample L in the previous formulas with the temperature-dependent L_{ϕ} . We then recover (36.2.30). With the assumption $\tau_{\phi} \propto T^{-p}$ for the inelastic relaxation time, $L_{\phi} \propto T^{-p/2}$, and we have

$$\sigma(T) = \begin{cases} \sigma_0 + \frac{e^2}{\pi^3 \hbar} \frac{1}{a} T^{p/2} & d = 3, \\ \sigma_0 + \frac{p}{2} \frac{e^2}{\pi^2 \hbar} \ln\left(\frac{T}{T_0}\right) & d = 2, \\ \sigma_0 - \frac{ae^2}{\pi \hbar} T^{-p/2} & d = 1, \end{cases}$$
(36.2.35)

where a is a microscopic length scale. The conductivity decreases in all three cases with decreasing temperature. This decrease is rather small in three dimensions, the quantum mechanical interference only gives a slight correction to the classical Drude result. Quantum corrections are more pronounced in two- and one-dimensional systems. The resistance of thin-film samples displayed in Fig. 36.11 exhibits one of the most spectacular consequences



Fig. 36.11. (a) Resistance of thin films vs. voltage on a logarithmic scale for various temperatures. (b) The plateau values of the resistance plotted against $\log T$ [Reprinted with permission from G. J. Dolan and D. D. Osheroff, *Phys. Rev. Lett.* 43, 721 (1979). (c) (1979) by the American Physical Society]

of weak localization, namely the logarithmic dependence of the resistance on temperature in a two-dimensional system.

As seen in the figure, the dependence of the resistance on the voltage is similarly logarithmic. The phase of the electrons can be modified by an external magnetic field and this can destroy the interference. The conductance increases (resistance decreases) when magnetic field is applied, as seen in Fig. 36.12. The measured field dependence is in good agreement with the prediction of the theory of weak localization.



Fig. 36.12. Low-field magnetoresistance of a silicon(111) MOSFET at several temperatures [Reprinted with permission from D. J. Bishop, R. C. Dynes, and D. C. Tsui, *Phys. Rev. B* **26**, 773 (1982). (c) (1982) by the American Physical Society]

36.2.6 Strong Localization, Hopping Conductivity

The semiclassical treatment of conduction with quantum corrections is applicable to the diffusive motion of electrons, when the electron states are extended. Electrons in localized states do not contribute to the conductivity at zero temperature. They may be thermally excited to extended states or to an empty localized state at finite temperature and electrical current may be generated by an electric field. Electrons can "hop" by quantum mechanical tunneling between localized states if there is a finite overlap between the wavefunctions. The system has to be at finite temperatures since the energy of the overlapping nearby states is normally different, and this energy difference has to be transferred to or gained from another degree of freedom, usually the phonon system.

The hopping probability is proportional to the overlap and depends on the energy mismatch. It is a plausible assumption that the contribution of hopping over a distance r to the conductivity depends exponentially on the distance and on the energy difference, that is

$$\sigma \propto \exp(-2\alpha r - \Delta \varepsilon / k_{\rm B}T)$$
. (36.2.36)

An electron can jump with the same probability to a greater spatial distance if the energy difference between the states is smaller. This mechanism is known as the *variable-range hopping* (VRH). Taking a *d*-dimensional sphere of radius r, the number of states in an energy interval ΔE is

$$Cr^d \rho(\varepsilon_{\rm F}) \Delta E$$
, (36.2.37)

where C is constant of order unity and $\rho(\varepsilon)$ is the density of states. The typical energy difference between the levels an electron sees, if it can hop to a distance r, is given by

$$\Delta \varepsilon = \frac{1}{Cr^d \rho(\varepsilon_{\rm F})}, \qquad (36.2.38)$$

The biggest contribution to the current comes from the most probable hopping distance determined from the extremum condition

$$\frac{\mathrm{d}}{\mathrm{d}r} \left(2\alpha r + \frac{1}{Cr^d \rho(\varepsilon_{\mathrm{F}})k_{\mathrm{B}}T} \right) = 0.$$
(36.2.39)

Assuming that the hops to the most probable distance, which increases with decreasing temperature as $T^{-1/(d+1)}$, dominate the conductivity, the temperature dependence of the conductivity exhibits an activated form,

$$\sigma \propto \exp\left[-(T_0/T)^{1/(d+1)}\right].$$
 (36.2.40)

The logarithm of the conductivity due to the variable-range hopping plotted against $T^{-1/4}$ shows a linear characteristic with negative slope for threedimensional systems. This relationship is known as the Mott $T^{-1/4}$ law.¹⁰

¹⁰ N. F. Mott, 1968.

The theory predicts the values -1/3 and -1/2 for the exponent for two- and one-dimensional systems, respectively. Hopping conduction has been observed in many materials. Figure 36.13(a) displays the temperature dependence of the conductivity of three differently doped compensated *n*-type GaAs samples. The temperature dependence is in agreement with MOTT's prediction for three-dimensional systems. Figure 36.13(b) shows the resistivity of a strongly disordered two-dimensional electron system produced in a semiconductor heterojunction. The density can be varied by changing the gate voltage. In the density range where the conductance is much smaller than the Mott minimum metallic conductance, the logarithm of the resistance varies as $T^{-1/3}$, as expected for two-dimensional systems.



Fig. 36.13. (a) Logarithm of the conductivity plotted against $T^{-1/4}$ for three samples of compensated *n*-type GaAs [Reprinted with permission from M. Benzaquen and D. Walsh, *Phys. Rev. B* **30**, 7287 (1984). \bigcirc (1984) by the American Physical Society]. (b) Temperature dependence of the resistance for a strongly disordered twodimensional electron gas generated in a GeAs/AlGeAs heterojunction [Reprinted with permission from H. W. Jiang, C. E. Johnson, and K. L. Wang, *Phys. Rev. B* **46**, 12830 (1992). \bigcirc (1992) by the American Physical Society]

Note that the Coulomb interaction between electrons has been neglected in MOTT's argument. This interaction has to be taken into account at very low temperatures, since screening is not effective in the regime where electrons are more or less localized. The temperature dependence of the conductivity is then given by the *Efros-Shklovskii law*¹¹

¹¹ A. L. EFROS and B. I. SHKLOVSKII, 1975.

$$\sigma \propto \exp\left[-(T_0/T)^{1/2}\right] \tag{36.2.41}$$

irrespective of the dimensionality.

The variable-range hopping mechanism gives a nonvanishing conductivity if the electrons can hop from one end of the sample to the other. This requires, in the language of percolation theory, a dopant concentration exceeding the percolation threshold. The conductance shows a power-law dependence on the dopant concentration in agreement with percolation theory.

36.2.7 Scaling Theory of Localization

The two particular cases treated until now, weak localization and strong localization, allowed us to determine the temperature dependence of the resistivity in the two limits. Weak localization is not really localization. As mentioned before, it is just the first sign of the wave nature of electrons in the electrical conductivity that reveals itself in the constructive interference of electron waves traveling along closed paths in opposite directions. Although one cannot tell from the perturbative result when the states become localized and when not, it is instructive to look at the length dependence of the conductivity given in (36.2.32), (36.2.33), and (36.2.34). The correction to the conductivity is small in three-dimensional systems and remains finite as the linear dimensions of the sample increase. The logarithmic correction in two-dimensional systems, if it is not destroyed by further corrections, can become comparable with σ_0 and the conductivity may vanish. A similar situation may occur in one-dimensional systems, where the conductivity decreases linearly with the system size. Thus, weak localization gives some hint that the resistance of one- and two-dimensional systems diverges as the system size increases, implying that the electron states become localized. This argument is only a naive extrapolation from the first corrections, but since we are interested in how the conductivity changes as the length of the system varies, the scaling considerations used, e.g., for critical phenomena, might be applicable to the localization problem. Indeed, earlier theories of the Anderson localization indicated that the dimensionless conductance

$$g(L) = \frac{G(L)}{G_0}$$
(36.2.42)

with $G_0 = e^2/\hbar$ has scaling properties as a function of the system size L.

The basic assumptions of the scaling theory of localization¹² can be formulated as follows. Consider a *d*-dimensional hypercubic sample of size *L* in all dimensions. The dimensionless conductance is a function of *L* and may depend on some other parameters, e.g., the degree of disorder. Denoting this parameter by *x*, we will consider the function g(L, x). Taking now a sample

¹² E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, 1979.

of size bL with b > 1, the dimensionless conductance, g(bL, x), of the larger sample is assumed to depend only on the change in the length scale and on the conductivity of the original sample, that is

$$g(bL, x) = f[b, g(L, x)],$$
 (36.2.43)

where f is an as yet unknown scaling function. This assumption implies that there is a unique characteristic length ξ in the problem, where of course ξ depends on the parameter x, and the conductance g(L, x) of a sample of size L is a function only of L/ξ ,

$$g(L, x) = g(L/\xi).$$
 (36.2.44)

This characteristic length is the localization length ξ_{loc} in the localized regime, while it is the correlation length ξ_{corr} in the metallic regime. Both of them diverge as the transition point is approached.

When the length scale is changed by a small amount, b = 1 + a with $a \ll 1$, both sides of (36.2.43) can be expanded to linear order in a. Collecting the zeroth- and first-order terms we get

$$g(L,x) = f\left[1, g(L,x)\right],$$

$$L\frac{\mathrm{d}g(L,x)}{\mathrm{d}L} = \left.\frac{\mathrm{d}f\left(b, g(L,x)\right)}{\mathrm{d}b}\right|_{b=1}.$$
(36.2.45)

Introducing the quantity

$$\beta(g(L,x)) = \left. \frac{1}{g(L,x)} \frac{\mathrm{d}f(b,g(L,x))}{\mathrm{d}b} \right|_{b=1}, \qquad (36.2.46)$$

it is a function of g(L, x) alone, and the scaling equation leads to

$$\beta(g(L,x)) = \frac{L}{g(L,x)} \frac{\mathrm{d}g(L,x)}{\mathrm{d}L} = \frac{\mathrm{d}\ln g(L,x)}{\mathrm{d}\ln L} \,. \tag{36.2.47}$$

The variation of the conductance can be determined provided the β function is known. The scaling theory uses the known results in the limiting cases, for weak and strong localization, to extrapolate to arbitrary g.

In a good conductor, the resistance is proportional to the length of the sample in the direction of the current divided by the cross section. In a d-dimensional hypercubic sample the conductance is

$$G = \sigma L^{d-2} \,, \tag{36.2.48}$$

and the dimensionless conductance is proportional to L^{d-2} . The logarithmic derivative of the functional form

$$g(L) \propto L^{d-2}$$
 (36.2.49)

leads to

$$\beta(g) = d - 2. \tag{36.2.50}$$

The first correction to this leading term in the β function can be calculated in the weak-localization limit from (36.2.31). The correction is proportional to 1/g in any dimension,

$$\beta(g) = d - 2 - \frac{c_d}{g}, \qquad (36.2.51)$$

where c_d is a positive number of order unity.

In the opposite limit, when the states near the Fermi energy are localized, and the localization can be characterized by a localization length ξ_{loc} , the conductance decays exponentially with the system size for $L \gg \xi_{\text{loc}}$, that is

$$g(L) \propto e^{-L/\xi_{\text{loc}}}$$
. (36.2.52)

from which, for small values of g,

$$\beta(g) = -\frac{L}{\xi_{\text{loc}}} = \ln g + \text{const}.$$
 (36.2.53)

Knowing the β function for large and small values of g, in the metallic and in the insulating regimes, it is natural to assume a smooth, monotonic interpolation between them. The expected profiles of the β function are depicted in Fig. 36.14 for d = 1, 2, and 3.



Fig. 36.14. Expected profiles of the β function of the localization problem for dimensions d = 1, 2, and 3

If the function $\beta(g)$ is smooth and the higher order corrections do not reverse the trends seen in the two limits, $\beta(g)$ is always negative for $d \leq 2$. This implies that the conductance decreases as the system size grows. There is a single fixed point, g = 0, and therefore all states become localized as $L \to \infty$. The conductivity of a small thin film or a short wire could seem
metallic, but the conductance decreases as the size increases and it finally disappears.

The localization length of two-dimensional systems can be estimated from the formulas of weak localization. It follows from (36.2.33) that

$$g(L) = g_0 - \frac{1}{\pi^2} \ln \frac{L}{l}, \qquad (36.2.54)$$

where

$$g_0 = \frac{1}{2\pi} k_{\rm F} l \,. \tag{36.2.55}$$

The localization length can be defined as the size where the correction to g_0 is comparable with g_0 itself, that is when

$$\frac{1}{\pi^2} \ln \frac{\xi_{\rm loc}}{l} = g_0 \,, \tag{36.2.56}$$

from which we get

$$\xi_{\rm loc} = l \exp\left(\frac{\pi}{2}k_{\rm F}l\right) \,. \tag{36.2.57}$$

The system is in the regime of weak localization when the localization length $\xi_{\rm loc}$ is larger than the phase-coherence length L_{ϕ} . The conductance decreases logarithmically with the system size. Strong, exponential localization sets in when $L_{\phi} > \xi_{\rm loc}$. The conductance is on the order of $e^2/2\pi^2\hbar$ at the crossover between the two regimes. This can be interpreted as the minimum metallic conductance in the sense that the conductance cannot be smaller if the underlying mechanism is the diffusive propagation of electrons.

An unstable fixed point exists for d > 2 at a g^* where $\beta(g^*) = 0$. When the dimensionless conductance is smaller than this critical value, $g < g^*$, the conductance decreases as the size increases. The electron states become localized and the system turns into an insulator. If, however, $g > g^*$, the conductance increases with the system size, the sample remains metallic. The initial value of the conductivity can be influenced by ordering or disordering the sample. A continuous Anderson metal–insulator transition may occur as the degree of disorder is changed.

The behavior near a second-order phase transition can be characterized by the critical exponents. To derive them we linearize the β function in the vicinity of the fixed point and define a quantity ν by the relation

$$\beta(g) = \frac{1}{\nu} \frac{g - g^*}{g^*} \approx \frac{1}{\nu} \frac{g - g^*}{g} \,. \tag{36.2.58}$$

As will be seen, ν will play the role of a critical exponent. Its value cannot be determined in the framework of this scaling theory, since the β function is known only for small and large values of g; nevertheless, several interesting features of the metal-insulator transition can be expressed in terms of this single parameter. Consider a sample where the mean free path and the conductance can be controlled by the degree of disorder. There is a critical value of disorder, x_c , where the conductance is equal to the fixed-point value,

$$g(L, x_{\rm c}) = g^*$$
. (36.2.59)

Since the conductance is scale independent at the fixed point, x_c is independent of the system size. We take now a sample with edge length equal to the mean free path and assume that the conductance g(l, x) is close to the fixed-point value,

$$g(l,x) = g^* + g^* C(x - x_c), \qquad (36.2.60)$$

with C > 0. The difference $x - x_c$, which characterizes the disorder, is positive on the metallic side and negative on the insulating side. Rearranging the linearized scaling equation

$$\frac{d\ln g}{d\ln L} = \frac{1}{\nu} \frac{g - g^*}{g}$$
(36.2.61)

into the form

$$\frac{\mathrm{d}g}{g - g^*} = \frac{1}{\nu} \frac{\mathrm{d}L}{L}$$
(36.2.62)

and integrating from l to L, that is from g(l) to g(L), we get

$$g(L) - g^* = \left[g(l) - g^*\right] \left(\frac{L}{l}\right)^{1/\nu} = g^* C(x - x_c) \left(\frac{L}{l}\right)^{1/\nu} .$$
 (36.2.63)

A localization length ξ_{loc} can be defined on the insulating side, for $x < x_c$, as the length where the change of the conductance is comparable with the fixed-point conductance itself, that is

$$C|x - x_{\rm c}| \left(\frac{\xi_{\rm loc}}{l}\right)^{1/\nu} \approx 1.$$
(36.2.64)

As we approach the metal-insulator transition by varying x, the localization length diverges with the critical exponent ν :

$$\xi_{\rm loc} \approx l |x - x_{\rm c}|^{-\nu}$$
. (36.2.65)

This linearized calculation, which yields a power-law dependence of the conductance on the length of the system, cannot be true close to the fixed point as it would give negative conductance. In a better treatment the β function is approximated in the vicinity of the fixed point by

$$\beta(g) = \frac{1}{\nu} \left(\ln g - \ln g^* \right) \,, \tag{36.2.66}$$

which coincides with (36.2.58) when $g - g^* \ll 1$. Integration of the scaling equation

$$\frac{\mathrm{d}\ln g}{\mathrm{d}\ln L} = \frac{1}{\nu} \ln \frac{g}{g^*} \tag{36.2.67}$$

then gives

$$\frac{\ln(g(L)/g^*)}{\ln(g(l)/g^*)} = \left(\frac{L}{l}\right)^{1/\nu},$$
(36.2.68)

or in another form

$$g(L) = g^* \left(\frac{g(l)}{g^*}\right)^{(L/l)^{1/\nu}}.$$
(36.2.69)

Combining with (36.2.60)

$$g(L) = g^* \left[1 + C(x - x_c) \right]^{(L/l)^{1/\nu}}.$$
 (36.2.70)

This expression can be taken as the expansion for small $x - x_c$ of the function

$$g(L) = g^* \exp\left[C(x - x_c) \left(\frac{L}{l}\right)^{1/\nu}\right].$$
 (36.2.71)

The conductance decreases exponentially with the system size on the insulating side, for $x < x_c$, a physically more reasonable result than the power-law behavior. The localization length ξ_{loc} given in (36.2.64) is identified as the linear extension L where the exponent takes the value -1. Combining (36.2.71) with (36.2.64),

$$g(L) = g^* \exp\left[-L/\xi_{\text{loc}}\right].$$
 (36.2.72)

On the metallic side, for $x > x_c$, the conductance increases with the system size. Quantum corrections should become negligible beyond some characteristic length ξ_{corr} , which is the natural length scale on this side of the metal-insulator transition, and the ohmic behavior

$$G = \sigma L^{d-2} \tag{36.2.73}$$

should be recovered. This happens when the β function becomes of order unity, or equivalently when the exponent in (36.2.71) is of order unity, that is

$$\xi_{\rm corr} \propto l(x - x_{\rm c})^{-\nu}$$
. (36.2.74)

The conductivity of a metal should be independent of the system size. Expressed in terms of the dimensionless conductance,

$$\sigma = \frac{2e^2}{\hbar} L^{d-2} g(L, x) = \frac{2e^2}{\hbar} L^{d-2} g(L/\xi_{\text{corr}}); \qquad (36.2.75)$$

hence, $g(L/\xi_{\rm corr})$ should be proportional to $(L/\xi_{\rm corr})^{-(d-2)}$. This gives

$$\sigma \propto \xi_{\rm corr}^{d-2} \propto (x - x_{\rm c})^{\nu(d-2)}$$
. (36.2.76)

The conductance does not exhibit a jump at the metal–insulator transition; it vanishes continuously with some power s of $x - x_c$. The exponent s satisfies the Wegner scaling law,¹³

$$s = \nu(d-2) \,. \tag{36.2.77}$$

This continuous vanishing of the conductance can be observed in the experimental results displayed in Fig. 36.11. The value s = 1 is obtained for the critical exponent of the conductivity by mapping the problem of Anderson localization to field theory models. This would give $\nu = 1$ for three-dimensional systems. The experiments and numerical solutions of models with various types of disorder give a different value. The value $\nu = 1.58$ was found numerically for the Anderson model with diagonal disorder. In the presence of an external magnetic field, when the hopping probability is modified by a phase factor containing the line integral of the vector potential, a somewhat different value, $\nu = 1.43$, was obtained. The numerical calculations allow us to reconstruct the β function. The results are in agreement with the scaling theory. The β function is found to have a zero, the scaling transformation has a nontrivial fixed point in three dimensions, while only the trivial fixed point $g^* = 0$ exists in one and two dimensions.

36.2.8 The Role of Electron–Electron Interaction

The scaling theory, as presented above, predicts that all electron states are localized in a large enough two-dimensional disordered system. This is corroborated by numerical calculations on models with different types of disorder. This implies that the conductance of two-dimensional systems should vanish at zero temperature. The logarithmic temperature dependence has indeed been observed on thin films. The experimental results displayed in Fig. 36.15 came therefore as a big surprise.

The two-dimensional electron system in the inversion layer of an Si:MOSFET at low carrier densities behaves as expected for an insulator showing a monotonic increase in resistivity with decreasing temperature. However, when the carrier density exceeds a critical value, the tendency is reversed, metallic behavior is found as $T \rightarrow 0$. The resistivity curves can be scaled by an appropriate choice of the temperature scale on two universal scaling curves, one for the metallic, the other for the insulating regime, demonstrating clearly that a metal–insulator transition takes place at zero temperature at a critical electron density. One explanation could be that this transition is the consequence of electron–electron interactions neglected until now. It can be shown that interaction effects are more important than weak-localization (interference) effects in three-dimensional samples. They become observable at temperatures satisfying $k_{\rm B}T \ll \hbar/\tau$ with the elastic mean free time. In contrast the interference effects dominate in wires. Two-dimensional systems are marginal in this respect. Electron–electron interactions give rise to a similar

¹³ F. Wegner, 1976.



Fig. 36.15. Temperature dependence of the resistivity of the two-dimensional electron gas in an Si:MOSFET for various carrier densities and the same data plotted against the scaled temperature [Reprinted with permission from S. V. Kravchenko et al., *Phys. Rev. B* 51, 7038 (1995). © (1995) by the American Physical Society]

logarithmic temperature dependence of the resistivity as disorder. Interaction effects and disorder should therefore be treated on an equal footing. Perturbative treatments of the interactions in the weak-localization regime indicate that localization effects may be suppressed. However, the full interplay between localization and interaction is a yet unsolved problem.

36.3 Spin Glasses

Our preceding discussion concerned systems with positional disorder of nonmagnetic atoms. We have seen in Chapter 35 that magnetic impurities give rise to interesting new effects in metals. At low concentrations, when the interaction between the impurities can be neglected, understanding the Kondo problem presented a big challenge. At high concentrations, when the concentration of the magnetic ions exceeds the percolation threshold, ferromagnetism may appear. We will discuss here an intermediate state occurring for an intermediate concentration range. The interaction between the randomly distributed magnetic ions cannot be neglected in the systems to be considered; nevertheless, the magnetic moments do not order even at low temperatures. The couplings between the magnetic ions, which can be ferromagnetic or antiferromagnetic depending on the separation between them, cannot align the spins in a crystallographically preferred direction. This new type of magnetic state with properties different from both paramagnets and ordered magnets is called *spin glass*.

36.3.1 Experimental Findings

Alloys of noble metals (copper or gold) with a few percent of manganese or iron atoms exhibit the following unusual properties:

1. As displayed in Fig. 36.16, the low-field susceptibility exhibits an increasingly sharp peak as the measuring field is lowered, turning into a cusp at some characteristic temperature $T_{\rm g}$ in the zero-field limit. A Curie-like behavior characteristic for random paramagnetic impurities is observed in the temperature range above $T_{\rm g}$. The susceptibility reaches a finite value there before starting to fall.



Fig. 36.16. Temperature dependence of the zero-field susceptibility of copper containing a few atomic percent of manganese atoms. The right panel shows the rounding of the cusp in weak fields on an enlarged scale [Reprinted with permission from V. Cannella and J. A. Mydosh, *Phys. Rev. B* **6**, 4220 (1972). \bigcirc (1972) by the American Physical Society]

2. The nonlinear terms become appreciable in the magnetization. The non-linear susceptibility χ_{nl} defined via

$$M = \chi H - \chi_{\rm nl} H^3 \tag{36.3.1}$$

diverges at $T_{\rm g}$ as $(T - T_{\rm g})^{-\gamma}$.

3. As displayed in Fig. 36.17, the cusp in the zero-field susceptibility is rounded off when the susceptibility is measured at finite frequencies.



Fig. 36.17. Temperature dependence of the zero-field susceptibility for copper with 0.94 at.% Mn at four different frequencies ranging from 1.33 kHz to 2.6 Hz [Reprinted with permission from C. A. M. Mulder et al., *Phys. Rev. B* **23**, 1384 (1981). © (1981) by the American Physical Society]

4. No magnetic ordering and no magnetic Bragg peaks characteristic of longrange order can be detected below $T_{\rm g}$ in neutron-scattering experiments. The magnetic moments are frozen into a static configuration, the time average of each individual moment is finite, but there are no long-range correlations between the orientations of different moments. The Fourier transform of the spatial distribution of the moments vanishes for any k,

$$\frac{1}{N}\sum_{i} \langle \boldsymbol{S}_{i} \rangle \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{i}} = 0. \qquad (36.3.2)$$

- 5. A remarkable feature is the lack of any visible anomaly in the heat capacity at $T_{\rm g}$. The heat capacity exhibits a broad peak slightly above $T_{\rm g}$.
- 6. The response to magnetic field depends on the history of the sample below $T_{\rm g}$. As seen in Fig. 36.18 the magnetization and susceptibility are higher for a field-cooled (FC) sample than for a zero-field-cooled (ZFC) sample. The latter corresponds to the usual situation: The magnetic field, in which the susceptibility is measured, is applied at the measurement temperature. On the other hand, in the field-cooled case the magnetic field is applied at a temperature above $T_{\rm g}$ before the sample is cooled to a temperature below $T_{\rm g}$ where the measurement is done.

The magnetization and the susceptibility are virtually constant in the field-cooled case, irrespective of whether the measurements are done on decreasing or increasing temperatures. The zero-field-cooled samples exhibit irreversibility. The susceptibility increases with temperature.



Fig. 36.18. The static susceptibility as a function of temperature taken in a weak field (H = 5.9 Oe) for two copper samples with 1.08 and 2.02 at.% Mn. Curves (a) and (c) were obtained on field-cooled samples and curves (b) and (d) were taken on zero-field-cooled samples for increasing temperature [Reprinted with permission from S. Nagata et al., *Phys. Rev. B* 19, 1633 (1979). \bigcirc (1979) by the American Physical Society]

- 7. When the external field applied to a field-cooled sample is switched off, the magnetization decreases rapidly to a value called remanent magnetization followed by a slow nonexponential decay of the remanent magnetization to zero. If we switch on the magnetic field below $T_{\rm g}$, a reversible component of the magnetization is developed immediately, followed by a slow increase of the magnetization. Saturation occurs only after a very long time.
- 8. The frequency dependence of the susceptibility and the relaxation phenomena do not define a unique characteristic relaxation time for the spins. Relaxation processes exist at all timescales, from microscopic (10^{-12} s) to macroscopic (10^5 s) times. The nonexponential decay of correlations can also be observed above $T_{\rm g}$, up to the temperature where the heat capacity has its maximum.
- 9. A characteristic feature of spin glasses is *aging*. The relaxation time of the magnetization of a field-cooled sample depends on its history, on the waiting time between the quench and the switch-off of the magnetic field.
- 10. As displayed in Fig. 36.19, there are examples where in a special range of concentrations the spin-glass phase goes over above $T_{\rm g}$ into a ferro-magnetic state and not into a paramagnetic phase.



Fig. 36.19. (a) Phase diagram of $\operatorname{Eu}_x \operatorname{Sr}_{1-x} \operatorname{S}$ as a function of x [Reprinted with permission from H. Maletta and P. Convert, *Phys. Rev. Lett.* **42**, 108 (1979). (c) (1979) by the American Physical Society]. (b) Phase diagram of gold containing 14 and 15 at.% Fe as a function of the quenching temperature [Reprinted with permission from S. Crane and H. Claus, *Phys. Rev. Lett.* **46**, 1693 (1981). (c) (1981) by the American Physical Society]

36.3.2 Models of Spin Glasses

Spin-glass behavior is observed experimentally in disordered alloys containing typically a relatively low concentration of magnetic ions. The randomly located magnetic moments interact with each other via some kind of exchange and freeze at low temperatures into random orientations without long-range order, because the competition between the couplings does not allow a global ordering. The exchange coupling could be the RKKY interaction, since the first known, so-called canonical spin glasses, AuFe and CuMn, are metallic, but it could as well be the superexchange, since there are several semiconducting and insulating spin glasses. Whatever the cause, the magnetic properties are described by the well-known Heisenberg model,

$$\mathcal{H} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j , \qquad (36.3.3)$$

where, however, the indices i and j refer to the random magnetic impurities. Assuming that the magnetic atoms randomly occupy the sites of an underlying regular lattice, the spin-glass model can be considered as a site-diluted Heisenberg model with an extra complication caused by the fact that the RKKY interaction oscillates with the distance between the magnetic atoms. It can be either ferro- or antiferromagnetic. Therefore, the strength and the sign of the coupling J_{ij} varies randomly in the sample.

While the experimentally investigated spin glasses are site diluted, most theoretical models assume random bonds. They have the common feature that the underlying perfect crystal lattice is preserved, a localized moment is supposed to sit on every site of a lattice, but the exchange coupling between them varies randomly, it can be antiferromagnetic or ferromagnetic with variable strength. The spins might be classical Ising variables and the coupling between them is an Ising-like interaction, or vector spins may interact with Heisenberg coupling. The models differ in the choice of the form of the random distribution for J_{ij} . In most work either a Gaussian probability distribution is taken with a width Δ ,

$$P(J_{ij}) = \frac{1}{(2\pi\Delta^2)^{1/2}} \exp\left(-\frac{J_{ij}^2}{2\Delta^2}\right),$$
(36.3.4)

or J_{ij} is given only two values, +J and -J, and the ferro- and antiferromagnetic couplings are distributed randomly with equal probability. The probability distribution of this symmetric bimodal model is given by

$$P(J_{ij}) = \frac{1}{2} \left[\delta(J_{ij} - J) + \delta(J_{ij} + J) \right].$$
 (36.3.5)

A bond-diluted bimodal model is obtained if the couplings $\pm J$ appear with probability p < 1 and the spins are not coupled with probability 1 - p,

$$P(J_{ij}) = p_{\frac{1}{2}} \left[\delta(J_{ij} - J) + \delta(J_{ij} + J) \right] + (1 - p) \delta(J_{ij}).$$
(36.3.6)

Ferro- or antiferromagnetic couplings may be preferred by shifting the center of the distribution function from zero.

More importantly, the spin-glass models differ in the range of the exchange interaction. Only nearest-neighbor spins are coupled in short-range models, while, as we will see, for computational reasons infinite-range models are often considered, where all spins are coupled irrespective of their separation.

36.3.3 Quenched Disorder

In the materials we are interested in, the spins are frozen into a nonequilibrium configuration by rapid cooling (quenching) during the preparation of the sample. The couplings between them are also frozen into fixed values for each sample. This quenched disorder should be treated differently from annealed disorder, which is achieved if the impurity spins are free to diffuse during the very slow cooling process to reach thermal equilibrium. The resulting J_{ij} s are then thermodynamic variables. The free energy of an annealed system is to be calculated from a partition function in which the trace is taken not only over the orientations of the spins but also over the positions of the magnetic impurities. Hence the partition function

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$$Z = \sum_{\{\boldsymbol{S}_i\}} \prod_{ij} \exp\left(J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j / k_{\rm B}T\right)$$
(36.3.7)

has to be averaged over the random spatial arrangements of the magnetic atoms (over the random distribution of the couplings), and the free energy is calculated from the logarithm of the averaged partition function. In contrast to that, in a quenched system, the partition function $Z\{J_{ij}\}$ and the free energy

$$F\{J_{ij}\} = -k_{\rm B}T\ln Z\{J_{ij}\}$$
(36.3.8)

corresponding to it have to be calculated in a first step for a fixed configuration $\{J_{ij}\}$ of the random couplings taking into account all possible states of the spins. We then imagine the macroscopic sample to be divided into a large number of subsystems, which are themselves macroscopic, such that the previous calculation is valid for each. To get the free energy of the entire system, the free energies of the subsystems are summed, which is equivalent to averaging over the random configurations of the couplings:

$$F = \left[F\{J_{ij}\}\right]_{\rm av} = -k_{\rm B}T\left[\ln Z\{J_{ij}\}\right]_{\rm av} .$$
 (36.3.9)

Thus, in the spin-glass problem, for a quenched disorder, the logarithm of the partition function has to be averaged and not the partition function. This is technically much more difficult than calculating the free energy of a disordered system in thermal equilibrium. This difficulty can partially be circumvented by the so-called *replica trick* which relies on the relation

$$\ln x = \lim_{n \to 0} \frac{1}{n} (x^n - 1).$$
 (36.3.10)

The free energy can formally be written in the form

$$F = -k_{\rm B}T \lim_{n \to 0} \frac{1}{n} \left\{ \left[Z^n \{ J_{ij} \} \right]_{\rm av} - 1 \right\}.$$
 (36.3.11)

Averaging the free energy over disorder leads to averaging Z^n over disorder. A simple interpretation of this trick is that we make n copies (replicas) of the real system with the same disorder and average the partition function of this effective system over disorder. Obviously n is integer and the calculation can be carried out in principle for all n. Then we analytically continue to small nto get the averaged free energy.

36.3.4 Frustration

It was mentioned in Chapter 14 that spins are frustrated in an antiferromagnetic chain, if the second-neighbor antiferromagnetic coupling is comparable to the nearest-neighbor coupling. This frustration is the consequence of the topology of the couplings in a geometrically ordered lattice. Similar frustration exists in the antiferromagnetic triangular lattice. If two neighboring spins are antiferromagnetically coupled and are therefore oppositely oriented, the orientation of the third spin at the vertex of an elementary triangle cannot be chosen so as to satisfy the antiferromagnetic couplings with both neighbors. The spins may resolve the frustration dilemma by forming a non-collinear magnetic structure. In other cases the spins remain disordered, resulting in a spin-singlet spin liquid the ground state.

The random distribution of ferro- and antiferromagnetic couplings in spin glasses may lead to frustration even when the topology of the lattice allows a nonfrustrated spin arrangement. This is illustrated in Fig. 36.20 for the example of a square plaquette with nearest-neighbor interactions, where three couplings are ferromagnetic and the fourth is antiferromagnetic.



Fig. 36.20. Frustrated spin configurations on a square plaquette with three ferromagnetic and one antiferromagnetic couplings. The spin orientations are chosen to satisfy three couplings. The unsatisfied bond is denoted by a slash

The spins would order ferromagnetically or antiferromagnetically if all couplings were ferromagnetic or antiferromagnetic. In the example, when one coupling is different from the three others, the spin orientations cannot be chosen to satisfy all four couplings. If classical spins are placed on three corners respecting the couplings between them to have the lowest energy, the fourth spin will be frustrated. Its two neighbors will want to orient it oppositely. The frustration is accompanied by a large degree of degeneracy. The spins with components $s_z = \pm 1/2$ can be placed in 16 ways on the plaquette. The ground states are doubly degenerate when all couplings are ferromagnetic. All spins are pointing up or all spins are pointing down. The classical antiferromagnetic state is eightfold degenerate when there are three ferromagnetic and one antiferromagnetic couplings on the plaquette. The eight degenerate spin configurations depicted in Fig. 36.20 are all frustrated; there is always one bond that cannot be satisfied.

To see the condition for frustration consider a closed path on a lattice with randomly arranged ferro- and antiferromagnetic couplings and take the product of the signs of the couplings,

$$\prod \operatorname{sgn} J_{ij} \,. \tag{36.3.12}$$

Obviously it takes the value +1 or -1. On paths where this product is negative, one of the spins is frustrated. Topological frustration on regular lattices with particular topology may lead to a spin liquid state even if the distribution of the couplings is uniform, while frustration is due to disorder in the spinglass phase. Spin liquids are in a global spin-singlet state, where the individual spins fluctuate rapidly. On the other hand, in a spin glass the individual spins are quenched into disordered directions and do not fluctuate.

36.3.5 Edwards–Anderson Model of Spin Glasses

The first attempt to theoretically describe the unusual properties of spin glasses is due to S. F. EDWARDS and P. W. ANDERSON (1975). They recognized that $\langle S_i \rangle$ is not a good order parameter. Although the spins are quenched below $T_{\rm g}$ and the mean value of any individual spin is finite, the spins point in different directions and hence their configurational average vanishes. Since the thermal fluctuations of the spins are slowed down, there is a nonvanishing probability that the spin points in the same direction at t = 0 and at a much later time. This can be formulated mathematically by the nonvanishing of the auto-correlation function, that is, the thermal average of the product of the same spin at site \mathbf{R}_i , for long time differences. The configurational average of this quantity,

$$q_{\rm EA} = \lim_{t \to \infty} \left[\left\langle \boldsymbol{S}_i(0) \boldsymbol{S}_i(t) \right\rangle_T \right]_{\rm av},\tag{36.3.13}$$

defines the *Edwards–Anderson order parameter*. Alternatively the configurational average of the square of the thermal average of the spin at site \mathbf{R}_i , that is

$$q = \left[\langle \boldsymbol{S}_i \rangle_T^2 \right]_{\text{av}}, \qquad (36.3.14)$$

can be used as an order parameter. The two should be identical in an ergodic system. As we will see, ergodicity is broken in spin glasses. Nevertheless, both $q_{\rm EA}$ and q can be used to characterize the spin-glass phase.

We apply the replica trick to determine the free energy. For a fixed quenched configuration of the couplings

$$Z^{n}\{J_{ij}\} = \operatorname{Tr} \prod_{\alpha=1}^{n} \exp\left(-\mathcal{H}\{J_{ij}, \boldsymbol{S}_{i}^{\alpha}\}/k_{\mathrm{B}}T\right)$$

= Tr exp $\left(-\sum_{\alpha=1}^{n} \mathcal{H}\{J_{ij}, \boldsymbol{S}_{i}^{\alpha}\}/k_{\mathrm{B}}T\right),$ (36.3.15)

where S_i^{α} denotes the spin at site \mathbf{R}_i in the α th replica. The trace should be taken over all possible states of all spins. With the use of the Hamiltonian given in (36.3.3) we have

$$Z^{n}\{J_{ij}\} = \operatorname{Tr} \prod_{\langle i,j \rangle} \exp\left(J_{ij} \sum_{\alpha=1}^{n} \boldsymbol{S}_{i}^{\alpha} \cdot \boldsymbol{S}_{j}^{\alpha} / k_{\mathrm{B}}T\right).$$
(36.3.16)

Averaging over the configurations of the exchange couplings requires calculating the quantity

$$\left[Z^{n}\left\{J_{ij}\right\}\right]_{\mathrm{av}} = \int_{-\infty}^{\infty} \left(\prod_{\langle i,j \rangle} \mathrm{d}J_{ij}P(J_{ij})\right) \mathrm{Tr} \prod_{\langle i,j \rangle} \exp\left(J_{ij}\sum_{\alpha=1}^{n} \boldsymbol{S}_{i}^{\alpha} \cdot \boldsymbol{S}_{j}^{\alpha}/k_{\mathrm{B}}T\right),$$
(36.3.17)

where $P(J_{ij})$ is the distribution function of the couplings. Assuming that the trace over the spin configurations and the averaging over the random configurations of the couplings can be interchanged in the replicated system, this expression is reduced to

$$\left[Z^{n}\left\{J_{ij}\right\}\right]_{\mathrm{av}} = \mathrm{Tr} \int_{-\infty}^{\infty} \prod_{\langle i,j \rangle} \mathrm{d}J_{ij} P(J_{ij}) \exp\left(J_{ij} \sum_{\alpha=1}^{n} \boldsymbol{S}_{i}^{\alpha} \cdot \boldsymbol{S}_{j}^{\alpha} / k_{\mathrm{B}}T\right). \quad (36.3.18)$$

EDWARDS and ANDERSON assumed a Gaussian distribution for the exchange couplings between nearest neighbors as given in (36.3.4). The averaging with this distribution can be carried out and we get

$$\int_{-\infty}^{\infty} \mathrm{d}J_{ij}P(J_{ij}) \exp\left\{\frac{J_{ij}}{k_{\mathrm{B}}T} \sum_{\alpha=1}^{n} \mathbf{S}_{i}^{\alpha} \cdot \mathbf{S}_{j}^{\alpha}\right\}$$

$$= \exp\left\{\frac{1}{2} \sum_{\alpha,\beta=1}^{n} \left(\mathbf{S}_{i}^{\alpha} \cdot \mathbf{S}_{j}^{\alpha}\right) \left(\mathbf{S}_{i}^{\beta} \cdot \mathbf{S}_{j}^{\beta}\right) \left(\frac{\Delta}{k_{\mathrm{B}}T}\right)^{2}\right\}.$$
(36.3.19)

Further approximations are needed in performing the trace over the spin configurations. If quantum fluctuations are negligible in the spin-glass phase, mean-field theory may be applicable. We thus assume that the spins are frozen in the direction of the effective field produced by the neighboring spins. This effective field is different for each moment owing to the disorder. Its selfconsistent calculation is a much more complicated task than in ordered magnetic systems.

Without going into details we mention that it seemed quite natural to assume that the replicas behave identically, the correlation between spins on the same site in different replicas,

$$q_{\alpha\beta} = \langle \boldsymbol{S}_i^{\alpha} \boldsymbol{S}_i^{\beta} \rangle, \qquad \alpha \neq \beta, \qquad (36.3.20)$$

are equal, $q_{\alpha\beta} = q$, and q is identical with the Edwards–Anderson order parameter, q_{EA} . The self-consistent solution for this order parameter gives q = 0 above a critical temperature T_{g} , while a nontrivial solution exists below it. The order parameter behaves as

$$q(T) = -\frac{1}{2} \left[1 - \left(\frac{T_{\rm g}}{T}\right)^2 \right] \approx \frac{T_{\rm g} - T}{T_{\rm g}}$$
(36.3.21)

in the vicinity of $T_{\rm g}$ given by

$$k_{\rm B}T_{\rm g} = \left(\sum_{j} \left\langle \frac{2}{9} J_{ij}^2 \right\rangle_{\rm av} \right)^{1/2}, \qquad (36.3.22)$$

and

$$q(T) = 1 - \left(\frac{2}{3\pi}\right)^{1/2} \frac{T}{T_{\rm g}}$$
(36.3.23)

at low temperatures, in the limit $T \to 0$.

The susceptibility takes the simple form

$$\chi(T) = \frac{g^2 \mu_{\rm B}^2 \mu_0}{3k_{\rm B}T} \left[1 - q(T)\right].$$
(36.3.24)

The 1/T Curie susceptibility is obtained above the glass transition temperature, but its increase with decreasing temperature stops at $T_{\rm g}$,

$$\chi(T) = \frac{g^2 \mu_{\rm B}^2 \mu_0}{3k_{\rm B} T_{\rm g}} - \mathcal{O}(T_{\rm g} - T)^2 , \qquad (36.3.25)$$

whereas at low temperatures

$$\chi(T) = \left(\frac{2}{3\pi}\right)^{1/2} \frac{g^2 \mu_{\rm B}^2 \mu_0}{3k_{\rm B} T_{\rm g}} \,. \tag{36.3.26}$$

This is in qualitative agreement with the measurements on field-cooled samples, where the behavior is reversible.

36.3.6 Sherrington–Kirkpatrick Model

Since the applicability of the mean-field approximation may be questioned for a short-range model, D. SHERRINGTON and S. KIRKPATRICK (1975) proposed a different model to describe the properties of spin glasses. They have taken Ising spins, but most importantly they assumed an infinite-range interaction. Each spin interacts with all other spins and the distribution function $P(J_{ij})$ is the same irrespective of the distance between the spins. The mean-field approximation is then exact; fluctuations can be neglected. If a spin interacts equally strongly with N-1 other spins, thermal averaging yields finite values in the thermodynamic limit provided the exchange coupling is proportional to 1/N. If ferromagnetic and antiferromagnetic couplings are not equally probable but the distribution is biased in one direction with a nonvanishing average, the distribution function can be chosen as

$$P(J_{ij}) = \left(\frac{N}{2\pi\Delta^2}\right)^{1/2} \exp\left(-\frac{N(J_{ij} - J_0/N)^2}{2\Delta^2}\right).$$
 (36.3.27)

The mean value and the width of the distribution are given by

$$[J_{ij}]_{av} = \frac{J_0}{N}$$
 and $[J_{ij}^2]_{av} - [J_{ij}]_{av}^2 = \frac{\Delta^2}{N}$. (36.3.28)

The order parameter has again to be solved self-consistently. Since the distribution of the couplings is centered around a finite value, a ferromagnetic solution may also exist. For this we allow a finite value for

$$m = \left[\langle S_i \rangle_T \right]_{\text{av}}.$$
 (36.3.29)

Obviously q is finite in the ferromagnetic phase as well. The spin-glass phase exists in the parameter range where the stable solution gives a finite q with m = 0.

The two order parameters, q and m, satisfy a coupled system of equations in the Sherrington–Kirkpatrick model:

$$q = \int_{-\infty}^{\infty} \frac{\mathrm{d}z}{(2\pi)^{1/2}} \mathrm{e}^{-z^2/2} \tanh^2 \left[\frac{\Delta q^{1/2} z}{k_{\mathrm{B}} T} + \frac{J_0 m}{k_{\mathrm{B}} T} \right],$$

$$m = \int_{-\infty}^{\infty} \frac{\mathrm{d}z}{(2\pi)^{1/2}} \mathrm{e}^{-z^2/2} \tanh \left[\frac{\Delta q^{1/2} z}{k_{\mathrm{B}} T} + \frac{J_0 m}{k_{\mathrm{B}} T} \right].$$
(36.3.30)

The phase diagram obtained from the self-consistent solution is displayed in Fig. 36.21.



Fig. 36.21. Phase diagram of the Sherrington-Kirkpatrick model of spin glasses

The spin-glass order parameter q(T) behaves rather similar to that found in the Edwards–Anderson model. It starts to increase linearly in $T_{\rm g} - T$ below $T_{\rm g}$ and approaches unity linearly at low temperatures. The susceptibility is Curie-like above the glass transition. The slope changes discontinuously at $T_{\rm g}$ and the susceptibility decreases slowly below $T_{\rm g}$ reaching a finite value at T = 0.

The infinite-range model turned out to be solvable for classical, *n*-component vector spins with Heisenberg exchange. The phase diagram is displayed in Fig. 36.22.



Fig. 36.22. Phase diagram of the infinite-range vector-spin model of spin glasses according to M. Gabay and G. Toulouse [Reprinted with permission from *Phys. Rev. Lett.* **47**, 201 (1981). (© (1981) by the American Physical Society]

The most important difference compared to the Ising spin glass is the appearance of mixed phases below the ferromagnetic phase for $J_0/\Delta > 1$. The phase denoted by M_1 is characterized by the coexistence of long-range ferromagnetic order with spin-glass order. The vector spins are aligned spontaneously in one direction and the transverse components of the spins exhibit spin-glass order. The other mixed phase denoted by M_2 exhibits the same coexistence of orderings as phase M_1 ; nevertheless, the two phases are separated by a well-defined transition line. To understand what happens, we have to present some further developments in spin-glass theory.

36.3.7 Recent Developments

The mean-field approximation based on the assumption that all replicas behave identically turned out to be internally inconsistent. It gives negative entropy at low temperatures. These inconsistencies could be corrected by assuming that replica symmetry may be broken at low temperatures and in weak fields. The replica-symmetric solution of the Sherrington–Kirkpatrick model was shown to become unstable below the *de Almeida–Thouless line*¹⁴ in the H-T plane. That is precisely what happens in the M₂ phase. The transition from phase M₁ to M₂ is characterized by the spontaneous breaking of

¹⁴ J. R. L. DE ALMEIDA and D. J. THOULESS, 1978.

the replica symmetry. The theory that can adequately describe the properties of the infinite-range spin-glass models was worked out by G. PARISI (1979). He pointed out that the spin-glass phase cannot be characterized by a scalar order parameter q when the replica symmetry is broken. A distribution of the $q_{\alpha\beta}$ parameters or a continuous function q(x,T) is needed, which depends, in addition to the temperature, on a continuous parameter defined in the interval $0 \le x \le 1$. Its calculation is a rather difficult task. We only mention that the Edwards-Anderson order parameter is equal to q(x,t) at x = 1,

$$q_{\rm EA}(T) = q(1,T),$$
 (36.3.31)

and the susceptibility is given by

$$\chi(T) = \frac{g^2 \mu_{\rm B}^2 \mu_0}{3k_{\rm B}T} \int_0^1 \left[1 - q(x, T)\right] \mathrm{d}x$$
(36.3.32)

instead of (36.3.24). This expression gives better agreement with the field-cooled measurements.

The study of the spin-glass problem raised some fundamental issues in the theory of disordered systems. A large number of configurations may exist in disordered systems owing to frustration, which all correspond to local energy minima, to metastable states. When the system finds itself in one of the valleys of the free energy landscape at low temperature, it may be stuck there and may be unable to overcome the barrier by thermal fluctuations to get into the true minimum. The ergodic hypothesis is a fundamental assumption of statistical physics, postulating that a system can explore the entire phase space over a long period of time, all microstates being equally probable, so that ensemble averages and time averages yield the same result. In spin glasses, though, ergodicity does not hold. Ergodicity breaking is not uncommon in solids. Whenever a symmetry is broken spontaneously, ergodicity is broken trivially. For example, when a paramagnetic system undergoes a phase transition to the ferromagnetic state, the system chooses one of the equivalent minima, which are related by the symmetry that is broken in the ordered phase. Since it would take an infinitely long time in the thermodynamic limit to go from one minimum to another, we only trace over a limited set of states about the selected minimum when physical quantities are calculated. A nontrivial ergodicity breaking occurs in the spin glass. A large number of valleys, not related by symmetry, appear below $T_{\rm g}$ in the space of states separated by high barriers. (The number of valleys separated by infinite barriers goes to infinity in the thermodynamic limit.) As the temperature is lowered, further new valleys appear inside each valley. This process goes on continuously down to T = 0. The properties of the system depend on which valley it is trapped in. Moreover, there are metastable states within each valley which are separated by finite free energy barriers. The time it takes to go from one metastable state to another depends on the barrier height between them. The broad distribution of the barrier heights explains why the dynamics of the system cannot be

described by a unique relaxation time and why a broad distribution of the relaxation times is needed. The quenched disorder is also the underlying reason of the remanence observed in spin glasses. From the theoretical point of view, the existence of the hierarchy of metastable states can help in understanding why the spin-glass phase cannot be described by a simple, Edwards–Andersonlike order parameter, but requires an order-parameter function as proposed in the Parisi theory.

The Parisi solution of the Sherrington–Kirkpatrick model gives a continuous phase transition from the paramagnetic to the spin-glass phase. However, the relevance of an infinite-ranged model for the low-temperature physics of three-dimensional spin-glass materials is questionable. Recently, large-scale numerical calculations have been performed on a wide class of more realistic short-range models. Consensus seems to emerge on the existence of a true phase transition for both Ising and Heisenberg spin glasses. The coherence length diverges as T approaches T_g . The critical behavior is probably universal. The same critical exponents are found for the Gaussian and bimodal models; moreover, bond dilution does not seem to modify the values. The critical exponent of the coherence length is $\nu = 2.45$ for the Ising spin glass and $\nu = 1.5$ for the Heisenberg spin glass.

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Response to External Perturbations

Conventionally statistical physics deals with the properties of systems in thermal equilibrium and with the methods to describe them. When experiments are performed on solids, the measurements are done, on many occasions, on samples that are out of equilibrium. We might study, for example, the electric current resulting from an electric field, the magnetization due to a magnetic field, or we might consider how the charge distribution is modified in the presence of a spatially varying potential. We might also be interested in processes that occur when the system is disturbed by a time-dependent external perturbation. When the external perturbation is weak and the variations in the observables (measurable physical quantities) are proportional to the strength of the perturbing field, the response of the system to the disturbance can be given in terms of retarded correlation functions calculated for the system in equilibrium. In this appendix we present the general formalism, the properties of response functions, and the procedures that can be used to calculate them. As an example we will consider in detail the response to an external scalar potential.

J.1 Linear Response Theory

Consider an interacting system described by a time-independent Hamiltonian \mathcal{H} and assume that the eigenfunctions $|\Psi_n\rangle$ and the energies E_n are known. When the system is in thermal equilibrium, the expectation value of an observable associated with the operator A can be calculated using the well-known formula

$$\langle A \rangle = \frac{1}{Z} \sum_{n} e^{-\beta E_n} \langle \Psi_n | A | \Psi_n \rangle , \qquad (J.1.1)$$

where the summation goes over the complete set of eigenstates and the normalizing factor Z is the partition function:

$$Z = \sum_{n} e^{-\beta E_n} \,. \tag{J.1.2}$$

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The expectation value can be written in a concise form as the trace (the sum of the diagonal matrix elements) of the product of A with the equilibrium density matrix,

$$\langle A \rangle = \operatorname{Tr}(\rho_0 A)$$
 (J.1.3)

with

$$\rho_0 = \frac{1}{Z} \mathrm{e}^{-\beta \mathcal{H}} \,. \tag{J.1.4}$$

When an external perturbation, e.g., a static electric or magnetic field, is switched on, the physical properties of the system may change. The external perturbation couples directly to an observable (for example, the magnetic field couples to the magnetization and the electric potential couples to the charge density), their product appearing in the Hamiltonian, but other physical quantities can also be influenced indirectly. When the external field is weak, the change in the expectation values of observables can be given in terms of generalized susceptibilities. Linear response theory expresses these susceptibilities in terms of retarded correlation functions of the equilibrium system.

J.1.1 Time-Dependent Response

Time-dependent external perturbations are described by a time-dependent Hamiltonian $\mathcal{H}_{\text{ext}}(t)$. When a space- and time-dependent external magnetic induction $\boldsymbol{B}(\boldsymbol{r},t)$ is applied,

$$\mathcal{H}_{\text{ext}}(t) = -\int d\boldsymbol{r} \, \boldsymbol{m}(\boldsymbol{r}) \cdot \boldsymbol{B}(\boldsymbol{r}, t) \,, \qquad (J.1.5)$$

where $\boldsymbol{m}(\boldsymbol{r})$ is the operator of the magnetic-moment density. An external scalar potential $\varphi_{\text{ext}}(\boldsymbol{r},t)$ couples to the charge density $\rho(\boldsymbol{r})$,

$$\mathcal{H}_{\text{ext}}(t) = \int d\boldsymbol{r} \,\rho(\boldsymbol{r})\varphi_{\text{ext}}(\boldsymbol{r},t) = \int d\boldsymbol{r} \,n(\boldsymbol{r})V_{\text{ext}}(\boldsymbol{r},t) \,. \tag{J.1.6}$$

We assume that the perturbation can be written quite generally in the form

$$\mathcal{H}_{\text{ext}}(t) = -\int \mathrm{d}\boldsymbol{r} \, B(\boldsymbol{r}) F(\boldsymbol{r}, t) \,, \qquad (J.1.7)$$

where $B(\mathbf{r})$ is an operator and the strength of the perturbation is given by $F(\mathbf{r}, t)$. Both B and F can be scalar or vector quantities. Owing to the locality of the interaction, the Hamiltonian of the external perturbation takes a simple form when expressed in terms of the Fourier transforms:

$$\mathcal{H}_{\text{ext}}(t) = -\frac{1}{V} \sum_{\boldsymbol{q}} B(-\boldsymbol{q}) F(\boldsymbol{q}, t) \,. \tag{J.1.8}$$

Assume for simplicity that the perturbation is spatially uniform but acts momentarily at t = 0 as a sharp impulse,

$$F(\mathbf{r},t) = F(t) = F_0\delta(t). \qquad (J.1.9)$$

If the amplitude F_0 of the perturbation is small, the change in the expectation value of an observable A can be written as

$$\langle \Delta A(t) \rangle = \chi_{AB}(t) F_0, \qquad (J.1.10)$$

and the coefficient $\chi_{AB}(t)$ is called the *response function*. Of course, such a perturbation can modify the physical quantities only for t > 0 owing to causality, that is the response function can take finite values only for t > 0 and has to vanish for t < 0.

When the perturbation varies continuously in time, it can be represented as a sequence of impulses. Written in an integral form

$$F(t) = \int_{-\infty}^{\infty} F(t')\delta(t-t') \,\mathrm{d}t' \,. \tag{J.1.11}$$

Owing to the linearity of the response, the effects of the impulses are added up. The change in the quantity A at time t is influenced only by the disturbance prior to t,

$$\left\langle \Delta A(t) \right\rangle = \int_{-\infty}^{t} \mathrm{d}t' \,\chi_{AB}(t-t')F(t') \,. \tag{J.1.12}$$

After a change of variables $t - t' \rightarrow t'$

$$\left\langle \Delta A(t) \right\rangle = \int_{0}^{\infty} \mathrm{d}t' \,\chi_{AB}(t') F(t-t') \,. \tag{J.1.13}$$

There are three interesting special cases for the time dependence of the perturbation. We may switch on the perturbation suddenly at t = 0 with amplitude F_0 . This corresponds to the choice

$$F(t) = \begin{cases} 0 & \text{for } t < 0, \\ F_0 & \text{for } t > 0. \end{cases}$$
(J.1.14)

The response of the system is then given by

$$\left\langle \Delta A(t) \right\rangle = \int_{0}^{t} \mathrm{d}t' \,\chi_{AB}(t') F_0 \,. \tag{J.1.15}$$

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The quantity

$$\Phi_{AB}^{\rm E}(t) = \int_{0}^{t} {\rm d}t' \,\chi_{AB}(t') \tag{J.1.16}$$

is called the *excitation function*.

A perturbing field which has been acting on the system for a long time already may be switched off suddenly at t = 0. We then study how the system relaxes to the new equilibrium state. This situation corresponds to

$$F(t) = \begin{cases} F_0 e^{\delta t} & \text{for } t < 0, \\ 0 & \text{for } t > 0, \end{cases}$$
(J.1.17)

where δ is a positive infinitesimal. The exponential factor describes the fact that initially the external perturbation was switched on adiabatically. The relaxation of the expectation value of A is given by

$$\langle \Delta A(t) \rangle = \int_{-\infty}^{0} \mathrm{d}t' \,\chi_{AB}(t-t')F_0 = \int_{t}^{\infty} \mathrm{d}t' \,\chi_{AB}(t')F_0 \,;$$
 (J.1.18)

therefore, the quantity

$$\Phi_{AB}^{\mathrm{R}}(t) = \int_{t}^{\infty} \mathrm{d}t' \,\chi_{AB}(t') \qquad (J.1.19)$$

is called the *relaxation function*.

Finally, we often study the case of periodically varying external perturbations. The response of the system is then described by frequency-dependent susceptibilities.

J.1.2 Generalized Susceptibilities

If the external perturbation varies in space, the response of the system is in general nonlocal. The variation of A at position r depends on the strength of the perturbation at other points of the system. Causality still holds, imposing that the expectation value of A at time t depends only on the values of the perturbation prior to t. The space- and time-dependent response function is defined by the linear relationship

$$\left\langle \Delta A(\boldsymbol{r},t) \right\rangle = \int_{-\infty}^{t} \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \,\chi_{AB}(\boldsymbol{r},\boldsymbol{r}',t-t') F(\boldsymbol{r}',t') \,. \tag{J.1.20}$$

If the unperturbed system is spatially uniform, the response may depend only on the difference between r and r', and we have

$$\left\langle \Delta A(\boldsymbol{r},t) \right\rangle = \int_{-\infty}^{t} \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \,\chi_{AB}(\boldsymbol{r}-\boldsymbol{r}',t-t') F(\boldsymbol{r}',t') \,. \tag{J.1.21}$$

Taking the Fourier transforms of $A(\mathbf{r}, t)$, $\chi_{AB}(\mathbf{r} - \mathbf{r}', t - t')$, and $F(\mathbf{r}', t')$ with respect to the spatial variables, the product of the Fourier components – instead of a convolution – appears on the right-hand side:

$$\left\langle \Delta A(\boldsymbol{q},t) \right\rangle = \int_{-\infty}^{t} \mathrm{d}t' \chi_{AB}(\boldsymbol{q},t-t') F(\boldsymbol{q},t') , \qquad (J.1.22)$$

or after a change of variables $t - t' \rightarrow t'$

$$\left\langle \Delta A(\boldsymbol{q},t) \right\rangle = \int_{0}^{\infty} \mathrm{d}t' \chi_{AB}(\boldsymbol{q},t') F(\boldsymbol{q},t-t') \,.$$
 (J.1.23)

A physically meaningful result is obtained only if the external perturbation is switched on adiabatically. This is achieved mathematically by including a factor $e^{-\delta|t|}$ in the amplitude $F(\mathbf{r}, t)$, with δ a positive infinitesimal.

The frequency Fourier transform of (J.1.22) yields

$$\langle \Delta A(\boldsymbol{q},\omega) \rangle = \chi_{AB}(\boldsymbol{q},\omega)F(\boldsymbol{q},\omega),$$
 (J.1.24)

where the quantity $\chi_{AB}(\boldsymbol{q},\omega)$ is the wave-vector- and frequency-dependent susceptibility. It determines the response of the system to an external perturbation with wave vector \boldsymbol{q} and angular frequency ω . In fact, since the response function vanishes for negative time argument, its Fourier transform is defined by

$$\chi_{AB}(\boldsymbol{q},\omega) = \int_{0}^{\infty} \chi_{AB}(\boldsymbol{q},t) \mathrm{e}^{\mathrm{i}\omega t} \,\mathrm{d}t \,. \tag{J.1.25}$$

As the response to a real perturbation is real, the complex susceptibilities have to satisfy the relation

$$\chi_{AB}(\boldsymbol{q},\omega) = \chi^*_{AB}(\boldsymbol{q},-\omega) \,. \tag{J.1.26}$$

When they are decomposed into real and imaginary parts in the form

$$\chi_{AB}(\boldsymbol{q},\omega) = \chi'_{AB}(\boldsymbol{q},\omega) + i\chi''_{AB}(\boldsymbol{q},\omega), \qquad (J.1.27)$$

the real part is an even function of the frequency, while the imaginary part is an odd function:

$$\chi'_{AB}(\boldsymbol{q},\omega) = \chi'_{AB}(\boldsymbol{q},-\omega), \qquad \chi''_{AB}(\boldsymbol{q},\omega) = -\chi''_{AB}(\boldsymbol{q},-\omega). \qquad (J.1.28)$$

J.1.3 Kubo Formula

Just as in an equilibrium situation, the expectation values of observables can also be calculated in terms of the density matrix in nonequilibrium systems:

$$\langle A \rangle = \operatorname{Tr}(\rho A).$$
 (J.1.29)

However, (J.1.4) cannot be generalized to a simple exponential form

$$\rho \neq \frac{1}{Z} e^{-\beta (\mathcal{H} + \mathcal{H}_{ext}(t))}$$
(J.1.30)

and rather has to be calculated from the equation of motion:

$$\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar} \big[\rho(t), \mathcal{H} + \mathcal{H}_{\mathrm{ext}}(t)\big]_{-}.$$
 (J.1.31)

This equation can be solved by making use of the relation

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{\mathrm{i}\mathcal{H}t/\hbar}\rho(t)\mathrm{e}^{-\mathrm{i}\mathcal{H}t/\hbar} = \frac{\mathrm{i}}{\hbar}\mathrm{e}^{\mathrm{i}\mathcal{H}t/\hbar} [\mathcal{H},\rho(t)]_{-}\mathrm{e}^{-\mathrm{i}\mathcal{H}t/\hbar}
+ \frac{\mathrm{i}}{\hbar}\mathrm{e}^{\mathrm{i}\mathcal{H}t/\hbar} [\rho(t),\mathcal{H}+\mathcal{H}_{\mathrm{ext}}(t)]_{-}\mathrm{e}^{-\mathrm{i}\mathcal{H}t/\hbar}
= \frac{\mathrm{i}}{\hbar}\mathrm{e}^{\mathrm{i}\mathcal{H}t/\hbar} [\rho(t),\mathcal{H}_{\mathrm{ext}}(t)]_{-}\mathrm{e}^{-\mathrm{i}\mathcal{H}t/\hbar} .$$
(J.1.32)

When this equation is integrated with the boundary condition $\rho(t \to -\infty) = \rho_0$ that follows from the adiabatic switching on of the perturbation, we get

$$\mathrm{e}^{\mathrm{i}\mathcal{H}t/\hbar}\rho(t)\mathrm{e}^{-\mathrm{i}\mathcal{H}t/\hbar} = \rho_0 + \frac{\mathrm{i}}{\hbar} \int_{-\infty}^t \mathrm{e}^{\mathrm{i}\mathcal{H}t'/\hbar} \big[\rho(t'), \mathcal{H}_{\mathrm{ext}}(t')\big]_{-} \mathrm{e}^{-\mathrm{i}\mathcal{H}t'/\hbar} \,\mathrm{d}t', \quad (\mathrm{J}.1.33)$$

which, after rearrangement, leads to an implicit integral equation:

$$\rho(t) = \rho_0 + \frac{\mathrm{i}}{\hbar} \int_{-\infty}^t \mathrm{e}^{-\mathrm{i}\mathcal{H}(t-t')/\hbar} \big[\rho(t'), \mathcal{H}_{\mathrm{ext}}(t')\big]_{-} \mathrm{e}^{\mathrm{i}\mathcal{H}(t-t')/\hbar} \,\mathrm{d}t' \,. \tag{J.1.34}$$

An iterative solution of this equation up to first order in the perturbation gives

$$\rho(t) = \rho_0 + \frac{\mathrm{i}}{\hbar} \int_{-\infty}^t \mathrm{e}^{-\mathrm{i}\mathcal{H}(t-t')/\hbar} \left[\rho_0, \mathcal{H}_{\mathrm{ext}}(t')\right]_{-} \mathrm{e}^{\mathrm{i}\mathcal{H}(t-t')/\hbar} \,\mathrm{d}t' \,. \tag{J.1.35}$$

Substituting this expression into (J.1.29) the second term on the right-hand side gives rise to a correction which is linear in the perturbing field. The change in the thermal average of A is then

$$\begin{split} \left\langle \Delta A(\boldsymbol{r},t) \right\rangle &= \frac{\mathrm{i}}{\hbar} \int_{-\infty}^{t} \operatorname{Tr} \left\{ A(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\mathcal{H}(t-t')/\hbar} \left[\rho_{0}, \mathcal{H}_{\mathrm{ext}}(t') \right]_{-} \mathrm{e}^{\mathrm{i}\mathcal{H}(t-t')/\hbar} \right\} \, \mathrm{d}t' \\ &= \frac{\mathrm{i}}{\hbar} \int_{-\infty}^{t} \operatorname{Tr} \left\{ A(\boldsymbol{r},t-t') \left[\rho_{0}, \mathcal{H}_{\mathrm{ext}}(t') \right]_{-} \right\} \, \mathrm{d}t' \\ &= -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{t} \operatorname{Tr} \left\{ \rho_{0} \left[A(\boldsymbol{r},t-t'), \mathcal{H}_{\mathrm{ext}}(t') \right]_{-} \right\} \, \mathrm{d}t' \end{split} \tag{J.1.36}$$

where we made use of the invariance of the trace under cyclic permutations of the operators and the time dependence of the operator A is given in the Heisenberg picture by the relation

$$A(t) = e^{i\mathcal{H}t/\hbar} A e^{-i\mathcal{H}t/\hbar} . \qquad (J.1.37)$$

For a perturbation given by (J.1.7) we have

$$\left\langle \Delta A(\boldsymbol{r},t) \right\rangle = \frac{\mathrm{i}}{\hbar} \int_{-\infty}^{t} \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}' \left\langle \left[A(\boldsymbol{r},t-t'), B(\boldsymbol{r}') \right]_{-} \right\rangle F(\boldsymbol{r}',t') \,. \qquad (J.1.38)$$

Comparison with (J.1.20) yields the explicit expression

$$\chi_{AB}(\boldsymbol{r}, \boldsymbol{r}', t - t') = \begin{cases} \frac{\mathrm{i}}{\hbar} \left\langle \left[A(\boldsymbol{r}, t - t'), B(\boldsymbol{r}') \right]_{-} \right\rangle & \text{for } t > t', \\ 0 & \text{for } t < t' \end{cases}$$
(J.1.39)

for the generalized susceptibility. After a rearrangement of the exponential factors associated with the time dependence of the operators we obtain

$$\chi_{AB}(\boldsymbol{r}, \boldsymbol{r}', t - t') = \begin{cases} \frac{i}{\hbar} \left\langle \left[A(\boldsymbol{r}, t), B(\boldsymbol{r}', t') \right]_{-} \right\rangle & \text{for } t > t', \\ 0 & \text{for } t < t'. \end{cases}$$
(J.1.40)

It is commonly written with the aid of the Heaviside unit step function as

$$\chi_{AB}(\boldsymbol{r},\boldsymbol{r}',t-t') = \frac{\mathrm{i}}{\hbar}\theta(t-t')\left\langle \left[A(\boldsymbol{r},t),B(\boldsymbol{r}',t')\right]_{-}\right\rangle.$$
(J.1.41)

This formula, which expresses the response to the perturbation in terms of a retarded correlation function of the equilibrium system, is known as the Kubo formula.¹

If the system is translation invariant, the response function depends only on r - r', and the Fourier transform with respect to the spatial variable is

¹ R. Kubo, 1956.

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$$\chi_{AB}(\boldsymbol{q},t-t') = \frac{\mathrm{i}}{\hbar} \theta(t-t') \frac{1}{V} \left\langle \left[A(\boldsymbol{q},t), B(-\boldsymbol{q},t') \right]_{-} \right\rangle.$$
(J.1.42)

Its Fourier transform with respect to time gives

$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \frac{1}{V} \Big\langle \big[A(\boldsymbol{q},t), B(-\boldsymbol{q},t') \big]_{-} \Big\rangle \,. \tag{J.1.43}$$

As we will see later, the integrand has to be cut off at infinity by a factor $\exp[-\delta(t-t')]$, which corresponds to the adiabatic switching on of the perturbation.

J.1.4 Alternative Form of the Kubo Formula

An alternative form of the generalized susceptibility can be derived by using the invariance of the trace of the product of operators under cyclic permutations:

$$\left\langle \left[A(\boldsymbol{r},t), B(\boldsymbol{r}',t') \right]_{-} \right\rangle = \operatorname{Tr} \left\{ \rho_0 A(\boldsymbol{r},t) B(\boldsymbol{r}',t') - \rho_0 B(\boldsymbol{r}',t') A(\boldsymbol{r},t) \right\}$$

=
$$\operatorname{Tr} \left\{ \left[B(\boldsymbol{r}',t'), \rho_0 \right]_{-} A(\boldsymbol{r},t) \right\},$$
 (J.1.44)

and the operator identity

$$\left[B(\mathbf{r}',t'),\rho_0\right]_{-} = -\mathrm{i}\rho_0 \int_{0}^{\beta\hbar} \mathrm{d}\lambda \dot{B}(\mathbf{r}',t'-\mathrm{i}\lambda),\qquad(\mathrm{J}.1.45)$$

where \dot{B} stands for the time derivative of B. This operator identity follows from

$$e^{\beta \mathcal{H}} B(\mathbf{r}', t') e^{-\beta \mathcal{H}} - B(\mathbf{r}', t') = \frac{1}{\hbar} \int_{0}^{\beta \hbar} d\lambda e^{\lambda \mathcal{H}/\hbar} [\mathcal{H}, B(\mathbf{r}', t')]_{-} e^{-\lambda \mathcal{H}/\hbar}$$
$$= \frac{1}{\hbar} \int_{0}^{\beta \hbar} d\lambda \left[\mathcal{H}, B(\mathbf{r}', t' - i\lambda)\right]_{-}, \qquad (J.1.46)$$

which can be readily checked by taking the matrix elements between the complete set of eigenstates of \mathcal{H} . We then find

$$\chi_{AB}(\boldsymbol{r},\boldsymbol{r}',t-t') = \frac{1}{\hbar}\theta(t-t')\int_{0}^{\beta\hbar} \mathrm{d}\lambda \left\langle \dot{B}(\boldsymbol{r}',t'-\mathrm{i}\lambda)A(\boldsymbol{r},t) \right\rangle \qquad (J.1.47)$$

and

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$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{1}{\hbar V} \int_{0}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} \int_{0}^{\beta\hbar} \mathrm{d}\lambda \, \left\langle \dot{B}(-\boldsymbol{q},-\mathrm{i}\lambda)A(\boldsymbol{q},t) \right\rangle. \tag{J.1.48}$$

Taking the classical limit $\hbar \to 0$ we obtain

$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{1}{k_{\rm B}TV} \int_{0}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \left\langle \dot{B}(-\boldsymbol{q},0)A(\boldsymbol{q},t) \right\rangle. \tag{J.1.49}$$

J.1.5 Analytic Properties of Susceptibilities

The thermal average can be calculated if we know the complete set of eigenstates of the Hamiltonian. The diagonal matrix elements between these states have to be weighted by the appropriate Boltzmann factors:

$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \frac{1}{V} \sum_{n} \frac{\mathrm{e}^{-\beta E_{n}}}{Z}$$

$$\times \left\langle \Psi_{n} \middle| A(\boldsymbol{q},t) B(-\boldsymbol{q},t') - B(-\boldsymbol{q},t') A(\boldsymbol{q},t) \middle| \Psi_{n} \right\rangle.$$
(J.1.50)

A complete set of states is inserted between the operators A and B using their completeness relation. Interchanging the labels $n \leftrightarrow m$ in the second term, we find

$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_{n}}}{Z} \\ \times \left[\langle \Psi_{n} | A(\boldsymbol{q},t) | \Psi_{m} \rangle \langle \Psi_{m} | B(-\boldsymbol{q},t') | \Psi_{n} \rangle \right. \\ \left. - \langle \Psi_{n} | B(-\boldsymbol{q},t') | \Psi_{m} \rangle \langle \Psi_{m} | A(\boldsymbol{q},t) | \Psi_{n} \rangle \right]$$

$$= \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_{n}}}{Z} \\ \times \langle \Psi_{n} | A(\boldsymbol{q},t) | \Psi_{m} \rangle \langle \Psi_{m} | B(-\boldsymbol{q},t') | \Psi_{n} \rangle \left[1 - \mathrm{e}^{-\beta(E_{m}-E_{n})} \right].$$

Writing out the time dependence explicitly,

$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_{n}}}{Z} \mathrm{e}^{\mathrm{i}(E_{n}-E_{m})(t-t')/\hbar} \times \left\langle \Psi_{n} | A(\boldsymbol{q}) | \Psi_{m} \right\rangle \left\langle \Psi_{m} | B(-\boldsymbol{q}) | \Psi_{n} \right\rangle \left[1 - \mathrm{e}^{-\beta(E_{m}-E_{n})} \right].$$
(J.1.52)

The time integral can be evaluated using the Fourier transform of the Heaviside step function given in (C.1.54) 586 J Response to External Perturbations

$$\int_{0}^{\infty} e^{i\omega(t-t')} d(t-t') = \int_{-\infty}^{\infty} \theta(t-t') e^{i\omega(t-t')} d(t-t') = \frac{i}{\omega+i\delta}.$$
 (J.1.53)

with δ a positive infinite simal. This result follows from the Fourier representation of the unit step function,

$$\theta(t - t') = -\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi \mathrm{i}} \frac{\mathrm{e}^{-\mathrm{i}\omega(t - t')}}{\omega + \mathrm{i}\delta}, \qquad (J.1.54)$$

which can be verified by closing the contour of integration in the lower halfplane, where the integrand has a simple pole at $\omega = -i\delta$ with residue -1 for t > t', while closing the contour in the upper half-plane for t < t'.

Performing now the time integral in (J.1.52) we obtain the spectral representation of the response function

$$\chi_{AB}(\boldsymbol{q},\omega) = -\frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \langle \Psi_n | A(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | B(-\boldsymbol{q}) | \Psi_n \rangle$$

$$\times \frac{1 - \mathrm{e}^{-\beta (E_m - E_n)}}{\hbar \omega - E_m + E_n + \mathrm{i}\delta} \,.$$
(J.1.55)

The same expression is obtained if the frequency-dependent susceptibility is defined by

$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')-\delta(t-t')} \frac{1}{V} \sum_{n} \frac{\mathrm{e}^{-\beta E_{n}}}{Z}$$

$$\times \left\langle \Psi_{n} \middle| A(\boldsymbol{q},t) B(-\boldsymbol{q},t') - B(-\boldsymbol{q},t') A(\boldsymbol{q},t) \middle| \Psi_{n} \right\rangle,$$
(J.1.56)

in which the perturbation is switched on adiabatically.

This form shows that if the variable ω is continued in the complex plane, the Fourier transform of the retarded response function is analytic in the upper half-plane. This statement about the analytic properties could be obtained much more simply and more generally by using the fact that the response function appearing in (J.1.22) is a well-behaved function in both the physical and mathematical sense. To demonstrate we write the response function in Fourier representation:

$$\chi_{AB}(\boldsymbol{q},t) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \chi_{AB}(\boldsymbol{q},\omega) \mathrm{e}^{-\mathrm{i}\omega t} \,. \tag{J.1.57}$$

When t < 0, the exponential factor of the integrand, $e^{-i\omega t}$, vanishes on the infinite semicircle in the upper half-plane and the integration path can be closed without changing the result by adding the integral on a semicircle of radius $R \to \infty$ in the upper half-plane, as shown in Fig. J.1.



Fig. J.1. Closing the integration contour in the upper half-plane for t < 0

Thus for negative times we have

$$\chi_{AB}(\boldsymbol{q},t) = \int_{C} \frac{\mathrm{d}\omega}{2\pi} \chi_{AB}(\boldsymbol{q},\omega) \mathrm{e}^{-\mathrm{i}\omega t} \,. \tag{J.1.58}$$

On the other hand we know that $\chi_{AB}(\boldsymbol{q},t)$ has to vanish for t < 0 owing to causality. Hence the integral vanishes on the closed contour C. This implies that the function $\chi_{AB}(\boldsymbol{q},\omega)$ may not have any singularity in the upper half-plane; it is analytic there. Its poles appear in the lower half-plane.

For physical reasons the response function is a retarded correlation function. One can define the advanced correlation function via

$$\chi^{\mathbf{A}}_{AB}(\boldsymbol{r},\boldsymbol{r}',t-t') = -\frac{1}{\hbar}\theta(t'-t)\Big\langle \big[A(\boldsymbol{r},t),B(\boldsymbol{r}',t')\big]_{-}\Big\rangle.$$
(J.1.59)

Its Fourier transform is

$$\chi^{\mathbf{A}}_{AB}(\boldsymbol{q},t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t'-t)\frac{1}{V}\Big\langle \big[A(\boldsymbol{q},t),B(-\boldsymbol{q},t')\big]_{-}\Big\rangle.$$
(J.1.60)

Taking the Fourier transform with respect to t we have

$$\chi^{\mathbf{A}}_{AB}(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{0} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')+\delta(t-t')} \frac{1}{V} \Big\langle \big[A(\boldsymbol{q},t), B(-\boldsymbol{q},t')\big]_{-} \Big\rangle \,.$$
(J.1.61)

The spectral representation now gives

$$\chi^{A}_{AB}(\boldsymbol{q},\omega) = -\frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_{n}}}{Z} \langle \Psi_{n} | A(\boldsymbol{q}) | \Psi_{m} \rangle \langle \Psi_{m} | B(-\boldsymbol{q}) | \Psi_{n} \rangle$$

$$\times \frac{1 - \mathrm{e}^{-\beta (E_{m} - E_{n})}}{\hbar \omega - E_{m} + E_{n} - \mathrm{i}\delta} \,. \tag{J.1.62}$$

The advanced function is analytic in the lower half-plane and has poles in the upper half-plane. Comparison with (J.1.55) shows that

$$\chi^{\mathbf{A}}_{AB}(\boldsymbol{q},\omega) = \chi^*_{B^{\dagger}A^{\dagger}}(\boldsymbol{q},\omega) \,. \tag{J.1.63}$$

When both A and B are observables and hence Hermitian operators, we have

$$\chi^{\mathbf{A}}_{AB}(\boldsymbol{q},\omega) = \chi^*_{BA}(\boldsymbol{q},\omega) \,. \tag{J.1.64}$$

J.1.6 Kramers–Kronig Relations

Let us consider now the integral

$$\int \frac{\chi_{AB}(\boldsymbol{q},\omega')}{\omega'-\omega+\mathrm{i}\delta}\,\mathrm{d}\omega'\,.\tag{J.1.65}$$

The positive infinitesimal δ ensures that the pole of the integrand at $\omega' = \omega - i\delta$ lies in the lower half-plane. The integrand is analytic in the upper half-plane and the integral has to vanish along any closed contour C in the upper halfplane:

$$\int_{C} \frac{\chi_{AB}(\boldsymbol{q},\omega')}{\omega'-\omega+\mathrm{i}\delta} \,\mathrm{d}\omega' = 0\,. \tag{J.1.66}$$

We will choose the contour as in Fig. J.1, closing the real axis on the upper half-plane by a semicircle with radius R tending to infinity.

If $\chi_{AB}(\boldsymbol{q},\omega')$ as a function of ω' decays fast enough at infinity, faster than $1/\omega'$, then not only does the integrand vanish on the semicircle, but the integral itself as well. Hence the integral on the real axis, too, has to vanish,

$$\int_{-\infty}^{\infty} d\omega' \frac{\chi_{AB}(\boldsymbol{q},\omega')}{\omega'-\omega+i\delta} = 0. \qquad (J.1.67)$$

Using the relationship

$$\frac{1}{x\pm \mathrm{i}\delta} = \mathrm{P}\frac{1}{x} \mp \mathrm{i}\pi\delta(x) \tag{J.1.68}$$

given in (C.3.3), where P denotes the principal value, we find

$$P\int_{-\infty}^{\infty} d\omega' \, \frac{\chi_{AB}(\boldsymbol{q},\omega')}{\omega'-\omega} - i\pi\chi_{AB}(\boldsymbol{q},\omega) = 0. \qquad (J.1.69)$$

This is the Cauchy relation for functions that are analytic in the upper halfplane.

It then follows that the real and imaginary parts of $\chi_{AB}(\mathbf{q},\omega)$ are Hilbert transforms of one another and satisfy the Kramers-Kronig relations:

$$\chi'_{AB}(\boldsymbol{q},\omega) = \frac{1}{\pi} \Pr \int_{-\infty}^{\infty} d\omega' \, \frac{\chi''_{AB}(\boldsymbol{q},\omega')}{\omega'-\omega} \,, \qquad (J.1.70\text{-a})$$

$$\chi_{AB}^{\prime\prime}(\boldsymbol{q},\omega) = -\frac{1}{\pi} \Pr \int_{-\infty}^{\infty} d\omega' \, \frac{\chi_{AB}^{\prime}(\boldsymbol{q},\omega')}{\omega'-\omega} \,, \qquad (J.1.70\text{-b})$$

and the full response function can be expressed in terms of its imaginary part as

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$$\chi_{AB}(\boldsymbol{q},\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \, \frac{\chi_{AB}''(\boldsymbol{q},\omega')}{\omega' - \omega - \mathrm{i}\delta} \,. \tag{J.1.71}$$

Since the real part is an even function of the frequency while the imaginary part is odd, the Kramers–Kronig relations can be written in the form

$$\chi'_{AB}(\boldsymbol{q},\omega) = \frac{2}{\pi} \Pr \int_{0}^{\infty} d\omega' \, \chi''_{AB}(\boldsymbol{q},\omega') \frac{\omega'}{{\omega'}^2 - \omega^2} \,, \qquad (J.1.72\text{-a})$$

$$\chi_{AB}^{\prime\prime}(\boldsymbol{q},\omega) = -\frac{2\omega}{\pi} \operatorname{P} \int_{0}^{\infty} \mathrm{d}\omega^{\prime} \,\chi_{AB}^{\prime}(\boldsymbol{q},\omega^{\prime}) \frac{1}{{\omega^{\prime}}^{2}-\omega^{2}} \,. \qquad (J.1.72\text{-b})$$

It follows from these relations that the static susceptibility can be given in terms of the imaginary part of the frequency-dependent susceptibility:

$$\chi_{AB} = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi_{AB}''(\omega)}{\omega} d\omega = \frac{2}{\pi} \int_{0}^{\infty} \frac{\chi_{AB}'(\omega)}{\omega} d\omega.$$
(J.1.73)

This is known as the *thermodynamic sum rule*.

J.1.7 Response Functions and Correlation Functions

The correlation function of two operators A and B is defined as

$$K_{AB}(\boldsymbol{r}-\boldsymbol{r}',t-t') = \left\langle A(\boldsymbol{r},t)B(\boldsymbol{r}',t') \right\rangle.$$
 (J.1.74)

Its Fourier transform with respect to the spatial variable is

$$K_{AB}(\boldsymbol{q},t-t') = \frac{1}{V} \left\langle A(\boldsymbol{q},t)B(-\boldsymbol{q},t') \right\rangle.$$
 (J.1.75)

Taking the Fourier transform with respect to time, too, we have

$$K_{AB}(\boldsymbol{q},\omega) = \frac{1}{V} \int_{-\infty}^{\infty} \left\langle A(\boldsymbol{q},t)B(-\boldsymbol{q},t') \right\rangle \mathrm{e}^{\mathrm{i}\omega(t-t')} \,\mathrm{d}(t-t') \,. \tag{J.1.76}$$

The correlations are invariant under inversion in a homogeneous system, hence

$$K_{AB}(\boldsymbol{q},\omega) = K_{AB}(-\boldsymbol{q},\omega). \qquad (J.1.77)$$

If the thermal average is written as the sum of the diagonal matrix elements weighted by the appropriate Boltzmann factors and a complete set of states is inserted using their completeness relation we find 590 J Response to External Perturbations

$$K_{AB}(\boldsymbol{q},\omega) = \int_{-\infty}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')}$$

$$\times \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \langle \Psi_n | A(\boldsymbol{q},t) | \Psi_m \rangle \langle \Psi_m | B(-\boldsymbol{q},t') | \Psi_n \rangle \,.$$
(J.1.78)

Since the states $|\Psi_m\rangle$ and $|\Psi_n\rangle$ are eigenstates of the Hamiltonian with energies E_m and E_n , respectively, the time dependence of the operators can be given explicitly, and the integral over the variable t - t' can be performed. We have

$$K_{AB}(\boldsymbol{q},\omega) = \int_{-\infty}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \mathrm{e}^{\mathrm{i}(E_n-E_m)(t-t')/\hbar} \\ \times \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \langle \Psi_n | A(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | B(-\boldsymbol{q}) | \Psi_n \rangle \qquad (J.1.79) \\ = 2\pi \hbar \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \langle \Psi_n | A(\boldsymbol{q}) | \Psi_m \rangle \\ \times \langle \Psi_m | B(-\boldsymbol{q}) | \Psi_n \rangle \delta(\hbar\omega + E_n - E_m) \,.$$

Comparison with (J.1.55) gives

$$\chi_{AB}(\boldsymbol{q},\omega) = -\frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} d\omega' \frac{K_{AB}(\boldsymbol{q},\omega')}{\omega - \omega' + \mathrm{i}\delta} \left(1 - \mathrm{e}^{-\beta\hbar\omega'}\right). \tag{J.1.80}$$

A similar relation holds for the advanced function:

$$\chi^{\mathbf{A}}_{AB}(\boldsymbol{q},\omega) = -\frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{K_{AB}(\boldsymbol{q},\omega')}{\omega - \omega' - \mathrm{i}\delta} \left(1 - \mathrm{e}^{-\beta\hbar\omega'}\right). \tag{J.1.81}$$

Therefore

$$\chi_{AB}(\boldsymbol{q},\omega) - \chi^{A}_{AB}(\boldsymbol{q},\omega) = \frac{\mathrm{i}}{\hbar} K_{AB}(\boldsymbol{q},\omega) \left(1 - \mathrm{e}^{-\beta\hbar\omega}\right). \qquad (J.1.82)$$

Let us consider now the correlation function

$$K_{BA}(\boldsymbol{q}, t - t') = \frac{1}{V} \langle B(\boldsymbol{q}, t) A(-\boldsymbol{q}, t') \rangle \qquad (J.1.83)$$
$$= \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \langle \Psi_n | B(\boldsymbol{q}, t) | \Psi_m \rangle \langle \Psi_m | A(-\boldsymbol{q}, t') | \Psi_n \rangle.$$

Its Fourier transform with respect to time is

$$K_{BA}(\boldsymbol{q},\omega) = \int_{-\infty} \mathrm{d}(t-t')\mathrm{e}^{\mathrm{i}\omega(t-t')}\mathrm{e}^{\mathrm{i}(E_n-E_m)(t-t')/\hbar} \\ \times \frac{1}{V}\sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \langle \Psi_n | B(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | A(-\boldsymbol{q}) | \Psi_n \rangle$$
(J.1.84)
$$= 2\pi\hbar \frac{1}{V}\sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \langle \Psi_n | A(-\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | B(\boldsymbol{q}) | \Psi_n \rangle \\ \times \mathrm{e}^{-\beta(E_m-E_n)} \delta(\hbar\omega + E_m - E_n) \,.$$

The labels n and m were interchanged in the last expression. Comparison with (J.1.79) leads to the relationship

$$K_{BA}(\boldsymbol{q},\omega) = e^{\beta\hbar\omega} K_{AB}(-\boldsymbol{q},-\omega) = e^{\beta\hbar\omega} K_{AB}(\boldsymbol{q},-\omega) \,. \tag{J.1.85}$$

Using this relationship in (J.1.80) we find

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$$\chi_{AB}(\boldsymbol{q},\omega) = -\frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{K_{AB}(\boldsymbol{q},\omega')}{\omega - \omega' + \mathrm{i}\delta} + \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{K_{BA}(\boldsymbol{q},-\omega')}{\omega - \omega' + \mathrm{i}\delta} \,. \tag{J.1.86}$$

J.1.8 Fluctuation–Dissipation Theorem

We encounter fairly often the situation where the operator B is the Hermitian adjoint of A. Then

$$\langle \Psi_n | A(\boldsymbol{q}) | \Psi_m \rangle^* = \langle \Psi_m | A^{\dagger}(-\boldsymbol{q}) | \Psi_n \rangle$$
 (J.1.87)

and hence

$$K_{AA^{\dagger}}(\boldsymbol{q},\omega) = 2\pi\hbar \frac{1}{V} \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} \left| \left\langle \Psi_n | A(\boldsymbol{q}) | \Psi_m \right\rangle \right|^2 \delta(\hbar\omega + E_n - E_m) \quad (J.1.88)$$

is a real positive semidefinite quantity. It follows from (J.1.80) that

$$\chi_{AA^{\dagger}}^{\prime\prime}(\boldsymbol{q},\omega) = \frac{1}{2\hbar} K_{AA^{\dagger}}(\boldsymbol{q},\omega) \left(1 - e^{-\beta\hbar\omega}\right), \qquad (J.1.89)$$

and thus

$$K_{AA^{\dagger}}(\boldsymbol{q},\omega) = 2\hbar \frac{1}{1 - e^{-\beta\hbar\omega}} \chi_{AA^{\dagger}}^{\prime\prime}(\boldsymbol{q},\omega) \,. \tag{J.1.90}$$

In the classical limit, when $\hbar \to 0$, we have

$$K_{AA^{\dagger}}(\boldsymbol{q},\omega) = 2\frac{k_{\rm B}T}{\omega}\chi_{AA^{\dagger}}^{\prime\prime}(\boldsymbol{q},\omega). \qquad (J.1.91)$$

The equal-time correlation function is obtained by integrating over the variable ω :

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$$K_{AA^{\dagger}}(\boldsymbol{q}) = \frac{1}{V} \langle A(\boldsymbol{q}) A^{\dagger}(-\boldsymbol{q}) \rangle = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} K_{AA^{\dagger}}(\boldsymbol{q},\omega)$$

$$= \frac{\hbar}{\pi} \int_{-\infty}^{\infty} \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega}} \chi_{AA^{\dagger}}''(\boldsymbol{q},\omega) \,\mathrm{d}\omega \,.$$
(J.1.92)

In the limit $T \to 0$ we have

$$K_{AA^{\dagger}}(\boldsymbol{q}) = \frac{\hbar}{\pi} \int_{0}^{\infty} \mathrm{d}\omega \, \chi_{AA^{\dagger}}'(\boldsymbol{q},\omega) \,. \tag{J.1.93}$$

If the operators appear in reversed order, then according to (J.1.85)

$$K_{A^{\dagger}A}(\boldsymbol{q},\omega) = \mathrm{e}^{\beta\hbar\omega} K_{AA^{\dagger}}(\boldsymbol{q},-\omega) \,. \tag{J.1.94}$$

Thus

$$K_{A^{\dagger}A}(\boldsymbol{q},\omega) = 2\hbar \frac{1}{\mathrm{e}^{\beta\hbar\omega} - 1} \chi_{AA^{\dagger}}^{\prime\prime}(\boldsymbol{q},\omega) \qquad (J.1.95)$$

and the static correlation function is

$$K_{A^{\dagger}A}(\boldsymbol{q}) = \frac{\hbar}{\pi} \int_{-\infty}^{\infty} \frac{1}{\mathrm{e}^{\beta\hbar\omega} - 1} \chi_{AA^{\dagger}}^{\prime\prime}(\boldsymbol{q},\omega) \,\mathrm{d}\omega \,. \tag{J.1.96}$$

The quantum mechanical transition rate between states $|\Psi_m\rangle$ and $|\Psi_n\rangle$ is independent of the direction of the transition, but the transition rates are weighted in the correlation functions by the thermal occupation of the states. This explains the above relationship between $K_{AA^{\dagger}}$ and $K_{A^{\dagger}A}$.

When we are interested in the fluctuations of an observable associated with the Hermitian operator A at a wave vector q, we have to consider the quantity

$$\frac{1}{V} \left\langle \left| A(\boldsymbol{q}) \right|^2 \right\rangle. \tag{J.1.97}$$

The volume factor appears for normalization. If the components at q and -q do not commute, the symmetric combination

$$\frac{1}{2V} \left\langle \left[A(\boldsymbol{q}) A^{\dagger}(-\boldsymbol{q}) + A^{\dagger}(-\boldsymbol{q}) A(\boldsymbol{q}) \right] \right\rangle$$
 (J.1.98)

should be retained. Using the expressions derived above we have

$$\frac{1}{V} \langle |A(\boldsymbol{q})|^{2} \rangle = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \frac{\mathrm{e}^{\beta\hbar\omega} + 1}{\mathrm{e}^{\beta\hbar\omega} - 1} \chi_{AA^{\dagger}}^{\prime\prime}(\boldsymbol{q},\omega) \,\mathrm{d}\omega$$

$$= \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} \coth \frac{\hbar\omega}{2k_{\mathrm{B}}T} \chi_{AA^{\dagger}}^{\prime\prime}(\boldsymbol{q},\omega) \,\mathrm{d}\omega \,. \tag{J.1.99}$$

The imaginary part of the susceptibility being an odd function of ω this can be written as

$$\frac{1}{V} \left\langle \left| A(\boldsymbol{q}) \right|^2 \right\rangle = \frac{\hbar}{\pi} \int_0^\infty \coth \frac{\hbar \omega}{2k_{\rm B}T} \chi_{AA^{\dagger}}''(\boldsymbol{q}, \omega) \,\mathrm{d}\omega \,. \tag{J.1.100}$$

The imaginary part of the susceptibility is related to the energy dissipated during the quantum mechanical transitions. For this reason this relationship, which expresses the fluctuations of $A(\mathbf{q})$ in terms of $\chi''_{AA^{\dagger}}(\mathbf{q},\omega)$, is known as the *fluctuation-dissipation theorem*.² It is the generalization of the Nyquist relation³ connecting the thermal noise of the electric current to the electrical resistance.

In the classical limit, when the thermal energy $k_{\rm B}T$ is larger than $\hbar\omega$ for the frequencies at which the energy is absorbed (where the imaginary part is finite), we have

$$\frac{1}{V} \langle \left| A(\boldsymbol{q}) \right|^2 \rangle = \frac{2k_{\rm B}T}{\pi} \int_{0}^{\infty} \frac{\chi_{AA\dagger}'(\boldsymbol{q},\omega)}{\omega} \,\mathrm{d}\omega \,. \tag{J.1.101}$$

J.2 Density–Density Response Function

It was shown in Chapter 29 [see (29.1.25)] that the dielectric function of the system of electrons can be written in the form

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2}\Pi(\boldsymbol{q},\omega)\,,\qquad({\rm J.2.1})$$

where $\Pi(\mathbf{q}, \omega)$ is the generalized susceptibility that relates the variations of the spatial distribution of electrons to the external potential. According to linear response theory this susceptibility is the Fourier transform with respect to both space and time of the retarded density-density correlation function

$$\Pi(\boldsymbol{r},\boldsymbol{r}',t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\Big\langle \big[n(\boldsymbol{r},t),n(\boldsymbol{r}',t')\big]_{-}\Big\rangle,\qquad(\mathrm{J.2.2})$$

that is

$$\Pi(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')} \Big\langle \big[n(\boldsymbol{q},t), n(-\boldsymbol{q},t') \big]_{-} \Big\rangle.$$
(J.2.3)

² H. B. CALLEN and T. A. WELTON, 1951.

³ H. Nyquist, 1928.
This susceptibility is defined with a negative sign since the perturbation Hamiltonian (J.1.6) does not have a negative sign in contrast to the general form (J.1.7).

The density-density correlation function

$$K_{nn}(\boldsymbol{q},t) = \frac{1}{V} \langle n(\boldsymbol{q},t)n(-\boldsymbol{q}) \rangle$$
 (J.2.4)

is simply related to the imaginary part of the response function. Because of the sign difference mentioned above we have

$$K_{nn}(\boldsymbol{q},\omega) = -2\hbar \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega}} \Pi''(\boldsymbol{q},\omega) \,. \tag{J.2.5}$$

A differently normalized quantity

$$\Gamma(\boldsymbol{q},t) = \frac{1}{N_{\rm e}} \langle n(\boldsymbol{q},t)n(-\boldsymbol{q},0) \rangle = \frac{1}{n_{\rm e}} K_{nn}(\boldsymbol{q},t) \qquad (J.2.6)$$

defined in (28.4.86) is often used in the literature. The dynamical structure factor $S(\mathbf{q}, \omega)$ is obtained from the Fourier transform of $\Gamma(\mathbf{q}, t)$ by discarding the $\mathbf{q} = 0$ component. We will show that the moments of the dielectric function and those of the structure factor satisfy exact relations, called *sum rules*. Their knowledge may help in the evaluation of optical absorption experiments. At the end of this section simple methods will be presented that allow us to calculate approximately the density–density response function.

J.2.1 Sum Rules

The dielectric function describes the causal relationship between the electric displacement and the electric field; hence, it satisfies the Kramers–Kronig relations. According to (16.1.65)

$$\epsilon_1(\boldsymbol{q},\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \mathrm{d}\omega' \,\epsilon_2(\boldsymbol{q},\omega') \frac{\omega'}{{\omega'}^2 - \omega^2} \,. \tag{J.2.7}$$

We know from (31.2.6) that the dielectric function is real for small values of q and sufficiently large values of ω and its asymptotic form is

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - \frac{\omega_{\rm p}^2}{\omega^2},$$
 (J.2.8)

where $\omega_{\rm p}$ is the plasma frequency defined in (16.1.69).

On the other hand, in that regime

$$\epsilon_1(\boldsymbol{q},\omega) = 1 - \frac{2}{\pi} \int_0^\infty \mathrm{d}\omega' \,\epsilon_2(\boldsymbol{q},\omega') \frac{\omega'}{\omega^2} \,. \tag{J.2.9}$$

Comparison of the two expressions leads to the first sum rule:

$$\int_{0}^{\infty} \omega \epsilon_2(\boldsymbol{q}, \omega) \, \mathrm{d}\omega = \frac{\pi}{2} \omega_{\mathrm{p}}^2.$$
 (J.2.10)

Making use of relationship (16.1.64) between the imaginary part of the dielectric function and the real part of the conductivity [see also (29.6.81)] we arrive at the *conductivity sum rule*

$$\int_{0}^{\infty} \operatorname{Re} \sigma(\boldsymbol{q}, \omega) \, \mathrm{d}\omega = \epsilon_0 \frac{\pi}{2} \omega_{\mathrm{p}}^2 = \pi \frac{n_{\mathrm{e}} e^2}{2m_{\mathrm{e}}} \,.$$
(J.2.11)

In optical experiments the optical constants $n(\omega)$ and $\kappa(\omega)$ (the real and imaginary parts of the complex refractive index) are used preferentially instead of the dielectric function or the optical conductivity. Their relationship is given in (25.1.44). We thus find a sum rule for the optical constants:

$$\int_{0}^{\infty} \omega n(\omega) \kappa(\omega) \, \mathrm{d}\omega = \frac{\pi}{4} \omega_{\mathrm{p}}^{2} \,. \tag{J.2.12}$$

The response function appearing in (29.1.25) describes a causal response; hence, the inverse of the dielectric function, too, satisfies the Kramers–Kronig relations. We find

$$\operatorname{Re} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega)} - 1 = \frac{2}{\pi} P \int_{0}^{\infty} \mathrm{d}\omega' \operatorname{Im} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega')} \frac{\omega'}{{\omega'}^{2} - \omega^{2}}.$$
 (J.2.13)

It then follows that for large values of ω

$$\operatorname{Re} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega)} - 1 = -\frac{2}{\pi} P \int_{0}^{\infty} \mathrm{d}\omega' \operatorname{Im} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega')} \frac{\omega'}{\omega^{2}}.$$
 (J.2.14)

On the other hand we know that

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{\omega_{\rm p}^2}{\omega^2}.$$
 (J.2.15)

Comparison of the two expressions yields the longitudinal f-sum rule:

$$\int_{0}^{\infty} \omega \operatorname{Im} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega)} \, \mathrm{d}\omega = -\frac{\pi}{2}\omega_{\mathrm{p}}^{2}.$$
(J.2.16)

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Looking at the static, $\omega = 0$ case the Kramers–Kronig relations give

$$\operatorname{Re} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q})} - 1 = \frac{2}{\pi} \operatorname{P} \int_{0}^{\infty} \frac{\mathrm{d}\omega'}{\omega'} \operatorname{Im} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega')} \,. \tag{J.2.17}$$

The static dielectric function diverges – its inverse vanishes – in metals in the long-wavelength $q \rightarrow 0$ limit as $1/q^2$, hence

$$\lim_{q \to 0} \int_{0}^{\infty} \operatorname{Im} \frac{1}{\epsilon_{\mathrm{r}}(\boldsymbol{q},\omega)} \frac{\mathrm{d}\omega}{\omega} = -\frac{\pi}{2} \,. \tag{J.2.18}$$

At T = 0, where the density-density correlation function vanishes for negative frequencies, it follows from (29.1.35) and (29.1.36) that the dynamical structure factor satisfies the relations

$$S(\boldsymbol{q},\omega) = -\frac{2\hbar}{n_{\rm e}} \Pi''(\boldsymbol{q},\omega) = -\frac{2\hbar}{n_{\rm e}} \frac{q^2}{4\pi \tilde{e}^2} \operatorname{Im} \frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} \quad \text{for } \omega > 0. \quad (J.2.19)$$

Substituting this into the sum rule (J.2.16) we find

$$\frac{1}{2\pi} \int_{0}^{\infty} \omega S(\boldsymbol{q}, \omega) \,\mathrm{d}\omega = \frac{\hbar q^2}{2m_{\rm e}} \,. \tag{J.2.20}$$

Inserting the same relation into (J.2.18) a sum rule

$$\frac{1}{2\pi} \int_{0}^{\infty} \frac{S(\boldsymbol{q}, \omega)}{\omega} \,\mathrm{d}\omega = \frac{\hbar q^2}{2m_{\rm e}\omega_{\rm p}^2} \tag{J.2.21}$$

valid for small but finite values of q is obtained.

The dynamical structure factor is sometimes defined in the literature without the factor $2\pi/N_{\rm e}$. This quantity will be denoted by $\widetilde{S}(\boldsymbol{q},\omega)$:

$$\widetilde{S}(\boldsymbol{q},\omega) = \sum_{mn} \frac{\mathrm{e}^{-\beta E_n}}{Z} |\langle \Psi_n | n(\boldsymbol{q}) | \Psi_m \rangle|^2 \delta(\omega - (E_m - E_n)/\hbar) \,. \tag{J.2.22}$$

When the sum rules are given for this quantity,

$$\int_{-\infty}^{\infty} \omega \widetilde{S}(\boldsymbol{q}, \omega) \,\mathrm{d}\omega = N_{\mathrm{e}} \frac{\hbar q^2}{2m_{\mathrm{e}}} \,, \qquad (J.2.23\text{-a})$$

$$\int_{0}^{\infty} \frac{\widetilde{S}(\boldsymbol{q},\omega)}{\omega} \,\mathrm{d}\omega = V \frac{\hbar q^2}{8\pi \tilde{e}^2} \,. \tag{J.2.23-b}$$

We can prove sum rule (J.2.20) for the first moment of the structure factor in a different way, too, which derivation leads to another, much used sum rule. We follow the procedure applied in Chapter 29 in calculating the dielectric function of semiconductors. For this let us consider the double commutator

$$\left[\left[n(\boldsymbol{q}),\mathcal{H}\right]_{-},n(-\boldsymbol{q})\right]_{-}.$$
 (J.2.24)

The inner commutator can readily be obtained:

$$[n(\boldsymbol{q}), \mathcal{H}]_{-} = -\frac{\hbar^{2}}{2m_{e}} \left[\sum_{i} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_{i}}, \sum_{j} \boldsymbol{\nabla}_{\boldsymbol{r}_{j}}^{2} \right]_{-}$$

$$= -i\boldsymbol{q} \frac{\hbar^{2}}{2m_{e}} \sum_{i} \left(\boldsymbol{\nabla}_{\boldsymbol{r}_{i}} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_{i}} + e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_{i}} \boldsymbol{\nabla}_{\boldsymbol{r}_{i}} \right).$$
(J.2.25)

This result is independent of the electron–electron interaction as the interaction Hamiltonian depends only on the spatial coordinates of electrons and hence commutes with the density.

Recognizing in this expression the current-density operator given in (29.6.7) we find that

$$[n(\boldsymbol{q}), \mathcal{H}]_{-} = \hbar \boldsymbol{q} \cdot \boldsymbol{j}(\boldsymbol{q}). \qquad (J.2.26)$$

This relationship could have been derived directly from the continuity equation as well. Evaluating now the second commutator we have

$$\left[\left[n(\boldsymbol{q}),\mathcal{H}\right]_{-},n(-\boldsymbol{q})\right]_{-}=\left[\hbar\boldsymbol{q}\cdot\boldsymbol{j}(\boldsymbol{q}),n(-\boldsymbol{q})\right]_{-}=\frac{N_{\mathrm{e}}\hbar^{2}q^{2}}{m_{\mathrm{e}}}.$$
 (J.2.27)

On the other hand, the ground-state expectation value of the double commutator can be calculated directly by inserting a complete set of eigenstates of the total Hamiltonian. We have

$$\langle \Psi_0 | [[n(\boldsymbol{q}), \mathcal{H}]_{-}, n(-\boldsymbol{q})]_{-} | \Psi_0 \rangle = \sum_m 2(E_m - E_0) | \langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle |^2.$$
 (J.2.28)

Comparison of the two equations yields the Bethe sum rule:⁴

$$\sum_{m} (E_m - E_0) \left| \left< \Psi_0 \left| n(q) \right| \Psi_m \right> \right|^2 = \frac{N_e \hbar^2 q^2}{2m_e} \,. \tag{J.2.29}$$

The dynamical structure factor as the Fourier transform of the density–density correlation function can also be given in a spectral representation. We readily find

$$S(\boldsymbol{q},\omega) = 2\pi\hbar \frac{1}{N_{\rm e}} \sum_{m} \langle \Psi_0 | n(\boldsymbol{q}) | \Psi_m \rangle \langle \Psi_m | n(-\boldsymbol{q}) | \Psi_0 \rangle \, \delta(\hbar\omega - E_m + E_0) \,. \tag{J.2.30}$$

⁴ H. Bethe, 1930.

The integral of the first moment of $S(\boldsymbol{q}, \omega)$ gives

$$\int_{-\infty}^{\infty} \omega S(\boldsymbol{q},\omega) \,\mathrm{d}\omega = \frac{2\pi}{\hbar} \frac{1}{N_{\mathrm{e}}} \sum_{m} (E_m - E_0) \left| \left\langle \Psi_0 \left| n(\boldsymbol{q}) \right| \Psi_m \right\rangle \right|^2. \tag{J.2.31}$$

Comparing this expression with (J.2.29) we recover the sum rule

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \omega S(\boldsymbol{q}, \omega) \,\mathrm{d}\omega = \frac{\hbar q^2}{2m_{\rm e}} \,. \tag{J.2.32}$$

The optical transitions from the ground state to the excited states were conveniently characterized by the oscillator strength defined in (25.2.13) when the optical properties of solids were studied. A formal comparison of the expression obtained for the dielectric function of electrons bound to atoms with the expression derived for itinerant electrons yields

$$f_{0m} = \frac{2m_{\rm e}}{\hbar^2 q^2} (E_m - E_0) \left| \left< \Psi_0 \left| n(q) \right| \Psi_m \right> \right|^2$$
(J.2.33)

for the oscillator strength of transitions in the electron system from the ground state to the excited state $|\Psi_m\rangle$. Summing the oscillator strengths over all excited states and comparing the expression with (J.2.29) we obtain

$$\sum_{m} f_{0m} = N_{\rm e} \,. \tag{J.2.34}$$

This relationship is known as the $f\text{-}sum\ rule$ or Thomas–Reiche–Kuhn sum rule. 5

J.2.2 Equation-of-Motion Method

The response function or generalized susceptibility can be considered as a many-particle-retarded Green function. The methods presented in the next appendix to calculate the Green functions can also be used to calculate the response functions. Although a consistent perturbation theory based on the Feynman diagram technique can only be formulated for the causal functions, the retarded functions can be obtained by analytic continuation in the ω -plane. The elements of diagram technique will be given in the next appendix on Green functions. Here we present a simpler approach based on the equation of motion of the operators appearing in the correlation functions.

Within this approach we still have several possibilities. We could write the equation of motion directly for the response function in the equilibrium system, or alternatively we could write an equation for the expectation value of

⁵ W. THOMAS, F. REICHE, and W. KUHN, 1925.

the operator A associated with the observable in the presence of the perturbing field. Whichever procedure is used, more complicated, higher order terms will appear in the equation of motion. Writing the equation of motion for them, a hierarchy is generated which has to be truncated at some point by decoupling the averages of products of operators. This decoupling procedure is well suited to get a rough picture of the behavior of the system although its accuracy is not well controlled.

As an example we consider the Fourier transform of the retarded density– density correlation function appearing in the dielectric function. It is defined by

$$\Pi(\boldsymbol{q},\omega) = -\frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}(t-t') \,\mathrm{e}^{\mathrm{i}\omega(t-t')-\delta(t-t')}$$

$$\times \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} \left\langle \left[c^{\dagger}_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t), c^{\dagger}_{\boldsymbol{k}'+\boldsymbol{q}\sigma'}(t')c_{\boldsymbol{k}'\sigma'}(t') \right]_{-} \right\rangle.$$
(J.2.35)

The thermal average has to be calculated for an equilibrium system taking into account the electron–electron interaction as precisely as possible. We will write the equation of motion for a single term of the sum over k and σ , for

$$\Pi_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{q},t-t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\frac{1}{V}\Big\langle \left[c_{\boldsymbol{k}\sigma}^{\dagger}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t),n_{\sigma'}(-\boldsymbol{q},t')\right]_{-}\Big\rangle.$$
(J.2.36)

Taking the time derivative with respect to t a Dirac delta function arising from the derivative of the Heaviside step function appears with the equaltime commutator of the operators $c^{\dagger}_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}+\boldsymbol{q}\sigma}$ and $n_{\sigma'}(-\boldsymbol{q})$. This commutator gives

$$\begin{bmatrix} c_{\boldsymbol{k}\sigma}^{\dagger}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t), n_{\sigma'}(-\boldsymbol{q},t) \end{bmatrix}_{-} = \delta_{\sigma\sigma'} \begin{bmatrix} c_{\boldsymbol{k}\sigma}^{\dagger}(t)c_{\boldsymbol{k}\sigma}(t) - c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \end{bmatrix}.$$
(J.2.37)

Besides that we need the commutators appearing in the expression

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(c_{\boldsymbol{k}\sigma}^{\dagger}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \right) = \frac{\mathrm{d}c_{\boldsymbol{k}\sigma}^{\dagger}(t)}{\mathrm{d}t} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) + c_{\boldsymbol{k}\sigma}^{\dagger}(t) \frac{\mathrm{d}c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t)}{\mathrm{d}t} \qquad (J.2.38)$$

$$= \frac{\mathrm{i}}{\hbar} \left[\mathcal{H}, c_{\boldsymbol{k}\sigma}^{\dagger}(t) \right]_{-} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) + \frac{\mathrm{i}}{\hbar} c_{\boldsymbol{k}\sigma}^{\dagger}(t) \left[\mathcal{H}, c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \right]_{-}.$$

For a homogeneous electron gas, where the one-particle potential is canceled by the q = 0 component of the Coulomb repulsion, we find

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}+\varepsilon_{\mathbf{k}}\right)c_{\mathbf{k}\sigma}^{\dagger}(t) = -\frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma''}U(\mathbf{q}')c_{\mathbf{k}+\mathbf{q}'\sigma}^{\dagger}(t)c_{\mathbf{k}'-\mathbf{q}'\sigma''}^{\dagger}(t)c_{\mathbf{k}'\sigma''}(t)$$
(J.2.39)

and

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}-\varepsilon_{\mathbf{k}+\mathbf{q}}\right)c_{\mathbf{k}+\mathbf{q}\sigma}(t) = \frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma''}U(\mathbf{q}')c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t)c_{\mathbf{k}'\sigma''}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t).$$
(J.2.40)

Multiplying the first equation by $c_{{\bm k}+{\bm q}\sigma}$ from the right and the second by $c_{{\bm k}\sigma}^\dagger$ from the left, they can be combined to yield

$$\begin{pmatrix} -\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} \end{pmatrix} c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \\ = -\frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma''} U(\mathbf{q}')c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t)c_{\mathbf{k}'\sigma''}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \\ + \frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma''} U(\mathbf{q}')c^{\dagger}_{\mathbf{k}\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t)c_{\mathbf{k}'\sigma''}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t) . \end{cases}$$
(J.2.41)

Using these expressions in the equation of motion for the response function we get

$$\begin{pmatrix} -\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} \end{pmatrix} \Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\ = \delta_{\sigma\sigma'}\delta(t-t')\frac{1}{V} \Big[\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}\sigma}(t) \rangle - \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle \Big] \\ + \frac{i}{\hbar}\theta(t-t')\frac{1}{V^2}\sum_{\mathbf{k}'\mathbf{q}'\sigma''} U(\mathbf{q}') \\ \times \Big\langle \Big[c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t)c_{\mathbf{k}'\sigma''}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \Big]_{-} \Big\rangle \\ - \frac{i}{\hbar}\theta(t-t')\frac{1}{V^2}\sum_{\mathbf{k}'\mathbf{q}'\sigma''} U(\mathbf{q}') \\ \times \Big\langle \Big[c^{\dagger}_{\mathbf{k}\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t)c_{\mathbf{k}'\sigma''}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \Big]_{-} \Big\rangle.$$

The first term on the right-hand side contains the occupation of the states with wave vectors k and k + q. They are given by the Fermi distribution function

$$\langle c_{\boldsymbol{k}\sigma}^{\dagger}c_{\boldsymbol{k}\sigma}\rangle = \langle n_{\boldsymbol{k}\sigma}\rangle = f_0(\varepsilon_{\boldsymbol{k}\sigma}).$$
 (J.2.43)

Neglecting for the moment the terms containing the electron–electron interaction we have

$$\left(-\frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} \right) \Pi_{0\sigma\sigma'}(\mathbf{k}, \mathbf{q}, t - t')$$

$$= \delta_{\sigma\sigma'} \delta(t - t') \frac{1}{V} \left[f_0(\varepsilon_{\mathbf{k}}) - f_0(\varepsilon_{\mathbf{k}+\mathbf{q}}) \right].$$

$$(J.2.44)$$

Its Fourier transform with respect to time satisfies the equation

$$(\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}) \Pi_{0\sigma\sigma'}(\boldsymbol{k}, \boldsymbol{q}, \omega) = \delta_{\sigma\sigma'} \frac{1}{V} [f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})]. \quad (J.2.45)$$

The formal solution

$$\Pi_{0\sigma\sigma'}(\boldsymbol{k},\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}}$$
(J.2.46)

is not quite correct. Also

$$\Pi_{0\sigma\sigma'}(\boldsymbol{k},\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}} + a\delta(\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}) \quad (J.2.47)$$

is a solution, and the value of a has to be determined from the correct analytic properties, dictated by the requirement that the retarded response function has to be analytic in the upper half-plane. This leads to

$$\Pi_{0\sigma\sigma'}(\boldsymbol{k},\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} \,. \tag{J.2.48}$$

Summing over \boldsymbol{k} and σ gives

$$\Pi_0(\boldsymbol{q},\omega) = \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta}, \qquad (J.2.49)$$

which is the well-known Lindhard function.

J.2.3 Decoupling Procedures

The equation of motion cannot be solved exactly when the electron–electron interaction is taken into account. As the simplest approximation we decouple the four-operator terms, that is we approximate the product of two equal-time operators by their expectation values. The two operators that are taken out of the commutator can be chosen in four different ways:

$$U(\mathbf{q}') \left\langle \left[c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle \\ \approx -\delta_{\mathbf{k}+\mathbf{q}',\mathbf{k}'} \delta_{\sigma\sigma''} U(\mathbf{k}'-\mathbf{k}) \left\langle c^{\dagger}_{\mathbf{k}'\sigma} c_{\mathbf{k}'\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle \\ + \delta_{\mathbf{q},\mathbf{q}'} U(\mathbf{q}) \left\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma} c_{\mathbf{k}+\mathbf{q}\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma''}(t) c_{\mathbf{k}'\sigma''}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle \quad (J.2.50) \\ + \delta_{\mathbf{q}',0} U(\mathbf{q}=0) \left\langle c^{\dagger}_{\mathbf{k}'\sigma''} c_{\mathbf{k}'\sigma''} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle \\ - \delta_{\mathbf{q}',\mathbf{k}'-\mathbf{k}-\mathbf{q}} \delta_{\sigma\sigma''} U(\mathbf{q}') \left\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma} c_{\mathbf{k}+\mathbf{q}\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma}(t) c_{\mathbf{k}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle$$

and similarly

$$\begin{split} U(\mathbf{q}') &\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \rangle \\ &\approx -\delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma''} U(\mathbf{q}') \langle c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \rangle \langle \left[c^{\dagger}_{\mathbf{k}-\mathbf{q}'\sigma}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \rangle \\ &+ \delta_{\mathbf{q}\mathbf{q}'} U(\mathbf{q}) \langle c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \rangle \langle \left[c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma''}(t) c_{\mathbf{k}'\sigma''}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \rangle \\ &+ \delta_{\mathbf{q}',0} U(\mathbf{q}'=0) \langle c^{\dagger}_{\mathbf{k}'\sigma''} c_{\mathbf{k}'\sigma''} \rangle \langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \rangle \\ &- \delta_{\mathbf{q},\mathbf{k}'-\mathbf{k}} \delta_{\sigma\sigma''} U(\mathbf{q}') \langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma} c_{\mathbf{k}'-\mathbf{q}'\sigma} \rangle \langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \rangle . \end{split}$$

We will consider the various terms separately.

Hartree–Fock Decoupling

As a first step we keep only the terms that contain the expression

$$\left\langle \left[c_{\boldsymbol{k}\sigma}^{\dagger}(t)c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t), n_{\sigma'}(-\boldsymbol{q},t') \right]_{-} \right\rangle.$$
 (J.2.52)

In this decoupling scheme

$$U(\mathbf{q}') \left\langle \left[c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q}, t') \right]_{-} \right\rangle$$

$$\approx -\delta_{\mathbf{k}+\mathbf{q}',\mathbf{k}'} \delta_{\sigma\sigma''} U(\mathbf{k}'-\mathbf{k}) \left\langle c^{\dagger}_{\mathbf{k}'\sigma} c_{\mathbf{k}'\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q}, t') \right]_{-} \right\rangle$$

$$+ \delta_{\mathbf{q}',0} U(\mathbf{q}=0) \left\langle c^{\dagger}_{\mathbf{k}'\sigma''} c_{\mathbf{k}'\sigma''} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q}, t') \right]_{-} \right\rangle$$

and

$$U(\mathbf{q}') \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle$$

$$\approx \delta_{\mathbf{q}',0} U(\mathbf{q}'=0) \left\langle c^{\dagger}_{\mathbf{k}'\sigma''} c_{\mathbf{k}'\sigma''} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle$$

$$- \delta_{\mathbf{q},\mathbf{k}'-\mathbf{k}} \delta_{\sigma\sigma''} U(\mathbf{q}') \left\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma} c_{\mathbf{k}'-\mathbf{q}'\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle.$$
(J.2.54)

Substituting these expressions into the equation of motion for $\Pi_{\sigma\sigma'}(\mathbf{k}, \mathbf{q}, t-t')$,

$$\begin{pmatrix} -\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} \end{pmatrix} \Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\ = \delta_{\sigma\sigma'}\delta(t-t')\frac{1}{V} [\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} \rangle - \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}+\mathbf{q}\sigma} \rangle] \\ + \frac{1}{V}\sum_{\mathbf{k}'\sigma''}\delta_{\sigma\sigma''}U(\mathbf{k}'-\mathbf{k})\langle c^{\dagger}_{\mathbf{k}'\sigma}c_{\mathbf{k}'\sigma} \rangle\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\ - \frac{1}{V}\sum_{\mathbf{k}'\sigma''}U(\mathbf{q}=0)\langle c^{\dagger}_{\mathbf{k}'\sigma''}c_{\mathbf{k}'\sigma''} \rangle\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\ + \frac{1}{V}\sum_{\mathbf{k}'\sigma''}U(\mathbf{q}=0)\langle c^{\dagger}_{\mathbf{k}'\sigma''}c_{\mathbf{k}'\sigma''} \rangle\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\ - \frac{1}{V}\sum_{\mathbf{q}'\sigma''}\delta_{\sigma\sigma''}U(\mathbf{q}')\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma} \rangle\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \,. \end{cases}$$
(J.2.55)

After a change of variables $q' \to k + q - k'$ we may recognize the Hartree–Fock self-energy correction of quasiparticles in the new terms appearing due to the interaction and we have

$$\left(-\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}}\right)\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\
= \delta_{\sigma\sigma'}\delta(t-t')\frac{1}{V}\left[\left\langle c_{\mathbf{k}\sigma}^{\dagger}c_{\mathbf{k}\sigma}\right\rangle - \left\langle c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger}c_{\mathbf{k}+\mathbf{q}\sigma}\right\rangle\right] \\
- \Sigma_{\mathbf{k}\sigma}\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') + \Sigma_{\mathbf{k}+\mathbf{q}\sigma}\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t').$$
(J.2.56)

Incorporating these corrections into the renormalized energies of the quasiparticles the equation of motion takes the form

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t} - \widetilde{\varepsilon}_{\mathbf{k}+\mathbf{q}} + \widetilde{\varepsilon}_{\mathbf{k}}\right)\Pi_{\sigma\sigma'}(\mathbf{k}, \mathbf{q}, t-t')
= \delta_{\sigma\sigma'}\delta(t-t')\frac{1}{V}\left[\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}\rangle - \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}+\mathbf{q}\sigma}\rangle\right].$$
(J.2.57)

It is natural to require that the occupation of the states be calculated with the renormalized energy, that is

$$\langle c^{\dagger}_{\boldsymbol{k}\sigma}c_{\boldsymbol{k}\sigma}\rangle = f_0(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}).$$
 (J.2.58)

The solution of the equation of motion then yields

$$\Pi_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \frac{f_0(\widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}}) - f_0(\widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}+\boldsymbol{q}} + \widetilde{\boldsymbol{\varepsilon}}_{\boldsymbol{k}} + \mathrm{i}\delta}, \qquad (J.2.59)$$

from which, after summation over \boldsymbol{k} and σ , we obtain

$$\Pi(\boldsymbol{q},\omega) = \frac{2}{V} \sum_{\boldsymbol{k}} \frac{f_0(\widetilde{\varepsilon}_{\boldsymbol{k}}) - f_0(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}} + \widetilde{\varepsilon}_{\boldsymbol{k}} + \mathrm{i}\delta} \,. \tag{J.2.60}$$

This decoupling thus corresponds to taking the self-energy corrections of the Hartree–Fock approximation into account in the Lindhard function. In diagrammatic language this approximation corresponds to independently dressing the electron and hole lines of the polarization bubble by the Hartree–Fock corrections.

The RPA

As a next approximation we take those terms from the decoupling that are proportional to U(q), that is we assume that

$$U(\mathbf{q}') \left\langle \left[c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q}, t') \right]_{-} \right\rangle$$

$$\approx \delta_{\mathbf{q}\mathbf{q}'} U(\mathbf{q}) \left\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma} c_{\mathbf{k}+\mathbf{q}\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma''}(t) c_{\mathbf{k}'\sigma''}(t), n_{\sigma'}(-\mathbf{q}, t') \right]_{-} \right\rangle$$
(J.2.61)

and

$$U(\mathbf{q}') \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle \\ \approx \delta_{\mathbf{q}\mathbf{q}'} U(\mathbf{q}) \left\langle c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma''}(t) c_{\mathbf{k}'\sigma''}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle.$$
(J.2.62)

The equation of motion then takes the form

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$$\left(-\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}}\right)\Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\
= \delta_{\sigma\sigma'}\delta(t-t')\frac{1}{V}\left[\left\langle c_{\mathbf{k}\sigma}^{\dagger}c_{\mathbf{k}\sigma}\right\rangle - \left\langle c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger}c_{\mathbf{k}+\mathbf{q}\sigma}\right\rangle\right] \\
- \frac{1}{V}\sum_{\mathbf{k}'\sigma''}U(\mathbf{q})\left\langle c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger}c_{\mathbf{k}+\mathbf{q}\sigma}\right\rangle\Pi_{\sigma''\sigma'}(\mathbf{k}'-\mathbf{q},\mathbf{q},t-t') \\
+ \frac{1}{V}\sum_{\mathbf{k}'\sigma''}U(\mathbf{q})\left\langle c_{\mathbf{k}\sigma}^{\dagger}c_{\mathbf{k}\sigma}\right\rangle\Pi_{\sigma''\sigma'}(\mathbf{k}'-\mathbf{q},\mathbf{q},t-t').$$
(J.2.63)

U(q) and the thermal average of the fermion occupation number can be taken out of the sum in the last two terms. The sum over k' gives the total spinresolved response function. Taking the frequency Fourier transform we have

$$(\hbar\omega - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}}) \Pi_{\sigma\sigma'}(\mathbf{k}, \mathbf{q}, \omega) = \delta_{\sigma\sigma'} \frac{1}{V} [f_0(\varepsilon_{\mathbf{k}}) - f_0(\varepsilon_{\mathbf{k}+\mathbf{q}})]$$
(J.2.64)

$$+ \frac{1}{V} [f_0(\varepsilon_{\mathbf{k}}) - f_0(\varepsilon_{\mathbf{k}+\mathbf{q}})] U(\mathbf{q}) \sum_{\sigma''} \Pi_{\sigma''\sigma'}(\mathbf{q}, \omega) ,$$

from which we find

$$\Pi_{\sigma\sigma'}(\boldsymbol{k},\boldsymbol{q},\omega) = \delta_{\sigma\sigma'} \frac{1}{V} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta}$$
(J.2.65)
+
$$\frac{1}{V} \frac{f_0(\varepsilon_{\boldsymbol{k}}) - f_0(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}} + \mathrm{i}\delta} U(\boldsymbol{q}) \sum_{\sigma''} \Pi_{\sigma''\sigma'}(\boldsymbol{q},\omega) \,.$$

Summation over the wave vector and spin gives

$$\Pi(\boldsymbol{q},\omega) = \Pi_0(\boldsymbol{q},\omega) + \Pi_0(\boldsymbol{q},\omega)U(\boldsymbol{q})\Pi(\boldsymbol{q},\omega).$$
 (J.2.66)

The solution of this equation,

$$\Pi(\boldsymbol{q},\omega) = \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - U(\boldsymbol{q})\Pi_0(\boldsymbol{q},\omega)}, \qquad (J.2.67)$$

is precisely identical to the result of the RPA. Thus this decoupling corresponds to summing the infinite series of polarization bubbles.

Hubbard Approximation

Finally, we consider the decoupling

$$U(\mathbf{q}') \left\langle \left[c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t), n_{\sigma'}(-\mathbf{q}, t') \right]_{-} \right\rangle$$
(J.2.68)
$$\approx -\delta_{\mathbf{q}',\mathbf{k}'-\mathbf{k}-\mathbf{q}} \delta_{\sigma\sigma''} U(\mathbf{q}') \left\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma} c_{\mathbf{k}+\mathbf{q}\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma}(t) c_{\mathbf{k}'\sigma}(t), n_{\sigma'}(-\mathbf{q}, t') \right]_{-} \right\rangle$$

and

$$U(\mathbf{q}') \left\langle \left[c^{\dagger}_{\mathbf{k}\sigma}(t) c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma''}(t) c_{\mathbf{k}'\sigma''}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle$$
(J.2.69)
$$\approx -\delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma''} U(\mathbf{q}') \left\langle c^{\dagger}_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} \right\rangle \left\langle \left[c^{\dagger}_{\mathbf{k}-\mathbf{q}'\sigma}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t), n_{\sigma'}(-\mathbf{q},t') \right]_{-} \right\rangle.$$

When this is inserted into the equation of motion we find

$$\begin{pmatrix} -\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} \end{pmatrix} \Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') = \delta_{\sigma\sigma'}\delta(t-t')\frac{1}{V} [\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} \rangle - \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}+\mathbf{q}\sigma} \rangle] \qquad (J.2.70) + \frac{1}{V}\sum_{\mathbf{k}'\sigma''}\delta_{\sigma\sigma''}U(\mathbf{k}+\mathbf{q}-\mathbf{k}')\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}+\mathbf{q}\sigma} \rangle \Pi_{\sigma\sigma'}(\mathbf{k}'-\mathbf{q},\mathbf{q},t-t') - \frac{1}{V}\sum_{\mathbf{q}'\sigma''}\delta_{\sigma\sigma''}U(\mathbf{q}')\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} \rangle \Pi_{\sigma\sigma'}(\mathbf{k}-\mathbf{q}',\mathbf{q},t-t') .$$

With a change of variables in the last term we have

$$\begin{pmatrix} -\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} \end{pmatrix} \Pi_{\sigma\sigma'}(\mathbf{k},\mathbf{q},t-t') \\ = \delta_{\sigma\sigma'}\delta(t-t')\frac{1}{V} [\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} \rangle - \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}+\mathbf{q}\sigma} \rangle] \qquad (J.2.71) \\ + \frac{1}{V}\sum_{\mathbf{k}'\sigma''}\delta_{\sigma\sigma''}U(\mathbf{k}+\mathbf{q}-\mathbf{k}')\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}c_{\mathbf{k}+\mathbf{q}\sigma} \rangle \Pi_{\sigma\sigma'}(\mathbf{k}'-\mathbf{q},\mathbf{q},t-t') \\ - \frac{1}{V}\sum_{\mathbf{k}'\sigma''}\delta_{\sigma\sigma''}U(\mathbf{k}+\mathbf{q}-\mathbf{k}')\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma} \rangle \Pi_{\sigma\sigma'}(\mathbf{k}'-\mathbf{q},\mathbf{q},t-t') .$$

The processes taken into account in this approximation can also be visualized by diagrams. They correspond to summing the contribution of the graphs depicted in Fig. J.2.



Fig. J.2. Diagrams taken into account in the Hubbard approximation

Unlike in the RPA, the potential $U(\mathbf{k} + \mathbf{q} - \mathbf{k}')$ cannot be taken out of the summation over \mathbf{k}' . Nevertheless, as pointed out by J. HUBBARD (1957), the new terms may be approximated by an expression proportional to $U(\mathbf{q})$. Taking the bare Coulomb repulsion for $U(\mathbf{q})$ and realizing that the most important contribution comes from terms in which $|\mathbf{k} - \mathbf{k}'|$ is close to the Fermi wave number,

$$U(\boldsymbol{q}) - U(\boldsymbol{k} + \boldsymbol{q} - \boldsymbol{k}')\delta_{\sigma,\sigma'} \approx 4\pi\tilde{e}^2 \left(\frac{1}{q^2} - \delta_{\sigma\sigma'}\frac{1}{q^2 + k_{\rm F}^2}\right).$$
(J.2.72)

Exchange is possible only between electrons of identical spins; therefore, the second term can compensate only half of the direct repulsion for large q values. Taking that into account, HUBBARD proposed the following approximate form

$$\sum_{\mathbf{k}'} U(\mathbf{k} + \mathbf{q} - \mathbf{k}') \Pi_{\sigma\sigma'}(\mathbf{k}' - \mathbf{q}, \mathbf{q}, t - t')$$

= $G(\mathbf{q}) \sum_{\mathbf{k}'} U(\mathbf{q}) \Pi_{\sigma\sigma'}(\mathbf{k}' - \mathbf{q}, \mathbf{q}, t - t')$ (J.2.73)

with

$$G(\boldsymbol{q}) = \frac{1}{2} \frac{q^2}{q^2 + k_{\rm F}^2}, \qquad (J.2.74)$$

as given in (29.2.70). There are also other, perhaps better, approximate forms in the literature, with somewhat different expressions for G(q).

Using this approximation in the equation of motion and comparing it with (J.2.63) obtained in the RPA, we see that the Hubbard decoupling leads to similar expressions as the RPA, except that the potential $U(\mathbf{q})$ is multiplied everywhere by $-G(\mathbf{q})$. Since the contributions corresponding to the two kinds of decoupling have to be added, the potential has to be multiplied by $1-G(\mathbf{q})$ compared to the RPA result, that is

$$\Pi(\boldsymbol{q},\omega) = \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - [1 - G(\boldsymbol{q})]U(\boldsymbol{q})\Pi_0(\boldsymbol{q},\omega)} \,. \tag{J.2.75}$$

Since the RPA is also known as the time-dependent Hartree approximation, the Hubbard approximation, where exchange terms are taken into account, might be called the time-dependent Hartree–Fock approximation.

Note that when the Hartree–Fock self-energy corrections are also taken into account, the Lindhard function $\Pi_0(\mathbf{q},\omega)$ should be calculated with the renormalized energies.

J.2.4 Alternative Derivation

In an alternative approach we solve the equation of motion for the induced electron density

$$n_{\rm ind}(\boldsymbol{q},t) = \left\langle n(\boldsymbol{q},t) \right\rangle = \sum_{\boldsymbol{k}\sigma} \left\langle c_{\boldsymbol{k}\sigma}^{\dagger}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \right\rangle \tag{J.2.76}$$

in the presence of an external perturbation

$$\mathcal{H}_{\text{ext}}(t) = \int V_{\text{ext}}(\boldsymbol{r}, t) n(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} = \frac{1}{V} \sum_{\boldsymbol{k} \boldsymbol{q} \sigma} V_{\text{ext}}(\boldsymbol{q}, t) c^{\dagger}_{\boldsymbol{k} + \boldsymbol{q} \sigma} c_{\boldsymbol{k} \sigma} \qquad (J.2.77)$$

to first order in V_{ext} , while trying to take into account the effect of the electronelectron interaction U(q) as precisely as we can. We first write the equation of motion for the product $c^{\dagger}_{k\sigma}(t)c_{k+q\sigma}(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(c_{\boldsymbol{k}\sigma}^{\dagger}(t) c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \right) = \frac{\mathrm{d}c_{\boldsymbol{k}\sigma}^{\dagger}(t)}{\mathrm{d}t} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) + c_{\boldsymbol{k}\sigma}^{\dagger}(t) \frac{\mathrm{d}c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t)}{\mathrm{d}t}
= \frac{\mathrm{i}}{\hbar} \left[\left(\mathcal{H} + \mathcal{H}_{\mathrm{ext}} \right), c_{\boldsymbol{k}\sigma}^{\dagger}(t) \right]_{-} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t)
+ \frac{\mathrm{i}}{\hbar} c_{\boldsymbol{k}\sigma}^{\dagger}(t) \left[\left(\mathcal{H} + \mathcal{H}_{\mathrm{ext}} \right), c_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) \right]_{-},$$
(J.2.78)

where \mathcal{H} is the sum of the kinetic energy term and the two-particle interaction. The time derivative of the creation and annihilation operators gives

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}+\varepsilon_{\mathbf{k}}\right)c_{\mathbf{k}\sigma}^{\dagger}(t) = -\frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma'}U(\mathbf{q}')c_{\mathbf{k}+\mathbf{q}'\sigma}^{\dagger}(t)c_{\mathbf{k}'-\mathbf{q}'\sigma'}^{\dagger}(t)c_{\mathbf{k}'\sigma'}(t)$$
$$-\frac{1}{V}\sum_{\mathbf{q}'}V_{\mathrm{ext}}(\mathbf{q}',t)c_{\mathbf{k}+\mathbf{q}'\sigma}^{\dagger}(t),\qquad(J.2.79)$$

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}-\varepsilon_{\mathbf{k}+\mathbf{q}}\right)c_{\mathbf{k}+\mathbf{q}\sigma}(t) = \frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma'}U(\mathbf{q}')c_{\mathbf{k}'-\mathbf{q}'\sigma'}^{\dagger}(t)c_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t) + \frac{1}{V}\sum_{\mathbf{q}'}V_{\mathrm{ext}}(\mathbf{q}',t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t).$$
(J.2.80)

Multiplying the first equation by $c_{\mathbf{k}+q\sigma}$ from the right and the second equation by $c_{\mathbf{k}\sigma}^{\dagger}$ from the left and taking the thermal average of the resulting expressions, the two equations can be combined to give

$$\begin{pmatrix} -\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}} \end{pmatrix} \langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle$$

$$= -\frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma'} U(\mathbf{q}') \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle$$

$$+ \frac{1}{V}\sum_{\mathbf{k}'\mathbf{q}'\sigma'} U(\mathbf{q}') \langle c^{\dagger}_{\mathbf{k}\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t) \rangle$$

$$- \frac{1}{V}\sum_{\mathbf{q}'} V_{\text{ext}}(\mathbf{q}',t) [\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle - \langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t) \rangle].$$

$$(J.2.81)$$

Being interested in the linear response, the thermal average in the last term should be calculated for the unperturbed system. Only the term q = q' contributes. A satisfactory treatment of the electron–electron interaction is more difficult. The four-operator terms could be decoupled into products of the thermal averages of two operators, as it is usually done in mean-field theory. The decoupling should be done in all possible ways, taking into account that

in normal metals the nonvanishing averages contain one creation and one annihilation operator. Accordingly the first term on the right-hand side of (J.2.81) is approximated as

$$\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\rangle$$

$$= \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\rangle \langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)\rangle$$

$$- \langle c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c_{\mathbf{k}'\sigma'}(t)\rangle \langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\rangle .$$

$$(J.2.82)$$

The sign of the terms is determined by the number of permutations of the fermion operators necessary to achieve the given order.

We want to collect the contributions that are proportional to the external potential. If one of the factors in the decoupled expression is assumed to be proportional to the perturbation, the other factor can be calculated for the unperturbed system. This linearization in the perturbation of the right-hand side of (J.2.82) leads to four terms. Taking into account that the only non-vanishing thermal average for an unperturbed normal system is the number of particles with a given wave vector, that is the creation and annihilation operators have to have the same momentum and spin, we find

$$\begin{split} \left\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\right\rangle \\ &= \delta_{\mathbf{q}',\mathbf{q}} \left\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\right\rangle \left\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)\right\rangle \\ &+ \delta_{\mathbf{q}',0} \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\right\rangle \left\langle c^{\dagger}_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)\right\rangle \\ &- \delta_{\mathbf{q}',\mathbf{k}'-\mathbf{k}}\delta_{\sigma,\sigma'} \left\langle c^{\dagger}_{\mathbf{k}'\sigma}(t)c_{\mathbf{k}'\sigma}(t)\right\rangle \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\right\rangle \\ &- \delta_{\mathbf{q}',\mathbf{k}'-\mathbf{k}-\mathbf{q}}\delta_{\sigma,\sigma'} \left\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma}(t)c_{\mathbf{k}'\sigma}(t)\right\rangle \left\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t)\right\rangle. \end{split}$$
(J.2.83)

If the Fermi distribution function is used for the occupation of electron states, we have

$$\langle c^{\dagger}_{\mathbf{k}+\mathbf{q}'\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle = \delta_{\mathbf{q}',\mathbf{q}}f_{0}(\varepsilon_{\mathbf{k}+\mathbf{q}})\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma'}(t)c_{\mathbf{k}'\sigma'}(t) \rangle + \delta_{\mathbf{q}',0}f_{0}(\varepsilon_{\mathbf{k}'})\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle - \delta_{\mathbf{q}',\mathbf{k}'-\mathbf{k}}\delta_{\sigma,\sigma'}f_{0}(\varepsilon_{\mathbf{k}'})\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle - \delta_{\mathbf{q}',\mathbf{k}'-\mathbf{k}-\mathbf{q}}\delta_{\sigma,\sigma'}f_{0}(\varepsilon_{\mathbf{k}+\mathbf{q}})\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma}(t)c_{\mathbf{k}'\sigma}(t) \rangle .$$
 (J.2.84)

A similar procedure for the second term on the right-hand side of (J.2.81) yields

$$\begin{split} \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t)\right\rangle \\ &= \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t)\right\rangle \left\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}'\sigma'}(t)\right\rangle \\ &- \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}'\sigma'}(t)\right\rangle \left\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}'\sigma'}(t)c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t)\right\rangle \end{split}$$

$$= \delta_{\mathbf{q}',\mathbf{q}} \langle c_{\mathbf{k}\sigma}^{\dagger}(t) c_{\mathbf{k}\sigma}(t) \rangle \langle c_{\mathbf{k}'-\mathbf{q}\sigma'}^{\dagger}(t) c_{\mathbf{k}'\sigma'}(t) \rangle$$

$$+ \delta_{\mathbf{q}',0} \langle c_{\mathbf{k}\sigma}^{\dagger}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle \langle c_{\mathbf{k}'\sigma'}^{\dagger}(t) c_{\mathbf{k}'\sigma'}(t) \rangle$$

$$- \delta_{\mathbf{k},\mathbf{k}'} \delta_{\sigma,\sigma'} \langle c_{\mathbf{k}\sigma}^{\dagger}(t) c_{\mathbf{k}\sigma}(t) \rangle \langle c_{\mathbf{k}-\mathbf{q}'\sigma}^{\dagger}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t) \rangle$$

$$- \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} \delta_{\sigma,\sigma'} \langle c_{\mathbf{k}\sigma}^{\dagger}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle \langle c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}^{\dagger}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t) \rangle$$

$$= \delta_{\mathbf{q}',\mathbf{q}} f_0(\varepsilon_{\mathbf{k}}) \langle c_{\mathbf{k}'-\mathbf{q}\sigma'}^{\dagger}(t) c_{\mathbf{k}'\sigma'}(t) \rangle + \delta_{\mathbf{q}',0} f_0(\varepsilon_{\mathbf{k}'}) \langle c_{\mathbf{k}\sigma}^{\dagger}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle$$

$$- \delta_{\mathbf{k},\mathbf{k}'} \delta_{\sigma,\sigma'} f_0(\varepsilon_{\mathbf{k}}) \langle c_{\mathbf{k}-\mathbf{q}'\sigma}^{\dagger}(t) c_{\mathbf{k}+\mathbf{q}-\mathbf{q}'\sigma}(t) \rangle$$

$$- \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} \delta_{\sigma,\sigma'} f_0(\varepsilon_{\mathbf{k}+\mathbf{q}-\mathbf{q}'}) \langle c_{\mathbf{k}\sigma}^{\dagger}(t) c_{\mathbf{k}+\mathbf{q}\sigma}(t) \rangle .$$
(J.2.85)

Substituting these expressions into (J.2.81) and after some algebra we have

$$\left(-\frac{\hbar}{i}\frac{d}{dt} - \varepsilon_{\mathbf{k}+\mathbf{q}} + \varepsilon_{\mathbf{k}}\right) \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \right\rangle \\
= \frac{1}{V}\sum_{\mathbf{k}'\sigma'} \left[U(\mathbf{k}-\mathbf{k}') - U(\mathbf{k}+\mathbf{q}-\mathbf{k}') \right] \delta_{\sigma,\sigma'} f_{0}(\varepsilon_{\mathbf{k}'}) \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \right\rangle \\
- \frac{1}{V}\sum_{\mathbf{k}'\sigma'} \left[U(\mathbf{q}) - U(\mathbf{k}+\mathbf{q}-\mathbf{k}')\delta_{\sigma,\sigma'} \right] \qquad (J.2.86) \\
\times \left[f_{0}(\varepsilon_{\mathbf{k}+\mathbf{q}}) - f_{0}(\varepsilon_{\mathbf{k}}) \right] \left\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma'}(t)c_{\mathbf{k}'\sigma'}(t) \right\rangle \\
+ \frac{1}{V}V_{\text{ext}}(\mathbf{q},t) \left[f_{0}(\varepsilon_{\mathbf{k}}) - f_{0}(\varepsilon_{\mathbf{k}+\mathbf{q}}) \right].$$

Note that the first term on the right-hand side gives precisely the Hartree– Fock corrections to $\varepsilon_{\mathbf{k}}$ and $\varepsilon_{\mathbf{k}+\mathbf{q}}$. The part containing $U(\mathbf{q})$ in the second term is proportional to the density $n(\mathbf{q})$. This is not true, however, for the other part containing $U(\mathbf{k} + \mathbf{q} - \mathbf{k}')$. A term proportional to $n(\mathbf{q})$ can be obtained by using the Hubbard approximation discussed previously. We assume that

$$\sum_{\mathbf{k}'} U(\mathbf{k} + \mathbf{q} - \mathbf{k}') \left\langle c^{\dagger}_{\mathbf{k}' - \mathbf{q}\sigma}(t) c_{\mathbf{k}'\sigma}(t) \right\rangle = G(\mathbf{q}) \sum_{\mathbf{k}'} U(\mathbf{q}) \left\langle c^{\dagger}_{\mathbf{k}' - \mathbf{q}\sigma}(t) c_{\mathbf{k}'\sigma}(t) \right\rangle$$
(J.2.87)

with

$$G(\boldsymbol{q}) = \frac{1}{2} \frac{q^2}{q^2 + k_{\rm F}^2} \,. \tag{J.2.88}$$

The procedure can be made self-consistent if the occupation of the states is determined for the renormalized energies. We then have

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t} - \widetilde{\varepsilon}_{\mathbf{k}+\mathbf{q}} + \widetilde{\varepsilon}_{\mathbf{k}}\right) \left\langle c_{\mathbf{k}\sigma}^{\dagger}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \right\rangle \\
= \frac{1}{V}\sum_{\mathbf{k}'\sigma'} U(\mathbf{q}) \left[1 - G(\mathbf{q})\right] \left\langle c_{\mathbf{k}'-\mathbf{q}\sigma'}^{\dagger}(t)c_{\mathbf{k}'\sigma'}(t) \right\rangle \left[f_{0}(\widetilde{\varepsilon}_{\mathbf{k}}) - f_{0}(\widetilde{\varepsilon}_{\mathbf{k}+\mathbf{q}})\right] \\
+ \frac{1}{V} V_{\mathrm{ext}}(\mathbf{q}, t) \left[f_{0}(\widetilde{\varepsilon}_{\mathbf{k}}) - f_{0}(\widetilde{\varepsilon}_{\mathbf{k}+\mathbf{q}})\right].$$
(J.2.89)

Taking the Fourier transform with respect to time we have

$$(\hbar\omega - \tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}} + \tilde{\varepsilon}_{\mathbf{k}}) \left\langle c^{\dagger}_{\mathbf{k}\sigma}(t)c_{\mathbf{k}+\mathbf{q}\sigma}(t) \right\rangle_{\mathrm{FT}} = \frac{1}{V} \left[V_{\mathrm{ext}}(\mathbf{q},\omega) + \sum_{\mathbf{k}'\sigma'} U(\mathbf{q}) \left[1 - G(\mathbf{q}) \right] \left\langle c^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma'}(t)c_{\mathbf{k}'\sigma'}(t) \right\rangle_{\mathrm{FT}} \right] \times \left[f_0(\tilde{\varepsilon}_{\mathbf{k}}) - f_0(\tilde{\varepsilon}_{\mathbf{k}+\mathbf{q}}) \right].$$
(J.2.90)

Dividing both sides by the energy factor and summing over k and σ , the Fourier component of the density appears:

$$\left\langle n(\boldsymbol{q},\omega)\right\rangle = \left[V_{\text{ext}}(\boldsymbol{q},\omega) + U(\boldsymbol{q}) \left[1 - G(\boldsymbol{q})\right] \left\langle n(\boldsymbol{q},\omega)\right\rangle \right] \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{f_0(\widetilde{\varepsilon}_{\boldsymbol{k}}) - f_0(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}} + \widetilde{\varepsilon}_{\boldsymbol{k}}},$$
(J.2.91)

from which we find

$$\langle n(\boldsymbol{q},\omega)\rangle = \frac{V_{\mathrm{ext}}(\boldsymbol{q},\omega)\Pi_0(\boldsymbol{q},\omega)}{1 - U(\boldsymbol{q})[1 - G(\boldsymbol{q})]\Pi_0(\boldsymbol{q},\omega)},$$
 (J.2.92)

where

$$\Pi_{0}(\boldsymbol{q},\omega) = \frac{1}{V} \sum_{\boldsymbol{k}\sigma} \frac{f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}}) - f_{0}(\widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}})}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}+\boldsymbol{q}} + \widetilde{\varepsilon}_{\boldsymbol{k}}}$$
(J.2.93)

is the Lindhard function calculated with the renormalized quasiparticle energies. The full response function has the same form as obtained in the Hubbard approximation,

$$\Pi(\boldsymbol{q},\omega) = \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - [1 - G(\boldsymbol{q})]U(\boldsymbol{q})\Pi_0(\boldsymbol{q},\omega)}, \qquad (J.2.94)$$

but with the renormalized $\Pi_0(q,\omega)$. Substituting this into (29.1.23) we get

$$\frac{1}{\epsilon_{\rm r}(\boldsymbol{q},\omega)} = 1 + \frac{4\pi\tilde{e}^2}{q^2} \frac{\Pi_0(\boldsymbol{q},\omega)}{1 - U(\boldsymbol{q})[1 - G(\boldsymbol{q})]\Pi_0(\boldsymbol{q},\omega)},\qquad(J.2.95)$$

and the dielectric function can be written as

$$\epsilon_{\rm r}(\boldsymbol{q},\omega) = 1 - U(\boldsymbol{q}) \frac{\Pi_0(\boldsymbol{q},\omega)}{1 + U(\boldsymbol{q})G(\boldsymbol{q})\Pi_0(\boldsymbol{q},\omega)} \,. \tag{J.2.96}$$

Further Reading

- G. D. Mahan, *Many-Particle Physics*, Third Edition, Plenum Press, New York (2000).
- S. W. Lovesey, Condensed Matter Physics: Dynamical Correlations, W. A. Benjamin, New York (1980).

 \mathbf{K}

Green Functions of the Many-Body Problem

Solids are inherently interacting many-particle systems. Correlations between the constituents and the response to external perturbations may be strongly influenced by the internal interactions. Therefore, the application of the methods of the many-body problem is often unavoidable in the theoretical description of the properties of solids. The methods based on calculating Green functions allow us to account for the effects of interactions, in principle exactly. Although we have referred to them in many places, and diagrams were used to visualize interaction processes, the consistent application of Green function methods and diagrammatic perturbation theory was avoided. In this appendix some basic concepts of many-body physics are presented. We give a physically motivated definition of Green functions and discuss the information they can provide about the system. The perturbative procedures to calculate the Green functions can be found in many classic textbooks on the many-body problem. We review only very briefly the fundamentals of diagram techniques. At the end, as an application of the Green function technique, we will present a simple treatment of superconductivity.

The path-integral formulation of quantum mechanics can also be applied to Green functions of the many-body problem. For fermions, which are of primary interest for us, the path integrals should be given in terms of Grassmann variables and not by functions owing to the anticommutation rules. The presentation of this method is beyond the scope of this appendix.

K.1 Green Functions

The basic elements of the many-body theory are the one-particle Green functions. We define them quite generally for fermion and boson systems and study their analytic properties and their relationship to the correlation functions. Although the Green functions can be defined for arbitrary temperature, special temperature Green functions have to be introduced to work out a consistent perturbation theory at finite temperatures.

K.1.1 One-Particle Green Function

Let us consider a system of bosons or fermions in the Heisenberg picture, where the time dependence of the operators is given by

$$\mathcal{A}(t) = e^{i\mathcal{H}t/\hbar} \mathcal{A} e^{-i\mathcal{H}t/\hbar}$$
(K.1.1)

with the full Hamiltonian, while the states are time independent. When we work with a grand canonical ensemble, $\mathcal{H} - \mu \mathcal{N}$ is used instead of \mathcal{H} with μ the chemical potential and \mathcal{N} the particle-number operator.

The field operator $\hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}', t')$ adds a particle with spin σ to the system at position \mathbf{r}' at time t'. Its propagation can be characterized by the retarded correlation function

$$\theta(t-t') \langle \hat{\psi}_{\sigma}(\boldsymbol{r},t), \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \rangle$$
 (K.1.2)

that gives the probability of finding the particle at a later time t at position r. The Heaviside unit step function $\theta(t - t')$ ensures that the propagation is forward in time. For mathematical reasons the *propagator* or *Green function* of the particle is defined by

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \Big\langle T \big\{ \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \big\} \Big\rangle, \qquad (\mathrm{K}.1.3)$$

where T is the time-ordering operator which orders the operators in decreasing time sequence from left to right. For bosons the operator T simply interchanges the operators, whereas for fermions a factor -1 appears every time two operators are interchanged. That is

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = \begin{cases} -\frac{i}{\hbar} \langle \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \rangle & \text{for } t > t', \\ \mp \frac{i}{\hbar} \langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \hat{\psi}_{\sigma}(\boldsymbol{r},t) \rangle & \text{for } t' > t. \end{cases}$$
(K.1.4)

Here and in what follows, the upper sign refers to bosons and the lower one to fermions. The time-ordered Green function is also referred to as the causal Green function. Note that if the spin of the particle can be flipped during the propagation due to scattering processes, the Green function matrix

$$G_{\sigma\sigma'}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \Big\langle T \big\{ \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}',t') \big\} \Big\rangle, \qquad (\mathrm{K}.1.5)$$

which has nondiagonal elements in the spin indices, has to be studied.

It is sometimes more convenient to work with the retarded Green function defined by

$$G^{\mathrm{R}}_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\Big\langle \big[\hat{\psi}_{\sigma}(\boldsymbol{r},t),\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}',t')\big]_{\mp}\Big\rangle,\qquad(\mathrm{K}.1.6)$$

where the commutator is used for bosons and the anticommutator for fermions. The advanced Green function

$$G^{\mathrm{A}}_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = \frac{\mathrm{i}}{\hbar}\theta(t'-t)\Big\langle \big[\hat{\psi}_{\sigma}(\boldsymbol{r},t),\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}',t')\big]_{\mp}\Big\rangle \tag{K.1.7}$$

accounts for the time development in the opposite direction. They obey the same equation of motion but differ in their analytic properties.

Instead of working with Green functions defined in space and time, it is often more convenient to use their Fourier transforms. If the field operators are written in terms of the creation and annihilation operators of plane-wave states in the form

$$\hat{\psi}_{\sigma}(\boldsymbol{r},t) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}(t) \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} ,$$
$$\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}'} c_{\boldsymbol{k}'\sigma}^{\dagger}(t') \mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}'} ,$$
(K.1.8)

we have

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'} \left\langle T\left\{c_{\boldsymbol{k}\sigma}(t)c_{\boldsymbol{k}'\sigma}^{\dagger}(t')\right\}\right\rangle \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}'} \,. \tag{K.1.9}$$

In a homogeneous system, where the Green function depends on r - r', only the term $\mathbf{k} = \mathbf{k}'$ gives a finite contribution. Equivalently we may say that the momentum $\hbar \mathbf{k}'$ of the particle added to the system has to be conserved in a translation-invariant system and so

$$G_{\sigma}(\boldsymbol{k}, t - t') = -\frac{\mathrm{i}}{\hbar} \left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}\sigma}^{\dagger}(t') \right\} \right\rangle.$$
(K.1.10)

The Green function of noninteracting particles can be calculated exactly. The time dependence of the creation and annihilation operators is given in the Heisenberg picture by

$$\begin{aligned} c_{\boldsymbol{k}\sigma}(t) &= \mathrm{e}^{\mathrm{i}\mathcal{H}_{0}t/\hbar}c_{\boldsymbol{k}\sigma}\mathrm{e}^{-\mathrm{i}\mathcal{H}_{0}t/\hbar} = c_{\boldsymbol{k}\sigma}\mathrm{e}^{-\mathrm{i}\varepsilon_{\boldsymbol{k}}t/\hbar} \,, \\ c_{\boldsymbol{k}\sigma}^{\dagger}(t) &= \mathrm{e}^{\mathrm{i}\mathcal{H}_{0}t/\hbar}c_{\boldsymbol{k}\sigma}^{\dagger}\mathrm{e}^{-\mathrm{i}\mathcal{H}_{0}t/\hbar} = c_{\boldsymbol{k}\sigma}^{\dagger}\mathrm{e}^{\mathrm{i}\varepsilon_{\boldsymbol{k}}t/\hbar} \,. \end{aligned} \tag{K.1.11}$$

We will consider a grand canonical ensemble in which the number of particles is not fixed. Then the time dependence of the operators has to be calculated by using $\mathcal{H}_0 - \mu \mathcal{N}$ instead of \mathcal{H}_0 and the excitation energies $\xi_{\mathbf{k}}$ are measured from the chemical potential, $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu$. Therefore we have

$$c_{\boldsymbol{k}}(t) = c_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\xi_{\boldsymbol{k}}t/\hbar}, \qquad c_{\boldsymbol{k}}^{\dagger}(t) = c_{\boldsymbol{k}}^{\dagger} \mathrm{e}^{\mathrm{i}\xi_{\boldsymbol{k}}t/\hbar}.$$
(K.1.12)

For the same reason the thermodynamic weight of a state with energy E and particle number N is

$$e^{-\beta(E-\mu N)}/Z \tag{K.1.13}$$

with

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$$Z = \operatorname{Tr} e^{-\beta(\mathcal{H}_0 - \mu \mathcal{N})}.$$
 (K.1.14)

We then find

$$G_{\sigma}^{(0)}(\boldsymbol{k}, t - t') = -\frac{\mathrm{i}}{\hbar} \mathrm{e}^{-\mathrm{i}\xi_{\boldsymbol{k}}(t - t')/\hbar} \begin{cases} \langle c_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}^{\dagger} \rangle & \text{for } t > t' \\ \pm \langle c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} \rangle & \text{for } t < t' \end{cases}$$
(K.1.15)

for the Fourier transform with respect to the spatial variable. If the expectation values are written in terms of the Bose or Fermi distribution functions,

$$G_{\sigma}^{(0)}(\boldsymbol{k}, t-t') = \begin{cases} -\frac{\mathrm{i}}{\hbar} (1 \pm n_{\boldsymbol{k}\sigma}) \mathrm{e}^{-\mathrm{i}\xi_{\boldsymbol{k}}(t-t')/\hbar} & \text{for } t > t', \\ \\ \mp \frac{\mathrm{i}}{\hbar} n_{\boldsymbol{k}\sigma} \mathrm{e}^{-\mathrm{i}\xi_{\boldsymbol{k}}(t-t')/\hbar} & \text{for } t < t', \end{cases}$$
(K.1.16)

where

$$n_{\boldsymbol{k}\sigma} = \frac{1}{\exp(\xi_{\boldsymbol{k}}/k_{\rm B}T) \mp 1} \,. \tag{K.1.17}$$

Its Fourier transform with respect to time is

$$G_{\sigma}^{(0)}(\boldsymbol{k},\omega) = \int_{-\infty}^{\infty} d(t-t') G_{\sigma}^{(0)}(\boldsymbol{k},t-t') e^{i\omega(t-t')}$$
$$= -\frac{i}{\hbar} \int_{-\infty}^{\infty} d(t-t') \theta(t-t') (1\pm n_{\boldsymbol{k}\sigma}) e^{i(\hbar\omega-\xi_{\boldsymbol{k}})(t-t')/\hbar} \quad (K.1.18)$$
$$\mp \frac{i}{\hbar} \int_{-\infty}^{\infty} d(t-t') \theta(t'-t) n_{\boldsymbol{k}\sigma} e^{i(\hbar\omega-\xi_{\boldsymbol{k}})(t-t')/\hbar}.$$

We use (J.1.53) and the analogous relation

$$\int_{-\infty}^{0} e^{i\omega(t-t')} d(t-t') = \int_{-\infty}^{\infty} \theta(t'-t) e^{i\omega(t-t')} d(t-t') = -\frac{i}{\omega - i\delta}$$
(K.1.19)

in evaluating these integrals. We then find

$$G_{\sigma}^{(0)}(\boldsymbol{k},\omega) = \frac{1 \pm n_{\boldsymbol{k}\sigma}}{\hbar\omega - \xi_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} \mp \frac{n_{\boldsymbol{k}\sigma}}{\hbar\omega - \xi_{\boldsymbol{k}\sigma} - \mathrm{i}\delta}.$$
 (K.1.20)

A similar calculation for the retarded and advanced Green functions of noninteracting particles gives

$$G_{\sigma}^{(0)R}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \xi_{\boldsymbol{k}\sigma} + \mathrm{i}\delta},$$

$$G_{\sigma}^{(0)A}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \xi_{\boldsymbol{k}\sigma} - \mathrm{i}\delta}.$$
(K.1.21)

When the electrons move in a one-particle potential, e.g., in the periodic potential of the lattice, and the complete set of eigenfunction $\phi_n(\mathbf{r})$ and eigenvalues ε_n are known, the field operators should be expanded in terms of the creation and annihilation operators of these states, and we find

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\sum_{n}\phi_{n}(\boldsymbol{r})\phi_{n}^{*}(\boldsymbol{r}')\mathrm{e}^{-\mathrm{i}(\varepsilon_{n}-\mu)(t-t')/\hbar} \qquad (\mathrm{K}.1.22)$$

in real space and time, while in frequency representation

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{n} \frac{\phi_{n}(\boldsymbol{r})\phi_{n}^{*}(\boldsymbol{r}')}{\hbar\omega - \varepsilon_{n} + \mu + \mathrm{i}\delta} \,. \tag{K.1.23}$$

The Green function of electrons in the presence of a periodic potential is defined conveniently in momentum representation not as the Fourier transform of $G_{\sigma}(\mathbf{r}, t; \mathbf{r}', t')$, but in terms of the creation and annihilation operators of Bloch electrons in the *n*th band:

$$G_{n\sigma}(\boldsymbol{k}, t - t') = -\frac{\mathrm{i}}{\hbar} \left\langle T \left\{ c_{n\boldsymbol{k}\sigma}(t) c_{n\boldsymbol{k}\sigma}^{\dagger}(t') \right\} \right\rangle.$$
(K.1.24)

The frequency Fourier transform of the Green function of noninteracting Bloch electrons has the simple form

$$G_{n\sigma}^{(0)}(\boldsymbol{k},\omega) = \frac{1 - n_{n\boldsymbol{k}\sigma}}{\hbar\omega - \varepsilon_{n\boldsymbol{k}\sigma} + \mu + \mathrm{i}\delta} + \frac{n_{n\boldsymbol{k}\sigma}}{\hbar\omega - \varepsilon_{n\boldsymbol{k}\sigma} + \mu - \mathrm{i}\delta}.$$
 (K.1.25)

The Green function of noninteracting particles exhibits an undamped oscillatory time dependence. The probability of finding the particle in its initial state is constant in time. The interaction between the particles will modify their energies and thereby the frequency of oscillations. Moreover, the particles will acquire a finite lifetime, and the probability of finding them decreases exponentially in time with a time constant which is the inverse of the lifetime. The Green function is expected to behave as

$$G_{\sigma}(\boldsymbol{k},t) \propto \mathrm{e}^{-\mathrm{i}(\widetilde{\varepsilon}_{\boldsymbol{k}\sigma}-\mu)t/\hbar} \mathrm{e}^{-\Gamma_{\boldsymbol{k}\sigma}t/\hbar},$$
 (K.1.26)

yielding

$$G_{\sigma}^{\mathrm{R,A}}(\boldsymbol{k},\omega) \approx \frac{Z_{\boldsymbol{k}\sigma}}{\hbar\omega - \widetilde{\varepsilon}_{\boldsymbol{k}\sigma} + \mu \pm \mathrm{i}\Gamma_{\boldsymbol{k}\sigma}}.$$
 (K.1.27)

When the Green function has such a form (this is not always the case as we will see in the next appendix), the retarded (advanced) Green function has a simple pole in the lower (upper) half-plane. When the lifetime is long enough, quasiparticles can be defined. The real part of the location of the pole gives the renormalized energy $\tilde{\epsilon}_{k\sigma}$ of the quasiparticle, while the imaginary part is proportional to the inverse of the lifetime, $1/\tau = \Gamma_{k\sigma}/\hbar$. The prefactor $Z_{k\sigma}$ is the quasiparticle weight. The methods of the many-body problem can be employed to calculate the Green function of interacting particles and to determine these quantities.

K.1.2 Phonon Propagator

The phonons being bosons, one could use the boson form of the Green function to describe the propagation of phonons in the system. It is, however, more convenient to treat phonons somewhat differently. The interaction of electrons with longitudinal acoustic phonons can be written in the simple form

$$\mathcal{H}_{\text{el-ph}} = g \sum_{\sigma} \int d\mathbf{r} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \hat{\phi}(\mathbf{r})$$
(K.1.28)

in terms of the continuous phonon field

$$\hat{\phi}(\boldsymbol{r}) = \frac{\mathrm{i}}{\sqrt{V}} \sum_{\boldsymbol{q}} \sqrt{\frac{\hbar\omega_{\boldsymbol{q}}}{2}} \left[a_{\boldsymbol{q}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} - a_{\boldsymbol{q}}^{\dagger} \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \right], \qquad (\mathrm{K}.1.29)$$

which is the gradient of the displacement field with $a_{\boldsymbol{q}}^{\dagger}$ and $a_{\boldsymbol{q}}$ the creation and annihilation operators for LA phonons.

The phonon Green function is then defined as

$$D(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \Big\langle T\Big\{ \hat{\phi}(\boldsymbol{r},t) \hat{\phi}(\boldsymbol{r}',t') \Big\} \Big\rangle.$$
(K.1.30)

In a homogeneous system, where the propagator depends on $\boldsymbol{r} - \boldsymbol{r}'$ and t - t', its Fourier transform is

$$D(\boldsymbol{q},\omega) = \int \mathrm{d}(\boldsymbol{r}-\boldsymbol{r}')\mathrm{e}^{-\mathrm{i}\boldsymbol{q}(\boldsymbol{r}-\boldsymbol{r}')} \int \mathrm{d}(t-t')\mathrm{e}^{\mathrm{i}\omega(t-t')}D(\boldsymbol{r}-\boldsymbol{r}',t-t') \,. \quad (\mathrm{K}.1.31)$$

The zero-temperature propagator of free phonons is

$$D^{(0)}(\boldsymbol{r} - \boldsymbol{r}', t - t') = -\frac{i}{V} \sum_{\boldsymbol{q}} \frac{\omega_{\boldsymbol{q}}}{2} \begin{cases} e^{i[\boldsymbol{q} \cdot (\boldsymbol{r} - \boldsymbol{r}') - \omega_{\boldsymbol{q}}(t - t')]} & \text{for } t > t', \\ e^{-i[\boldsymbol{q} \cdot (\boldsymbol{r} - \boldsymbol{r}') - \omega_{\boldsymbol{q}}(t - t')]} & \text{for } t' > t, \end{cases}$$
(K.1.32)

and in Fourier representation

$$D^{(0)}(\boldsymbol{q},\omega) = \frac{\omega_{\boldsymbol{q}}}{2} \left[\frac{1}{\omega - \omega_{\boldsymbol{q}} + \mathrm{i}\delta} - \frac{1}{\omega + \omega_{\boldsymbol{q}} - \mathrm{i}\delta} \right] = \frac{\omega_{\boldsymbol{q}}^2}{\omega^2 - \omega_{\boldsymbol{q}}^2 + \mathrm{i}\delta} \,. \quad (\mathrm{K}.1.33)$$

K.1.3 Spectral Representation

The thermal average appearing in the definition of the Green function can be expressed by using a complete set of eigenstates $|\Psi_n^N\rangle$ of the full Hamiltonian. Working with a grand canonical ensemble the upper index stands for the number of particles. Denoting the energy of this state by E_n^N we find

$$G_{\sigma}(\boldsymbol{k},t) = -\frac{\mathrm{i}}{\hbar} \left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}\sigma}^{\dagger}(0) \right\} \right\rangle$$

$$= \begin{cases} -\frac{\mathrm{i}}{\hbar} \sum_{N,n} \frac{1}{Z} \mathrm{e}^{-\beta \left(E_{n}^{N} - \mu N \right)} \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}\sigma}^{\dagger}(0) \left| \Psi_{n}^{N} \right\rangle & t > 0, \\ \\ \mp \frac{\mathrm{i}}{\hbar} \sum_{N,n} \frac{1}{Z} \mathrm{e}^{-\beta \left(E_{n}^{N} - \mu N \right)} \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma}^{\dagger}(0) c_{\boldsymbol{k}\sigma}(t) \left| \Psi_{n}^{N} \right\rangle & t < 0. \end{cases}$$

Inserting the completeness relation

$$\sum_{N',m} \left| \Psi_m^{N'} \right\rangle \left\langle \Psi_m^{N'} \right| = 1 \tag{K.1.35}$$

between the creation and annihilation operators we find

$$G_{\sigma}(\boldsymbol{k},t) = \begin{cases} -\frac{\mathrm{i}}{\hbar} \sum_{N,n,m} \frac{1}{Z} \mathrm{e}^{-\beta \left(E_{n}^{N}-\mu N\right)} \mathrm{e}^{\mathrm{i}\left(E_{n}^{N}-E_{m}^{N+1}+\mu\right)t/\hbar} \\ \times \left| \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{m}^{N+1} \right\rangle \right|^{2} & t > 0 \,, \\ \mp \frac{\mathrm{i}}{\hbar} \sum_{N,n,m} \frac{1}{Z} \mathrm{e}^{-\beta \left(E_{n}^{N}-\mu N\right)} \mathrm{e}^{\mathrm{i}\left(E_{m}^{N-1}-E_{n}^{N}+\mu\right)t/\hbar} \\ \times \left| \left\langle \Psi_{m}^{N-1} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{n}^{N} \right\rangle \right|^{2} & t < 0 \,. \end{cases}$$
(K.1.36)

With a change of variables for t < 0 we have

$$G_{\sigma}(\boldsymbol{k},t) = \begin{cases} -\frac{\mathrm{i}}{\hbar} \sum_{N,n,m} \frac{1}{Z} \mathrm{e}^{-\beta \left(E_{n}^{N} - \mu N\right)} \mathrm{e}^{\mathrm{i}\left(E_{n}^{N} - E_{m}^{N+1} + \mu\right)t/\hbar} \\ \times \left| \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{m}^{N+1} \right\rangle \right|^{2} & t > 0 \,, \\ \mp \frac{\mathrm{i}}{\hbar} \sum_{N,n,m} \frac{1}{Z} \mathrm{e}^{-\beta \left(E_{n}^{N} - \mu N\right)} \mathrm{e}^{\mathrm{i}\left(E_{n}^{N} - E_{m}^{N+1} + \mu\right)t/\hbar} \\ \times \mathrm{e}^{\beta \left(E_{n}^{N} - E_{m}^{N+1} + \mu\right)} \left| \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{m}^{N+1} \right\rangle \right|^{2} & t < 0 \,. \end{cases}$$
(K.1.37)

The Fourier transform with respect to time gives

$$G_{\sigma}(\boldsymbol{k},\omega) = \frac{1}{Z} \sum_{N,n,m} e^{-\beta \left(E_{n}^{N}-\mu N\right)} \left| \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{m}^{N+1} \right\rangle \right|^{2}$$
(K.1.38)

$$\times \left\{ \frac{1 \mp e^{\beta \left(E_{n}^{N}-E_{m}^{N+1}+\mu\right)}}{\hbar\omega + E_{n}^{N}-E_{m}^{N+1}+\mu} - i\pi\delta \left(\hbar\omega + E_{n}^{N}-E_{m}^{N+1}+\mu\right) \left(1 \pm e^{-\beta\hbar\omega}\right) \right\}.$$

Let us introduce the spectral function $A_{\sigma}(\pmb{k},\omega)$ with the definition

$$A_{\sigma}(\boldsymbol{k},\omega) = 2\pi\hbar \left(1 \mp e^{-\beta\hbar\omega}\right) \frac{1}{Z} \sum_{N,n,m} e^{-\beta \left(E_{n}^{N}-\mu N\right)}$$

$$\times \left|\left\langle \Psi_{n}^{N}\right| c_{\boldsymbol{k}\sigma} \left|\Psi_{m}^{N+1}\right\rangle\right|^{2} \delta(\hbar\omega + E_{n}^{N} - E_{m}^{N+1} + \mu).$$
(K.1.39)

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The real part of the Green function can then be written as

$$\operatorname{Re} G_{\sigma}(\boldsymbol{k},\omega) = \frac{1}{2\pi\hbar} \operatorname{P} \int_{-\infty}^{\infty} \frac{A_{\sigma}(\boldsymbol{k},\omega')}{\omega - \omega'} \,\mathrm{d}\omega \,, \qquad (K.1.40)$$

while the imaginary part is

$$\operatorname{Im} G_{\sigma}(\boldsymbol{k},\omega) = \begin{cases} -\frac{1}{2\hbar} A_{\sigma}(\boldsymbol{k},\omega) \operatorname{coth} \frac{\beta\hbar\omega}{2} & \text{for bosons,} \\ -\frac{1}{2\hbar} A_{\sigma}(\boldsymbol{k},\omega) \tanh \frac{\beta\hbar\omega}{2} & \text{for fermions.} \end{cases}$$
(K.1.41)

We then find

$$G_{\sigma}(\boldsymbol{k},\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \left[\mathrm{P}\frac{1}{\omega-\omega'} - \mathrm{i}\pi\delta(\omega-\omega') \coth\frac{\beta\hbar\omega'}{2} \right] A_{\sigma}(\boldsymbol{k},\omega') \quad (\mathrm{K}.1.42)$$

for bosons, while for fermions

$$G_{\sigma}(\boldsymbol{k},\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \left[\mathrm{P}\frac{1}{\omega-\omega'} - \mathrm{i}\pi\delta(\omega-\omega')\tanh\frac{\beta\hbar\omega'}{2} \right] A_{\sigma}(\boldsymbol{k},\omega') \,. \tag{K.1.43}$$

The thermal factors can be written in terms of the distribution functions of the Bose–Einstein and Fermi–Dirac statistics, respectively:

$$\coth\frac{\beta\hbar\omega}{2} = 1 + 2g_0(\hbar\omega), \qquad \tanh\frac{\beta\hbar\omega}{2} = 1 - 2f_0(\hbar\omega), \qquad (K.1.44)$$

with

$$g_0(\varepsilon) = \frac{1}{\mathrm{e}^{\beta\varepsilon} - 1}$$
 and $f_0(\varepsilon) = \frac{1}{\mathrm{e}^{\beta\varepsilon} + 1}$. (K.1.45)

Using these formulas we get

$$G_{\sigma}(\boldsymbol{k},\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \left[\frac{1 + g_0(\hbar\omega')}{\omega - \omega' + \mathrm{i}\delta} - \frac{g_0(\hbar\omega')}{\omega - \omega' - \mathrm{i}\delta} \right] A_{\sigma}(\boldsymbol{k},\omega') \qquad (K.1.46)$$

for bosons and

$$G_{\sigma}(\boldsymbol{k},\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \left[\frac{1 - f_0(\hbar\omega')}{\omega - \omega' + \mathrm{i}\delta} + \frac{f_0(\hbar\omega')}{\omega - \omega' - \mathrm{i}\delta} \right] A_{\sigma}(\boldsymbol{k},\omega') \qquad (\mathrm{K}.1.47)$$

for fermions. This representation of the Green function in terms of the spectral function is known as the Lehmann representation or Källén–Lehmann representation.¹

¹ G. Källén, 1952, H. Lehmann, 1954.

The time dependence of the Green function is obtained by inverting the Fourier transform. The integral over ω along the real axis can be closed by an infinite semicircle in the lower half-plane if t > 0 or in the upper half-plane for t < 0. The integral can be evaluated using the residue theorem. We get

$$G_{\sigma}(\boldsymbol{k},t) = \begin{cases} -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{e}^{-\mathrm{i}\omega t} A_{\sigma}(\boldsymbol{k},\omega) \left[1+g_{0}(\hbar\omega)\right] & t > 0\\ -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{e}^{-\mathrm{i}\omega t} A_{\sigma}(\boldsymbol{k},\omega) g_{0}(\hbar\omega) & t < 0 \end{cases}$$
(K.1.48)

for bosons and

$$G_{\sigma}(\boldsymbol{k},t) = \begin{cases} -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{e}^{-\mathrm{i}\omega t} A_{\sigma}(\boldsymbol{k},\omega) \left[1 - f_{0}(\hbar\omega)\right] & t > 0\\ \frac{\mathrm{i}}{\hbar} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{e}^{-\mathrm{i}\omega t} A_{\sigma}(\boldsymbol{k},\omega) f_{0}(\hbar\omega) & t < 0 \end{cases}$$
(K.1.49)

for fermions.

The retarded and advanced Green functions can also be represented in terms of the spectral function. Using the definition of the retarded Green function and repeating the same steps used for the causal Green function

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},t) = -\frac{\mathrm{i}}{\hbar} \sum_{N,n,m} \frac{1}{Z} \mathrm{e}^{-\beta \left(E_{n}^{N}-\mu N\right)} \mathrm{e}^{\mathrm{i}\left(E_{n}^{N}-E_{m}^{N+1}+\mu\right)t/\hbar} \times \left|\left\langle \Psi_{n}^{N}\right| c_{\boldsymbol{k}\sigma} \left|\Psi_{m}^{N+1}\right\rangle\right|^{2} \left[1 \mp \mathrm{e}^{\beta \left(E_{n}^{N}-E_{m}^{N+1}+\mu\right)}\right].$$
(K.1.50)

Its Fourier transform is

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},\omega) = \frac{1}{Z} \sum_{N,n,m} \mathrm{e}^{-\beta \left(E_{n}^{N}-\mu N\right)} \left| \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{m}^{N+1} \right\rangle \right|^{2} \\ \times \frac{1 \mp \mathrm{e}^{\beta \left(E_{n}^{N}-E_{m}^{N+1}+\mu\right)}}{\hbar \omega + E_{n}^{N}-E_{m}^{N+1}+\mu + \mathrm{i}\delta} \,.$$
(K.1.51)

It is readily seen that

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \frac{1}{\omega - \omega' + \mathrm{i}\delta} A_{\sigma}(\boldsymbol{k},\omega') \,. \tag{K.1.52}$$

A similar calculation for the advanced Green function yields

$$G_{\sigma}^{A}(\boldsymbol{k},\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \frac{1}{\omega - \omega' - \mathrm{i}\delta} A_{\sigma}(\boldsymbol{k},\omega') \,. \tag{K.1.53}$$

The retarded function is analytic in the upper half-plane, while the advanced function is analytic in the lower half-plane. Their difference along the real axis is just the spectral function:

$$A_{\sigma}(\boldsymbol{k},\omega) = \mathrm{i}\hbar \left[G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},\omega) - G_{\sigma}^{\mathrm{A}}(\boldsymbol{k},\omega) \right].$$
(K.1.54)

To understand the physical meaning of the spectral function we calculate the expectation value of the particle number. It follows from the definition of the Green function that in the limit $t \to 0 - \delta$

$$\lim_{t \to 0-\delta} G_{\sigma}(\boldsymbol{k}, t) = \mp \langle n_{\boldsymbol{k}\sigma} \rangle , \qquad (K.1.55)$$

and thus

$$\langle n_{\boldsymbol{k}\sigma} \rangle = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} A_{\sigma}(\boldsymbol{k},\omega) \begin{cases} g_0(\hbar\omega), \\ f_0(\hbar\omega). \end{cases}$$
(K.1.56)

The total number of particles is

$$N = V \sum_{\sigma} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} A_{\sigma}(\boldsymbol{k},\omega) \begin{cases} g_0(\hbar\omega), \\ f_0(\hbar\omega). \end{cases}$$
(K.1.57)

Thus $A_{\sigma}(\mathbf{k}, \omega)$ is related to the density of states via

$$\rho_{\sigma}(\varepsilon) = \frac{1}{2\pi\hbar} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3} A_{\sigma}(\boldsymbol{k},\varepsilon/\hbar) \,. \tag{K.1.58}$$

On the other hand, when we integrate over the frequency, the spectral function satisfies the relation

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} A_{\sigma}(\boldsymbol{k},\omega) = 1. \qquad (K.1.59)$$

This relation can be derived from the defining equation of the spectral function. It can be readily shown that

$$\int_{-\infty}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \left\langle c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}\sigma}^{\dagger}(0) \right\rangle = A_{\sigma}(\boldsymbol{k},\omega) \frac{\mathrm{e}^{\beta\hbar\omega}}{\mathrm{e}^{\beta\hbar\omega} \mp 1} \tag{K.1.60}$$

and

$$\int_{-\infty}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \left\langle c_{\boldsymbol{k}\sigma}^{\dagger}(0) c_{\boldsymbol{k}\sigma}(t) \right\rangle = A_{\sigma}(\boldsymbol{k},\omega) \frac{1}{\mathrm{e}^{\beta\hbar\omega} \mp 1} \,, \qquad (\mathrm{K}.1.61)$$

and therefore

$$\int_{-\infty}^{\infty} \mathrm{d}t \,\mathrm{e}^{\mathrm{i}\omega t} \left\langle \left[c_{\boldsymbol{k}\sigma}(t), c_{\boldsymbol{k}\sigma}^{\dagger}(0) \right]_{\mp} \right\rangle = A_{\sigma}(\boldsymbol{k}, \omega) \,. \tag{K.1.62}$$

Integrating both sides over ω and making use of the commutation (anticommutation) relations of the creation and annihilation operators, we indeed recover (K.1.59).

For noninteracting particles

$$A_{\sigma}(\boldsymbol{k},\omega) = 2\pi\hbar\delta(\hbar\omega - \xi_{\boldsymbol{k}}). \qquad (K.1.63)$$

The operator $c_{\boldsymbol{k}\sigma}^{\dagger}$ is not the creation operator of an exact one-particle state in an interacting system. The added particle decays in time, and the uncertainty in time is accompanied by an uncertainty in the energy. Therefore $A_{\sigma}(\boldsymbol{k},\omega)$ as a function of ω is a broadened Lorentzian with half-width $\Gamma_{\boldsymbol{k}}$,

$$A_{\sigma}(\boldsymbol{k},\omega) \sim \frac{\Gamma_{\boldsymbol{k}}}{(\hbar\omega - \tilde{\xi}_{\boldsymbol{k}})^2 + \Gamma_{\boldsymbol{k}}^2}.$$
 (K.1.64)

Note that if this functional form is used for the spectral function, we recover (K.1.27) for the retarded and advanced Green functions.



Fig. K.1. Spectral function at a fixed wave vector as a function of frequency

The spectral function is displayed in Fig. K.1. The position of the peak corresponds to the renormalized energy of the one-particle excitation and the width is proportional to the inverse of the decay time. This is easily seen if the time dependence of the Green function calculated from the inverse Fourier transform of the spectral representation is compared with the form given in (K.1.26).

The spectral function has an incoherent background in addition to the Lorentzian peak. The integral of $A_{\sigma}(\mathbf{k}, \omega)$ over ω has to satisfy (K.1.59). When only the coherent part corresponding to the Lorentzian peak is integrated, it gives the quasiparticle weight $Z_{\mathbf{k}\sigma} < 1$. The remaining part comes from the incoherent background.

Finally, we note also that the total energy of the interacting electron system,

$$\langle \mathcal{H} \rangle = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} \langle c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \rangle + \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{k}'\sigma\sigma'} U(\boldsymbol{q}) \langle c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma} c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'} c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma} \rangle, \quad (K.1.65)$$

can be written in terms of the spectral function. When the equation of motion for the creation operator,

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$$\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'} - \varepsilon_{\boldsymbol{k}}\right)c_{\boldsymbol{k}\sigma}^{\dagger}(t') = \frac{1}{V}\sum_{\boldsymbol{k}'\boldsymbol{q}\sigma'}U(\boldsymbol{q})c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^{\dagger}(t')c_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}(t')c_{\boldsymbol{k}'\sigma'}(t'), \quad (\mathrm{K.1.66})$$

is multiplied by $c_{{\bm k}\sigma}(t)$ from the right and the similar equation for the annihilation operator,

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t}-\varepsilon_{\boldsymbol{k}}\right)c_{\boldsymbol{k}\sigma}(t) = \frac{1}{V}\sum_{\boldsymbol{k}'\boldsymbol{q}\sigma'}U(\boldsymbol{q})c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}(t)c_{\boldsymbol{k}'\sigma'}(t)c_{\boldsymbol{k}-\boldsymbol{q}\sigma}(t)\,,\quad(\mathrm{K}.1.67)$$

is multiplied by $c^{\dagger}_{\boldsymbol{k}\sigma}(t')$ from the left, we find

$$\lim_{t' \to t} \frac{1}{4} \sum_{\boldsymbol{k}\sigma} \left(-\frac{\hbar}{i} \frac{\mathrm{d}}{\mathrm{d}t} + \frac{\hbar}{i} \frac{\mathrm{d}}{\mathrm{d}t'} - 2\varepsilon_{\boldsymbol{k}} \right) c^{\dagger}_{\boldsymbol{k}\sigma}(t') c_{\boldsymbol{k}\sigma}(t) \qquad (K.1.68)$$
$$= \frac{1}{2V} \sum_{\boldsymbol{k}\boldsymbol{k}'\boldsymbol{q}\sigma\sigma'} U(\boldsymbol{q}) c^{\dagger}_{\boldsymbol{k}+\boldsymbol{q}\sigma}(t) c^{\dagger}_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}(t) c_{\boldsymbol{k}'\sigma'}(t) c_{\boldsymbol{k}\sigma}(t) \,.$$

The contribution of the interaction to the total energy can thus be expressed in terms of $\langle c^{\dagger}_{k\sigma}(t')c_{k\sigma}(t)\rangle$ and the total energy is

$$\langle \mathcal{H} \rangle = \lim_{t' \to t} \frac{1}{4} \sum_{\boldsymbol{k}\sigma} \left(2\varepsilon_{\boldsymbol{k}} - \frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t} + \frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t'} \right) \left\langle c_{\boldsymbol{k}\sigma}^{\dagger}(t') c_{\boldsymbol{k}\sigma}(t) \right\rangle$$

$$= \lim_{t' \to t+\delta} \frac{1}{4} \sum_{\boldsymbol{k}\sigma} \left(2\varepsilon_{\boldsymbol{k}} - \frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t} + \frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t'} \right) \frac{\hbar}{\mathrm{i}} G_{\sigma}(\boldsymbol{k}, t - t') \,.$$
(K.1.69)

When the Green function is written in terms of the spectral function we find

$$\langle \mathcal{H} \rangle = \sum_{\boldsymbol{k}\sigma} \int \frac{\mathrm{d}\omega}{2\pi} \frac{1}{2} (\varepsilon_{\boldsymbol{k}} + \hbar\omega) f_0(\hbar\omega) A_\sigma(\boldsymbol{k},\omega) \,. \tag{K.1.70}$$

K.1.4 Green Function and Density of States

The density of states was shown to be related to the spectral function via (K.1.58). Since

$$\operatorname{Im} G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},\omega) = -\frac{1}{2\hbar} A_{\sigma}(\boldsymbol{k},\omega') \qquad (\mathrm{K}.1.71)$$

according to (K.1.52), the density of states can be expressed in terms of the retarded Green function as

$$\rho_{\sigma}(\varepsilon) = -\frac{1}{\pi} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3} \mathrm{Im} \, G_{\sigma}^{\mathrm{R}}(\boldsymbol{k}, \varepsilon/\hbar) \,. \tag{K.1.72}$$

We derive here a generalized relationship in another representation.

The Green operator of a system described by the Hamiltonian ${\mathcal H}$ is defined via

$$G^{\pm}(\omega) = \frac{1}{\hbar\omega - \mathcal{H} \pm \mathrm{i}\delta} \,. \tag{K.1.73}$$

Suppose we know the complete set of eigenstates of the Schrödinger equation

$$\mathcal{H}|\Psi_n\rangle = E_n|\Psi_n\rangle. \tag{K.1.74}$$

Using the completeness relation we readily find that

$$G^{\pm}(\omega) = \sum_{n} \frac{|\Psi_n\rangle \langle \Psi_n|}{\hbar \omega - E_n \pm \mathrm{i}\delta} \,. \tag{K.1.75}$$

The retarded and advanced Green functions are obtained by taking the matrix elements of the Green operator between a complete set of basis functions. Working in real space

$$G^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{n} \frac{\langle \boldsymbol{r} | \Psi_n \rangle \langle \Psi_n | \boldsymbol{r}' \rangle}{\hbar \omega - E_n + \mathrm{i}\delta} = \sum_{n} \frac{\Psi_n(\boldsymbol{r}) \Psi_n^*(\boldsymbol{r}')}{\hbar \omega - E_n + \mathrm{i}\delta}, \qquad (\mathrm{K}.1.76)$$

while in k-space

$$G^{\mathrm{R}}(\boldsymbol{k}, \boldsymbol{k}', \omega) = \sum_{n} \frac{\langle \boldsymbol{k} | \Psi_{n} \rangle \langle \Psi_{n} | \boldsymbol{k}' \rangle}{\hbar \omega - E_{n} + \mathrm{i}\delta} \,. \tag{K.1.77}$$

Taking the imaginary part of the diagonal terms,

Im
$$G^{\mathrm{R}}(\boldsymbol{k},\omega) = -\pi \sum_{n} |\langle \boldsymbol{k} | \Psi_n \rangle|^2 \delta(\hbar \omega - E_n).$$
 (K.1.78)

When this is summed over k, making use of the completeness relation yields

$$\sum_{\boldsymbol{k}} \operatorname{Im} G^{\mathrm{R}}(\boldsymbol{k}, \omega) = -\pi \sum_{n} \delta(\hbar \omega - E_{n}). \quad (K.1.79)$$

Recognizing that the density of states

$$\rho(\varepsilon) = \frac{1}{V} \sum_{n} \delta(\varepsilon - E_n)$$
 (K.1.80)

appears on the right-hand side apart from simple factors, we find the relation

$$\rho(\varepsilon) = -\frac{1}{\pi} \frac{1}{V} \sum_{\boldsymbol{k}} \operatorname{Im} G^{\mathrm{R}}(\boldsymbol{k}, \varepsilon/\hbar)$$
 (K.1.81)

between the density of states and the Green function. For particles with spin, a sum over the spin variables is needed to get the full density of states.

Note that more generally

$$\operatorname{Im} G^{+}(\omega) = -\pi \sum_{n} |\Psi_{n}\rangle \langle \Psi_{n} | \delta(\hbar \omega - E_{n}), \qquad (K.1.82)$$

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and the density of states is the sum of the diagonal matrix elements,

$$\rho(\varepsilon) = -\frac{1}{\pi} \operatorname{Tr} \operatorname{Im} G^+(\varepsilon/\hbar) \,. \tag{K.1.83}$$

The quantity obtained from the diagonal matrix elements of the real-space Green function $G^{\rm R}(\boldsymbol{r}, \boldsymbol{r}', \omega)$,

$$\rho(\boldsymbol{r},\varepsilon) = -\frac{1}{\pi} \frac{1}{V} \operatorname{Im} G^{\mathrm{R}}(\boldsymbol{r},\boldsymbol{r},\varepsilon/\hbar), \qquad (\mathrm{K}.1.84)$$

can be considered as the local density of states. Its integral over the volume gives the full density of states:

$$\rho(\varepsilon) = \int \rho(\boldsymbol{r}, \varepsilon) \,\mathrm{d}\boldsymbol{r} \,. \tag{K.1.85}$$

K.1.5 Temperature Green Function

The Green function introduced above was defined for arbitrary temperature. However, as will be discussed later in this appendix, a consistent perturbation theory can be worked out for it only at zero temperature. At finite temperatures the thermal average is taken with the appropriate real Boltzmann weights,

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \frac{1}{Z} \mathrm{Tr} \left(\mathrm{e}^{-\beta \mathcal{H}} T \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') \right\} \right), \qquad (\mathrm{K}.1.86)$$

while the time dependence of the operators is given in the Heisenberg representation by complex factors,

$$\mathcal{A}(t) = e^{i\mathcal{H}t/\hbar} \mathcal{A} e^{-i\mathcal{H}t/\hbar} . \tag{K.1.87}$$

In a perturbative treatment of the Green function both the real Boltzmann factor and the complex exponentials coming from the time dependence of the operators have to be expanded in powers of the perturbation. Owing to the mixing of the real and complex coefficients, this expression cannot be consistently treated in perturbation theory. As a way out T. MATSUBARA (1955) proposed to formally introduce an imaginary time variable τ . The "time" dependence of the field operators is given by

$$\hat{\psi}_{\sigma}(\boldsymbol{r},\tau) = \mathrm{e}^{\tau \mathcal{H}/\hbar} \hat{\psi}_{\sigma}(\boldsymbol{r}) \mathrm{e}^{-\tau \mathcal{H}/\hbar}, \qquad \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r},\tau) = \mathrm{e}^{\tau \mathcal{H}/\hbar} \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}) \mathrm{e}^{-\tau \mathcal{H}/\hbar}, \quad (\mathrm{K}.1.88)$$

and the imaginary-time Green function known as the temperature Green function or Matsubara Green function is defined by

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \left\langle T_{\tau} \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},\tau) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau') \right\} \right\rangle$$

$$= -\frac{1}{\hbar} \frac{1}{Z} \operatorname{Tr} \left(e^{-\beta \mathcal{H}} T_{\tau} \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},\tau) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau') \right\} \right).$$
(K.1.89)

Here T_{τ} is again an ordering operator, ordering the field operators according to the value of the argument τ , with the smallest on the right. For fermions a sign factor $(-1)^P$ is also included, where P is the number of permutations needed to go from the original ordering to the "time-ordered" form. Note that $\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r},\tau)$ is not the Hermitian adjoint of $\hat{\psi}_{\sigma}(\boldsymbol{r},\tau)$ if τ is real.

If the Hamiltonian is independent of time, the Green function depends only on $\tau - \tau'$. This is easily seen using the invariance of the trace under a cyclic permutation of the operators. Writing out the τ dependence of the operators explicitly,

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \frac{1}{Z} \operatorname{Tr} \left(\mathrm{e}^{-\beta\mathcal{H}} T_{\tau} \left\{ \mathrm{e}^{\tau\mathcal{H}/\hbar} \hat{\psi}_{\sigma}(\boldsymbol{r}) \mathrm{e}^{-\tau\mathcal{H}/\hbar} \mathrm{e}^{\tau'\mathcal{H}/\hbar} \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}') \mathrm{e}^{-\tau'\mathcal{H}/\hbar} \right\} \right).$$
(K.1.90)

Cyclic permutation yields

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \frac{1}{Z} \operatorname{Tr} \left(e^{-\beta \mathcal{H}} T_{\tau} \left\{ e^{(\tau-\tau')\mathcal{H}/\hbar} c_{\boldsymbol{k}\sigma} e^{-(\tau-\tau')\mathcal{H}/\hbar} c_{\boldsymbol{k}\sigma}^{\dagger} \right\} \right) = \mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\tau-\tau').$$
(K.1.91)

The temperature Green function, as defined above, is meaningful only when both τ and τ' are in the interval $[0, \beta\hbar]$. High-energy states would otherwise give a divergent contribution, which is not compensated by the smallness of their thermodynamic weight. The "time" difference $\tau - \tau'$ is then restricted to the interval $-\beta\hbar \leq \tau - \tau' \leq \beta\hbar$.

A periodic extension to arbitrary τ and τ' is, however, possible. Choosing τ' in the interval $[0, \beta\hbar]$ and using again the cyclic property of the trace we find

$$\begin{aligned} \mathcal{G}_{\sigma}(\boldsymbol{r},\beta\hbar;\boldsymbol{r}',\tau') &= -\frac{1}{\hbar}\frac{1}{Z}\operatorname{Tr}\left(\mathrm{e}^{-\beta\mathcal{H}}\mathrm{e}^{\beta\mathcal{H}}\hat{\psi}_{\sigma}(\boldsymbol{r})\mathrm{e}^{-\beta\mathcal{H}}\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau')\right) \\ &= -\frac{1}{\hbar}\frac{1}{Z}\operatorname{Tr}\left(\mathrm{e}^{-\beta\mathcal{H}}\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau')\hat{\psi}_{\sigma}(\boldsymbol{r})\right) \\ &= \mp\frac{1}{\hbar}\frac{1}{Z}\operatorname{Tr}\left(\mathrm{e}^{-\beta\mathcal{H}}T_{\tau}\left\{\hat{\psi}_{\sigma}(\boldsymbol{r})\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau')\right\}\right) \\ &= \pm\mathcal{G}_{\sigma}(\boldsymbol{r},0;\boldsymbol{r}',\tau')\,, \end{aligned}$$
(K.1.92)

and similarly

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\tau;\boldsymbol{r}',\beta\hbar) = \pm \mathcal{G}_{\sigma}(\boldsymbol{r},\tau;\boldsymbol{r}',0). \qquad (K.1.93)$$

The temperature Green function is then defined for arbitrary τ and τ' by requiring that it be periodic (antiperiodic) in each "time" variable with period $\beta\hbar$. As a function of the difference $\tau - \tau'$ the Green function is then periodic with period $2\beta\hbar$ both for bosons and for fermions.

As a periodic function, $\mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\tau-\tau')$ may be expanded in a Fourier series:

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\tau-\tau') = \frac{k_{\rm B}T}{\hbar} \sum_{n} \mathrm{e}^{-\mathrm{i}\omega_{n}(\tau-\tau')} G_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\omega_{n}), \qquad (\mathrm{K}.1.94)$$

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where $\omega_n = n\pi k_{\rm B}T/\hbar$. The Fourier coefficients are given by

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\omega_n) = \frac{1}{2} \int_{-\hbar\beta}^{\hbar\beta} \mathrm{d}(\tau-\tau') \mathrm{e}^{\mathrm{i}\omega_n(\tau-\tau')} \mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\tau-\tau') \,. \tag{K.1.95}$$

There is an extra symmetry that allows for further simplifications. When $-\beta\hbar \leq \tau - \tau' \leq 0$, and therefore $\tau - \tau' + \beta\hbar > 0$, the cyclic property of the trace yields

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\tau-\tau'<0) = \pm \mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\tau-\tau'+\beta\hbar). \qquad (K.1.96)$$

Owing to this property only those Fourier coefficients which correspond to even frequencies (ω_n with n even) are finite for bosons, while only the coefficients belonging to n odd survive for fermions. Therefore

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\omega_n) = \int_{0}^{\hbar\beta} \mathrm{d}(\tau-\tau') \mathrm{e}^{\mathrm{i}\omega_n(\tau-\tau')} \mathcal{G}_{\sigma}(\boldsymbol{r},\boldsymbol{r}',\tau-\tau') \qquad (\mathrm{K}.1.97)$$

with

$$\omega_n = \begin{cases} 2n\pi k_{\rm B}T/\hbar & \text{for bosons},\\ (2n+1)\pi k_{\rm B}T/\hbar & \text{for fermions}. \end{cases}$$
(K.1.98)

For a noninteracting system the real-space temperature Green function reduces to

$$\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) = \sum_j \frac{\phi_j(\boldsymbol{r})\phi_j^*(\boldsymbol{r}')}{\mathrm{i}\hbar\omega_n - \varepsilon_j + \mu}, \qquad (K.1.99)$$

where $\phi_j(\mathbf{r})$ is an eigenfunction of the unperturbed Hamiltonian with energy ε_j .

In a translation-invariant system, where the Green function depends on r - r' only, it is convenient to work in momentum representation. The Green function is defined in terms of the creation and annihilation operators via

$$\mathcal{G}_{\sigma}(\boldsymbol{k},\tau,\tau') = -\frac{1}{\hbar} \left\langle T_{\tau} \left\{ c_{\boldsymbol{k}\sigma}(\tau) c_{\boldsymbol{k}\sigma}^{\dagger}(\tau') \right\} \right\rangle$$

$$= -\frac{1}{\hbar} \frac{1}{Z} \operatorname{Tr} \left(e^{-\beta \mathcal{H}} T_{\tau} \left\{ c_{\boldsymbol{k}\sigma}(\tau) c_{\boldsymbol{k}\sigma}^{\dagger}(\tau') \right\} \right) .$$
(K.1.100)

For noninteracting particles we find

$$\mathcal{G}_{\sigma}^{(0)}(\boldsymbol{k},\omega_n) = \frac{1}{\mathrm{i}\hbar\omega_n - \xi_{\boldsymbol{k}\sigma}} \,. \tag{K.1.101}$$

K.1.6 Relation Between the Retarded, Advanced, and Temperature Green Functions

When the thermal average is written as the sum of the matrix elements over a complete set of states with the appropriate Boltzmann weight, and the same complete set is inserted between the creation and annihilation operators,

$$\begin{aligned} \mathcal{G}_{\sigma}(\boldsymbol{k},\tau>0) &= -\frac{1}{\hbar} \sum_{N,n,m} \frac{1}{Z} \mathrm{e}^{-\beta(E_{n}^{N}-\mu N)} \mathrm{e}^{(E_{n}^{N}-E_{m}^{N+1}+\mu)\tau/\hbar} \\ &\times \left| \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{m}^{N+1} \right\rangle \right|^{2}. \end{aligned} \tag{K.1.102}$$

Calculating the Fourier coefficients from the integral

$$\mathcal{G}_{\sigma}(\boldsymbol{k},\omega_n) = \int_{0}^{\hbar\beta} \mathrm{d}\tau \mathrm{e}^{\mathrm{i}\omega_n \tau} \mathcal{G}_{\sigma}(\boldsymbol{k},\tau-\tau')$$
(K.1.103)

we find

$$\mathcal{G}_{\sigma}(\boldsymbol{k},\omega_{n}) = \frac{1}{Z} \sum_{N,n,m} e^{-\beta(E_{n}^{N}-\mu N)} \left| \left\langle \Psi_{n}^{N} \right| c_{\boldsymbol{k}\sigma} \left| \Psi_{m}^{N+1} \right\rangle \right|^{2} \\ \times \frac{1 \mp e^{\beta(E_{n}^{N}-E_{m}^{N+1}+\mu)}}{i\hbar\omega_{n}+E_{n}^{N}-E_{m}^{N+1}+\mu} \,.$$
(K.1.104)

When expressed in terms of the spectral function we have

$$\mathcal{G}_{\sigma}(\boldsymbol{k},\omega_n) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \frac{1}{\mathrm{i}\omega_n - \omega'} A_{\sigma}(\boldsymbol{k},\omega') \,. \tag{K.1.105}$$

Introduce now the function

$$\Gamma_{\sigma}(\boldsymbol{k}, z) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi\hbar} \frac{1}{z - \omega'} A_{\sigma}(\boldsymbol{k}, \omega'), \qquad (\mathrm{K}.1.106)$$

where z is a complex variable. Clearly it reproduces the temperature Green function at the discrete points $z = i\omega_n$ along the imaginary axis:

$$\Gamma_{\sigma}(\boldsymbol{k}, i\omega_n) = \mathcal{G}_{\sigma}(\boldsymbol{k}, \omega_n).$$
 (K.1.107)

On the other hand, the retarded or advanced Green functions are recovered when z approaches the real axis from above or from below. Comparison with (K.1.52) and (K.1.53) shows that

$$G^{\rm R}_{\sigma}(\boldsymbol{k},\omega) = \Gamma_{\sigma}(\boldsymbol{k},\omega+{\rm i}\delta),$$

$$G^{\rm A}_{\sigma}(\boldsymbol{k},\omega) = \Gamma_{\sigma}(\boldsymbol{k},\omega-{\rm i}\delta).$$
(K.1.108)

Thus, once the temperature Green function has been determined by some method in the discrete points $i\omega_n$, and the expression is analytically continued in the upper (lower) half-plane, the value on the real axis gives the retarded (advanced) Green function. This is formally achieved by the substitution $i\omega_n = \omega \pm i\delta$,

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},\omega) = \mathcal{G}_{\sigma}(\boldsymbol{k},\omega_n)|_{\mathrm{i}\omega_n = \omega + \mathrm{i}\delta},$$

$$G_{\sigma}^{\mathrm{A}}(\boldsymbol{k},\omega) = \mathcal{G}_{\sigma}(\boldsymbol{k},\omega_n)|_{\mathrm{i}\omega_n = \omega - \mathrm{i}\delta}.$$
(K.1.109)

The spectral function is then obtained via

$$A_{\sigma}(\boldsymbol{k},\omega) = i\hbar \Big[\mathcal{G}_{\sigma}(\boldsymbol{k},\omega_n) |_{i\omega_n = \omega + i\delta} - \mathcal{G}_{\sigma}(\boldsymbol{k},\omega_n) |_{i\omega_n = \omega - i\delta} \Big], \qquad (K.1.110)$$

from which the physical quantities can be calculated.

K.2 Calculating the Green Functions

A convenient procedure for calculating the Green function is to solve its equation of motion. As an example we will consider a system of fermions moving in a one-particle potential $V(\mathbf{r})$ and interacting with each other via a twoparticle potential $U(\mathbf{r}_i - \mathbf{r}_j)$. The equation of motion for the field operators or for the creation and annihilation operators leads to terms with three operators. Therefore, two-particle Green functions appear in the equation of motion for the one-particle Green function. Their equations of motion contain even higher order Green functions, and an infinite hierarchy may appear. This hierarchy may be truncated at some point by a decoupling procedure, and a closed system of equations can be obtained, which might be solvable. A drawback of this procedure is that the accuracy is difficult to estimate. A different method is based on perturbation theory. A consistent theory can be worked out both at zero and at finite temperature and the contribution of the various processes can be visualized by Feynman diagrams. The accuracy is then set by the processes that can be taken into account.

K.2.1 Equation of Motion for Green Functions

The equation of motion for the retarded Green function of interacting fermions has already been given in (31.1.9). To better see the relationship to the diagram technique we consider now the equation of motion for the causal Green function:

$$\begin{bmatrix}
\frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}t'} + \frac{\hbar^2}{2m_{\mathrm{e}}} \nabla_{\mathbf{r}'}^2 - V(\mathbf{r}') \\
-\frac{\mathrm{i}}{\hbar} \sum_{\sigma'} \int \mathrm{d}\mathbf{r}_2 U(\mathbf{r}' - \mathbf{r}_2) \\
\times \left\langle T \left\{ \hat{\psi}_{\sigma}(\mathbf{r}, t) \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}', t') \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}_2, t') \hat{\psi}_{\sigma'}(\mathbf{r}_2, t') \right\} \right\rangle.$$
(K.2.1)

Neglecting for the moment the interaction between the particles, the Green function of particles exposed only to the one-particle potential is

$$\left[\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}t'} + \frac{\hbar^2}{2m_{\mathrm{e}}}\boldsymbol{\nabla}_{\boldsymbol{r}'}^2 - V(\boldsymbol{r}')\right]G_{\sigma}^{(0)}(\boldsymbol{r},t;\boldsymbol{r}',t') = \delta(t-t')\delta(\boldsymbol{r}-\boldsymbol{r}'). \quad (\mathrm{K}.2.2)$$

The equation for the full Green function can then be formally integrated:

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = G_{\sigma}^{(0)}(\boldsymbol{r},t;\boldsymbol{r}',t') \qquad (K.2.3)$$
$$-\frac{\mathrm{i}}{\hbar} \sum_{\sigma'} \int \mathrm{d}\boldsymbol{r}_{1} \int_{-\infty}^{\infty} \mathrm{d}t_{1} \int \mathrm{d}\boldsymbol{r}_{2} G_{\sigma}^{(0)}(\boldsymbol{r}_{1},t_{1},\boldsymbol{r}',t') U(\boldsymbol{r}_{1}-\boldsymbol{r}_{2})$$
$$\times \left\langle T \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}_{1},t_{1}) \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}_{2},t_{1}) \hat{\psi}_{\sigma'}(\boldsymbol{r}_{2},t_{1}) \right\} \right\rangle.$$

The contributions to the one-particle Green function can be visualized pictorially by Feynman diagrams.² The full Green function $G_{\sigma}(\mathbf{r}, t; \mathbf{r}', t')$ that describes the propagation of a particle in the interacting system from \mathbf{r}' , where it is added to the system at time t', to \mathbf{r} , where it is measured at time t, is represented by a heavy solid line, while thin lines denote the free propagation of particles between two successive scattering events. A wavy line represents the interaction between the particles. The expression containing four operators in the second term on the right-hand side can be thought of as describing the propagation of two interacting particles. The two-particle propagator with two incoming and two outgoing lines is shown in Fig. K.2. Equation (K.2.3) describing the propagation of a single particle is visualized by the diagrams in Fig. K.3.



Fig. K.2. Graphical representation of the two-particle propagator



Fig. K.3. Graphical equation for the propagation of a particle in real space

The processes displayed in the diagrammatic equation can be summarized as follows. It may happen that the particle propagates freely from r' to r^{-2} R. P. FEYNMAN, 1948.
without being involved in any scattering process. In other cases, the particle propagates freely only until the first interaction. This takes place at some point r_1 at time t_1 , while the particle with which it interacts is at some other point r_2 at the same time. Since r_1 and r_2 can be anywhere in the sample, we have to integrate over these variables. Similarly we have to integrate over the time variable of the first interaction. As a result of this scattering process the electron is scattered into another state while an electron-hole pair is created. As the two electrons and the hole propagate further in the system, they may interact with each other and with the other electrons of the Fermi system until an electron arrives at r at time t, while the Fermi system returns to its initial state.

In a homogeneous system that is invariant under arbitrary translations the Green function depends only on $\mathbf{r} - \mathbf{r}'$ and t - t' and it is often more convenient to work in the momentum representation. The equation of motion for $G_{\sigma}(\mathbf{k}, t - t')$ has a similar structure,

$$G_{\sigma}(\boldsymbol{k}, t-t') = G_{\sigma}^{(0)}(\boldsymbol{k}, t-t') - \frac{\mathrm{i}}{\hbar} \frac{1}{V^2} \sum_{\boldsymbol{q}\boldsymbol{k}'\sigma'} \int_{-\infty}^{\infty} \mathrm{d}t_1 G_{\sigma}^{(0)}(\boldsymbol{k}, t_1-t') U(\boldsymbol{q}) \qquad (\mathrm{K.2.4})$$
$$\times \left\langle T \left\{ c_{\boldsymbol{k}\sigma}(t) c_{\boldsymbol{k}+\boldsymbol{q},\sigma}^{\dagger}(t_1) c_{\boldsymbol{k}'\sigma'}^{\dagger}(t_1) c_{\boldsymbol{k}'\sigma'}(t_1) \right\} \right\rangle.$$

Note that the wave vector (momentum) is conserved both in the elementary interaction process and in the two-particle propagator. The diagrammatic equation in momentum space is shown in Fig. K.4.



Fig. K.4. Graphical representation of (K.2.5) describing the propagation of an electron in momentum space

The part of the diagram that is linked to the incoming and outgoing electron lines is the improper (reducible) self-energy Σ^* . In this approach it is defined by the relation

$$G_{\sigma}(\mathbf{r}, t; \mathbf{r}', t') = G_{\sigma}^{(0)}(\mathbf{r}, t; \mathbf{r}', t') + \int d\mathbf{r}_{1} \int_{-\infty}^{\infty} dt_{1} \int d\mathbf{r}_{2} \int_{-\infty}^{\infty} dt_{2} G_{\sigma}^{(0)}(\mathbf{r}_{1}, t_{1}, \mathbf{r}', t')$$
 (K.2.5)
 $\times \Sigma_{\sigma}^{*}(\mathbf{r}_{2}, t_{2}, \mathbf{r}_{1}, t_{1}) G_{\sigma}^{(0)}(\mathbf{r}, t; \mathbf{r}_{2}, t_{2})$

in the real-space representation and via

$$G_{\sigma}(\boldsymbol{k},\omega) = G_{\sigma}^{(0)}(\boldsymbol{k},\omega) + G_{\sigma}^{(0)}(\boldsymbol{k},\omega)\Sigma_{\sigma}^{*}(\boldsymbol{k},\omega)G_{\sigma}^{(0)}(\boldsymbol{k},\omega)$$
(K.2.6)

when the Fourier transforms are used. The proper (irreducible) self-energy will be defined later.

The simplest way to truncate the hierarchy of Green functions is to decouple the four-operator term on the right-hand side of (K.2.3). For general space and time arguments we have

$$\left\langle T\left\{ \hat{\psi}_{\sigma}(\boldsymbol{r}_{1},t_{1})\hat{\psi}_{\sigma'}(\boldsymbol{r}_{2},t_{2})\hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}_{3},t_{3})\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}_{4},t_{4})\right\} \right\rangle$$

$$= \left\langle T\left\{ \hat{\psi}_{\sigma}(\boldsymbol{r}_{1},t_{1})\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}_{4},t_{4})\right\} \right\rangle \left\langle T\left\{ \hat{\psi}_{\sigma'}(\boldsymbol{r}_{2},t_{2})\hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}_{3},t_{3})\right\} \right\rangle$$

$$- \left\langle T\left\{ \hat{\psi}_{\sigma}(\boldsymbol{r}_{1},t_{1})\hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}_{3},t_{3})\right\} \right\rangle \left\langle T\left\{ \hat{\psi}_{\sigma'}(\boldsymbol{r}_{2},t_{2})\hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}_{4},t_{4})\right\} \right\rangle.$$

$$(K.2.7)$$

In both terms, the two particles propagate independently of each other; there is no interaction between them, as shown diagrammatically in Fig. K.5. The heavy lines indicate that the propagators are renormalized; the self-energy corrections due to the interaction with the rest of the system are incorporated in the Green functions. As we will see, this approximation is equivalent to the Hartree–Fock approximation. The first process is the direct process, the second the exchange term.



Fig. K.5. Self-consistent Hartree–Fock approximation for the two-particle propagator in real space

The same decoupling procedure in the momentum representation can be visualized by the diagrams shown in Fig. K.6.



Fig. K.6. Self-consistent Hartree–Fock approximation for the two-particle propagator in momentum representation

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Applying this decoupling in real-space representation to (K.2.3) we have

$$\left\langle T \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}_{1},t_{1}) \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}_{2},t_{1}) \hat{\psi}_{\sigma'}(\boldsymbol{r}_{2},t_{1}) \right\} \right\rangle$$

$$= \left\langle \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}_{2},t_{1}) \hat{\psi}_{\sigma'}(\boldsymbol{r}_{2},t_{1}) \right\rangle \left\langle T \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}_{1},t_{1}) \right\} \right\rangle$$

$$- \left\langle \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}_{1},t_{1}) \hat{\psi}_{\sigma'}(\boldsymbol{r}_{2},t_{1}) \right\rangle \left\langle T \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},t) \hat{\psi}_{\sigma'}^{\dagger}(\boldsymbol{r}_{2},t_{1}) \right\} \right\rangle,$$

$$(K.2.8)$$

and the equation of motion yields

$$G_{\sigma}(\mathbf{r} - \mathbf{r}', t - t') = G_{\sigma}^{(0)}(\mathbf{r} - \mathbf{r}', t - t')$$

$$+ \sum_{\sigma'} \iint d\mathbf{r}_{1} d\mathbf{r}_{2} \int dt_{1} G_{\sigma}^{(0)}(\mathbf{r}_{1} - \mathbf{r}', t_{1} - t')$$

$$\times U(\mathbf{r}_{1} - \mathbf{r}_{2}) \langle \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}_{2}, t_{1}) \hat{\psi}_{\sigma'}(\mathbf{r}_{2}, t_{1}) \rangle G_{\sigma}(\mathbf{r} - \mathbf{r}_{1}, t - t_{1})$$

$$- \sum_{\sigma'} \iint d\mathbf{r}_{1} d\mathbf{r}_{2} \int dt_{1} G_{\sigma}^{(0)}(\mathbf{r}_{1} - \mathbf{r}', t_{1} - t') \delta_{\sigma\sigma'}$$

$$\times U(\mathbf{r}_{1} - \mathbf{r}_{2}) \langle \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}_{1}, t_{1}) \hat{\psi}(\mathbf{r}_{2}, t_{1}) \rangle G_{\sigma}(\mathbf{r} - \mathbf{r}_{2}, t - t_{1}) .$$

In momentum representation we find

$$G_{\sigma}(\boldsymbol{k}, t - t') = G_{\sigma}^{(0)}(\boldsymbol{k}, t - t')$$

$$-i\hbar \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} \int dt_1 G_{\sigma}^{(0)}(\boldsymbol{k}, t_1 - t') U(\boldsymbol{q} = 0) G_{\sigma'}(\boldsymbol{k}', -\delta) G_{\sigma}(\boldsymbol{k}, t - t_1)$$

$$+i\hbar \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} \int dt_1 G_{\sigma}^{(0)}(\boldsymbol{k}, t_1 - t') \delta_{\sigma\sigma'} U(\boldsymbol{k}' - \boldsymbol{k}) G_{\sigma}(\boldsymbol{k}', -\delta) G_{\sigma}(\boldsymbol{k}, t - t_1) .$$
(K.2.10)

The graphical representations of these equations are shown in Fig. K.7.



Fig. K.7. Graphical representation of the electron propagation in the Hartree–Fock approximation: (a) in real space and (b) in momentum space

As mentioned already, the decoupling used in the four-operator term in the equation of motion is analogous to the decoupling of the interaction term of the Hamiltonian in the Hartree–Fock approximation. We show here that the quasiparticle energies determined from the pole of the Green function are indeed the renormalized energies of the Hartree–Fock theory. For this we take the Fourier transform of (K.2.10) with respect to time. We obtain an algebraic equation for $G_{\sigma}(\mathbf{k}, \omega)$:

$$G_{\sigma}(\boldsymbol{k},\omega) = G_{\sigma}^{(0)}(\boldsymbol{k},\omega) + \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} G_{\sigma}^{(0)}(\boldsymbol{k},\omega) U(\boldsymbol{q}=0) \langle n_{\boldsymbol{k}'\sigma'} \rangle G_{\sigma}(\boldsymbol{k},\omega) - \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} G_{\sigma}^{(0)}(\boldsymbol{k},\omega) \delta_{\sigma\sigma'} U(\boldsymbol{k}'-\boldsymbol{k}) \langle n_{\boldsymbol{k}'\sigma} \rangle G_{\sigma}(\boldsymbol{k},\omega) . \quad (K.2.11)$$

Its formal solution is

$$G_{\sigma}(\boldsymbol{k},\omega) = \frac{1}{[G_{\sigma}^{(0)}(\boldsymbol{k},\omega)]^{-1} - \Sigma_{\sigma}(\boldsymbol{k},\omega)} = \frac{1}{\hbar\omega - \xi_{\boldsymbol{k}\sigma} - \Sigma_{\sigma}(\boldsymbol{k})}, \quad (K.2.12)$$

with

$$\Sigma_{\sigma}(\boldsymbol{k},\omega) = \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} U(\boldsymbol{q}=0) \langle n_{\boldsymbol{k}'\sigma'} \rangle - \frac{1}{V} \sum_{\boldsymbol{k}'\sigma'} \delta_{\sigma\sigma'} U(\boldsymbol{k}'-\boldsymbol{k}) \langle n_{\boldsymbol{k}'\sigma} \rangle , \quad (K.2.13)$$

which is precisely the self-energy correction in the Hartree–Fock approximation. The first correction to the unperturbed Green function on the right-hand side of Fig. K.7(b), the so-called tadpole diagram, corresponds to the Hartree approximation. The other diagram represents the Fock term. The contribution of the tadpole diagram is proportional to U(q = 0); hence, it vanishes for the homogeneous electron gas, where the uniform positive background precisely cancels the q = 0 Fourier component of the Coulomb potential, indicating that there is no forward scattering in a neutral medium.

Expression (K.2.12) gives correctly the real part of the causal Green function. An imaginary part proportional to

$$\delta(\hbar\omega - \xi_{\boldsymbol{k}\sigma} - \Sigma_{\sigma}(\boldsymbol{k})) \tag{K.2.14}$$

might be added to it. To get its amplitude correctly we calculate first the retarded and advanced Green functions. They satisfy exactly the same equations, but differ in their analytic properties: the retarded (advanced) Green function is analytic in the upper (lower) half-plane. The Green function of interacting electrons,

$$G_{\sigma}^{\mathrm{R}}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \xi_{\boldsymbol{k}\sigma} - \Sigma_{\sigma}(\boldsymbol{k}) + \mathrm{i}\delta},$$

$$G_{\sigma}^{\mathrm{A}}(\boldsymbol{k},\omega) = \frac{1}{\hbar\omega - \xi_{\boldsymbol{k}\sigma} - \Sigma_{\sigma}(\boldsymbol{k}) - \mathrm{i}\delta},$$
(K.2.15)

has similar structure as that of free particles given in (K.1.21). It has a simple pole at the quasiparticle energy. $\Sigma_{\sigma}(\mathbf{k})$ is real in the Hartree–Fock approximation, hence the spectral function is

$$A_{\sigma}(\boldsymbol{k},\omega) = 2\pi\hbar\delta(\hbar\omega - \xi_{\boldsymbol{k}\sigma} - \Sigma_{\sigma}(\boldsymbol{k})). \qquad (K.2.16)$$

Substituting this into (K.1.47) we have

$$G_{\sigma}(\boldsymbol{k},\omega) = \frac{1 - f_0(\xi_{\boldsymbol{k}\sigma})}{\hbar\omega - \tilde{\xi}_{\boldsymbol{k}\sigma} + \mathrm{i}\delta} + \frac{f_0(\xi_{\boldsymbol{k}\sigma})}{\hbar\omega - \tilde{\xi}_{\boldsymbol{k}\sigma} - \mathrm{i}\delta}, \qquad (\mathrm{K.2.17})$$

where $\tilde{\xi}_{k\sigma} = \varepsilon_{k\sigma} + \Sigma_{\sigma}(k) - \mu$ is the quasiparticle energy measured from the chemical potential.

If we wish to go beyond the Hartree–Fock approximation, the search for higher order corrections is greatly facilitated by the diagrammatic representation of the interaction processes. Figure K.8 shows the first- and second-order diagrams taken into account in the self-consistent calculation if $\langle n_{\mathbf{k}'\sigma} \rangle$ in the Hartree–Fock self-energy (K.2.13) is calculated from the renormalized Green function.



Fig. K.8. First- and second-order self-energy corrections in the self-consistent Hartree–Fock approximation

In the next step we recall that the Coulomb potential is screened in the electron gas and the effect of the screening can be incorporated into an effective potential which corresponds to dressing the wavy line of the potential by an infinite series of electron-hole bubbles. These diagrams are contained already in the iterative solution of the Hartree term with the full Green function in the loop, but not in the Fock term. Screening can thus be taken into account in the Fock term by replacing the bare potential with the screened one. The thick wavy line in the Fock term in Fig. K.9 denotes the screened potential.

Figure K.10(*a*) shows the lowest order (second-order) new self-energy correction that is accounted for by this procedure. However, even with this extension only a small fraction of all interaction processes are taken into account. For example, the contribution of the second-order process shown in Fig. K.10(*b*) is still missing.



Fig. K.9. Graphical representation of the equation describing the propagation of an electron when the bare potential in the Fock term is replaced by the screened one



Fig. K.10. (a) Second-order process taken into account when the screened potential is used in the Fock term. (b) A still missing second-order process in two equivalent representations

While the equation of motion could be written down equally well for the retarded, advanced, or causal Green functions, and the equations have similar form at zero or finite temperature, a consistent perturbative account of higher order processes can be achieved only for the causal Green functions. In the latter case the contribution of all self-energy corrections to the Green function up to a given order in the interaction are visualized by Feynman diagrams and can be calculated using the Feynman rules. However, as we will see, different procedures and different rules have to be applied depending on whether the calculations are done for T = 0 or for finite temperature.

K.2.2 Perturbation Theory at Zero Temperature

The Green functions have been defined in the Heisenberg picture, where all time dependence is ascribed to the operators and the wavefunction is time independent. The time dependence of an operator \mathcal{A} is given in (K.1.1), that is the operators satisfy the equation

$$\frac{\partial \mathcal{A}(t)}{\partial t} = \frac{\mathrm{i}}{\hbar} \left[\mathcal{H}, \mathcal{A} \right]_{-}.$$
 (K.2.18)

To work out a consistent perturbation theory it is convenient to switch to the interaction picture, where the time dependence of an operator is defined by

$$\tilde{\mathcal{A}}(t) = \mathrm{e}^{\mathrm{i}\mathcal{H}_0 t/\hbar} \mathcal{A} \mathrm{e}^{-\mathrm{i}\mathcal{H}_0 t/\hbar} \,, \tag{K.2.19}$$

so that the operators satisfy the equation

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$$\frac{\partial \tilde{\mathcal{A}}(t)}{\partial t} = \frac{\mathrm{i}}{\hbar} \big[\mathcal{H}_0, \tilde{\mathcal{A}}(t) \big]_-, \qquad (K.2.20)$$

where \mathcal{H}_0 is the unperturbed Hamiltonian of a solvable problem, whereas the interaction described by the Hamiltonian \mathcal{H}_{int} is treated as a perturbation and its effects are incorporated into the time dependence of the wavefunction via the equation

$$\frac{\partial |\Psi(t)\rangle}{\partial t} = -\frac{\mathrm{i}}{\hbar} \tilde{\mathcal{H}}_{\mathrm{int}}(t) |\tilde{\Psi}(t)\rangle \,. \tag{K.2.21}$$

In what follows the tilde above an operator or wavefunction denotes that the quantity is given in the interaction picture.

Formal integration of the differential equation for the wavefunction from t_0 to t gives

$$|\tilde{\Psi}(t)\rangle = |\tilde{\Psi}(t_0)\rangle - \frac{\mathrm{i}}{\hbar} \int_{t_0}^t \tilde{\mathcal{H}}_{\mathrm{int}}(t') |\tilde{\Psi}(t')\rangle \,\mathrm{d}t' \,. \tag{K.2.22}$$

The evolution of the wavefunction from t_0 to t can be given in terms of the time-development operator $S(t, t_0)$ via

$$|\tilde{\Psi}(t)\rangle = S(t,t_0)|\tilde{\Psi}(t_0)\rangle, \qquad (K.2.23)$$

where $S(t, t_0)$ satisfies the equation

$$\frac{\partial}{\partial t}S(t,t_0) = -\frac{\mathrm{i}}{\hbar}\tilde{\mathcal{H}}_{\mathrm{int}}(t)S(t,t_0). \qquad (K.2.24)$$

The solution of this equation,

$$S(t,t_0) = e^{i\mathcal{H}_0 t/\hbar} e^{-i\mathcal{H}(t-t_0)/\hbar} e^{-i\mathcal{H}_0 t_0/\hbar}, \qquad (K.2.25)$$

is Hermitian and unitary,

$$S(t,t_0) = S^{\dagger}(t_0,t), \qquad S(t,t_0)S^{\dagger}(t,t_0) = 1.$$
 (K.2.26)

Moreover it clearly possesses the group property

$$S(t_2, t_1)S(t_1, t_0) = S(t_2, t_0).$$
 (K.2.27)

A more convenient expression is obtained if the differential equation is formally integrated with the boundary condition $S(t_0, t_0) = 1$. We get

$$S(t,t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t \tilde{\mathcal{H}}_{int}(t_1) S(t_1,t_0) dt_1.$$
 (K.2.28)

Iteration of this equation leads to

$$S(t,t_0) = 1 - \frac{\mathrm{i}}{\hbar} \int_{t_0}^t \tilde{\mathcal{H}}_{\mathrm{int}}(t_1) \,\mathrm{d}t_1 + \cdots$$

$$+ \left(-\frac{\mathrm{i}}{\hbar}\right)^n \int_{t_0}^t \tilde{\mathcal{H}}_{\mathrm{int}}(t_1) \,\mathrm{d}t_1 \dots \int_{t_0}^{t_{n-1}} \tilde{\mathcal{H}}_{\mathrm{int}}(t_n) \,\mathrm{d}t_n + \cdots$$
(K.2.29)

This expression can be written in a symmetric form using the time-ordering operator T that orders the operators chronologically according to their time arguments with the latest time farthest to the left and multiplies the time-ordered sequence by a factor $(-1)^P$, where P is the number of permutations needed to go from the original to the time-ordered sequence. We have

$$S(t,t_0) = 1 - \frac{\mathrm{i}}{\hbar} \int_{t_0}^t \tilde{\mathcal{H}}_{\mathrm{int}}(t_1) \,\mathrm{d}t_1 + \cdots$$

$$+ \left(-\frac{\mathrm{i}}{\hbar} \right)^n \frac{1}{n!} \int_{t_0}^t \mathrm{d}t_1 \dots \int_{t_0}^t \mathrm{d}t_n T \left\{ \tilde{\mathcal{H}}_{\mathrm{int}}(t_1) \dots \tilde{\mathcal{H}}_{\mathrm{int}}(t_n) \right\} + \cdots$$

$$= \sum_{n=0}^{\infty} \left(-\frac{\mathrm{i}}{\hbar} \right)^n \frac{1}{n!} \int_{t_0}^t \mathrm{d}t_1 \dots \int_{t_0}^t \mathrm{d}t_n T \left\{ \tilde{\mathcal{H}}_{\mathrm{int}}(t_1) \dots \tilde{\mathcal{H}}_{\mathrm{int}}(t_n) \right\}.$$
(K.2.30)

This can be reexponentiated to give

$$S(t,t_0) = T \left\{ \exp\left(-\frac{\mathrm{i}}{\hbar} \int_{t_0}^t \mathrm{d}t' \tilde{\mathcal{H}}_{\mathrm{int}}(t')\right) \right\}.$$
 (K.2.31)

Note that the relationship between the operators in the Heisenberg and interaction pictures can be given in terms of the same unitary operator S,

$$\mathcal{A}(t) = e^{i\mathcal{H}t/\hbar} \mathcal{A} e^{-i\mathcal{H}t/\hbar} = e^{i\mathcal{H}t/\hbar} e^{-i\mathcal{H}_0 t/\hbar} \tilde{\mathcal{A}}(t) e^{i\mathcal{H}_0 t/\hbar} e^{-i\mathcal{H}t/\hbar} = S(0,t) \tilde{\mathcal{A}}(t) S(t,0) .$$
(K.2.32)

The operators given in the Heisenberg and interaction pictures coincide at t = 0 and the time-independent ground-state wavefunction $|\Psi_0\rangle$ in the Heisenberg picture is identified with the wavefunction in the interaction picture at t = 0. To find this state we should know the wavefunction at some time t_0 , and then we should be able to follow its time evolution until t = 0. For this we rely on the adiabatic hypothesis and the *Gell-Mann and Low theorem.*³ We assume that the interaction \mathcal{H}_{int} is switched on infinitely slowly at time $t = -\infty$ so as to reach full strength at time t = 0, and it is then switched off

 $^{^3}$ M. Gell-Mann and F. Low, 1951.

again very slowly to vanish as t goes to $+\infty$. This is achieved mathematically by including a factor $\exp(-\delta|t|)$ into \mathcal{H}_{int} with δ a positive infinitesimal. The time-development operator can be defined in the same way as before,

$$|\tilde{\Psi}(t)\rangle = S_{\delta}(t, t_0) |\tilde{\Psi}(t_0)\rangle, \qquad (K.2.33)$$

where

$$S_{\delta}(t,t_0) = \sum_{n=0}^{\infty} \left(-\frac{\mathrm{i}}{\hbar}\right)^n \frac{1}{n!} \int_{t_0}^t \mathrm{d}t_1 \dots \int_{t_0}^t \mathrm{d}t_n \times \mathrm{e}^{-\delta(|t_1|+\dots+|t_n|)} T\left\{\tilde{\mathcal{H}}_{\mathrm{int}}(t_1)\dots\tilde{\mathcal{H}}_{\mathrm{int}}(t_n)\right\}.$$
(K.2.34)

Since the ground state at $t = -\infty$ is the ground state $|\Phi_0\rangle$ of the unperturbed system, it is expected to develop into an exact eigenstate

$$|\Psi_0\rangle = S_\delta(0, -\infty)|\Phi_0\rangle \tag{K.2.35}$$

of the interacting system. This state is indeed a good eigenstate as long as δ is finite. However, it diverges to become meaningless in the limit $\delta \to 0$. Gell-Mann and Low have shown that this divergence can be eliminated by an appropriately chosen phase factor. Their theorem states, and can be proven exactly, that if $|\Phi_0\rangle$ is a nondegenerate ground state of the unperturbed system and perturbation theory can be applied, that is the limit

$$\lim_{\delta \to 0} \frac{S_{\delta}(0, -\infty) |\Phi_0\rangle}{\langle \Phi_0 | S_{\delta}(\infty, -\infty) | \Phi_0 \rangle}$$
(K.2.36)

exists for all orders in the perturbation theory, then the state that develops from the unperturbed ground state is an eigenstate of the full Hamiltonian. This theorem does not guarantee that the new state is the ground state of the interacting system, but we can assume that the eigenstates of the unperturbed system evolve continuously, without level crossings, in normal systems if no transition occurs to a new kind of broken-symmetry state as the interaction is switched on, and thus that the ground state of the noninteracting system develops into the ground state of the interacting system. This adiabatic hypothesis is not valid in superconductors where the new ground state cannot be obtained in perturbation theory.

Knowing now how the operators and the ground-state wavefunction can be written in the interaction representation, simple algebraic manipulations using (K.2.27) lead to

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \frac{\langle \Phi_0 | T\{\psi_{\sigma}(\boldsymbol{r},t)\psi_{\sigma}^{\dagger}(\boldsymbol{r}',t')S(\infty,-\infty)\} | \Phi_0 \rangle}{\langle \Phi_0 | S(\infty,-\infty) | \Phi_0 \rangle} .$$
(K.2.37)

When the quantity $S(\infty, -\infty)$ in the numerator is expanded in powers of the interaction Hamiltonian we find

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{\mathrm{i}}{\hbar}\right)^{n+1} \int_{-\infty}^{\infty} \mathrm{d}t_1 \dots \int_{-\infty}^{\infty} \mathrm{d}t_n \qquad (K.2.38)$$
$$\times \frac{\langle \boldsymbol{\Phi}_0 | T\{\tilde{\psi}_{\sigma}(\boldsymbol{r},t)\tilde{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t')\tilde{\mathcal{H}}_{\mathrm{int}}(t_1)\dots\tilde{\mathcal{H}}_{\mathrm{int}}(t_n)\} | \boldsymbol{\Phi}_0 \rangle}{\langle \boldsymbol{\Phi}_0 | S(\infty,-\infty) | \boldsymbol{\Phi}_0 \rangle}.$$

The various terms in the perturbation series contain the ground-state expectation value of the time-ordered product of a large number of field operators. These expectation values can be evaluated using the *Wick theorem.*⁴

Before presenting this theorem we introduce the concepts of normal ordering and contraction (pairing). In a normal product, all creation operators are placed to the left of all annihilation operators, and a factor -1 is included for every interchange of fermion operators. In a Fermi system, where the one-particle states are filled up to the Fermi energy in the ground state, the states above and below the Fermi energy should be treated differently. States above the Fermi energy should be treated as electron states whereas states below the Fermi energy as hole states and the creation and annihilation operators of holes should be used in the normal ordering. This ensures that the ground-state expectation value of a normal-ordered product vanishes identically.

The contraction of two operators is defined as the difference between their time-ordered and normal products,

$$A^{c}B^{c} = T\{AB\} - N(AB).$$
 (K.2.39)

The contraction of two creation operators or two annihilation operators vanishes, while that of a creation and an annihilation operator is a *c*-number, not an operator. It is just the ground-state expectation value of the time-ordered product. For fermion fields, for example,

$$\hat{\psi}^{c}_{\sigma}(\boldsymbol{r},t)\hat{\psi}^{\dagger c}_{\sigma'}(\boldsymbol{r}',t') = \delta_{\sigma\sigma'} \left\langle T\{\hat{\psi}_{\sigma}(\boldsymbol{r},t)\hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}',t')\}\right\rangle, \qquad (K.2.40)$$

which is the Green function of noninteracting particles apart from a factor $-i/\hbar$:

$$\hat{\psi}^{c}_{\sigma}(\boldsymbol{r},t)\hat{\psi}^{\dagger c}_{\sigma'}(\boldsymbol{r}',t') = i\hbar G(\boldsymbol{r},t;\boldsymbol{r}',t')\delta_{\sigma\sigma'}.$$
(K.2.41)

Similar relationships hold for bosons as well. To prove these relations the field operators have to be written in terms of the creation and annihilation operators and

$$c_{\boldsymbol{k}\sigma}^{c}(t)c_{\boldsymbol{k}'\sigma'}^{\dagger c}(t') = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\sigma\sigma'}e^{-i\varepsilon_{\boldsymbol{k}}(t-t')/\hbar} \begin{cases} 1-n_{\boldsymbol{k}} & t-t'>0\\ -n_{\boldsymbol{k}} & t-t'<0 \end{cases}$$
(K.2.42)

has to be used, where $n_{\bm k}$ is unity inside the Fermi sphere and vanishes outside. This gives

⁴ G. C. WICK, 1950.

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$$c^{c}_{\boldsymbol{k}\sigma}(t)c^{\dagger c}_{\boldsymbol{k}'\sigma'}(t') = i\hbar G(\boldsymbol{k}, t - t')\delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\sigma\sigma'}. \qquad (K.2.43)$$

We are now in the position to state the Wick theorem: if A, B, C, etc., denote field operators or creation and annihilation operators, their time-ordered product can be decomposed into a sum over normal products with zero, one, two, etc., contractions by pairing the operators in all possible ways:

$$T\{ABCD \dots UVW\} = N(ABCD \dots UVW) + N(A^c B^c CD \dots UVW) + N(A^c BC^c D \dots UVW) + \cdots$$
(K.2.44)
+ N(A^c BCD \ldots UVW^c) + \cdots
+ N(A^c B^{cc} C^{ccc} D \ldots U^{ccc} V^{cc} W^c) .

We know that the ground-state expectation value of a normal product vanishes. Therefore, when the ground-state expectation value of a time-ordered product is taken, only those terms survive in which all operators are paired with another operator. Thus we find

$$\langle T\{ABCD\dots UVW\} \rangle = \langle T\{AB\} \rangle \langle T\{CD\} \rangle \cdots \langle T\{VW\} \rangle$$
 (K.2.45)

$$\pm \langle T\{AC\} \rangle \langle T\{BD\} \rangle \cdots \langle T\{VW\} \rangle \pm \cdots$$

All possible contractions have to be taken on the right-hand side. The sign is determined by the parity of the number of interchanges of fermion operators.

Returning now to (K.2.38) which gives the Green function in the interaction picture and applying the Wick theorem to the numerator, it can be decomposed into a sum of terms each of which contains the product of interaction potentials and one-particle propagators of noninteracting particles. The Wick theorem thus leads to an expansion of the full Green function in terms of the free propagators. The individual terms in the expansion can be visualized graphically by Feynman diagrams. The rules will be given below. A similar decomposition is possible for the expression given in the denominator. It can be shown that the role of the denominator is to cancel the disconnected parts of the diagrams. We then have

$$G_{\sigma}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar} \Big\langle \Phi_0 \big| T \big\{ \tilde{\psi}_{\sigma}(\boldsymbol{r},t) \tilde{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',t') S(\infty,-\infty) \big\} \big| \Phi_0 \big\rangle_{\mathrm{con}} \,, \quad (\mathrm{K}.2.46)$$

where the subscript con indicates that only the connected diagrams have to be considered.

The Feynman rules for finding the analytic expression corresponding to a diagram for a system with two-particle interactions can be summarized as follows:

1. In *n*th order of perturbation theory, draw all topologically distinct connected diagrams having two external points (an initial point \mathbf{r}', t' and a terminal point \mathbf{r}, t), *n* wavy interaction lines, and 2n + 1 oriented solid lines. One solid line starts at the point \mathbf{r}', t' and one ends at the point \mathbf{r}, t . One line is entering and one is leaving the vertices of the interaction

lines. A solid line runs continuously from the point \mathbf{r}', t' to \mathbf{r}, t . The other solid fermion lines close on themselves, forming closed fermion loops.

- 2. Label each internal vertex point with the space-time variables r_i, t_i .
- 3. Assign a spin label σ_i to each oriented line.
- 4. Associate the propagator $G_{\sigma}^{(0)}(\boldsymbol{r}_j, t_j; \boldsymbol{r}_i, t_i)$ with the oriented solid line running from \boldsymbol{r}_i, t_i to \boldsymbol{r}_j, t_j with spin σ .
- 5. Associate the factor $U(\mathbf{r}_i \mathbf{r}_j)\delta(t_i t_j)$ with the interaction line connecting \mathbf{r}_i, t_i with \mathbf{r}_j, t_j . When the interaction is spin dependent, the spin variables of the lines entering and leaving the vertices are assigned to the spin variables of the interaction.
- 6. Integrate over the 2n independent position variables and the n independent time variables and sum over the independent spin variables of the internal lines.
- A Green function with equal-time arguments should be interpreted as G⁽⁰⁾_σ(**r**_j, t_j; **r**_i, t_j + δ) with an infinitesimal δ.

 Multiply the contribution by (iħ)ⁿ(-1)^F, where F is the number of closed
- 8. Multiply the contribution by $(i\hbar)^n(-1)^F$, where F is the number of closed fermion loops.

Similar rules apply in momentum space:

- 1. Draw all topologically distinct connected diagrams consisting of two external points, n directed wavy interaction lines, and 2n + 1 oriented solid lines; one of them is an incoming line, another is an outgoing line. A solid line runs continuously from the incoming line to the outgoing line. The other solid lines form closed fermion loops.
- 2. Assign the momentum and frequency variable k, ω and the spin label σ to the incoming and outgoing lines.
- 3. Associate a momentum and frequency variable k_i, ω_i and a spin label σ_i with each oriented internal solid line and a momentum variable q_i with each interaction line by requiring the conservation of momentum and frequency at each internal vertex.
- 4. Associate the propagator

$$G_{\sigma_i}^{(0)}(\boldsymbol{k}_i,\omega_i) = \frac{1}{\hbar\omega_i - \xi_{\boldsymbol{k}_i} + \mathrm{i}\delta\operatorname{sgn}\xi_{\boldsymbol{k}_i}}$$
(K.2.47)

of free particles with the oriented solid line. This form is obtained from (K.1.20) by taking the zero-temperature limit.

- 5. Associate the factor $U(\mathbf{q}_j)$ with each interaction line. When the interaction is spin dependent, the spin variables of the lines entering and leaving the vertices are assigned to the spin variables of the interaction.
- 6. Integrate over the n independent momentum and frequency variables with the weight

$$\int \frac{\mathrm{d}\boldsymbol{k}_i}{(2\pi)^3} \int \frac{\mathrm{d}\omega_i}{2\pi} \tag{K.2.48}$$

and sum over the independent spin variables of the internal lines.

- 7. A solid line that is linked to the same interaction line is interpreted as $e^{i\omega_i\delta}G_{\sigma}(\mathbf{k}_i,\omega_i)$.
- 8. Multiply the contribution by $(i\hbar)^n(-1)^F$, where F is the number of closed fermion loops.

The rules are somewhat different for an interacting electron–phonon system, where the elementary vertex has one entering and one leaving fermion line and one phonon line.

The diagrams for the Green function can be divided into parts by cutting a single fermion line. A part of the diagram that is connected to the rest of the diagram only by two fermion lines and cannot be separated into two parts by cutting a single line is called an irreducible or proper self-energy part. The proper self-energy Σ_{σ} (self-energy in short) is the sum of all possible irreducible self-energy parts. Any diagram for the Green function consists of a chain of self-energy diagrams joined by a solid line. The Green function can then be shown to satisfy the Dyson equation,⁵ which in Fourier representation has the form

$$G_{\sigma}(\boldsymbol{k},\omega) = G_{\sigma}^{(0)}(\boldsymbol{k},\omega) + G_{\sigma}^{(0)}(\boldsymbol{k},\omega)\Sigma_{\sigma}(\boldsymbol{k},\omega)G_{\sigma}^{(0)}(\boldsymbol{k},\omega) + G_{\sigma}^{(0)}(\boldsymbol{k},\omega)\Sigma_{\sigma}(\boldsymbol{k},\omega)G_{\sigma}^{(0)}(\boldsymbol{k},\omega)\Sigma_{\sigma}(\boldsymbol{k},\omega)G_{\sigma}^{(0)}(\boldsymbol{k},\omega) + \cdots = G_{\sigma}^{(0)}(\boldsymbol{k},\omega) + G_{\sigma}^{(0)}(\boldsymbol{k},\omega)\Sigma_{\sigma}(\boldsymbol{k},\omega)G_{\sigma}(\boldsymbol{k},\omega) = \frac{1}{\left[G_{\sigma}^{(0)}(\boldsymbol{k},\omega)\right]^{-1} - \Sigma_{\sigma}(\boldsymbol{k},\omega)}.$$
 (K.2.49)

K.2.3 Finite-Temperature Diagram Technique

The "time" dependence of the operators in the temperature Green function was defined in (K.1.88) with the full Hamiltonian. In analogy to the zero-temperature technique, one can introduce an "interaction representation" in which the τ dependence is given by the unperturbed Hamiltonian,

$$\tilde{\mathcal{A}}(\tau) = e^{\mathcal{H}_0 \tau/\hbar} \mathcal{A} e^{-\mathcal{H}_0 \tau/\hbar} .$$
 (K.2.50)

The "time" dependence of the operators in the two pictures can be related by an operator S,

$$\mathcal{A}(\tau) = \mathcal{S}^{-1}(\tau)\tilde{\mathcal{A}}(\tau)\mathcal{S}(\tau), \qquad (K.2.51)$$

where \mathcal{S} is defined by

$$\mathcal{S}(\tau) = e^{\mathcal{H}_0 \tau/\hbar} e^{-\mathcal{H}\tau/\hbar} = T_\tau \left\{ \exp\left(-\frac{1}{\hbar} \int_0^\tau d\tau' \tilde{\mathcal{H}}_{int}(\tau')\right) \right\}.$$
(K.2.52)

The Boltzmann factor giving the thermodynamic weight of the states can also be expressed in terms of the same S at $\tau = \hbar\beta$,

⁵ F. J. Dyson, 1949.

$$e^{-\beta \mathcal{H}} = e^{-\beta \mathcal{H}_0} \mathcal{S}(\hbar\beta), \qquad (K.2.53)$$

and the partition function is

$$Z = \operatorname{Tr} \left[e^{-\beta \mathcal{H}_0} \mathcal{S}(\hbar \beta) \right] = \left\langle \mathcal{S}(\hbar \beta) \right\rangle_0.$$
 (K.2.54)

The Green function can then be written as

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \frac{\left\langle T_{\tau} \left\{ \tilde{\psi}_{\sigma}(\boldsymbol{r},\tau) \tilde{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau') \mathcal{S}(\hbar\beta) \right\} \right\rangle_{0}}{\langle \mathcal{S}(\hbar\beta) \rangle_{0}}, \qquad (K.2.55)$$

where $\langle \cdots \rangle_0$ denotes the thermodynamic average calculated for the unperturbed system using the noninteracting Hamiltonian.

Expansion of the exponential in the operator \mathcal{S} yields

$$\mathcal{S}(\hbar\beta) = \sum_{n=0}^{\infty} \left(\frac{-1}{\hbar}\right)^n \frac{1}{n!} \int_{0}^{\hbar\beta} \dots \int_{0}^{\hbar\beta} d\tau_1 \dots d\tau_n T_\tau \left\{ \tilde{\mathcal{H}}_{int}(\tau_1) \dots \tilde{\mathcal{H}}_{int}(\tau_n) \right\}.$$
(K 2.56)

Substitution of this expansion into (K.2.55) leads to an expression for the Green function which contains the expectation value of the "time"-ordered product of a large number of field operators. The Wick theorem can be generalized to this situation. It can be shown that this expectation value is equal to the sum of terms obtained by pairing the operators in all possible ways, provided the pairing (contraction) of two operators is defined by

$$A^{c}B^{c} = \left\langle T_{\tau}\{AB\}\right\rangle_{0}. \tag{K.2.57}$$

The pairing of field operators is thus equal to the temperature Green function in a noninteracting system apart from a trivial factor.

The terms in the decomposition can be visualized by diagrams. The only role of the denominator in (K.2.55) is to cancel the disconnected parts, and thus

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\tau,\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \left\langle T_{\tau} \left\{ \tilde{\psi}_{\sigma}(\boldsymbol{r},\tau) \tilde{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau') \mathcal{S}(\hbar\beta) \right\} \right\rangle_{\text{con}} .$$
(K.2.58)

The rules for finding the contribution of the diagrams in momentum representation are as follows:

- 1. Draw all topologically distinct connected diagrams consisting of two external points, n wavy interaction lines and 2n + 1 oriented solid lines, one of which is an incoming line and another is an outgoing line.
- 2. Assign the momentum and discrete frequency variables \mathbf{k}, ω_n and the spin label σ to the incoming and outgoing lines.
- 3. Associate a momentum and frequency variable $\mathbf{k}_i, \omega_{n,i}$ and a spin label σ_i with each oriented internal solid line; assign a direction to each interaction line and a momentum variable \mathbf{q}_i by requiring the conservation of momentum and frequency at each internal vertex.

4. Associate the propagator

$$\mathcal{G}_{\sigma}^{(0)}(\boldsymbol{k},\omega_n) = \frac{1}{\mathrm{i}\hbar\omega_n - \xi_{\boldsymbol{k}\sigma}} \tag{K.2.59}$$

of free particles with the oriented solid line.

- 5. Assign the factor $U(q_j)$ to each interaction line. When the interaction is spin dependent, the spin variables of the lines entering and leaving the vertices are assigned to the spin variables of the interaction.
- 6. Integrate over the n independent wave vectors with weight

$$\int \frac{\mathrm{d}\boldsymbol{k}_i}{(2\pi)^3} \tag{K.2.60}$$

and sum over the n independent frequencies and spin variables of the internal lines.

7. Multiply the contribution by $(-\hbar k_{\rm B}T)^n (-1)^F$, where F is the number of closed fermion loops.

The sums over the discrete frequencies can be converted into integrals in the complex plane using the analytic properties of the functions $\tanh z$ and $\coth z$. The function $\tanh z$ has simple poles at $z = i(n + \frac{1}{2})\pi$,

$$\tanh z = \sum_{n=-\infty}^{\infty} \frac{1}{z - i(n+1/2)\pi},$$
(K.2.61)

and hence

$$f_0(\hbar z) = \frac{1}{e^{\hbar z/k_B T} + 1} = \frac{1}{2} \left(1 - \tanh \frac{\hbar z}{2k_B T} \right) = \frac{1}{2} + k_B T \sum_{n = -\infty}^{\infty} \frac{1}{i\hbar\omega_n - \hbar z}$$
(K.2.62)

with $\omega_n = (2n+1)\pi k_{\rm B}T/\hbar$. If a function F has to be summed over the odd frequencies ω_n , the sum can be converted into an integral. Application of the residue theorem gives

$$\sum_{n} F(i\omega_{n}) = -\frac{1}{2\pi i} \frac{\hbar}{k_{\rm B}T} \int_{C} \frac{F(z)}{e^{\hbar z/k_{\rm B}T} + 1} dz$$

$$= \frac{1}{4\pi i} \frac{\hbar}{k_{\rm B}T} \int_{C} F(z) \tanh \frac{\hbar z}{2k_{\rm B}T} dz,$$
(K.2.63)

where the contour C encircles the imaginary axis counterclockwise as shown in Fig. K.11(a).

For bosons, where the summation goes over even frequencies, similar considerations give

$$\sum_{n} F(i\omega_{n}) = \frac{1}{2\pi i} \frac{\hbar}{k_{B}T} \int_{C} \frac{F(z)}{e^{\hbar z/k_{B}T} - 1} dz$$

$$= \frac{1}{4\pi i} \frac{\hbar}{k_{B}T} \int_{C} F(z) \coth \frac{\hbar z}{2k_{B}T} dz.$$
(K.2.64)



Fig. K.11. The contour used to calculate the frequency sum as an integral in the complex plane. (a) Contour around the imaginary axis. (b) Deformed contour by leaving out the poles of F

If the function F(z) decays fast enough at infinity, the integration path can be deformed to an infinite circle, leaving out the eventual poles of F(z). This deformed contour is shown in Fig. K.11(b). If, for example,

$$F(i\omega_n) = \frac{g(i\omega_n)}{i\omega_n - z_0}, \qquad (K.2.65)$$

where g does not have poles in the complex plane, but decays fast enough, that is F(z) has a simple pole at $z = z_0$, then we readily get

$$\sum_{n} \frac{g(\mathrm{i}\omega_n)}{\mathrm{i}\omega_n - z_0} = \frac{\beta\hbar}{\mathrm{e}^{\hbar z_0/k_{\mathrm{B}}T} + 1} g(z_0) \tag{K.2.66}$$

for fermions, whereas for bosons

$$\sum_{n} \frac{g(\mathrm{i}\omega_n)}{\mathrm{i}\omega_n - z_0} = \frac{-\beta\hbar}{\mathrm{e}^{\hbar z_0/k_{\mathrm{B}}T} - 1} g(z_0) \,. \tag{K.2.67}$$

K.3 Green Functions in Superconductivity

We have seen in Chapter 34 that the most general description of superconductors relies on using the Green functions of the many-body problem. We presented the Gorkov equations, but their solution was not given. Here we solve them in the most simple case, for homogeneous superconductors. We point out the difficulties arising from the nonanalyticity of the causal Green functions and how that problem can be avoided by using the temperature Green functions.

K.3.1 Gorkov Equations

The equations of motion for the real-time normal and anomalous Green functions have been given in (34.4.36) and (34.4.37). They have the form

$$\left(-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial t}-\mathcal{H}_{\mathrm{e}}\right)G(\boldsymbol{r},t;\boldsymbol{r}',t')-\Delta(\boldsymbol{r})F^{*}(\boldsymbol{r},t;\boldsymbol{r}',t')=\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t'),$$

$$-\Delta^*(\mathbf{r})G(\mathbf{r},t;\mathbf{r}',t') + \left(-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial t} + \mathcal{H}_{\mathrm{e}}^*\right)F^*(\mathbf{r},t;\mathbf{r}',t') = 0.$$
(K.3.1)

This system of equations has to be solved with the self-consistency conditions

$$\Delta(\mathbf{r}) = -i\hbar V_0 F(\mathbf{r}, t+\delta; \mathbf{r}, t), \quad \Delta^*(\mathbf{r}) = i\hbar V_0 F^*(\mathbf{r}, t+\delta; \mathbf{r}, t), \quad (K.3.2)$$

where the positive infinitesimal δ ensures the correct order of the operators.

These equations can easily be solved in Fourier representation for a homogeneous system in the absence of external electromagnetic field. Assuming that the eigenvalues $\xi_{\mathbf{k}}$ of the one-particle Hamiltonian \mathcal{H}_{e} are known, we find the algebraic equations

$$(\hbar\omega - \xi_{\mathbf{k}})G(\mathbf{k},\omega) - \Delta F^*(\mathbf{k},\omega) = 1,$$

$$-\Delta^* G(\mathbf{k},\omega) + (\hbar\omega + \xi_{\mathbf{k}})F^*(\mathbf{k},\omega) = 0.$$
 (K.3.3)

After eliminating the anomalous Green function we get

$$\left[(\hbar\omega)^2 - \xi_{\boldsymbol{k}}^2 - |\Delta|^2\right] G(\boldsymbol{k}, \omega) = \hbar\omega + \xi_{\boldsymbol{k}}, \qquad (K.3.4)$$

and the formal solution is

$$G(\mathbf{k},\omega) = \frac{\hbar\omega + \xi_{\mathbf{k}}}{(\hbar\omega)^2 - \xi_{\mathbf{k}}^2 - |\Delta|^2},$$

$$F^*(\mathbf{k},\omega) = \frac{\Delta^*}{(\hbar\omega)^2 - \xi_{\mathbf{k}}^2 - |\Delta|^2}.$$
(K.3.5)

Recognizing in the denominator the energy $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta|^2}$ of the quasiparticles of the superconducting state, the Green functions can be written in terms of the coherence factors that relate the quasiparticles to the electrons and holes via the Bogoliubov transformation (34.2.68). Using the expressions given in (34.2.29) and (34.2.30),

$$|u_{\mathbf{k}}|^2 = \frac{E_{\mathbf{k}} + \xi_{\mathbf{k}}}{2E_{\mathbf{k}}}, \quad |v_{\mathbf{k}}|^2 = \frac{E_{\mathbf{k}} - \xi_{\mathbf{k}}}{2E_{\mathbf{k}}}, \quad u_{\mathbf{k}}^* v_{\mathbf{k}} = \frac{\Delta}{2E_{\mathbf{k}}}, \quad (K.3.6)$$

we find

$$G(\mathbf{k},\omega) = \frac{\hbar\omega + \xi_{\mathbf{k}}}{(\hbar\omega)^2 - E_{\mathbf{k}}^2} = \frac{|u_{\mathbf{k}}|^2}{\hbar\omega - E_{\mathbf{k}}} + \frac{|v_{\mathbf{k}}|^2}{\hbar\omega + E_{\mathbf{k}}},$$

$$F^*(\mathbf{k},\omega) = \frac{\Delta^*}{(\hbar\omega)^2 - E_{\mathbf{k}}^2} = \frac{u_{\mathbf{k}}v_{\mathbf{k}}^*}{\hbar\omega - E_{\mathbf{k}}} - \frac{u_{\mathbf{k}}v_{\mathbf{k}}^*}{\hbar\omega + E_{\mathbf{k}}},$$
(K.3.7)

showing that the Green functions have poles at the quasiparticle energies for superconductors as well.

The equations can be satisfied even if terms like $\delta(\hbar\omega \pm E_k)$ are added to the solution found above. These terms fix the analytic properties by positioning the poles in the complex ω plane. The correct form can be easily found with the aid of the retarded and advanced Green functions. Once these functions are known, the spectral function is obtained using (K.1.54), and then the real and imaginary parts of the causal Green function are given by (K.1.40) and (K.1.41), respectively.

The retarded Green functions defined by

$$G^{\mathrm{R}}(\boldsymbol{r},t;\boldsymbol{r}',t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\left\langle \left[\hat{\psi}_{\uparrow}(\boldsymbol{r},t),\hat{\psi}_{\uparrow}^{\dagger}(\boldsymbol{r}',t')\right]_{+}\right\rangle,$$

$$F^{\mathrm{R}^{*}}(\boldsymbol{r},t;\boldsymbol{r}',t') = \frac{\mathrm{i}}{\hbar}\theta(t-t')\left\langle \left[\hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},t),\hat{\psi}_{\uparrow}^{\dagger}(\boldsymbol{r}',t')\right]_{+}\right\rangle$$
(K.3.8)

satisfy the same equations of motion as the causal functions, but their analytic properties are simpler in that they have to be analytic in the upper half-plane, hence

$$G^{\mathbf{R}}(\boldsymbol{k},\omega) = \frac{\hbar\omega + \xi_{\boldsymbol{k}}}{(\hbar\omega - E_{\boldsymbol{k}} + \mathrm{i}\delta)(\hbar\omega + E_{\boldsymbol{k}} + \mathrm{i}\delta)}$$
$$= \frac{|u_{\boldsymbol{k}}|^2}{\hbar\omega - E_{\boldsymbol{k}} + \mathrm{i}\delta} + \frac{|v_{\boldsymbol{k}}|^2}{\hbar\omega + E_{\boldsymbol{k}} + \mathrm{i}\delta}$$
(K.3.9)

and

$$F^{\mathbf{R}^{*}}(\boldsymbol{k},\omega) = \frac{\Delta^{*}}{(\hbar\omega_{n} - E_{\boldsymbol{k}} + \mathrm{i}\delta)(\hbar\omega + E_{\boldsymbol{k}} + \mathrm{i}\delta)}$$
$$= \frac{u_{\boldsymbol{k}}v_{\boldsymbol{k}}^{*}}{\hbar\omega - E_{\boldsymbol{k}} + \mathrm{i}\delta} - \frac{u_{\boldsymbol{k}}v_{\boldsymbol{k}}^{*}}{\hbar\omega + E_{\boldsymbol{k}} + \mathrm{i}\delta}.$$
(K.3.10)

The advanced Green function is analytic in the lower half-plane. It is obtained from the retarded one by reversing the sign of the infinitesimal imaginary term in the denominator. The spectral function is

$$A(\mathbf{k},\omega) = 2\pi\hbar \left[|u_{\mathbf{k}}|^2 \delta(\hbar\omega - E_{\mathbf{k}}) + |v_{\mathbf{k}}|^2 \delta(\hbar\omega + E_{\mathbf{k}}) \right]$$
(K.3.11)

and the imaginary part of the Green function is

$$\operatorname{Im} G(\boldsymbol{k},\omega) = -\pi \left[|u_{\boldsymbol{k}}|^2 \delta(\hbar\omega - E_{\boldsymbol{k}}) + |v_{\boldsymbol{k}}|^2 \delta(\hbar\omega + E_{\boldsymbol{k}}) \right] \tanh \frac{\hbar\omega}{2k_{\mathrm{B}}T}.$$
(K.3.12)

The full normal Green function can then be written in the form

$$G(\mathbf{k},\omega) = \frac{|u_{\mathbf{k}}|^2}{\hbar\omega - E_{\mathbf{k}} + \mathrm{i}\delta} + \frac{|v_{\mathbf{k}}|^2}{\hbar\omega + E_{\mathbf{k}} - \mathrm{i}\delta} + 2\pi\mathrm{i}f_0(E_{\mathbf{k}})[|u_{\mathbf{k}}|^2\delta(\hbar\omega - E_{\mathbf{k}}) - |v_{\mathbf{k}}|^2\delta(\hbar\omega + E_{\mathbf{k}})].$$
(K.3.13)

Knowing the imaginary part of the normal Green function the imaginary part of the anomalous Green function can be calculated from the equation of motion:

Im
$$F^*(\mathbf{k},\omega) = -\pi \frac{\Delta^*}{2E_{\mathbf{k}}} \left[\delta(\hbar\omega - E_{\mathbf{k}}) - \delta(\hbar\omega + E_{\mathbf{k}}) \right] \tanh \frac{\hbar\omega}{2k_{\rm B}T}$$
, (K.3.14)

and the full expression is

$$F^{*}(\boldsymbol{k},\omega) = \frac{\Delta^{*}}{(\hbar\omega_{n} - E_{\boldsymbol{k}} + \mathrm{i}\delta)(\hbar\omega + E_{\boldsymbol{k}} - \mathrm{i}\delta)} + \mathrm{i}\pi \frac{\Delta^{*}}{E_{\boldsymbol{k}}} f_{0}(E_{\boldsymbol{k}}) \left[\delta(\hbar\omega - E_{\boldsymbol{k}}) + \delta(\hbar\omega + E_{\boldsymbol{k}})\right].$$
(K.3.15)

The self-consistency condition (34.4.33) for the energy gap leads to the equation

$$\Delta^* = i\hbar \frac{V_0}{V} \sum_{\boldsymbol{k}} \int \frac{d\omega}{2\pi} e^{-i\delta\omega} F^*(\boldsymbol{k},\omega) \,. \tag{K.3.16}$$

Substituting the expression derived above for $F^*(\mathbf{k}, \omega)$ into this equation the integral of the first term over the frequency can be performed by closing the integration path in the lower half-plane. We get

$$\Delta^* = \frac{V_0}{V} \sum_{k} \frac{\Delta^*}{2E_k} \left[1 - 2f_0(E_k) \right], \qquad (K.3.17)$$

which is equivalent to (34.2.97) from which the temperature dependence of the energy gap has been calculated.

K.3.2 Temperature Green Functions for Superconductors

The same result can be derived much more simply by using the temperature Green functions. Considering only conventional *s*-wave superconductors, the normal Green function defined in the usual way,

$$\mathcal{G}_{\sigma}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \left\langle T_{\tau} \left\{ \hat{\psi}_{\sigma}(\boldsymbol{r},\tau) \hat{\psi}_{\sigma}^{\dagger}(\boldsymbol{r}',\tau') \right\} \right\rangle, \qquad (K.3.18)$$

is independent of the spin orientation and the spin index will be dropped. The anomalous Green functions

$$\mathcal{F}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \left\langle T_{\tau} \left\{ \hat{\psi}_{\uparrow}(\boldsymbol{r},\tau) \hat{\psi}_{\downarrow}(\boldsymbol{r}',\tau') \right\} \right\rangle,$$

$$\overline{\mathcal{F}}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = -\frac{1}{\hbar} \left\langle T_{\tau} \left\{ \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},\tau) \hat{\psi}_{\uparrow}^{\dagger}(\boldsymbol{r}',\tau') \right\} \right\rangle$$
(K.3.19)

appear in the equation of motion. Note that $\overline{\mathcal{F}}$ is not the Hermitian adjoint of \mathcal{F} . The pairing potential $\Delta(\mathbf{r})$ can be given in terms of these functions in the form

$$\Delta(\mathbf{r}) = V_0 \mathcal{F}(\mathbf{r}, \tau + \delta; \mathbf{r}, \tau), \quad \Delta^*(\mathbf{r}) = V_0 \overline{\mathcal{F}}(\mathbf{r}, \tau + \delta; \mathbf{r}, \tau). \quad (K.3.20)$$

Using the BCS Hamiltonian in real space representation as given in (34.4.3), the τ -dependent operators satisfy the equations

$$\begin{split} &\hbar \frac{\mathrm{d}}{\mathrm{d}\tau} \hat{\psi}_{\uparrow}(\boldsymbol{r},\tau) = -\mathcal{H}_{\mathrm{e}} \hat{\psi}_{\uparrow}(\boldsymbol{r},\tau) + \Delta(\boldsymbol{r}) \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},\tau) ,\\ &\hbar \frac{\mathrm{d}}{\mathrm{d}\tau} \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},\tau) = \mathcal{H}_{\mathrm{e}}^{*} \hat{\psi}_{\downarrow}^{\dagger}(\boldsymbol{r},\tau) + \Delta^{*}(\boldsymbol{r}) \hat{\psi}_{\uparrow}(\boldsymbol{r},\tau) , \end{split}$$
(K.3.21)

and the equations of motion of the Green functions are

$$\left(-\hbar \frac{\mathrm{d}}{\mathrm{d}\tau} - \mathcal{H}_{\mathrm{e}}\right) \mathcal{G}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') + \Delta(\boldsymbol{r})\overline{\mathcal{F}}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = \delta(\boldsymbol{r}-\boldsymbol{r}')\delta(\tau-\tau'),$$

$$\left(\hbar \frac{\mathrm{d}}{\mathrm{d}\tau} - \mathcal{H}_{\mathrm{e}}^{*}\right) \overline{\mathcal{F}}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') - \Delta^{*}(\boldsymbol{r})\mathcal{G}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = 0.$$
(K.3.22)

It is more convenient to work in momentum and frequency representation for a homogeneous system. The Fourier transforms defined via

$$\mathcal{G}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = \frac{k_{\mathrm{B}}T}{\hbar} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^{3}} \sum_{n} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \mathrm{e}^{-\mathrm{i}\omega_{n}(\tau-\tau')} \mathcal{G}(\boldsymbol{k},\omega_{n}),$$

$$\overline{\mathcal{F}}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = \frac{k_{\mathrm{B}}T}{\hbar} \int \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^{3}} \sum_{n} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \mathrm{e}^{-\mathrm{i}\omega_{n}(\tau-\tau')} \overline{\mathcal{F}}(\boldsymbol{k},\omega_{n})$$
(K.3.23)

satisfy the algebraic equations

1

$$(i\hbar\omega_n - \xi_k)\mathcal{G}(k,\omega_n) + \Delta\overline{\mathcal{F}}(k,\omega_n) = 1,$$

$$(-i\hbar\omega_n - \xi_k)\overline{\mathcal{F}}(k,\omega_n) - \Delta^*\mathcal{G}(k,\omega_n) = 0.$$
(K.3.24)

These equations are readily solved to give

$$\mathcal{G}(\boldsymbol{k},\omega_n) = -\frac{\mathrm{i}\hbar\omega_n + \xi_{\boldsymbol{k}}}{(\hbar\omega_n)^2 + \xi_{\boldsymbol{k}}^2 + |\Delta|^2} = \frac{u_{\boldsymbol{k}}^2}{\mathrm{i}\hbar\omega_n - E_{\boldsymbol{k}}} + \frac{v_{\boldsymbol{k}}^2}{\mathrm{i}\hbar\omega_n + E_{\boldsymbol{k}}} \qquad (K.3.25)$$

and

$$\overline{\mathcal{F}}(\boldsymbol{k},\omega_n) = \frac{\Delta^*}{(\hbar\omega_n)^2 + \xi_{\boldsymbol{k}}^2 + |\Delta|^2} = -\frac{u_{\boldsymbol{k}}v_{\boldsymbol{k}}}{i\hbar\omega_n - E_{\boldsymbol{k}}} + \frac{u_{\boldsymbol{k}}v_{\boldsymbol{k}}}{i\hbar\omega_n + E_{\boldsymbol{k}}}.$$
 (K.3.26)

Note that the normal Green function satisfies the relation

$$\mathcal{G}(\boldsymbol{k},\omega_n) = G^{\mathrm{R}}(\boldsymbol{k},\mathrm{i}\omega_n), \qquad (\mathrm{K}.3.27)$$

which was derived in (K.1.109), while for the anomalous Green function

$$\overline{\mathcal{F}}(\boldsymbol{k},\omega_n) = -F^{\mathrm{R}^*}(\boldsymbol{k},\mathrm{i}\omega_n). \qquad (\mathrm{K}.3.28)$$

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The self-consistency condition for the gap leads to

$$\Delta^* = V_0 \overline{\mathcal{F}}(\boldsymbol{r}, \tau + \delta; \boldsymbol{r}, \tau) = \frac{V_0}{V} k_{\rm B} T \sum_{\boldsymbol{k}} \sum_n \overline{\mathcal{F}}(\boldsymbol{k}, \omega_n)$$

$$= \frac{V_0}{V} k_{\rm B} T \sum_{\boldsymbol{k}} \sum_n \frac{\Delta^*}{(\hbar\omega_n)^2 + \xi_{\boldsymbol{k}}^2 + |\Delta|^2}.$$
 (K.3.29)

The sum over the discrete frequencies can be converted into a contour integral with the aid of (K.2.63) or we could use the relation

$$\tanh \frac{z}{2k_{\rm B}T} = 2k_{\rm B}T \sum_{n=-\infty}^{\infty} \frac{z}{z^2 + (\hbar\omega_n)^2}$$
(K.3.30)

given in (34.2.109). In either way we arrive at (34.2.97).

K.3.3 Derivation of the Ginzburg–Landau Equations

The Gorkov equations can be generalized to inhomogeneous superconductors. Assuming that we are dealing with a stationary system, the Green functions depend on $\tau - \tau'$ only. If the Green functions are written in Fourier series, in analogy with (K.1.94), the Fourier coefficients defined by

$$\mathcal{G}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = \frac{k_{\mathrm{B}}T}{\hbar} \sum_{n} \mathrm{e}^{-\mathrm{i}\omega_{n}(\tau-\tau')} \mathcal{G}(\boldsymbol{r},\boldsymbol{r}',\omega_{n}),$$

$$\overline{\mathcal{F}}(\boldsymbol{r},\tau;\boldsymbol{r}',\tau') = \frac{k_{\mathrm{B}}T}{\hbar} \sum_{n} \mathrm{e}^{-\mathrm{i}\omega_{n}(\tau-\tau')} \overline{\mathcal{F}}(\boldsymbol{r},\boldsymbol{r}',\omega_{n})$$
(K.3.31)

satisfy the system of equations

$$(i\hbar\omega_n - \mathcal{H}_e) \mathcal{G}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) + \Delta(\boldsymbol{r})\overline{\mathcal{F}}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) = \delta(\boldsymbol{r} - \boldsymbol{r}'), (-i\hbar\omega_n - \mathcal{H}_e^*) \overline{\mathcal{F}}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) - \Delta^*(\boldsymbol{r})\mathcal{G}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) = 0.$$
(K.3.32)

The vector potential appears in these equations through \mathcal{H}_{e} . In weak fields, the equations can be solved to first order in the vector potential. A nonlocal relationship is obtained between the current density and the vector potential and a microscopic expression can be derived for the Pippard coherence length. In the remaining part we will show how the Ginzburg–Landau equations can be obtained from an expansion in powers of $\Delta(\mathbf{r})$ in the neighborhood of the transition temperature.

We introduce the Green function $\mathcal{G}^{(0)}$ of the normal system. It satisfies the equation

$$(i\hbar\omega_n - \mathcal{H}_e) \mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) = \delta(\boldsymbol{r} - \boldsymbol{r}'). \qquad (K.3.33)$$

It is easily verified by differentiation that the Gorkov equations can be written in an integral form with the aid of this function

$$\mathcal{G}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) = \mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) - \int \mathrm{d}\boldsymbol{r}_1 \mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}_1, \omega_n) \Delta(\boldsymbol{r}_1) \overline{\mathcal{F}}(\boldsymbol{r}_1, \boldsymbol{r}', \omega_n)$$
(K.3.34)

and

$$\overline{\mathcal{F}}(\boldsymbol{r},\boldsymbol{r}',\omega_n) = \int \mathrm{d}\boldsymbol{r}_1 \mathcal{G}^{(0)}(\boldsymbol{r}_1,\boldsymbol{r},-\omega_n) \Delta^*(\boldsymbol{r}_1) \mathcal{G}(\boldsymbol{r}_1,\boldsymbol{r}',\omega_n) \,. \tag{K.3.35}$$

Iteration of the equations leads to

$$\overline{\mathcal{F}}(\boldsymbol{r},\boldsymbol{r}',\omega_n) = \int d\boldsymbol{r}_1 \mathcal{G}^{(0)}(\boldsymbol{r}_1,\boldsymbol{r},-\omega_n) \Delta^*(\boldsymbol{r}_1) \mathcal{G}^{(0)}(\boldsymbol{r}_1,\boldsymbol{r}',\omega_n)$$
(K.3.36)
$$-\iiint d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 \mathcal{G}^{(0)}(\boldsymbol{r}_1,\boldsymbol{r},-\omega_n) \Delta^*(\boldsymbol{r}_1) \mathcal{G}^{(0)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_n)$$
$$\times \Delta(\boldsymbol{r}_2) \mathcal{G}^{(0)}(\boldsymbol{r}_3,\boldsymbol{r}_2,-\omega_n) \Delta^*(\boldsymbol{r}_3) \mathcal{G}^{(0)}(\boldsymbol{r}_3,\boldsymbol{r}',\omega_n) + \cdots .$$

When the two leading terms in this expansion are substituted into the selfconsistency condition for the gap we find

$$\Delta^{*}(\boldsymbol{r}) = k_{\mathrm{B}}TV_{0}\sum_{n} \left[\int \mathrm{d}\boldsymbol{r}_{1}\mathcal{G}^{(0)}(\boldsymbol{r}_{1},\boldsymbol{r},-\omega_{n})\Delta^{*}(\boldsymbol{r}_{1})\mathcal{G}^{(0)}(\boldsymbol{r}_{1},\boldsymbol{r},\omega_{n}) - \iiint \mathrm{d}\boldsymbol{r}_{1}\mathrm{d}\boldsymbol{r}_{2}\mathrm{d}\boldsymbol{r}_{3}\mathcal{G}^{(0)}(\boldsymbol{r}_{1},\boldsymbol{r},-\omega_{n})\Delta^{*}(\boldsymbol{r}_{1})\mathcal{G}^{(0)}(\boldsymbol{r}_{1},\boldsymbol{r}_{2},\omega_{n}) \times \Delta(\boldsymbol{r}_{2})\mathcal{G}^{(0)}(\boldsymbol{r}_{3},\boldsymbol{r}_{2},-\omega_{n})\Delta^{*}(\boldsymbol{r}_{3})\mathcal{G}^{(0)}(\boldsymbol{r}_{3},\boldsymbol{r},\omega_{n}) \right].$$
(K.3.37)

The Green function of normal systems is well known in the absence of external magnetic field. We have

$$\mathcal{G}^{(0)}(\boldsymbol{r}, \boldsymbol{r}', \omega_n) = \sum_{\boldsymbol{k}} \frac{\psi_{\boldsymbol{k}}(\boldsymbol{r})\psi_{\boldsymbol{k}}^*(\boldsymbol{r}')}{\mathrm{i}\hbar\omega_n - \xi_{\boldsymbol{k}}}, \qquad (\mathrm{K.3.38})$$

where $\psi_{\mathbf{k}}(\mathbf{r})$ is the wavefunction of the state with energy $\xi_{\mathbf{k}}$. For pure metals, where plane waves can be used for the wavefunction, the integrals in (K.3.37) can be evaluated. After some tedious algebra we arrive at the first Ginzburg– Landau equation for the order parameter Δ . The calculations can be done for impure superconductors as well. In the "dirty" limit the equations are very similar to the pure case, only the parameters are somewhat different.

To get the second Ginzburg–Landau equation, we start from the quantum mechanical expression for the current density. This quantity can be readily expressed in terms of the normal Green function. Substitution of the two leading terms of the iterative solution of the Gorkov equations for the normal Green function,

$$\mathcal{G}(\boldsymbol{r},\boldsymbol{r}',\omega_n) = \mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega_n) - \iint \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \mathcal{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}_1,\omega_n) \Delta(\boldsymbol{r}_1) (\mathrm{K}.3.39)$$
$$\times \mathcal{G}^{(0)}(\boldsymbol{r}_2,\boldsymbol{r}_1,-\omega_n) \Delta^*(\boldsymbol{r}_2) \mathcal{G}^{(0)}(\boldsymbol{r}_2,\boldsymbol{r}',\omega_n) ,$$

into the expression for the current leads precisely to the second Ginzburg–Landau equation.

Further Reading

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Field Theory of Luttinger Liquids

As has been shown in Chapter 32, there are no fermionic quasiparticles in Luttinger liquids even though the archetype, the Tomonaga–Luttinger model, is a seemingly innocent model of interacting fermions. The excitation spectrum consists only of bosonic branches. The properties of the model can be described equivalently working with either the fermionic or the bosonic degrees of freedom, although the difficulties in one or the other formalism may be different. The same is true when the effects of interactions beyond the Tomonaga– Luttinger model (backward and umklapp scattering) are considered. Their treatment is often simpler when bosonic degrees of freedom are used, especially when they are described by continuous boson fields. We present the elements of this theory in this appendix. First, we show how the discrete harmonic chain can be represented by a boson field. Then the Hamiltonians of one-dimensional interacting fermions with and without spin are reduced to similar form and the correlation functions are determined.

L.1 Field Theory of the Harmonic Chain

Consider a harmonic chain of atoms with mass M. The spring constant of the elastic coupling between nearest-neighbor atoms at equilibrium distance a is denoted by K. The system is described by the well-known Lagrangian

$$\mathcal{L} = \sum_{n=1}^{N} \left[\frac{1}{2} M \dot{u}_n^2 - \frac{1}{2} K \left(u_{n+1} - u_n \right)^2 \right], \qquad (L.1.1)$$

where u_n is the displacement of the *n*th atom from its equilibrium position. The corresponding Hamiltonian is

$$\mathcal{H} = \sum_{n=1}^{N} \left[\frac{p_n^2}{2M} + \frac{1}{2} K \left(u_{n+1} - u_n \right)^2 \right], \qquad (L.1.2)$$

where p_n is the canonical momentum. The displacement and the canonical momentum satisfy the canonical commutation relation

$$\left[u_n, p_{n'}\right]_{-} = \mathrm{i}\hbar\delta_{nn'} \,. \tag{L.1.3}$$

The macroscopic properties are mainly determined by the long-wavelength, low-frequency (low-energy) excitations, for which the variations of u_n are slow compared to the lattice constant. If we are not concerned with the behavior on the atomic scale, it is allowed to neglect the discreteness of the lattice and to describe the system in terms of a continuous displacement field u(x) which takes the value u_n at x = na. This function can be obtained by smearing out the function

$$u(x) = a \sum_{n} u_n \delta(x - na) \tag{L.1.4}$$

or taking the limit $a \to 0$. Using the relations

$$\sum_{n=1}^{N} \approx \frac{1}{a} \int_{0}^{L} \mathrm{d}x \tag{L.1.5}$$

and

$$u_{n+1} - u_n \approx \frac{\partial u(x)}{\partial x} a$$
, (L.1.6)

which are valid when a is small compared to L = Na, the Lagrangian takes the form

$$\mathcal{L} = \int_{0}^{L} \mathrm{d}x \left[\frac{M}{2a} \dot{u}^{2}(x) - \frac{Ka}{2} \left(\partial_{x} u(x) \right)^{2} \right], \qquad (L.1.7)$$

where ∂_x is a short-hand notation for $\partial/\partial x$. The Lagrangian equation of motion

$$\frac{\partial \mathcal{L}(x)}{\partial u(x)} - \frac{\partial}{\partial t} \frac{\partial \mathcal{L}(x)}{\partial \dot{u}(x)} - \frac{\partial}{\partial x} \frac{\partial \mathcal{L}(x)}{\partial (\partial_x u(x))} = 0$$
(L.1.8)

for the density

$$\mathcal{L}(x) = \frac{M}{2a}\dot{u}^2(x) - \frac{Ka}{2} \left(\partial_x u(x)\right)^2 \tag{L.1.9}$$

leads to

$$-\frac{M}{a}\frac{\partial^2 u(x)}{\partial t^2} + Ka\frac{\partial^2 u(x)}{\partial x^2} = 0.$$
 (L.1.10)

This equation describes the propagation of a wave with velocity

$$c = \sqrt{\frac{Ka^2}{M}} \tag{L.1.11}$$

in agreement with (11.2.11) which gives the velocity of acoustic vibrations for a linear chain.

The continuum version of p_n is naturally defined as $p(x) = M\dot{u}(x)$. However, it follows from the commutation relation (L.1.3) that the commutator of u(x) and p(x') contains an extra factor a,

$$[u(x), p(x')]_{-} = i\hbar a\delta(x - x').$$
 (L.1.12)

We therefore introduce a new, dimensionless field, $\phi(x) = u(x)/a$, and the dimensionless conjugate momentum $\Pi(x) = p(x)/\hbar$, which satisfy the commutation relation

$$[\phi(x), \Pi(x')]_{-} = i\delta(x - x').$$
 (L.1.13)

When the kinetic energy and the harmonic potential energy are given in terms of them we have

$$\mathcal{H} = \int dx \left[\frac{\hbar^2}{2Ma} \Pi^2(x) + \frac{1}{2} K a^3 \left(\frac{\partial \phi(x)}{\partial x} \right)^2 \right]$$

= $\frac{1}{2} \hbar c \int dx \left[\mu \Pi^2(x) + \frac{1}{\mu} \left(\frac{\partial \phi(x)}{\partial x} \right)^2 \right],$ (L.1.14)

where $\mu = \hbar/cMa$ is a dimensionless parameter which governs the power-law decay of all correlation functions. Based on this analogy, we can speak of a harmonic model when the Hamiltonian of the Luttinger model is transformed into a similar form.

L.2 Fermion–Boson Equivalence

For the sake of simplicity, we first consider spinless fermions and express the field operators of fermions propagating in one dimension in terms of boson fields. The expressions will then be generalized to physical fermions with spin without going into the mathematical details.

L.2.1 Phase Field for Spinless Fermions

The field operator of spinless fermions propagating along a chain of length L can be decomposed into right- and left-moving components:

$$\hat{\psi}(x) = \hat{\psi}_{+}(x) + \hat{\psi}_{-}(x)$$
 (L.2.1)

with

$$\hat{\psi}_{+}(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{i(k_{\rm F}+k)x} c_{k_{\rm F}+k},$$

$$\hat{\psi}_{-}(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{i(-k_{\rm F}+k)x} d_{-k_{\rm F}+k},$$

(L.2.2)

where $c_{k_{\rm F}+k}$ and $d_{-k_{\rm F}+k}$ are the annihilation operators of electron states near the Fermi points $k_{\rm F}$ and $-k_{\rm F}$, respectively, and $k = (2\pi/L)n_k$ with integer n_k if periodic boundary condition is used. The operators defined by factoring out the fast oscillating factor $\exp(\pm k_{\rm F} x)$,

$$R(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{ikx} c_{k_{\rm F}+k} = e^{-ik_{\rm F}x} \hat{\psi}_{+}(x) ,$$

$$L(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{ikx} d_{-k_{\rm F}+k} = e^{ik_{\rm F}x} \hat{\psi}_{-}(x) ,$$
(L.2.3)

contain only the long-wavelength components and are slowly varying on the scale of the lattice spacing. Although the physics is governed by the states near the Fermi points, a mathematically rigorous treatment is only possible if n_k in $k = (2\pi/L)n_k$ can take any integer values from $-\infty$ to ∞ for both the right- and the left-moving branches. It follows from the anticommutation rules of the fermion operators that the field operators of the right- and left-moving fermions satisfy the anticommutation relations characteristic of fermion fields,

$$\left[\hat{\psi}_{\lambda}(x), \hat{\psi}_{\lambda'}^{\dagger}(x')\right]_{+} = \delta_{\lambda\lambda'}\delta(x - x') \qquad \lambda, \lambda' = \pm, \qquad (L.2.4)$$

where the variables x and x' take values in the range [0, L]. In deriving these relations we have used

$$\frac{1}{L}\sum_{n_k=-\infty}^{\infty} e^{2\pi i n_k x/L} = \sum_{h=-\infty}^{\infty} \delta(x-hL)$$
(L.2.5)

that follows from (C.1.46).

The divergent contributions arising from the infinitely deep Fermi sea can be eliminated by normal ordering the operators. The creation operators are ordered to the left of the annihilation operators in a product with the proviso that states below the Fermi energy are treated in the hole representation, i.e., the creation operators of holes are ordered to the left of the annihilation operators of holes. The chiral density of right- and left-moving fermions is

$$n_{\lambda}(x) = : \hat{\psi}_{\lambda}^{\dagger}(x) \hat{\psi}_{\lambda}(x) : .$$
 (L.2.6)

Thus

$$n_{+}(x) = :R^{\dagger}(x)R(x):$$
 and $n_{-}(x) = :L^{\dagger}(x)L(x):$ (L.2.7)

Writing the chiral density of right-moving fermions in terms of the creation and annihilation operators and separating out the terms where the two operators have identical momenta,

$$n_{+}(x) = \frac{1}{L} \sum_{kk'} e^{-i(k-k')x} : c^{\dagger}_{k_{\rm F}+k} c_{k_{\rm F}+k'} :$$

$$= \frac{1}{L} \sum_{k} : c^{\dagger}_{k_{\rm F}+k} c_{k_{\rm F}+k} : + \frac{1}{L} \sum_{q \neq 0} e^{iqx} n_{+}(q) , \qquad (L.2.8)$$

where

$$n_{+}(q) = \sum_{k} c^{\dagger}_{k_{\rm F}+k} c_{k_{\rm F}+k+q}$$
 (L.2.9)

is the known expression for the Fourier transform of the density. The normal ordering sign was omitted in the second term as being redundant when the two fermion operators have different momenta. The first term which contains the number operators of right-moving particles is independent of the position. The integral of $n_+(x)$ over the chain gives

$$\delta N_{+} = \sum_{k} : c_{k_{\rm F}+k}^{\dagger} c_{k_{\rm F}+k} := \sum_{k>0} c_{k_{\rm F}+k}^{\dagger} c_{k_{\rm F}+k} - \sum_{k<0} c_{k_{\rm F}+k} c_{k_{\rm F}+k}^{\dagger} . \qquad (\text{L.2.10})$$

In the ground state of the noninteracting system

$$\delta N_+ |\Psi_{\rm FS}\rangle = 0, \qquad (L.2.11)$$

thus δN_+ gives in fact the number of right-moving particles added to or removed from the system in the excited states. The quantities $n_+(q)$ correspond to long-wavelength density fluctuations. The spatial variations in $n_+(x)$ are slow compared to the lattice constant, i.e., compared to the inverse of $k_{\rm F}$, and a local Fermi wave number can be defined via

$$k_{\rm F+}(x) = k_{\rm F} + 2\pi n_+(x)$$
. (L.2.12)

These slow fluctuations can be interpreted as arising from the slowly varying phase of a plane wave and we find

$$\partial_x \phi_+(x) = 2\pi n_+(x) \,. \tag{L.2.13}$$

An analogous relation will be found between the operator of the chiral density and the bosonic phase field.

Similar expressions are valid for the left movers:

$$n_{-}(x) = \frac{1}{L} \sum_{kk'} e^{-i(k-k')x} : d^{\dagger}_{-k_{\rm F}+k} d_{-k_{\rm F}+k'} :$$

$$= \frac{1}{L} \delta N_{-} + \frac{1}{L} \sum_{q \neq 0} e^{iqx} n_{-}(q), \qquad (L.2.14)$$

with

$$n_{-}(q) = \sum_{k} d^{\dagger}_{-k_{\rm F}+k} d_{-k_{\rm F}+k+q}$$
(L.2.15)

and

$$\delta N_{-} = \sum_{k} : d^{\dagger}_{-k_{\rm F}+k} d_{-k_{\rm F}+k} :$$

$$= \sum_{k<0} d^{\dagger}_{-k_{\rm F}+k} d_{-k_{\rm F}+k} - \sum_{k>0} d_{-k_{\rm F}+k} d^{\dagger}_{-k_{\rm F}+k} . \qquad (L.2.16)$$

In the ground state of the noninteracting system

$$\delta N_{-}|\Psi_{\rm FS}\rangle = 0. \qquad (L.2.17)$$

Thus δN_{-} gives the number of left-moving particles added to or removed from the system in the excited states.

Sums going to infinity have to be regularized by an exponential factor with a positive infinitesimal α (this will be used repeatedly) and we write

$$n_{\lambda}(x) = \frac{1}{L} \sum_{q \neq 0} \mathrm{e}^{\mathrm{i}qx - \alpha|q|/2} n_{\lambda}(q) + \frac{1}{L} \delta N_{\lambda} \,. \tag{L.2.18}$$

As has been proved in Chapter 32, the long-wavelength Fourier components of the chiral densities satisfy the Kac–Moody commutation relations,

$$\left[n_{+}(q), n_{+}(-q')\right]_{-} = \delta_{qq'} \frac{qL}{2\pi}, \quad \left[n_{-}(q), n_{-}(-q')\right]_{-} = -\delta_{qq'} \frac{qL}{2\pi}, \quad (L.2.19)$$

in the Tomonaga–Luttinger model [see (32.3.16) and (32.3.17)]. We show here that these relations are exact in the Luttinger model.

Using the anticommutators of the fermion operators

$$\left[n_{+}(q), n_{+}(q')\right]_{-} = \sum_{k} \left(c_{k_{\mathrm{F}}+k}^{\dagger} c_{k_{\mathrm{F}}+k+q+q'} - c_{k_{\mathrm{F}}+k-q'}^{\dagger} c_{k_{\mathrm{F}}+k+q}\right). \quad (\mathrm{L}.2.20)$$

When $q \neq q'$, the summation variable can be changed in the first term from k to k-q'. The two terms cancel each other and the commutator vanishes. The calculation is more subtle for q = q' because we would subtract two infinite quantities in

$$[n_{+}(q), n_{+}(-q)]_{-} = \sum_{k} c^{\dagger}_{k_{\mathrm{F}}+k} c_{k_{\mathrm{F}}+k} - \sum_{k} c^{\dagger}_{k_{\mathrm{F}}+k+q} c_{k_{\mathrm{F}}+k+q} \,. \tag{L.2.21}$$

We may avoid this by rewriting the particle-number operators in normalordered form:

$$[n_{+}(q), n_{+}(-q)]_{-} = \sum_{k} \left(:c^{\dagger}_{k_{\mathrm{F}}+k}c_{k_{\mathrm{F}}+k} - c^{\dagger}_{k_{\mathrm{F}}+k+q}c_{k_{\mathrm{F}}+k+q} : \right)$$

+
$$\sum_{k} \left(\left\langle c^{\dagger}_{k_{\mathrm{F}}+k}c_{k_{\mathrm{F}}+k} \right\rangle_{0} - \left\langle c^{\dagger}_{k_{\mathrm{F}}+k+q}c_{k_{\mathrm{F}}+k+q} \right\rangle_{0} \right).$$
 (L.2.22)

The shift of the variables $k + q \rightarrow k$ in the second term of the first line can be safely done and the two terms cancel each other, while the difference between the two terms in the second line is equal to the number of particles in the ground state in an interval of width q. This reproduces exactly the commutation relation given above.

It then follows, using (L.2.5), that in the limit $L \to \infty$ the real-space densities satisfy the relations

$$[n_{+}(x), n_{+}(x')]_{-} = \frac{1}{L^{2}} \sum_{qq'} e^{iqx} e^{-iq'x'} [n_{+}(q), n_{+}(-q')]_{-}$$
$$= \frac{1}{L^{2}} \sum_{q} e^{iq(x-x')} \frac{Lq}{2\pi} =$$
$$= -\frac{i}{2\pi} \frac{\partial}{\partial x} \frac{1}{L} \sum_{q} e^{iq(x-x')} = -\frac{i}{2\pi} \partial_{x} \delta(x-x')$$
(L.2.23)

and

$$[n_{-}(x), n_{-}(x')]_{-} = \frac{i}{2\pi} \partial_x \delta(x - x'). \qquad (L.2.24)$$

The densities can be expressed in terms of bosonic creation and annihilation operators introduced in analogy with (32.3.23) by the relations

$$b_{q} = \begin{cases} \left(\frac{2\pi}{Lq}\right)^{1/2} n_{+}(q) &= \sum_{k} \left(\frac{2\pi}{Lq}\right)^{1/2} c_{k_{\mathrm{F}}+k}^{\dagger} c_{k_{\mathrm{F}}+k+q} & q > 0, \\ \left(\frac{2\pi}{L|q|}\right)^{1/2} n_{-}(q) &= \sum_{k} \left(\frac{2\pi}{L|q|}\right)^{1/2} d_{-k_{\mathrm{F}}+k}^{\dagger} d_{-k_{\mathrm{F}}+k+q} & q < 0, \end{cases}$$
(L.2.25)

$$b_{q}^{\dagger} = \begin{cases} \left(\frac{2\pi}{Lq}\right)^{1/2} n_{+}(-q) = \sum_{k} \left(\frac{2\pi}{Lq}\right)^{1/2} c_{k_{\mathrm{F}}+k+q}^{\dagger} c_{k_{\mathrm{F}}+k} & q > 0, \\ \left(\frac{2\pi}{L|q|}\right)^{1/2} n_{-}(-q) = \sum_{k} \left(\frac{2\pi}{L|q|}\right)^{1/2} d_{-k_{\mathrm{F}}+k+q}^{\dagger} d_{-k_{\mathrm{F}}+k} & q < 0. \end{cases}$$

The chiral densities can be expressed as

$$n_{+}(x) = \frac{1}{L} \sum_{q>0} \left(\frac{Lq}{2\pi}\right)^{1/2} \left(e^{iqx}b_{q} + e^{-iqx}b_{q}^{\dagger}\right) e^{-\alpha q/2} + \frac{1}{L}\delta N_{+} \qquad (L.2.26)$$

and

$$n_{-}(x) = \frac{1}{L} \sum_{q < 0} \left(\frac{L|q|}{2\pi} \right)^{1/2} \left(e^{iqx} b_q + e^{-iqx} b_q^{\dagger} \right) e^{-\alpha |q|/2} + \frac{1}{L} \delta N_{-}$$

$$= \frac{1}{L} \sum_{q > 0} \left(\frac{Lq}{2\pi} \right)^{1/2} \left(e^{iqx} b_{-q}^{\dagger} + e^{-iqx} b_{-q} \right) e^{-\alpha q/2} + \frac{1}{L} \delta N_{-} .$$
(L.2.27)

The boson operators defined for $q \neq 0$ commute with the particle-number operators defined for q = 0,

$$\left[b_q, \delta N_{\pm}\right]_{-} = \left[b_q^{\dagger}, \delta N_{\pm}\right]_{-} = 0. \qquad (L.2.28)$$

The bosonic parts describe the density fluctuations, while the quantum numbers δN_{\pm} are related to topological excitations.

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The key element in bosonization is the introduction of bosonic phase fields $\varphi_{\lambda}(x)$:

$$\varphi_{\lambda}(x) = -i\frac{2\pi}{L}\sum_{q>0}\frac{1}{q}e^{iqx-\alpha q/2}n_{\lambda}(q) + \frac{\pi x}{L}\delta N_{\lambda},$$

$$\varphi_{\lambda}^{\dagger}(x) = i\frac{2\pi}{L}\sum_{q>0}\frac{1}{q}e^{-iqx-\alpha q/2}n_{\lambda}(-q) + \frac{\pi x}{L}\delta N_{\lambda},$$
(L.2.29)

and their Hermitian linear combination,

$$\phi_{\lambda}(x) = \varphi_{\lambda}(x) + \varphi_{\lambda}^{\dagger}(x) = -i\frac{2\pi}{L}\sum_{q\neq 0}\frac{1}{q}e^{iqx-\alpha|q|/2}n_{\lambda}(q) + \frac{2\pi x}{L}\delta N_{\lambda}.$$
 (L.2.30)

In terms of the bosonic creation and annihilation operators we have

$$\varphi_{+}(x) = -i \sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} e^{iqx - \alpha q/2} b_{q} + \frac{\pi x}{L} \delta N_{+} ,$$

$$\varphi_{+}^{\dagger}(x) = i \sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} e^{-iqx - \alpha q/2} b_{q}^{\dagger} + \frac{\pi x}{L} \delta N_{+} ,$$
(L.2.31)

and

$$\phi_{+}(x) = -i\sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} \left(e^{iqx}b_{q} - e^{-iqx}b_{q}^{\dagger}\right)e^{-\alpha q/2} + \frac{2\pi x}{L}\delta N_{+}.$$
 (L.2.32)

Similarly

$$\varphi_{-}(x) = i \sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} e^{iqx - \alpha q/2} b_{-q} + \frac{\pi x}{L} \delta N_{-},$$

$$\varphi_{-}^{\dagger}(x) = -i \sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} e^{-iqx - \alpha q/2} b_{-q}^{\dagger} + \frac{\pi x}{L} \delta N_{-},$$
(L.2.33)

and

$$\phi_{-}(x) = -i \sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} \left(e^{iqx} b_{-q}^{\dagger} - e^{-iqx} b_{-q}\right) e^{-\alpha q/2} + \frac{2\pi x}{L} \delta N_{-} . \quad (L.2.34)$$

Comparison of (L.2.18) and (L.2.30) leads to the relation

$$n_{\lambda}(x) = \frac{1}{2\pi} \partial_x \phi_{\lambda}(x) , \qquad (L.2.35)$$

which was announced in (L.2.13). The name phase field is justified by the property that it changes by 2π every time we pass a fermion of chirality λ .¹

The commutator of the chiral density with the phase field is easily obtained:

$$[n_{+}(x), \phi_{+}(x')]_{-} = \frac{i}{L} \sum_{q,q'>0} \left\{ e^{i(qx-q'x')-\alpha(q+q')/2} [b_{q}, b_{q'}^{\dagger}]_{-} - e^{-i(qx-q'x')-\alpha(q+q')/2} [b_{q}^{\dagger}, b_{q'}]_{-} \right\}$$
$$= \frac{i}{L} \left[\sum_{q>0} e^{iq(x-x')-\alpha q} + \sum_{q>0} e^{-iq(x-x')-\alpha q} \right]. \quad (L.2.36)$$

Converting the sums to integrals

$$[n_{+}(x), \phi_{+}(x')]_{-} = \frac{i}{2\pi} \int_{0}^{\infty} dq \left[e^{iq(x-x')-\alpha q} + e^{-iq(x-x')-\alpha q} \right]$$

= $-\frac{1}{2\pi} \left[\frac{1}{x-x'+i\alpha} - \frac{1}{x-x'-i\alpha} \right]$
= $i\delta(x-x').$ (L.2.37)

Similarly

$$[n_{-}(x), \phi_{-}(x')]_{-} = -i\delta(x - x').$$
 (L.2.38)

The evaluation of the commutator of the phase fields is somewhat more delicate.

$$\left[\phi_{+}(x),\phi_{+}(x')\right]_{-} = \sum_{q>0} \frac{2\pi}{Lq} \left[e^{iq(x-x')-\alpha q} - e^{-iq(x-x')-\alpha q}\right].$$
 (L.2.39)

Since q can take the values $n_q 2\pi/L$ with integer n_q ,

$$\begin{split} \left[\phi_{+}(x),\phi_{+}(x')\right]_{-} &= \sum_{n_{q}=1}^{\infty} \frac{1}{n_{q}} \left[e^{2\pi i n_{q}(x-x')/L} - e^{-2\pi i n_{q}(x-x')/L} \right] e^{-\alpha 2\pi n_{q}/L} \\ &= -\ln\left(1 - e^{2\pi i (x-x')/L - \alpha 2\pi/L}\right) \\ &+ \ln\left(1 - e^{-2\pi i (x-x')/L - \alpha 2\pi/L}\right). \end{split}$$
(L.2.40)

In the last step we used the series expansion of the function $\ln(1-x)$. Keeping only the leading term in the limit $L \to \infty$, we find

¹ The conventions in which the phase field is defined by a factor $1/\pi$, $1/\sqrt{\pi}$, or $1/\sqrt{2\pi}$ in this formula and in which the topological terms are not included are also common.

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$$\left[\phi_{+}(x), \phi_{+}(x') \right]_{-} = -\ln \left(2\pi \left[-i(x - x') + \alpha \right] / L \right)$$

+ $\ln \left(2\pi \left[i(x - x') + \alpha \right] / L \right)$ (L.2.41)
= $\ln \frac{\alpha + i(x - x')}{\alpha - i(x - x')} .$

Taking now the limit $\alpha \to 0$ and making use of the relation

$$\arctan x = \frac{1}{2i} \ln \frac{1+ix}{1-ix}$$
 (L.2.42)

we find

$$[\phi_{+}(x), \phi_{+}(x')]_{-} = i\pi \operatorname{sgn}(x - x')$$
 (L.2.43)

and similarly

$$[\phi_{-}(x), \phi_{-}(x')]_{-} = -i\pi \operatorname{sgn}(x - x').$$
 (L.2.44)

This result can be derived more simply by rewriting (L.2.39) as

$$\left[\phi_{+}(x),\phi_{+}(x')\right]_{-} = 2i\sum_{q>0}\frac{2\pi}{Lq}\sin[q(x-x')]e^{-\alpha q}$$
(L.2.45)

and converting the sum to an integral

$$\left[\phi_{+}(x),\phi_{+}(x')\right]_{-} = 2i \int_{0}^{\infty} dq \frac{\sin[q(x-x')]}{q} e^{-\alpha q}.$$
 (L.2.46)

The integral is now convergent without the factor $e^{-\alpha q}$,

$$\int_{0}^{\infty} dq \frac{\sin[q(x-x')]}{q} = \frac{\pi}{2} \operatorname{sgn}(x-x'), \qquad (L.2.47)$$

and we recover the previous result.

It is convenient to introduce dual fields by the linear combinations

$$\phi(x) = \frac{1}{\sqrt{4\pi}} \left[\phi_+(x) + \phi_-(x) \right]$$

= $-\frac{i}{\sqrt{4\pi}} \frac{2\pi}{L} \sum_{q \neq 0} \frac{1}{q} e^{iqx - \alpha|q|/2} \left[n_+(q) + n_-(q) \right] + \frac{\sqrt{\pi}x}{L} \delta N$ (L.2.48)

and

$$\theta(x) = \frac{1}{\sqrt{4\pi}} \left[\phi_+(x) - \phi_-(x) \right]$$

= $-\frac{i}{\sqrt{4\pi}} \frac{2\pi}{L} \sum_{q \neq 0} \frac{1}{q} e^{iqx - \alpha|q|/2} \left[n_+(q) - n_-(q) \right] + \frac{\sqrt{\pi}x}{L} J,$ (L.2.49)

where

$$\delta N = \delta N_+ + \delta N_-$$
 and $J = \delta N_+ - \delta N_-$. (L.2.50)

Note that the total particle density and the current density are related to ϕ and θ via

$$n(x) = n_{+}(x) + n_{-}(x) = \frac{1}{\sqrt{\pi}} \partial_{x} \phi(x) ,$$

$$j(x) = v_{\rm F} \left[n_{+}(x) - n_{-}(x) \right] = \frac{v_{\rm F}}{\sqrt{\pi}} \partial_{x} \theta(x) .$$
(L.2.51)

The commutation relation of these fields is

$$[\phi(x), \theta(x')]_{-} = \frac{1}{2} i \operatorname{sgn}(x - x').$$
 (L.2.52)

The field $\Pi(x)$ defined by

$$\Pi(x) = -\partial_x \theta(x) \tag{L.2.53}$$

is conjugate to the phase field since they satisfy the canonical commutation relation

$$\left[\phi(x),\Pi(x')\right]_{-} = \mathrm{i}\delta(x-x')\,. \tag{L.2.54}$$

The conjugate field can also be expressed in terms of the density fluctuations in the form

$$\Pi(x) = -\sqrt{\pi} \left[n_{+}(x) - n_{-}(x) \right]$$

= $-\frac{\sqrt{\pi}}{L} \sum_{q \neq 0} e^{iqx - \alpha |q|/2} \left[n_{+}(q) - n_{-}(q) \right] - J \frac{\sqrt{\pi}}{L}.$ (L.2.55)

Note that the momentum conjugate to the dual field $\theta(x)$ is $-\partial_x \phi(x)$, since

$$\left[\theta(x), -\partial_x \phi(x)\right]_{-} = \mathrm{i}\delta(x - x'). \qquad (\mathrm{L.2.56})$$

L.2.2 Klein Factors

The Hilbert space generated by the boson operators b_q^{\dagger} is identical to the Hilbert space of all excited states of the Luttinger model for fixed particle number. The boson operators conserve the number of particle in each branch; therefore, the matrix elements of operators that are written exclusively in terms of the bosonic densities vanish between Hilbert spaces with different numbers of particles. That is why the bosonic description in Chapter 32 had to be completed by adding the q = 0 fermion-number operators δN_{λ} that have integer eigenvalues. The communication between sectors with different numbers of particles is achieved in the field-theoretical description by introducing *Klein factors* F_{λ}^{\dagger} and F_{λ} which connect the ground states of different charge sectors of the Hilbert space. Let $|\delta N_{\lambda}\rangle_0$ denote the lowest energy state with δN_{λ} extra particles on branch λ relative to the ground-state $|\Psi_{\rm FS}\rangle$. It has no particle-hole excitations and is the vacuum for bosonic excitations in the δN_{λ} -particle sector,

$$b_q |\delta N_\lambda\rangle_0 = 0. \tag{L.2.57}$$

The Klein factors take this state into the lowest energy state with $\delta N_{\lambda} \pm 1$ particles by putting a particle into the lowest energy empty state or removing the particle from the highest energy filled state:

$$F_{\lambda}^{\dagger}|\delta N_{\lambda}\rangle_{0} = |\delta N_{\lambda} + 1\rangle_{0}, \qquad F_{\lambda}|\delta N_{\lambda}\rangle_{0} = |\delta N_{\lambda} - 1\rangle_{0}.$$
(L.2.58)

Accordingly,

$$F_{\lambda}^{\dagger}F_{\lambda} = F_{\lambda}F_{\lambda}^{\dagger} = 1, \qquad (L.2.59)$$

that is they are unitary operators satisfying the relation $F_{\lambda}^{\dagger} = F_{\lambda}^{-1}$, and

$$\left[N_{\lambda}, F_{\lambda'}^{\dagger}\right]_{-} = \delta_{\lambda\lambda'} F_{\lambda}^{\dagger}, \qquad \left[N_{\lambda}, F_{\lambda'}\right]_{-} = -\delta_{\lambda\lambda'} F_{\lambda}. \tag{L.2.60}$$

The Klein factors commute with the boson operators:

$$\left[F_{\lambda}^{\dagger}, b_{q}\right]_{-} = \left[F_{\lambda}^{\dagger}, b_{q}^{\dagger}\right]_{-} = \left[F_{\lambda}, b_{q}\right]_{-} = \left[F_{\lambda}, b_{q}^{\dagger}\right]_{-} = 0.$$
 (L.2.61)

Thus if F_{λ}^{\dagger} or F_{λ} acts on an excited state of the δN_{λ} -particle sector with several electron-hole pairs, the new state contains the same set of particlehole excitations but created on the ground state with $\delta N_{\lambda} + 1$ or $\delta N_{\lambda} - 1$ particles,

$$F_{\lambda}^{\dagger}|\delta N_{\lambda}\rangle = F_{\lambda}^{\dagger}f[\{b^{\dagger}\}]|\delta N_{\lambda}\rangle_{0} = f[\{b^{\dagger}\}]|\delta N_{\lambda} + 1\rangle_{0}$$
(L.2.62)

and

$$F_{\lambda}|\delta N_{\lambda}\rangle = F_{\lambda}f[\{b^{\dagger}\}]|\delta N_{\lambda}\rangle_{0} = f[\{b^{\dagger}\}]|\delta N_{\lambda} - 1\rangle_{0}.$$
 (L.2.63)

If the number of particles is nonzero for both the right- and left-moving branch, we have to specify the ordering of the operators associated with the branches and the application of the Klein factor gives an extra phase factor. Assuming that the creation operators of right movers are ordered to the left of left movers,

$$\begin{aligned} F_{+}^{\dagger} |\delta N_{+}, \delta N_{-}\rangle_{0} &= |\delta N_{+} + 1, \delta N_{-}\rangle_{0} \,, \\ F_{-}^{\dagger} |\delta N_{+}, \delta N_{-}\rangle_{0} &= (-1)^{\delta N_{+}} |\delta N_{+}, \delta N_{-} + 1\rangle_{0} \,, \\ F_{+} |\delta N_{+}, \delta N_{-}\rangle_{0} &= |\delta N_{+} - 1, \delta N_{-}\rangle_{0} \,, \\ F_{-} |\delta N_{+}, \delta N_{-}\rangle_{0} &= (-1)^{\delta N_{+}} |\delta N_{+}, \delta N_{-} - 1\rangle_{0} \,. \end{aligned}$$
(L.2.64)

The Klein factors obey the Clifford algebra

$$\left[F_{\lambda}^{\dagger}, F_{\lambda'}\right]_{+} = 2\delta_{\lambda\lambda'} \tag{L.2.65}$$

and

$$\left[F_{\lambda}^{\dagger}, F_{\lambda'}^{\dagger}\right]_{+} = \left[F_{\lambda}, F_{\lambda'}\right]_{+} = 0 \quad \text{for} \quad \lambda \neq \lambda'. \quad (L.2.66)$$

L.2.3 Bosonized Form of the Fermion Field Operators

We are now in the position to write the fermion creation and annihilation operators in terms of the boson fields. Without going in the mathematical details we only give plausibility arguments. For this consider the commutator

$$\left[n_{\lambda}(x), \hat{\psi}_{\lambda}(x')\right]_{-} = -\delta(x - x')\hat{\psi}_{\lambda}(x'). \qquad (L.2.67)$$

They can easily be checked in the fermion representation. Similar expressions are obtained in the boson representation between $n_{\lambda}(x)$ and $\exp(\pm i\phi_{\lambda}(x'))$:

$$[n_{+}(x), e^{i\phi_{+}(x')}]_{-} = -\delta(x - x')e^{i\phi_{+}(x')},$$

$$[n_{-}(x), e^{-i\phi_{-}(x')}]_{-} = -\delta(x - x')e^{-i\phi_{-}(x')}.$$
(L.2.68)

They can be verified using (L.2.37). It is therefore expected that the fermion field operator is proportional to this exponential and, of course, a Klein factor has to appear to ensure that the fermion operators anticommute. With the correct prefactor we have

$$\hat{\psi}_{+}(x) = \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{+} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}\phi_{+}(x)}$$

$$= \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{+} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}\sqrt{\pi}[\phi(x)+\theta(x)]}$$
(L.2.69)

and

$$\hat{\psi}_{-}(x) = \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{-} e^{-ik_{F}x} e^{-i\phi_{-}(x)}$$

$$= \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{-} e^{-ik_{F}x} e^{-i\sqrt{\pi}[\phi(x) - \theta(x)]}.$$
(L.2.70)

The boson representation of the adjoint operators is

$$\hat{\psi}_{+}^{\dagger}(x) = \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{+}^{\dagger} e^{-ik_{F}x} e^{-i\phi_{+}(x)}$$

$$= \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{+}^{\dagger} e^{-ik_{F}x} e^{-i\sqrt{\pi}[\phi(x) + \theta(x)]}$$
(L.2.71)

and

$$\hat{\psi}^{\dagger}_{-}(x) = \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F^{\dagger}_{-} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}\phi_{-}(x)}$$
$$= \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F^{\dagger}_{-} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}\sqrt{\pi}[\phi(x) - \theta(x)]}.$$
(L.2.72)

The correctness of the factor $(2\pi\alpha)^{-1/2}$ can be checked by calculating the ground-state expectation value of $\hat{\psi}^{\dagger}_{+}(x)\hat{\psi}_{+}(x')$ both in the fermion and in the boson representation. In the fermion language we have
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$$\langle \Psi_{\rm FS} | \hat{\psi}^{\dagger}_{+}(x) \hat{\psi}_{+}(x') | \Psi_{\rm FS} \rangle = \frac{1}{L} \sum_{k<0} \mathrm{e}^{-\mathrm{i}k(x-x')} \,.$$
 (L.2.73)

The sum can be made convergent by a factor $e^{\alpha k}$ and we find

$$\langle \Psi_{\rm FS} | \hat{\psi}^{\dagger}_{+}(x) \hat{\psi}_{+}(x') | \Psi_{\rm FS} \rangle = \int_{-\infty}^{0} \frac{\mathrm{d}k}{2\pi} \mathrm{e}^{[\alpha - \mathrm{i}(x - x')]k} = \frac{1}{2\pi} \frac{1}{\alpha - \mathrm{i}(x - x')} \,. \quad (\mathrm{L.2.74})$$

On the other hand, in the boson representation we have to evaluate the ground-state average

$$\langle 0|\hat{\psi}_{+}^{\dagger}(x)\hat{\psi}_{+}(x')|0\rangle = \frac{1}{2\pi\alpha}\langle 0|e^{-i\phi_{+}(x)}e^{i\phi_{+}(x')}|0\rangle.$$
 (L.2.75)

This can be done by using the Baker–Hausdorff formula

$$e^{A}e^{B} = e^{A+B}e^{\frac{1}{2}[A,B]_{-}}$$
 (L.2.76)

given in (13.3.9), which is valid if the commutator of A and B commutes with both A and B. We thus have

$$\left\langle 0 \left| \hat{\psi}_{+}^{\dagger}(x) \hat{\psi}_{+}(x') \right| 0 \right\rangle = \frac{1}{2\pi\alpha} \left\langle 0 \left| e^{-i[\phi_{+}(x) - \phi_{+}(x')]} e^{\frac{1}{2}[\phi_{+}(x),\phi_{+}(x')]} \right| 0 \right\rangle.$$
(L.2.77)

The commutator has been calculated in (L.2.41) and we find

$$e^{\frac{1}{2}[\phi_{+}(x),\phi_{+}(x')]_{-}} = \left(\frac{\alpha + i(x - x')}{\alpha - i(x - x')}\right)^{1/2}.$$
 (L.2.78)

The expectation value of the remaining exponential factor can be calculated using

$$\langle e^{iC} \rangle = e^{-\frac{1}{2} \langle C^2 \rangle}$$
 (L.2.79)

given in (13.3.11), which is valid if C is a linear combination of bosonic creation and annihilation operators. With the choice $C = -[\phi_+(x) - \phi_+(x')]$ and substituting the bosonic expansion of the phase field we get

$$-\frac{1}{2}\langle 0|\left[\phi_{+}(x)-\phi_{+}(x')\right]^{2}|0\rangle = -\frac{1}{2}\sum_{q>0}\frac{2\pi}{Lq}\left[2-e^{iq(x-x')}-e^{-iq(x-x')}\right]e^{-\alpha q}.$$
(L.2.80)

The sums can be evaluated with the trick used in (L.2.40). For example

$$\langle \phi_{+}(x)\phi_{+}(x')\rangle = \sum_{q>0} \frac{2\pi}{Lq} e^{iq(x-x')-\alpha q}$$

$$= \sum_{n_{q}=1}^{\infty} \frac{1}{n_{q}} e^{2\pi i n_{q}(x-x')/L-\alpha 2\pi n_{q}/L}$$

$$= -\ln\left(1 - e^{i2\pi (x-x'+i\alpha)/L}\right)$$

$$= -\ln\left(2\pi [\alpha - i(x-x')]/L\right).$$

$$(L.2.81)$$

Collecting together all the terms we get

$$-\frac{1}{2} \langle 0 | [\phi_{+}(x) - \phi_{+}(x')]^{2} | 0 \rangle = \ln(2\pi\alpha/L) - \frac{1}{2} \ln\left(2\pi[\alpha - i(x - x')]/L\right) \\ -\frac{1}{2} \ln\left(2\pi[\alpha + i(x - x')]/L\right). \quad (L.2.82)$$

Exponentiation of this expression and multiplication with (L.2.78) yields

$$\langle 0 | e^{-i\phi_{+}(x)} e^{i\phi_{+}(x')} | 0 \rangle = \langle 0 | e^{i\phi_{+}(x)} e^{-i\phi_{+}(x')} | 0 \rangle = \frac{\alpha}{\alpha - i(x - x')}. \quad (L.2.83)$$

Together with the factor $1/2\pi\alpha$ we recover the expression which was obtained in (L.2.74) in the fermion language.

Note that the field operator can be written in a simpler form in terms of the bosonic fields $\varphi_{\lambda}(x)$ and $\varphi_{\lambda}^{\dagger}(x)$. It follows from the commutation relation

$$\begin{split} \left[\varphi_{+}(x),\varphi_{+}^{\dagger}(x')\right]_{-} &= \sum_{q>0} \frac{2\pi}{Lq} e^{iq(x-x')-\alpha q} \\ &= \sum_{n_{q}=1}^{\infty} \frac{1}{n_{q}} e^{2\pi i n_{q}(x-x')/L} e^{-\alpha 2\pi n_{q}/L} \\ &= -\ln\left(1 - e^{2\pi i (x-x')/L - \alpha 2\pi/L}\right) \\ &= -\ln\left(2\pi \left[\alpha - i(x-x')\right]/L\right), \end{split}$$
(L.2.84)

which was calculated analogous to (L.2.40), that

$$e^{i\varphi_{+}^{\dagger}(x)}e^{i\varphi_{+}(x)} = e^{i(\varphi_{+}^{\dagger}(x)+\varphi_{+}(x))} \left(\frac{L}{2\pi\alpha}\right)^{1/2},$$
 (L.2.85)

and hence

$$\hat{\psi}_{+}(x) = \frac{1}{\sqrt{L}} F_{+} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}\varphi_{+}^{\dagger}(x)} \mathrm{e}^{\mathrm{i}\varphi_{+}(x)} \,. \tag{L.2.86}$$

Analogous calculation yields

$$\hat{\psi}_{-}(x) = \frac{1}{\sqrt{L}} F_{-} \mathrm{e}^{-\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{-\mathrm{i}\varphi_{-}^{\dagger}(x)} \mathrm{e}^{-\mathrm{i}\varphi_{-}(x)} \,. \tag{L.2.87}$$

Since the boson operators are normal ordered in these expressions, the divergent factors $1/\sqrt{\alpha}$ that regularize the field operators in (L.2.69) and (L.2.70) disappear.

It can be checked, using the commutators of the bosonic fields, that the fermionic field operators written in this bosonized form anticommute. Equation (L.2.4) is satisfied, and the correct relationship

$$n_{\lambda}(x) = :\hat{\psi}_{\lambda}^{\dagger}(x)\hat{\psi}_{\lambda}(x) := \lim_{x' \to x} \left(:\hat{\psi}_{\lambda}^{\dagger}(x')\hat{\psi}_{\lambda}(x) : \right) = \frac{1}{2\pi}\partial_{x}\phi_{\lambda}(x) \qquad (L.2.88)$$

holds between the chiral density and the phase field.

L.2.4 Boson Representation of the Spin Operators

The spin-1/2 operators can be represented by the creation and annihilation operators of spinless fermions using the Jordan–Wigner transformation

$$S_{j}^{+} = c_{j}^{\dagger} \exp\left(i\pi \sum_{l=1}^{j-1} c_{l}^{\dagger} c_{l}\right),$$

$$S_{j}^{-} = \exp\left(-i\pi \sum_{l=1}^{j-1} c_{l}^{\dagger} c_{l}\right) c_{j},$$

$$S_{j}^{z} = c_{j}^{\dagger} c_{j} - \frac{1}{2}.$$
(L.2.89)

The term -1/2 in S_j^z can be eliminated by normal ordering the fermion operators. The continuum version of the z-component of the spin operator, $S^z(x)$, is defined by requiring the same Fourier spectrum as for the discrete S_j^z operators. This implies that the continuum version should take the value

$$S^{z}(x = ja) = \frac{1}{a}S_{j}^{z}$$
 (L.2.90)

at the discrete lattice points x = ja. It is given by the particle density

$$S^{z}(x) = :\psi^{\dagger}(x)\psi(x):$$

=: $\psi^{\dagger}_{+}(x)\psi_{+}(x): + :\psi^{\dagger}_{-}(x)\psi_{-}(x):$
+: $\psi^{\dagger}_{+}(x)\psi_{-}(x): + :\psi^{\dagger}_{-}(x)\psi_{+}(x):$. (L.2.91)

The boson representation of the spinless fermion field gives

$$S^{z}(x) = \frac{1}{2\pi} \left[\partial_{x} \phi_{+}(x) + \partial_{x} \phi_{-}(x) \right] + \frac{1}{2\pi\alpha} \left[F_{+}^{\dagger} F_{-} e^{-i2k_{F}x} e^{-i\phi_{+}(x)} e^{-i\phi_{-}(x)} + h.c. \right]$$
(L.2.92)
$$= \frac{1}{\sqrt{\pi}} \partial_{x} \phi(x) + \frac{1}{2\pi\alpha} \left[F_{+}^{\dagger} F_{-} e^{-i2k_{F}x} e^{-i\sqrt{4\pi}\phi(x)} + h.c. \right].$$

This expression has a slowly varying part and an oscillating component. Since $k_{\rm F} = \pi/2a$ in the unpolarized ground state,

$$e^{\mp i2k_F x} = (-1)^{x/a},$$
 (L.2.93)

that is the oscillating term alternates with the lattice site.

Considering now the S_j^+ operator, the string operator in the exponent gives

$$i\pi \sum_{l=1}^{j-1} c_l^{\dagger} c_l = i\pi \sum_{l=1}^{j-1} \left(:c_l^{\dagger} c_l : +\frac{1}{2} \right) \rightarrow i\pi \int_{-L/2}^{x} dy : \hat{\psi}^{\dagger}(y) \hat{\psi}(y) : +i\pi \frac{x}{2a} = i\pi \int_{-L/2}^{x} dy [n_+(y) + n_-(y)] + ik_F x = \frac{1}{2} i \int_{-L/2}^{x} dy [\partial_y \phi_+(y) + \partial_y \phi_-(y)] + ik_F x = \frac{1}{2} i [\phi_+(x) + \phi_-(x)] + ik_F x.$$
 (L.2.94)

The continuum version of c_j^{\dagger} is

$$\psi^{\dagger}(x) = \frac{1}{\sqrt{2\pi\alpha}} \left(F_{+}^{\dagger} \mathrm{e}^{-\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{-\mathrm{i}\phi_{+}(x)} + F_{-}^{\dagger} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}\phi_{-}(x)} \right).$$
(L.2.95)

Collecting together these factors we find

$$S^{+}(x) \propto e^{ik_{F}x} e^{\frac{1}{2}i\left[\phi_{+}(x)+\phi_{-}(x)\right]} \left(F^{\dagger}_{+}e^{-ik_{F}x}e^{-i\phi_{+}(x)} + F^{\dagger}_{-}e^{ik_{F}x}e^{i\phi_{-}(x)}\right)$$
$$= F^{\dagger}_{+}e^{-i\sqrt{\pi}\theta(x)} + e^{i2k_{F}x}F^{\dagger}_{-}e^{i\sqrt{\pi}(2\phi(x)-\theta(x))}.$$
(L.2.96)

A similar calculation gives

$$S^{-}(x) \propto F_{+} e^{i\sqrt{\pi}\theta(x)} + e^{-i2k_{F}x} F_{-} e^{-i\sqrt{\pi}(2\phi(x) - \theta(x))}.$$
 (L.2.97)

L.2.5 Fermions with Spin

The generalization of the bosonization procedure to fermions with spin is straightforward. The spin index σ should appear everywhere in addition to the chirality index λ . When the field operators are decomposed into right- and left-moving parts we have

$$\hat{\psi}_{+,\sigma}(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{i(k_{\rm F}+k)x} c_{k_{\rm F}+k,\sigma},$$

$$\hat{\psi}_{-,\sigma}(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{i(-k_{\rm F}+k)x} d_{-k_{\rm F}+k,\sigma}.$$
(L.2.98)

The slowly varying chiral fields are defined via

$$R_{\sigma}(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{ikx} c_{k_{\rm F}+k,\sigma},$$

$$L_{\sigma}(x) = \frac{1}{\sqrt{L}} \sum_{k} e^{ikx} d_{-k_{\rm F}+k,\sigma}.$$
(L.2.99)

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When the densities are expressed in terms of the bosonic creation and annihilation operators defined for the two spin orientations we find

$$n_{+,\sigma}(x) = \frac{1}{L} \sum_{q>0} \left(\frac{Lq}{2\pi}\right)^{1/2} \left(e^{iqx} b_{q\sigma} + e^{-iqx} b_{q\sigma}^{\dagger}\right) e^{-\alpha q/2} + \frac{1}{L} \delta N_{+,\sigma} \quad (L.2.100)$$

and

$$n_{-,\sigma}(x) = \frac{1}{L} \sum_{q>0} \left(\frac{Lq}{2\pi}\right)^{1/2} \left(e^{iqx} b^{\dagger}_{-q\sigma} + e^{-iqx} b_{-q\sigma}\right) e^{-\alpha q/2} + \frac{1}{L} \delta N_{-,\sigma} \,.$$
(L.2.101)

The phase fields defined via

$$\partial_x \phi_{\lambda,\sigma}(x) = 2\pi n_{\lambda,\sigma}(x)$$
 (L.2.102)

are then given by

$$\phi_{+,\sigma}(x) = -\mathrm{i}\sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} \left(\mathrm{e}^{\mathrm{i}qx}b_{q\sigma} - \mathrm{e}^{-\mathrm{i}qx}b_{q\sigma}^{\dagger}\right) \mathrm{e}^{-\alpha q/2} + \delta N_{+,\sigma}\frac{2\pi x}{L} \quad (\mathrm{L}.2.103)$$

and

$$\phi_{-,\sigma}(x) = -i \sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} \left(e^{iqx} b^{\dagger}_{-q\sigma} - e^{-iqx} b_{-q\sigma}\right) e^{-\alpha q/2} + \delta N_{-,\sigma} \frac{2\pi x}{L},$$
(L.2.104)

and they satisfy the commutation relations

$$[\phi_{\pm,\sigma}(x),\phi_{\pm,\sigma'}(x')]_{-} = \pm i\pi \delta_{\sigma\sigma'} \operatorname{sgn}(x-x')$$
(L.2.105)

and

$$[n_{\pm,\sigma}(x),\phi_{\pm,\sigma'}(x')]_{-} = \pm \mathrm{i}\delta_{\sigma\sigma'}\,\delta(x-x')\,. \tag{L.2.106}$$

We introduce the linear combinations

$$\begin{split} \phi_{\rm c}(x) &= \frac{1}{\sqrt{8\pi}} \left[\phi_{+,\uparrow}(x) + \phi_{+,\downarrow}(x) + \phi_{-,\uparrow}(x) + \phi_{-,\downarrow}(x) \right], \\ \phi_{\rm s}(x) &= \frac{1}{\sqrt{8\pi}} \left[\phi_{+,\uparrow}(x) - \phi_{+,\downarrow}(x) + \phi_{-,\uparrow}(x) - \phi_{-,\downarrow}(x) \right], \\ \theta_{\rm c}(x) &= \frac{1}{\sqrt{8\pi}} \left[\phi_{+,\uparrow}(x) + \phi_{+,\downarrow}(x) - \phi_{-,\uparrow}(x) - \phi_{-,\downarrow}(x) \right], \\ \theta_{\rm s}(x) &= \frac{1}{\sqrt{8\pi}} \left[\phi_{+,\uparrow}(x) - \phi_{+,\downarrow}(x) - \phi_{-,\uparrow}(x) + \phi_{-,\downarrow}(x) \right]. \end{split}$$
(L.2.107)

It follows from the commutation relations of the phase fields $\phi_{\lambda,\sigma}$ that

$$\begin{bmatrix} \phi_{\rm c}(x), \theta_{\rm c}(x') \end{bmatrix}_{-} = \frac{1}{2} i \operatorname{sgn}(x - x'), \\ \begin{bmatrix} \phi_{\rm s}(x), \theta_{\rm s}(x') \end{bmatrix}_{-} = \frac{1}{2} i \operatorname{sgn}(x - x').$$
 (L.2.108)

It is convenient to use the fields $\Pi_{\rm c}(x)$ and $\Pi_{\rm s}(x)$ defined via

$$\partial_x \theta_{\rm c}(x) = -\Pi_{\rm c}(x)$$
 and $\partial_x \theta_{\rm s}(x) = -\Pi_{\rm s}(x)$ (L.2.109)

instead of the dual fields $\theta_{\rm c}(x)$ and $\theta_{\rm s}(x)$, since they are canonically conjugate to the fields $\phi_{\rm c}(x)$ and $\phi_{\rm s}(x)$ satisfying the canonical commutation relations

$$\begin{bmatrix} \phi_{c}(x), \Pi_{c}(x') \end{bmatrix}_{-} = i\delta(x - x'), \\ \begin{bmatrix} \phi_{s}(x), \Pi_{s}(x') \end{bmatrix}_{-} = i\delta(x - x'). \end{aligned}$$
 (L.2.110)

When they are expressed in terms of the density fluctuations we have

$$\Pi_{\rm c}(x) = -\sqrt{\frac{\pi}{2}} \left[n_{+,\uparrow}(x) + n_{+,\downarrow}(x) - n_{-,\uparrow}(x) - n_{-,\downarrow}(x) \right],$$
(L.2.111)
$$\Pi_{\rm s}(x) = -\sqrt{\frac{\pi}{2}} \left[n_{+,\uparrow}(x) - n_{+,\downarrow}(x) - n_{-,\uparrow}(x) + n_{-,\downarrow}(x) \right].$$

The fermionic field operators can be written in terms of the boson fields if four Klein factors, $F_{\lambda,\sigma}$ for $\lambda = \pm$ and $\sigma = \uparrow, \downarrow$, are introduced. They are natural generalizations of the factors in the spinless case. We have

$$\hat{\psi}_{+,\sigma}(x) = \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{+,\sigma} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}\phi_{+,\sigma}(x)} ,$$

$$\hat{\psi}_{-,\sigma}(x) = \lim_{\alpha \to 0} \frac{1}{\sqrt{2\pi\alpha}} F_{-,\sigma} \mathrm{e}^{-\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{-\mathrm{i}\phi_{-,\sigma}(x)} .$$
 (L.2.112)

L.3 Boson Representation of the Hamiltonian

We now show that the Hamiltonian of the Luttinger model can be written in a form analogous to the Hamiltonian of the harmonic chain in spite of the interactions. We also give the boson representation of backward and umklapp scattering.

L.3.1 Free Spinless Fermions

The kinetic energy of spinless fermions can be written as

$$\mathcal{H}_{0} = \sum_{k} \hbar v_{\rm F} k \, c^{\dagger}_{k_{\rm F}+k} c_{k_{\rm F}+k} - \sum_{k} \hbar v_{\rm F} k \, d^{\dagger}_{-k_{\rm F}+k} d_{-k_{\rm F}+k} \,, \tag{L.3.1}$$

if the energy is measured from the chemical potential. The infinite sea of negative energy states that makes the energy unbounded from below can be removed by taking the normal-ordered products:

$$\mathcal{H}_{0} = \sum_{k} \hbar v_{\mathrm{F}} k : c_{k_{\mathrm{F}}+k}^{\dagger} c_{k_{\mathrm{F}}+k} : -\sum_{k} \hbar v_{\mathrm{F}} k : d_{-k_{\mathrm{F}}+k}^{\dagger} d_{-k_{\mathrm{F}}+k} : .$$
(L.3.2)

Owing to the linear dispersion relation this expression can be written in terms of the fermion field operators defined in (L.2.2) as

$$\mathcal{H}_{0} = \hbar v_{\mathrm{F}} \sum_{\lambda=\pm} \int \mathrm{d}x : \hat{\psi}_{\lambda}^{\dagger}(x) \left[\lambda \frac{1}{\mathrm{i}} \partial_{x} - k_{\mathrm{F}} \right] \hat{\psi}_{\lambda}(x) :$$

$$= -\mathrm{i}\hbar v_{\mathrm{F}} \int \mathrm{d}x : \left[R^{\dagger}(x) \partial_{x} R(x) - L^{\dagger}(x) \partial_{x} L(x) \right] : .$$
(L.3.3)

When we attempt to bosonize this expression directly by writing the fermion field operators in terms of the phase fields using (L.2.69) and (L.2.70), we have to be careful in avoiding the divergences occurring for identical arguments of the operators. This can be achieved by applying the point-splitting technique. The normal-ordered product of the right-moving part can be determined from

$$: R^{\dagger}(x)\partial_{x}R(x) := \lim_{\epsilon \to 0} \left[R^{\dagger}(x+\epsilon)\partial_{x}R(x) - \left\langle R^{\dagger}(x+\epsilon)\partial_{x}R(x)\right\rangle \right] , \quad (L.3.4)$$

where the derivative is calculated from

$$\partial_x R(x) = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[R(x) - R(x - \epsilon) \right].$$
 (L.3.5)

Straightforward but lengthy calculation gives

$$: R^{\dagger}(x)\partial_{x}R(x) := \frac{i}{4\pi} \left[\partial_{x}\phi_{+}(x)\right]^{2}, \qquad : L^{\dagger}(x)\partial_{x}L(x) := -\frac{i}{4\pi} \left[\partial_{x}\phi_{-}(x)\right]^{2},$$
(L.3.6)

and we find

$$\mathcal{H}_{0} = \hbar v_{\mathrm{F}} \frac{1}{4\pi} \int \mathrm{d}x \left[\left(\partial_{x} \phi_{+}(x) \right)^{2} + \left(\partial_{x} \phi_{-}(x) \right)^{2} \right].$$
(L.3.7)

Alternatively we could start from the expression of the noninteracting Hamiltonian in terms of the boson creation and annihilation operators. In the spinless case (32.3.30) gives

$$\mathcal{H}_{0} = \sum_{q>0} \hbar v_{\mathrm{F}} q \, b_{q}^{\dagger} b_{q} + \sum_{q>0} \hbar v_{\mathrm{F}} q \, b_{-q}^{\dagger} b_{-q} + \frac{\hbar \pi v_{\mathrm{F}}}{L} \left(\delta N_{+}^{2} + \delta N_{-}^{2} \right). \tag{L.3.8}$$

It is readily seen using relations (L.2.26) and (L.2.27) that this expression is equivalent to

$$\mathcal{H}_{0} = \hbar v_{\rm F} \pi \int dx \left[n_{+}^{2}(x) + n_{-}^{2}(x) \right], \qquad (L.3.9)$$

which is identical to (L.3.7) if it is written in terms of the phase fields $\phi_+(x)$ and $\phi_-(x)$. Using the field $\phi(x)$ and its dual, $\theta(x)$, or the conjugate momentum we find

$$\mathcal{H}_{0} = \frac{1}{2}\hbar v_{\mathrm{F}} \int \mathrm{d}x \left[\left(\partial_{x}\theta(x) \right)^{2} + \left(\partial_{x}\phi(x) \right)^{2} \right]$$

$$= \frac{1}{2}\hbar v_{\mathrm{F}} \int \mathrm{d}x \left[\Pi^{2}(x) + \left(\partial_{x}\phi(x) \right)^{2} \right].$$
 (L.3.10)

This has exactly the same form as the Hamiltonian of the harmonic chain.

L.3.2 Boson Form of the Full Hamiltonian

The interactions were defined in the g-ology model in (32.3.63). Since the coupling constants are independent of the momentum transfer, the interaction is local in real space. In the spinless Tomonaga–Luttinger model, where backscattering and umklapp processes are excluded, the Hamiltonian of the forward-scattering processes can be written in real space as

$$\mathcal{H}_{\text{int}} = g_2 \int \mathrm{d}x \, \hat{\psi}_+^{\dagger}(x) \hat{\psi}_+(x) \hat{\psi}_-^{\dagger}(x) \hat{\psi}_-(x) \qquad (\text{L.3.11}) \\ + \frac{1}{2} g_4 \int \mathrm{d}x \left[\hat{\psi}_+^{\dagger}(x) \hat{\psi}_+(x) \hat{\psi}_+^{\dagger}(x) \hat{\psi}_+(x) + \hat{\psi}_-^{\dagger}(x) \hat{\psi}_-(x) \hat{\psi}_-^{\dagger}(x) \hat{\psi}_-(x) \right].$$

Written in terms of the chiral densities

$$\mathcal{H}_{\text{int}} = g_2 \int \mathrm{d}x \, n_+(x) n_-(x) + \frac{1}{2} g_4 \int \mathrm{d}x \left[n_+(x) n_+(x) + n_-(x) n_-(x) \right].$$
(L.3.12)

The chiral densities can be expressed in terms of Π and $\partial_x \phi$ via

$$n_{+}(x) = \frac{1}{\sqrt{4\pi}} \left[\partial_{x} \phi(x) - \Pi(x) \right],$$

$$n_{-}(x) = \frac{1}{\sqrt{4\pi}} \left[\partial_{x} \phi(x) + \Pi(x) \right],$$

(L.3.13)

hence

$$n_{+}(x)n_{-}(x) = \frac{1}{4\pi} \left[\left(\partial_{x} \phi(x) \right)^{2} - \Pi^{2}(x) \right]$$
(L.3.14)

and

$$n_{+}^{2}(x) + n_{-}^{2}(x) = \frac{1}{2\pi} \left[\left(\partial_{x} \phi(x) \right)^{2} + \Pi^{2}(x) \right].$$
 (L.3.15)

Combining these expressions with the noninteracting part of the Hamiltonian, the boson form of the spinless Tomonaga–Luttinger model is

$$\mathcal{H} = \frac{1}{2}\hbar u \int \mathrm{d}x \left[K\Pi^2(x) + \frac{1}{K} (\partial_x \phi(x))^2 \right], \qquad (L.3.16)$$

where

$$\hbar u = \left(\hbar v_{\rm F} - \frac{g_2}{2\pi} + \frac{g_4}{2\pi}\right)^{1/2} \left(\hbar v_{\rm F} + \frac{g_2}{2\pi} + \frac{g_4}{2\pi}\right)^{1/2} \tag{L.3.17}$$

and

$$K = \left(\hbar v_{\rm F} - \frac{g_2}{2\pi} + \frac{g_4}{2\pi}\right)^{1/2} \left(\hbar v_{\rm F} + \frac{g_2}{2\pi} + \frac{g_4}{2\pi}\right)^{-1/2}.$$
 (L.3.18)

With the dimensionless coupling constants $\tilde{g} = g/(2\pi\hbar v_{\rm F})$ we have

$$u = v_{\rm F} \left(1 - \tilde{g}_2 + \tilde{g}_4\right)^{1/2} \left(1 + \tilde{g}_2 + \tilde{g}_4\right)^{1/2} = v_{\rm F} \left[\left(1 + \tilde{g}_4\right)^2 - \tilde{g}_2^2 \right]^{1/2} \quad ({\rm L.3.19})$$

and

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$$K = \left(\frac{1 + \tilde{g}_4 - \tilde{g}_2}{1 + \tilde{g}_4 + \tilde{g}_2}\right)^{1/2} .$$
 (L.3.20)

Thus the Tomonaga–Luttinger interactions only lead to a renormalization of the velocity of the bosonic excitations from $v_{\rm F}$ to u and to the appearance of a factor K in the current term and a factor 1/K in the density term of the Hamiltonian.

L.3.3 Boson Form of the Umklapp Scattering

Only small-momentum transfer, forward-scattering processes are allowed in the Luttinger model. Large-momentum-transfer, umklapp processes are also possible between spinless fermions, and they may become relevant at half filling. When written in terms of the fermion field operators the umklapp term of the Hamiltonian is

$$\mathcal{H}_{u} = g_{3} \int dx \Big[e^{iGx} \hat{\psi}_{+}^{\dagger}(x) \hat{\psi}_{+}^{\dagger}(x) \hat{\psi}_{-}(x) \hat{\psi}_{-}(x) + e^{-iGx} \hat{\psi}_{-}^{\dagger}(x) \hat{\psi}_{-}^{\dagger}(x) \hat{\psi}_{+}(x) \hat{\psi}_{+}(x) \Big], \qquad (L.3.21)$$

where G is a vector of the reciprocal lattice. In boson representation we find

$$\mathcal{H}_{\rm u} = \frac{2g_3}{(2\pi\alpha)^2} \int dx \cos\left[\sqrt{16\pi}\phi(x) + (4k_{\rm F} - G)x\right].$$
 (L.3.22)

For a half-filled band, where $k_{\rm F} = \pi/2a$,

$$\mathcal{H}_{u} = \frac{2g_3}{(2\pi\alpha)^2} \int dx \cos\left[\sqrt{16\pi}\phi(x)\right].$$
 (L.3.23)

The relevance or irrelevance of this term will be discussed in the last section of this appendix.

L.3.4 Fermions with Spin

The kinetic energy of fermions with spin is analogous to (L.3.3), except that we have to sum over the spin quantum numbers. The same applies to the boson forms (L.3.9) and (L.3.7):

$$\mathcal{H}_{0} = \hbar v_{\mathrm{F}} \pi \sum_{\sigma} \int \mathrm{d}x \left[n_{+,\sigma}^{2}(x) + n_{-,\sigma}^{2}(x) \right]$$

$$= \hbar v_{\mathrm{F}} \frac{1}{4\pi} \sum_{\sigma} \int \mathrm{d}x \left[(\partial_{x} \phi_{+,\sigma}(x))^{2} + (\partial_{x} \phi_{-,\sigma}(x))^{2} \right].$$
 (L.3.24)

Taking the charge and spin phase fields and their duals we have

$$\mathcal{H}_{0} = \frac{1}{2} \hbar v_{\mathrm{F}} \int \mathrm{d}x \left[\left(\partial_{x} \theta_{\mathrm{c}}(x) \right)^{2} + \left(\partial_{x} \phi_{\mathrm{c}}(x) \right)^{2} \right] + \frac{1}{2} \hbar v_{\mathrm{F}} \int \mathrm{d}x \left[\left(\partial_{x} \theta_{\mathrm{s}}(x) \right)^{2} + \left(\partial_{x} \phi_{\mathrm{s}}(x) \right)^{2} \right], \qquad (L.3.25)$$

or if the conjugate fields are used,

~

$$\mathcal{H}_{0} = \frac{1}{2}\hbar v_{\mathrm{F}} \int \mathrm{d}x \left[\Pi_{\mathrm{c}}^{2}(x) + \left(\partial_{x}\phi_{\mathrm{c}}(x)\right)^{2} \right] + \frac{1}{2}\hbar v_{\mathrm{F}} \int \mathrm{d}x \left[\Pi_{\mathrm{s}}^{2}(x) + \left(\partial_{x}\phi_{\mathrm{s}}(x)\right)^{2} \right].$$
(L.3.26)

The momentum operator given in (32.3.59) can also be expressed in terms of these fields. We find

$$P = -\hbar \int \mathrm{d}x \left[k_{\mathrm{F}} + \sqrt{\pi/2} \partial_x \phi_{\mathrm{c}}(x) \right] \frac{\Pi_{\mathrm{c}}(x)}{\sqrt{\pi/2}} - \hbar \int \mathrm{d}x \left(\partial_x \phi_{\mathrm{s}}(x) \right) \Pi_{\mathrm{s}}(x). \quad (\mathrm{L.3.27})$$

The forward-scattering terms of (32.3.63) can be written in terms of the chiral densities for fermions with spin, too:

$$\mathcal{H}_{\text{int}} = \sum_{\sigma} \int dx \Big[(g_{2\parallel} - g_{1\parallel}) n_{+,\sigma}(x) n_{-,\sigma}(x) + g_{2\perp} n_{+,\sigma}(x) n_{-,-\sigma}(x) \\ + \frac{1}{2} g_{4\parallel} \big(n_{+,\sigma}(x) n_{+,\sigma}(x) + n_{-,\sigma}(x) n_{-,\sigma}(x) \big) \\ + \frac{1}{2} g_{4\perp} \big(n_{+,\sigma}(x) n_{+,-\sigma}(x) + n_{-,\sigma}(x) n_{-,-\sigma}(x) \big) \Big].$$
(L.3.28)

When written in terms of the phase fields and their conjugates, the terms containing the charge and spin fields are decoupled. The Hamiltonian is the sum of two similar terms:

$$\mathcal{H} = \mathcal{H}_{\rm c} + \mathcal{H}_{\rm s} \,, \tag{L.3.29}$$

where - similar to (L.3.16) - the interaction gives rise to a renormalization of the velocity of the boson modes and to the appearance of a correlation factor K. We find

$$\mathcal{H}_{\rm c} = \frac{1}{2}\hbar u_{\rm c} \int \mathrm{d}x \left[K_{\rm c} \Pi_{\rm c}^2(x) + \frac{1}{K_{\rm c}} \left(\partial_x \phi_{\rm c}(x) \right)^2 \right]$$
(L.3.30)

for the charge part, where, when written in terms of the dimensionless couplings

$$\tilde{g}_i = g_i / (2\pi v_{\rm F}) \,, \tag{L.3.31}$$

we have

$$u_{\rm c} = v_{\rm F} \left[\left(1 + \tilde{g}_{4\parallel} + \tilde{g}_{4\perp} \right)^2 - \left(\tilde{g}_{1\parallel} - \tilde{g}_{2\parallel} - \tilde{g}_{2\perp} \right)^2 \right]^{1/2}$$
(L.3.32)

and

$$K_{\rm c} = \left[\frac{1 + \tilde{g}_{4\parallel} + \tilde{g}_{4\perp} + \left(\tilde{g}_{1\parallel} - \tilde{g}_{2\parallel} - \tilde{g}_{2\perp}\right)}{1 + \tilde{g}_{4\parallel} + \tilde{g}_{4\perp} - \left(\tilde{g}_{1\parallel} - \tilde{g}_{2\parallel} - \tilde{g}_{2\perp}\right)}\right]^{1/2}.$$
 (L.3.33)

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The expressions for the spin modes are similar:

$$\mathcal{H}_{\rm s} = \frac{1}{2}\hbar u_{\rm s} \int \mathrm{d}x \left[K_{\rm s} \Pi_{\rm s}^2(x) + \frac{1}{K_{\rm s}} \left(\partial_x \phi_{\rm s}(x) \right)^2 \right], \qquad (\mathrm{L.3.34})$$

where

$$u_{\rm s} = v_{\rm F} \left[\left(1 + \tilde{g}_{4\parallel} - \tilde{g}_{4\perp} \right)^2 - \left(\tilde{g}_{1\parallel} - \tilde{g}_{2\parallel} + \tilde{g}_{2\perp} \right)^2 \right]^{1/2}$$
(L.3.35)

and

$$K_{\rm s} = \left[\frac{1 + \tilde{g}_{4\parallel} - \tilde{g}_{4\perp} + \left(\tilde{g}_{1\parallel} - \tilde{g}_{2\parallel} + \tilde{g}_{2\perp}\right)}{1 + \tilde{g}_{4\parallel} - \tilde{g}_{4\perp} - \left(\tilde{g}_{1\parallel} - \tilde{g}_{2\parallel} + \tilde{g}_{2\perp}\right)}\right]^{1/2}.$$
 (L.3.36)

The large-momentum-transfer processes of the backward and umklapp scattering, which in fermion representation have the form

$$\mathcal{H}_{\text{int}} = \sum_{\sigma} \int \mathrm{d}x \, g_{1\perp} \hat{\psi}^{\dagger}_{+,\sigma}(x) \hat{\psi}^{\dagger}_{-,-\sigma}(x) \hat{\psi}_{+,-\sigma}(x) \hat{\psi}_{-,\sigma}(x) \qquad (\text{L.3.37})$$
$$+ \frac{1}{2} \sum_{\sigma} \int \mathrm{d}x \, g_{3\perp} \left[\mathrm{e}^{\mathrm{i}Gx} \hat{\psi}^{\dagger}_{+,\sigma}(x) \hat{\psi}^{\dagger}_{+,-\sigma}(x) \hat{\psi}_{-,-\sigma}(x) \hat{\psi}_{-,\sigma}(x) + \text{h.c.} \right],$$

cannot be written in simple form in terms of the chiral densities. When given in terms of the phase fields, we find

$$\mathcal{H}_{\text{back}} = \frac{2g_{1\perp}}{(2\pi\alpha)^2} \int dx \cos\left(\sqrt{8\pi}\phi_{\text{s}}(x)\right)$$
(L.3.38)

for the backward scattering, while

$$\mathcal{H}_{\rm u} = \frac{2g_{3\perp}}{(2\pi\alpha)^2} \int \mathrm{d}x \cos\left(\sqrt{8\pi}\phi_{\rm c}(x)\right) \tag{L.3.39}$$

for the umklapp processes in the half-filled case, when $4k_{\rm F} = G$. The spincharge separation still holds. Only the spin modes are involved in backward scattering and only the charge modes in the umklapp processes.

L.4 Correlation Functions

The real advantage of the boson representation is that it allows us to calculate correlation functions in real space much more easily than in the fermion representation. This makes it easier to study the relevance or irrelevance of perturbations.

L.4.1 Noninteracting Spinless Fermions

The retarded correlation function of spinless noninteracting fermions,

$$K(x,t) = -\frac{i}{\hbar}\theta(t) \langle \hat{\psi}(x,t)\hat{\psi}^{\dagger}(0,0) \rangle = -\frac{i}{\hbar}\theta(t) \langle \hat{\psi}_{+}(x,t)\hat{\psi}^{\dagger}_{+}(0,0) + \hat{\psi}_{-}(x,t)\hat{\psi}^{\dagger}_{-}(0,0) \rangle,$$
(L.4.1)

can be simply evaluated in the space–time representation. Taking the right-moving part at T=0 we have

$$K_{+}(x,t) = -\frac{\mathrm{i}}{\hbar} \frac{1}{L} \theta(t) \sum_{k>0} \mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \mathrm{e}^{\mathrm{i}k(x-v_{\mathrm{F}}t)} \,. \tag{L.4.2}$$

In the limit $L \to \infty$ the summation over $k = (2\pi/L)n_k$ can be replaced with an integral,

$$K_{+}(x,t) = -\frac{\mathrm{i}}{\hbar}\theta(t)\mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x} \int_{0}^{\infty} \frac{\mathrm{d}k}{2\pi} \mathrm{e}^{\mathrm{i}k(x-v_{\mathrm{F}}t)} \,. \tag{L.4.3}$$

Using (J.1.53) we find

$$K_{+}(x,t) = \frac{\mathrm{e}^{\mathrm{i}k_{\mathrm{F}}x}}{2\pi\hbar} \frac{\theta(t)}{x - v_{\mathrm{F}}t + \mathrm{i}\delta} \,. \tag{L.4.4}$$

Similar calculation for left-moving fermions yields

$$K_{-}(x,t) = -\frac{e^{-ik_{F}x}}{2\pi\hbar} \frac{\theta(t)}{x + v_{F}t - i\delta}.$$
 (L.4.5)

The advanced correlation functions can be calculated analogously. For the causal Green function we get

$$G_{+}(x,t) = -\frac{i}{\hbar} \left\langle T \left\{ \hat{\psi}_{+}(x,t) \hat{\psi}_{+}^{\dagger}(0,0) \right\} \right\rangle = \frac{1}{2\pi\hbar} \frac{e^{ik_{F}x}}{x - v_{F}t + i\delta \text{sgn}t} ,$$

$$G_{-}(x,t) = -\frac{i}{\hbar} \left\langle T \left\{ \hat{\psi}_{-}(x,t) \hat{\psi}_{-}^{\dagger}(0,0) \right\} \right\rangle = -\frac{1}{2\pi\hbar} \frac{e^{-ik_{F}x}}{x + v_{F}t - i\delta \text{sgn}t} .$$
(L.4.6)

The same result can be derived in a somewhat more tedious calculation in the boson representation, where (L.2.69) and (L.2.70) are used for the fermion fields:

$$K_{+}(x,t) = -\frac{i}{2\pi\alpha\hbar}\theta(t)e^{ik_{F}x} \langle e^{i\phi_{+}(x,t)}e^{-i\phi_{+}(0,0)} \rangle.$$
(L.4.7)

Owing to the linear dispersion of the boson spectrum,

$$b_q(t) = e^{-iv_F|q|t}b_q, \qquad b_q^{\dagger}(t) = e^{iv_F|q|t}b_q^{\dagger}, \qquad (L.4.8)$$

and the time dependence of the boson field, apart from the time-independent topological term, is given by

$$\begin{split} \phi_{+}(x,t) &= -i\sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} \left(e^{iq(x-v_{\rm F}t)}b_{q} - e^{-iq(x-v_{\rm F}t)}b_{q}^{\dagger}\right) e^{-\alpha q/2}, \\ (L.4.9) \\ \phi_{-}(x,t) &= -i\sum_{q>0} \left(\frac{2\pi}{Lq}\right)^{1/2} \left(e^{iq(x+v_{\rm F}t)}b_{-q}^{\dagger} - e^{-iq(x+v_{\rm F}t)}b_{-q}\right) e^{-\alpha q/2}. \end{split}$$

That is

$$\phi_{+}(x,t) = \phi_{+}(x - v_{\rm F}t) \tag{L.4.10}$$

for the right-moving field and

$$\phi_{-}(x,t) = \phi_{-}(x+v_{\rm F}t) \tag{L.4.11}$$

for the left-moving field.

The exponential factors in (L.4.7) can be reduced to a single exponential by using the Baker-Hausdorff formula (L.2.76) and the averaging can be done in the exponent using (L.2.79). The resulting expression is identical to (L.2.83) with the variable $x - v_{\rm F}t$:

$$\langle 0 | \mathrm{e}^{\mathrm{i}\phi_+(x,t)} \mathrm{e}^{-\mathrm{i}\phi_+(0,0)} | 0 \rangle = \frac{\alpha}{\alpha - \mathrm{i}(x - v_{\mathrm{F}}t)} \,.$$
 (L.4.12)

Equation (L.4.4) is indeed recovered if $\alpha = \delta$. Analogous calculation for the left-moving fermions gives

$$\langle 0 | \mathrm{e}^{\mathrm{i}\phi_{-}(x,t)} \mathrm{e}^{-\mathrm{i}\phi_{-}(0,0)} | 0 \rangle = \frac{\alpha}{\alpha + \mathrm{i}(x + v_{\mathrm{F}}t)}.$$
 (L.4.13)

The correlation function

$$K_{\beta_+,\beta_-}(x,t) = \left\langle \mathcal{O}_{\beta_+,\beta_-}(x,t)\mathcal{O}^{\dagger}_{\beta_+,\beta_-}(0,0) \right\rangle$$
(L.4.14)

of a more general operator

$$\mathcal{O}_{\beta_{+},\beta_{-}}(x,t) = e^{i[\beta_{+}\phi_{+}(x,t)+\beta_{-}\phi_{-}(x,t)]}$$
(L.4.15)

can easily be calculated using the results given above. Since $\phi_+(x,t)$ and $\phi_-(x,t)$ commute,

$$K_{\beta_{+},\beta_{-}}(x,t) = \left\langle e^{i\beta_{+}\phi_{+}(x,t)} e^{-i\beta_{+}\phi_{+}(0,0)} \right\rangle \left\langle e^{i\beta_{-}\phi_{-}(x,t)} e^{-i\beta_{-}\phi_{-}(0,0)} \right\rangle, \quad (L.4.16)$$

and hence

$$K_{\beta_+,\beta_-}(x,t) = \left(\frac{\alpha}{\alpha - i(x - v_F t)}\right)^{\beta_+^2} \left(\frac{\alpha}{\alpha + i(x + v_F t)}\right)^{\beta_-^2} .$$
(L.4.17)

When the fields ϕ and θ introduced in (L.2.48) and (L.2.49) are used, the correlation function

$$K_{m,n}(x,t) = \left\langle \mathcal{O}_{m,n}(x,t)\mathcal{O}_{m,n}^{\dagger}(0,0) \right\rangle$$
(L.4.18)

of the operator

$$\mathcal{O}_{m,n}(x,t) = e^{i\sqrt{\pi}[m\phi(x,t)+n\theta(x,t)]}$$
(L.4.19)

takes the form

$$K_{m,n}(x,t) = \left(\frac{\alpha}{\alpha - i(x - v_{\rm F}t)}\right)^{2\Delta_+} \left(\frac{\alpha}{\alpha + i(x + v_{\rm F}t)}\right)^{2\Delta_-} \propto \left(\frac{1}{x - v_{\rm F}t + i\alpha}\right)^{2\Delta_+} \left(\frac{1}{x + v_{\rm F}t - i\alpha}\right)^{2\Delta_-},$$
(L.4.20)

where

$$\Delta_{+} = (m+n)^2/8, \qquad \Delta_{-} = (m-n)^2/8.$$
 (L.4.21)

L.4.2 Interacting Spinless Fermions

While the evaluation of the correlation function is much simpler in the fermion representation in the absence of interactions, it is much more difficult when interactions are taken into account. The calculation of the correlation functions can be carried out exactly in the fermion space-time representation using Ward identities, but it is a rather lengthy and cumbersome procedure. This is where the power of the boson representation makes itself felt. Introducing the scaled phase fields

$$\widetilde{\phi} = \phi / \sqrt{K} = \frac{1}{\sqrt{4\pi K}} (\phi_+ + \phi_-) ,$$

$$\widetilde{\theta} = \sqrt{K} \theta = \sqrt{\frac{K}{4\pi}} (\phi_+ - \phi_-) ,$$
(L.4.22)

and the scaled conjugate momentum

$$\widetilde{\Pi} = \sqrt{K}\Pi \,, \tag{L.4.23}$$

the Hamiltonian of the interacting system takes the same form as that of a noninteracting one, except that the velocity $v_{\rm F}$ is replaced by u. The correlation functions of the scaled fields of the interacting system are readily obtained from (L.4.20):

$$K_{m,n}(x,t) = \left\langle e^{i\sqrt{\pi}[m\widetilde{\phi}(x,t)+n\widetilde{\theta}(x,t)]} e^{-i\sqrt{\pi}[m\widetilde{\phi}(0,0)+n\widetilde{\theta}(0,0)]} \right\rangle$$
$$\propto \left(\frac{1}{x-ut+i\alpha}\right)^{2\Delta_{+}} \left(\frac{1}{x+ut-i\alpha}\right)^{2\Delta_{-}}, \qquad (L.4.24)$$

with Δ_{\pm} given in (L.4.21).

Consider now an arbitrary operator

$$\mathcal{O}_{\delta N_{+},\delta N_{-}}(x,t) = e^{-i[\delta N_{+}\phi_{+}(x,t) - \delta N_{-}\phi_{-}(x,t)]}$$
(L.4.25)

that adds δN_+ particles to the right-moving branch and δN_- particles to the left-moving branch. The fields ϕ_+ and ϕ_- are related to the scaled fields via

$$\phi_{\pm} = \sqrt{\pi} \left[\sqrt{K} \widetilde{\phi} \pm \frac{1}{\sqrt{K}} \widetilde{\theta} \right]; \qquad (L.4.26)$$

hence, the operator takes the form

$$\mathcal{O}_{\delta N_{+},\delta N_{-}}(x,t) = e^{-i\sqrt{\pi}[J\phi(x,t)+\delta N\theta(x,t)]}$$

= $e^{-i\sqrt{\pi}[J\sqrt{K}\widetilde{\phi}(x,t)+\delta N\widetilde{\theta}(x,t)/\sqrt{K}]}$. (L.4.27)

The correlation function of these operators is

$$\left\langle \mathcal{O}_{\delta N_{+},\delta N_{-}}(x,t)\mathcal{O}_{\delta N_{+},\delta N_{-}}^{\dagger}(0,0)\right\rangle \\ \propto \frac{1}{(x-ut+\mathrm{i}\alpha)^{2\Delta_{+}}(x+ut-\mathrm{i}\alpha)^{2\Delta_{-}}}$$
(L.4.28)

with

$$\Delta_{\pm} = \frac{1}{8} \left(\sqrt{K}J \pm \frac{1}{\sqrt{K}} \delta N \right)^2 = \left(KJ \pm \delta N \right)^2 / 8K, \qquad (L.4.29)$$

as given in (32.5.33).

This result can be applied to calculate the correlation functions of the anisotropic S = 1/2 Heisenberg chain. Using the boson representation of the spin operators given in (L.2.92) and (L.2.96), the explicit expressions for the longitudinal and transverse correlation functions given in (32.5.36) and (32.5.37) can be recovered. We consider here the role of umklapp scattering in the spinless-fermion representation.

If the operator $\mathcal{O}_{\delta N_+,\delta N_-}$ appears in the Hamiltonian as a perturbation, the strength of its coupling constant, $\lambda_{\delta N_+,\delta N_-}$, increases or decreases under renormalization depending on the value of the scaling dimension $d_{\delta N_+,\delta N_-}$ of the operator. It can be calculated from the asymptotic, large x behavior of the correlation function. From our earlier results we find

$$\left\langle \mathcal{O}_{\delta N_{+},\delta N_{-}}(x,t)\mathcal{O}_{\delta N_{+},\delta N_{-}}^{\dagger}(0,0)\right\rangle \propto |x|^{-2d_{\delta N_{+},\delta N_{-}}}$$
 (L.4.30)

with

$$d_{\delta N_{+},\delta N_{-}} = \Delta_{+} + \Delta_{-} = \frac{1}{4} \left[\frac{1}{K} (\delta N)^{2} + K J^{2} \right].$$
(L.4.31)

An operator is relevant if its scaling dimension is less than 2. When $d_{\delta N_+,\delta N_-} = 2$, the operator is marginal, while it is irrelevant if the scaling dimension is

larger than 2. The umklapp scattering between spinless fermions ($\delta N_+ = 2$, $\delta N_- = -2$ or vice versa, that is $\delta N = 0$, $J = \pm 4$) is irrelevant for K > 1/2. This is the case for the spin-1/2 anisotropic Heisenberg chain discussed in Chapter 15 in the region $-1 < \Delta < 1$. The umklapp processes are still marginal in the isotropic antiferromagnetic point $\Delta = -1$. That is why the planar and isotropic antiferromagnetic spin chains behave as Luttinger liquids. Umklapp processes become relevant for $\Delta < -1$, where K < 1/2. They generate a gap in the excitation spectrum.

L.4.3 Fermions with Spin

The procedure can be easily generalized to fermions with spin. We consider the operator

$$\mathcal{O}_{\delta N_{\lambda,\sigma}}(x,t) = \mathrm{e}^{-\mathrm{i}\left[\delta N_{+,\uparrow}\phi_{+,\uparrow}(x,t) + \delta N_{+,\uparrow}\phi_{+,\uparrow}(x,t) - \delta N_{-,\uparrow}\phi_{-,\uparrow}(x,t) - \delta N_{-,\uparrow}\phi_{-,\uparrow}(x,t)\right]}$$
(L.4.32)

that adds $\delta N_{\lambda,\sigma}$ particles to the branch with indices λ, σ . Written in terms of the charge and spin phase fields and their duals,

$$\mathcal{O}_{\delta N_{\lambda,\sigma}}(x,t) = \mathrm{e}^{-\mathrm{i}\sqrt{\pi/2} \left[J_{\mathrm{c}}\phi_{\mathrm{c}}(x,t) + J_{\mathrm{s}}\phi_{\mathrm{s}}(x,t) + \delta N_{\mathrm{c}}\theta_{\mathrm{c}}(x,t) + N_{\mathrm{s}}\theta_{\mathrm{s}}(x,t) \right]}, \qquad (\mathrm{L}.4.33)$$

with

$$\begin{split} \delta N_{\rm c} &= \delta N_{+,\uparrow} + \delta N_{+,\downarrow} + \delta N_{-,\uparrow} + \delta N_{-,\downarrow} ,\\ N_{\rm s} &= \delta N_{+,\uparrow} - \delta N_{+,\downarrow} + \delta N_{-,\uparrow} - \delta N_{-,\downarrow} ,\\ J_{\rm c} &= \delta N_{+,\uparrow} + \delta N_{+,\downarrow} - \delta N_{-,\uparrow} - \delta N_{-,\downarrow} ,\\ J_{\rm s} &= \delta N_{+,\uparrow} - \delta N_{+,\downarrow} - \delta N_{-,\uparrow} + \delta N_{-,\downarrow} \end{split}$$
(L.4.34)

introduced in (32.3.50). Since the spin and charge degrees of freedom are separated, the correlation functions are the product of the contributions of the charge and spin modes:

$$\left\langle \mathcal{O}_{\delta N_{\lambda,\sigma}}(x,t) \mathcal{O}_{\delta N_{\lambda,\sigma}}^{\dagger}(0,0) \right\rangle$$

$$= \left\langle e^{-i\sqrt{\pi/2}[J_{c}\phi_{c}(x,t)+\delta N_{c}\theta_{c}(x,t)]} e^{i\sqrt{\pi/2}[J_{c}\phi_{c}(0,0)+\delta N_{c}\theta_{c}(0,0)]} \right\rangle$$

$$\times \left\langle e^{-i\sqrt{\pi/2}[J_{s}\phi_{s}(x,t)+N_{s}\theta_{s}(x,t)]} e^{i\sqrt{\pi/2}[J_{s}\phi_{s}(0,0)+N_{s}\theta_{s}(0,0)]} \right\rangle.$$

$$(L.4.35)$$

The results derived for the spinless case can be taken over:

$$\left\langle e^{-i\sqrt{\pi/2}(J_{c}\phi_{c}(x,t)+\delta N_{c}\theta_{c}(x,t))}e^{i\sqrt{\pi/2}[J_{c}\phi_{c}(0,0)+\delta N_{c}\theta_{c}(0,0)]}\right\rangle$$

$$\propto \frac{1}{(x-u_{c}t+i\alpha)^{2\Delta_{c,+}}(x+u_{c}t-i\alpha)^{2\Delta_{c,-}}},$$

$$\left\langle e^{-i\sqrt{\pi/2}(J_{s}\phi_{s}(x,t)+N_{s}\theta_{s}(x,t))}e^{i\sqrt{\pi/2}[J_{s}\phi_{s}(0,0)+N_{s}\theta_{s}(0,0)]}\right\rangle$$

$$\propto \frac{1}{(x-u_{s}t+i\alpha)^{2\Delta_{s,+}}(x+u_{s}t-i\alpha)^{2\Delta_{s,-}}}$$

$$(L.4.36)$$

with

$$\Delta_{\mathrm{c},\pm} = \frac{1}{16} \left(\frac{1}{\sqrt{K_{\mathrm{c}}}} \delta N_{\mathrm{c}} \pm \sqrt{K_{\mathrm{c}}} J_{\mathrm{c}} \right)^{2},$$

$$\Delta_{\mathrm{s},\pm} = \frac{1}{16} \left(\frac{1}{\sqrt{K_{\mathrm{s}}}} N_{\mathrm{s}} \pm \sqrt{K_{\mathrm{s}}} J_{\mathrm{s}} \right)^{2}.$$
(L.4.37)

The factor 1/16 instead of 1/8 is due to the extra factor $1/\sqrt{2}$ in the exponent of the operators. This form reproduces the expression given in (32.3.125).

Further Reading

- J. van Delft and H. Schoeller, Bosonization for beginners refermionization for experts, Ann. Phys. 4, 225 (1998).
- A. O. Gogolin, A. A. Nersesyan, and A. M. Tsvelik, *Bosonization and Strongly Correlated Systems*, Cambridge University Press, Cambridge (1998).
- 3. N. Nagaosa, *Quantum Field Theory in Strongly Correlated Electronic Systems*, Texts and Monographs in Physics, Springer-Verlag, Berlin (1999).

Renormalization and Scaling in Solid-State Physics

The renormalization procedure and the renormalization group widely used for field theory models have gained widespread applications in statistical physics and solid-state physics, particularly since the works by K. G. WILSON. While the aim of renormalization in field theory is the elimination of unphysical divergences occurring in perturbation theory, the challenge in statistical physics is the proper treatment of the long-wavelength fluctuations near the critical point of a second-order phase transition. The solid-state physics problems for which the renormalization group method can provide a better understanding are different again. Infrared divergences resulting from the continuum of lowenergy excitations are encountered quite commonly. Logarithmically singular corrections to, e.g., the scattering amplitudes, correlation functions, susceptibilities, or thermodynamic quantities are obtained in any order of perturbation theory in the Kondo problem, near the X-ray absorption edge, and in one-dimensional electron systems, to mention just a few. The renormalizationgroup procedure allows the summation of the leading and subleading logarithmic terms to all orders of the coupling constants. Other formulations of the renormalization transformation afford a nonperturbative treatment of the infrared divergences. The perhaps most spectacular result was the solution of the Kondo problem. In this appendix we outline some basic ideas of the application of renormalization and scaling to solid-state physics problems.

M.1 Poor Man's Scaling

The actual renormalization and scaling procedures applied to solid-state physics problems can be quite different from one another. A common element in a large class of them is the gradual elimination of degrees of freedom. This can be the decimation of the lattice points in a lattice model or a reduction of the bandwidth in an electronic problem. The physics of the transformed model would normally be different from the original one unless the coupling constants characterizing the interactions are renormalized. Eventually new types of interactions have to be included, e.g., a next-nearest-neighbor interaction in a lattice model with only nearest-neighbor interaction. This type of renormalization is usually called scaling, since the physical properties are studied under variation of the energy or length scale. The simplest procedure applicable to electronic problems is the "poor man's scaling" proposed by P. W. ANDERSON (1970).

M.1.1 General Considerations

Assume that the electrons lying in a band of width 2D about the Fermi energy interact with each other or – as in the case of the Kondo problem – with an impurity. The interaction is characterized by a set of coupling constants g_1, g_2, \ldots , or J. When the bandwidth is reduced from 2D to $2(D - \delta D)$, as depicted in Fig. M.1, while keeping the density of states constant, the number of degrees of freedom is reduced.



Fig. M.1. Elimination of a part of the degrees of freedom by reducing the bandwidth

Even though the eliminated states are far from the Fermi energy, the physical properties of the original system are not correctly reproduced by the new model. Those high-order scattering processes are missing in which at least one electron or one hole is found in the vicinity of the upper or lower band edge, respectively, in an intermediate state. The physical properties may be made invariant under this reduction of the bandwidth (scaling of the cutoff) by choosing a renormalized Hamiltonian \mathcal{H}' instead of \mathcal{H} . The contribution of the missing states can be compensated in the simplest case by simultaneously changing (scaling, renormalizing) the values of the coupling constants. This may not be sufficient in some cases. New types of couplings, such as manyparticle interactions or retarded, frequency-dependent interactions, may be needed. The renormalization procedure is relatively simple if the new couplings are not relevant, in the sense that they do not affect the physical behavior.

As the bandwidth is successively reduced, a sequence of renormalized Hamiltonians, \mathcal{H}' , \mathcal{H}'' , \mathcal{H}''' , etc., and a sequence of couplings, g'_i , g''_i , g'''_i , etc., are obtained. If the series converges to a fixed-point Hamiltonian \mathcal{H}^* , the fixed-point values of the coupling constants and the way the model approaches

the fixed point can be used to describe the behavior of the system. If the coupling constant of an interaction weakens in the course of the cutoff scaling and the fixed-point value vanishes, this interaction can be scaled out of the problem; it is irrelevant. An interaction is marginal if its coupling constant remains invariant, while relevant couplings grow during the scaling procedure to reach a strong-coupling fixed point.

We have not yet specified what we mean by requiring the invariance of the physical properties under cutoff scaling. Normally the invariance of the free energy is required in the study of critical phenomena. ANDERSON proposed the use of the scattering *T*-matrix for electronic problems. Its invariance for scattering of the physically most relevant electrons, those that lie near the Fermi energy, should be required.

Consider a system described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{int}} \,, \tag{M.1.1}$$

where \mathcal{H}_0 is the noninteracting part and \mathcal{H}_{int} is the interaction. The scattering matrix is defined by

$$T(z) = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{int}} G_0(z) T(z), \qquad (M.1.2)$$

where

$$G_0(z) = \frac{1}{z - \mathcal{H}_0}$$
 (M.1.3)

is the Green function of the noninteracting system. A projection operator P is introduced which projects onto states containing at least one electron in the range $(D - \delta D, D)$ near the upper band edge or at least one hole in the range $(-D, -D + \delta D)$ near the lower band edge. It is used to separate the contributions of the processes which are not affected by the cutoff scaling from those which are eliminated in the course of renormalization, in other words those processes for which all electrons are in the reduced band even in the intermediate state from those in which at least one electron or one hole lies near the band edge in one of the intermediate states. Dividing formally the second term of (M.1.2) into two parts we write

$$T = \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{int}}(1-P)G_0T + \mathcal{H}_{\text{int}}PG_0T.$$
(M.1.4)

Iteration of the equation gives

$$T = \mathcal{H}_{int} + \mathcal{H}_{int}(1-P)G_0T$$

+ $\mathcal{H}_{int}PG_0[\mathcal{H}_{int} + \mathcal{H}_{int}(1-P)G_0T + \mathcal{H}_{int}PG_0T]$
= $[\mathcal{H}_{int} + \mathcal{H}_{int}PG_0\mathcal{H}_{int}] + [\mathcal{H}_{int} + \mathcal{H}_{int}PG_0\mathcal{H}_{int}](1-P)G_0T$
+ $\mathcal{H}_{int}PG_0\mathcal{H}_{int}PG_0T$ (M.1.5)
= $[\mathcal{H}_{int} + \mathcal{H}_{int}PG_0\mathcal{H}_{int} + \mathcal{H}_{int}PG_0\mathcal{H}_{int}PG_0\mathcal{H}_{int} + \cdots]$
+ $[\mathcal{H}_{int} + \mathcal{H}_{int}PG_0\mathcal{H}_{int} + \mathcal{H}_{int}PG_0\mathcal{H}_{int}PG_0\mathcal{H}_{int} + \cdots](1-P)G_0T$
+ $\mathcal{H}_{int}PG_0\mathcal{H}_{int}PG_0\mathcal{H}_{int} \cdots PG_0T$.

We treat scattering processes where the electrons and holes of both the initial and the final states are in the reduced band by considering the reduced T-matrix

$$T' = (1 - P)T(1 - P).$$
(M.1.6)

Multiplying (M.1.5) by 1 - P from the left and from the right and neglecting the last term, which contains an arbitrarily high power of the interaction, the reduced *T*-matrix can be written as

$$T' = \mathcal{H}'_{\text{int}} + \mathcal{H}'_{\text{int}} G_0 T', \qquad (M.1.7)$$

where

$$\mathcal{H}_{\rm int}' = (1-P) \big[\mathcal{H}_{\rm int} + \mathcal{H}_{\rm int} P G_0 \mathcal{H}_{\rm int} + \mathcal{H}_{\rm int} P G_0 \mathcal{H}_{\rm int} P G_0 \mathcal{H}_{\rm int} + \cdots \big] (1-P) \,.$$
(M.1.8)

This shows that the *T*-matrix remains invariant in the reduced Hilbert space if the interaction part of the Hamiltonian is renormalized to \mathcal{H}'_{int} .

This derivation does not take into account that the norm of the initial and final states may be changed in the presence of the interaction. This can be corrected if the matrix elements of the scattering matrix between the properly normalized initial and final states,

$$T_{if} = \frac{\langle f | \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{int}} G_0 T | i \rangle}{\langle f | 1 + G_0 T | f \rangle^{1/2} \langle i | 1 + G_0 T | i \rangle^{1/2}}, \qquad (M.1.9)$$

are required to remain invariant. The changes in the normalization of the initial and final states are caused by processes in which the electrons of the Fermi sea are excited in the intermediate states. Similarly, when calculating the numerator, we have to take into account processes corresponding to virtual excitations of the initial and final states. Denoting the physical values of the coupling constants by g_1 , g_2 , g_3 , etc., and the renormalized values by $g_j + \delta g_j$, we require

$$T_{if}(D, g_1, g_2, g_3, \dots) = T_{if}(D - \delta D, g_1 + \delta g_1, g_2 + \delta g_2, g_3 + \delta g_3, \dots)$$
(M.1.10)

for all relevant processes. Written in differential form

$$\frac{\partial T_{if}}{\partial g_1} \delta g_1 + \frac{\partial T_{if}}{\partial g_2} \delta g_2 + \frac{\partial T_{if}}{\partial g_3} \delta g_3 + \dots = \frac{\partial T_{if}}{\partial D} \delta D.$$
(M.1.11)

This renormalization procedure was applied in Chapters 32 and 35 to the one-dimensional electron gas and to the Kondo problem. Some technical details are given below.

M.1.2 Scaling Theory of the One-Dimensional Electron Gas

The g-ology model of the interacting one-dimensional electron gas was defined in (32.3.63). We will consider here, for the sake of simplicity, a non-half-filled band so that the umklapp processes can be neglected. We will omit the chiral forward-scattering processes too, since their contribution is not logarithmically singular. They only give rise to a renormalization of the Fermi velocity. Three types of scattering process are permitted when a right-moving and a left-moving electron collide. The coupling constant is denoted by $g_{1\parallel} - g_{2\parallel}$ when the two particles have identical spins. Backward- and forward-scattering processes can be distinguished when the electrons participating in the scattering process have opposite spins. The coupling constants are $g_{1\perp}$ and $g_{2\perp}$, respectively.

The perturbative corrections to the renormalized Hamiltonian can be calculated straightforwardly using (M.1.8). The analysis of the term

$$\mathcal{H}_{\rm int} P \frac{1}{z - \mathcal{H}_0} \mathcal{H}_{\rm int} \tag{M.1.12}$$

requires the enumeration of all processes in which there is an electron in an intermediate state near the upper band edge in a range of width δD or a hole near the lower band edge. A simpler procedure is offered if the full matrix elements are calculated for two-particle scattering processes and the invariance of the matrix elements is required under a simultaneous scaling of the bandwidth and the couplings.

To describe two-particle scattering processes, both the initial and the final states are chosen to contain two extra electrons in addition to the Fermi sea:

$$|i\rangle = c^{\dagger}_{k_{\rm F}+k,\alpha} d^{\dagger}_{-k_{\rm F}+k',\beta} |\Psi_{\rm FS}\rangle, \qquad |f\rangle = d^{\dagger}_{-k_{\rm F}+k+q,\gamma} c^{\dagger}_{k_{\rm F}+k'-q,\delta} |\Psi_{\rm FS}\rangle. \tag{M.1.13}$$

In lowest order in the interaction we find

$$T_{if}^{(0)} = \langle f | \mathcal{H}_{\text{int}} | i \rangle = \frac{1}{L} \left[(g_{1\parallel} - g_{2\parallel}) \delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\alpha\beta} + g_{1\perp} \delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\alpha,-\beta} - g_{2\perp} \delta_{\alpha\delta} \delta_{\beta\gamma} \delta_{\alpha,-\beta} \right]$$
(M.1.14)

The diagrams representing the second-order scattering processes of the extra electrons are depicted in Fig. M.2.



Fig. M.2. Second-order scattering processes

A simpler diagrammatic representation is obtained if the interaction is denoted by a dot. The four diagrams in the upper row and the four diagrams in the lower row are then represented by the skeleton diagrams shown in Fig. M.3. This representation has the advantage that the structure of the diagram, whether it has a particle–particle pair or a particle–hole pair in the intermediate state, is better seen.



Fig. M.3. Skeleton diagrams representing the second-order processes

The contribution of all these diagrams can easily be determined for the case when the extra electrons are on the Fermi surface and the only remaining variable is z. If the matrix elements of the T-matrix are decomposed according to their spin dependence in the form

$$T_{if} = \frac{1}{L} \left[T_{\parallel} \delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\alpha\beta} + T_{1\perp} \delta_{\alpha\gamma} \delta_{\beta\delta} \delta_{\alpha,-\beta} - T_{2\perp} \delta_{\alpha\delta} \delta_{\beta\gamma} \delta_{\alpha,-\beta} \right], \quad (M.1.15)$$

up to second order we find

$$T_{\parallel}(z) = g_{1\parallel} - g_{2\parallel} + \frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \ln \frac{z}{2D} ,$$

$$T_{1\perp}(z) = g_{1\perp} + \frac{1}{\pi\hbar v_{\rm F}} g_{1\perp}(g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \ln \frac{z}{2D} ,$$

$$T_{2\perp}(z) = g_{2\perp} + \frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \ln \frac{z}{2D} .$$

(M.1.16)

The invariance of these matrix elements under a simultaneous change of the cutoff and the couplings leads to

$$\begin{split} \delta g_{1\parallel} - \delta g_{2\parallel} &= -\frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \frac{\delta D}{D} - \frac{1}{\pi\hbar v_{\rm F}} g_{1\perp} \delta g_{1\perp} \ln \frac{z}{2D} ,\\ \delta g_{1\perp} &= -\frac{1}{\pi\hbar v_{\rm F}} g_{1\perp} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \frac{\delta D}{D} \\ &- \frac{1}{\pi\hbar v_{\rm F}} \delta g_{1\perp} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \ln \frac{z}{2D} \\ &- \frac{1}{\pi\hbar v_{\rm F}} g_{1\perp} (\delta g_{1\parallel} - \delta g_{2\parallel} + \delta g_{2\perp}) \ln \frac{z}{2D} ,\\ \delta g_{2\perp} &= -\frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \frac{\delta D}{D} - \frac{1}{\pi\hbar v_{\rm F}} g_{1\perp} \delta g_{1\perp} \ln \frac{z}{2D} . \end{split}$$
(M.1.17)

The leading corrections to the change of the couplings are of second order:

$$\delta g_{1\parallel} - \delta g_{2\parallel} = -\frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \frac{\delta D}{D} ,$$

$$\delta g_{1\perp} = -\frac{1}{\pi\hbar v_{\rm F}} g_{1\perp} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \frac{\delta D}{D} , \qquad (M.1.18)$$

$$\delta g_{2\perp} = -\frac{1}{2\pi\hbar v_{\rm F}} g_{1\perp}^2 \frac{\delta D}{D} .$$

These equations were listed in (32.5.46).



Fig. M.4. Skeleton diagrams of the third-order scattering processes

The skeleton diagrams of the next-order scattering processes are depicted in Fig. M.4. Note that the third-order processes, except for the last two, can be obtained from the second-order processes of Fig. M.3 by replacing the elementary interaction with a second-order vertex. These are the so-called parquet diagrams. Their contributions are proportional to $\ln^2 z/2D$. The contributions of the two other diagrams are only proportional to $\ln z/2D$. The analytic results with the correct combinations of the coupling constants are

$$T_{\parallel}^{(3)}(z) = \frac{1}{2\pi^{2}\hbar^{2}v_{\rm F}^{2}}g_{1\perp}^{2}(g_{1\parallel} - g_{2\parallel} + g_{2\perp})\ln^{2}\frac{z}{2D} + \frac{1}{4\pi^{2}\hbar^{2}v_{\rm F}^{2}}\left[-(g_{1\parallel} - g_{2\parallel})^{3} + g_{1\perp}^{2}g_{2\perp} - (g_{1\parallel} - g_{2\parallel})g_{2\perp}^{2}\right]\ln\frac{z}{2D},$$

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$$T_{1\perp}^{(3)}(z) = \frac{1}{2\pi^2 \hbar^2 v_{\rm F}^2} g_{1\perp} \left[(g_{1\parallel} - g_{2\parallel} + g_{2\perp})^2 + g_{1\perp}^2 \right] \ln^2 \frac{z}{2D} + \frac{1}{2\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel}) g_{1\perp} g_{2\perp} \ln \frac{z}{2D} , \qquad (M.1.19) T_{2\perp}^{(3)}(z) = \frac{1}{2\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) g_{1\perp}^2 \ln^2 \frac{z}{2D} + \frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} \left[(g_{1\parallel} - g_{2\parallel}) g_{1\perp}^2 - (g_{1\parallel} - g_{2\parallel})^2 g_{2\perp} - g_{2\perp}^3 \right] \ln \frac{z}{2D} .$$

In this order we have to take into account the self-energy corrections to the incoming and outgoing particles represented by the diagrams in Fig. M.5.



Fig. M.5. Third-order processes contributing to the renormalization of the wavefunction of the incoming and outgoing particles

The contributions of the self-energy processes to T_{if} are easily obtained. The lowest order expression for T_{if} given in (M.1.14) has to be multiplied by the factor

$$\langle \Psi_{\rm FS} | c_{k_{\rm F}+k,\alpha} (1+G_0 T) c_{k_{\rm F}+k,\alpha}^{\dagger} | \Psi_{\rm FS} \rangle$$
 (M.1.20)

to account for the self-energy correction due to the incoming right-moving electron. Similar factors,

$$\langle \Psi_{\rm FS} | d_{-k_{\rm F}+k',\beta} (1+G_0 T) d^{\dagger}_{-k_{\rm F}+k',\beta} | \Psi_{\rm FS} \rangle ,$$

$$\langle \Psi_{\rm FS} | d_{-k_{\rm F}+k+q,\gamma} (1+G_0 T) d^{\dagger}_{-k_{\rm F}+k+q,\gamma} | \Psi_{\rm FS} \rangle ,$$

$$\langle \Psi_{\rm FS} | c_{k_{\rm F}+k'-q,\delta} (1+G_0 T) c^{\dagger}_{k_{\rm F}+k'-q,\delta} | \Psi_{\rm FS} \rangle ,$$

$$(M.1.21)$$

account for the self-energy corrections due to the incoming left-moving as well as the outgoing left- and right-moving fermions, respectively. When all incoming and outgoing particles are on the Fermi surface, these factors take the same value:

$$1 + \frac{1}{8\pi^2 \hbar^2 v_{\rm F}^2} \left[(g_{1\parallel} - g_{2\parallel})^2 + g_{1\perp}^2 + g_{2\perp}^2 \right] \ln \frac{z}{2D} \,. \tag{M.1.22}$$

Similar factors appear due to the proper normalization of the wavefunction of the incoming and outgoing electrons. Taking all these corrections into account we find

$$T_{\parallel}^{(3)}(z) = \frac{1}{2\pi^2 \hbar^2 v_{\rm F}^2} g_{1\perp}^2 (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \ln^2 \frac{z}{2D} + \frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) g_{1\perp}^2 \ln \frac{z}{2D} ,$$

$$\begin{split} T_{1\perp}^{(3)}(z) &= \frac{1}{2\pi^2 \hbar^2 v_{\rm F}^2} g_{1\perp} \left[(g_{1\parallel} - g_{2\parallel} + g_{2\perp})^2 + g_{1\perp}^2 \right] \ln^2 \frac{z}{2D} \\ &+ \frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} \left[(g_{1\parallel} - g_{2\parallel} + g_{2\perp})^2 g_{1\perp} + g_{1\perp}^3 \right] \ln \frac{z}{2D} , \ ({\rm M}.1.23) \\ T_{2\perp}^{(3)}(z) &= \frac{1}{2\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) g_{1\perp}^2 \ln^2 \frac{z}{2D} \\ &+ \frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) g_{1\perp}^2 \ln \frac{z}{2D} . \end{split}$$

The renormalized couplings are obtained from the invariance of the sum of (M.1.16) and (M.1.23). It turns out that the corrections coming from the $\ln^2 z/2D$ contributions of the third-order parquet diagrams cancel out and so do not contribute to the scaling equations. This is a consequence of the self-consistency of the scaling theory. As the parquet diagrams are generated by successively replacing a bare vertex with a logarithmic bubble, their $\ln^n z/2D$ contributions are generated by solving the scaling equations with the elementary bubbles as inputs. Only the nonparquet diagrams contribute new terms to the scaling equations.

The third-order corrections to the renormalized couplings are given by

$$\begin{split} \delta g_{1\parallel}^{(3)} &- \delta g_{2\parallel}^{(3)} = -\frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) g_{1\perp}^2 \frac{\delta D}{D} ,\\ \delta g_{1\perp}^{(3)} &= -\frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} \big[(g_{1\parallel} - g_{2\parallel} + g_{2\perp})^2 g_{1\perp} + g_{1\perp}^3 \big] \frac{\delta D}{D} , \qquad ({\rm M}.1.24) \\ \delta g_{2\perp}^{(3)} &= -\frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) g_{1\perp}^2 \frac{\delta D}{D} . \end{split}$$

It is readily seen that the combination $g_{1\parallel}^{(3)}-g_{2\parallel}^{(3)}-g_{2\perp}^{(3)}$ remains invariant in this order, too,

$$\delta \left(g_{1\parallel}^{(3)} - g_{2\parallel}^{(3)} - g_{2\perp}^{(3)} \right) = 0, \qquad (M.1.25)$$

while

$$\delta(g_{1\parallel}^{(3)} - g_{2\parallel}^{(3)} + g_{2\perp}^{(3)}) = -\frac{1}{2\pi^2 \hbar^2 v_{\rm F}^2} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) g_{1\perp}^2 \frac{\delta D}{D} . \qquad (M.1.26)$$

Combining these expressions with the result derived in second order we have

$$\begin{split} \delta(g_{1\parallel} - g_{2\parallel} + g_{2\perp}) &= -\frac{1}{\pi \hbar v_{\rm F}} g_{1\perp}^2 \Big[1 + \frac{1}{2\pi \hbar v_{\rm F}} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \Big] \frac{\delta D}{D} ,\\ \delta g_{1\perp} &= -\frac{1}{\pi \hbar v_{\rm F}} g_{1\perp} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \frac{\delta D}{D} \qquad ({\rm M}.1.27) \\ &- \frac{1}{4\pi^2 \hbar^2 v_{\rm F}^2} \Big[(g_{1\parallel} - g_{2\parallel} + g_{2\perp})^2 g_{1\perp} + g_{1\perp}^3 \Big] \frac{\delta D}{D} , \end{split}$$

or in differential form

$$\frac{\mathrm{d}(g_{1\parallel} - g_{2\parallel} + g_{2\perp})}{\mathrm{d}D} = \frac{1}{\pi\hbar v_{\mathrm{F}}} \frac{1}{D} g_{1\perp}^2 \left[1 + \frac{1}{2\pi\hbar v_{\mathrm{F}}} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \right],$$
$$\frac{\mathrm{d}g_{1\perp}}{\mathrm{d}D} = \frac{1}{\pi\hbar v_{\mathrm{F}}} \frac{1}{D} g_{1\perp} (g_{1\parallel} - g_{2\parallel} + g_{2\perp}) \qquad (\mathrm{M.1.28})$$
$$+ \frac{1}{4\pi^2 \hbar^2 v_{\mathrm{F}}^2} \frac{1}{D} \left[(g_{1\parallel} - g_{2\parallel} + g_{2\perp})^2 g_{1\perp} + g_{1\perp}^3 \right].$$

The line $g_{1\perp} = 0$ is a fixed line of the model. It describes the Tomonaga– Luttinger behavior. Otherwise the one-dimensional Fermi gas scales to a strong-coupling fixed point. Its location, however, cannot be obtained from this perturbative treatment.

M.1.3 Scaling Theory of the Kondo Problem

Consider an anisotropic Kondo problem where the interaction of the conduction electrons with the impurity spin S located at the origin is described by the Hamiltonian

$$\mathcal{H}_{\rm int} = \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'\alpha\beta} \left[J_{\pm} \left(S^+ \sigma^-_{\alpha\beta} + S^- \sigma^+_{\alpha\beta} \right) + J_z S^z \sigma^z_{\alpha\beta} \right] c^{\dagger}_{\boldsymbol{k}'\alpha} c_{\boldsymbol{k}\beta} \,. \tag{M.1.29}$$

The first correction to the renormalized interaction defined by (M.1.8) is

$$\delta \mathcal{H}_{\text{int}}' = \left(\frac{1}{V}\right)^2 \sum_{\boldsymbol{k}_1 \boldsymbol{k}_2 \alpha \beta} \left[J_{\pm} \left(S^+ \sigma_{\alpha\beta}^- + S^- \sigma_{\alpha\beta}^+ \right) + J_z S^z \sigma_{\alpha\beta}^z \right] c_{\boldsymbol{k}_1 \alpha}^\dagger c_{\boldsymbol{k}_2 \beta} \right]$$

$$\times P \frac{1}{z - \mathcal{H}_0} \sum_{\boldsymbol{k}_3 \boldsymbol{k}_4 \gamma \delta} \left[J_{\pm} \left(S^+ \sigma_{\gamma\delta}^- + S^- \sigma_{\gamma\delta}^+ \right) + J_z S^z \sigma_{\gamma\delta}^z \right] c_{\boldsymbol{k}_3 \gamma}^\dagger c_{\boldsymbol{k}_4 \delta} \,.$$
(M.1.30)

We show that this expression, given already in (35.2.43), can be written as

$$\delta \mathcal{H}_{\rm int}' = \frac{1}{V} \sum_{\boldsymbol{k}\boldsymbol{k}'\alpha\beta} \left[\delta J_{\pm} \left(S^+ \sigma_{\alpha\beta}^- + S^- \sigma_{\alpha\beta}^+ \right) + \delta J_z S^z \sigma_{\alpha\beta}^z \right] c_{\boldsymbol{k}'\alpha}^{\dagger} c_{\boldsymbol{k}\beta} \qquad (M.1.31)$$

with appropriately chosen δJ_{\pm} and δJ_z .

The expression in (M.1.30) describes a two-step scattering process of an electron by the impurity if the electron created by $c^{\dagger}_{\mathbf{k}_{3}\gamma}$ in the first step is destroyed in the second scattering process by the operator $c_{\mathbf{k}_{2}\beta}$ or if the hole created by $c^{\dagger}_{\mathbf{k}_{4}\delta}$ in the first step is filled by $c^{\dagger}_{\mathbf{k}_{1}\alpha}$ in the second step. These processes were depicted in Fig. 35.14. We therefore have

$$\delta \mathcal{H}_{int}' = \left(\frac{1}{V}\right)^{2} \sum_{\mathbf{k}_{1}\mathbf{k}_{2}\mathbf{k}_{4}\alpha\beta\delta} c_{\mathbf{k}_{1}\alpha}^{\dagger} c_{\mathbf{k}_{2}\beta} P \frac{1}{z - \xi_{\mathbf{k}_{2}} + \xi_{\mathbf{k}_{4}}} c_{\mathbf{k}_{2}\beta}^{\dagger} c_{\mathbf{k}_{4}\delta}$$

$$\times \left[J_{\pm} \left(S^{+} \sigma_{\alpha\beta}^{-} + S^{-} \sigma_{\alpha\beta}^{+}\right) + J_{z} S^{z} \sigma_{\alpha\beta}^{z}\right]$$

$$\times \left[J_{\pm} \left(S^{+} \sigma_{\beta\delta}^{-} + S^{-} \sigma_{\beta\delta}^{+}\right) + J_{z} S^{z} \sigma_{\beta\delta}^{z}\right]$$

$$+ \left(\frac{1}{V}\right)^{2} \sum_{\mathbf{k}_{1}\mathbf{k}_{2}\mathbf{k}_{3}\alpha\beta\gamma} c_{\mathbf{k}_{1}\alpha}^{\dagger} c_{\mathbf{k}_{2}\beta} P \frac{1}{z - \xi_{\mathbf{k}_{3}} + \xi_{\mathbf{k}_{1}}} c_{\mathbf{k}_{3}\gamma}^{\dagger} c_{\mathbf{k}_{1}\alpha}$$

$$\times \left[J_{\pm} \left(S^{+} \sigma_{\alpha\beta}^{-} + S^{-} \sigma_{\alpha\beta}^{+}\right) + J_{z} S^{z} \sigma_{\alpha\beta}^{z}\right]$$

$$\times \left[J_{\pm} \left(S^{+} \sigma_{\gamma\alpha}^{-} + S^{-} \sigma_{\gamma\alpha}^{+}\right) + J_{z} S^{z} \sigma_{\gamma\alpha}^{z}\right].$$
(M.1.32)

The projection operator selects those processes in which there is at least one electron near the upper band edge or one hole near the lower band edge. Otherwise the projection gives zero. Hence the first term gives nonvanishing contribution if the energy of the state with wave vector \mathbf{k}_2 is in the range between $D-\delta D$ and D. The energy will be approximated by D and $c_{\mathbf{k}_2\beta}c_{\mathbf{k}_2\beta}^{\dagger} = 1$, since the states near the upper band edge are empty. Similarly, the energy of the state with wave vector \mathbf{k}_1 has to be in the range between -D and $-D+\delta D$ in the second term. It can be approximated by -D, and $c_{\mathbf{k}_1\beta}^{\dagger}c_{\mathbf{k}_1\beta} = 1$, since the states near the lower band edge are filled in the Fermi sea. Taking a constant density of states ρ in the band, using the multiplication rules of the Pauli matrices [see (F.3.11)] and the commutation relations of the spin operators, the summation over the repeated momenta and spin indices can be performed. We get

$$\begin{split} \delta \mathcal{H}_{\text{int}}' &= \frac{1}{2V} \sum_{\boldsymbol{k}_1 \boldsymbol{k}_4 \alpha \delta} \frac{\delta D \,\rho}{z - D + \xi_{\boldsymbol{k}_4}} c^{\dagger}_{\boldsymbol{k}_1 \alpha} c_{\boldsymbol{k}_4 \delta} \Big[J_{\pm \frac{1}{2}}^{2} \left(S^+ S^- + S^- S^+ \right) \delta_{\alpha \delta} \\ &+ J_z^2 (S^z)^2 \delta_{\alpha \delta} - J_{\pm} J_z \left(S^+ \sigma^-_{\alpha \delta} + S^- \sigma^+_{\alpha \delta} \right) - J_{\pm}^2 S^z \sigma^z_{\alpha \delta} \Big] \qquad (M.1.33) \\ &+ \frac{1}{2V} \sum_{\boldsymbol{k}_2 \boldsymbol{k}_3 \beta \gamma} \frac{\delta D \,\rho}{z - \xi_{\boldsymbol{k}_3} - D} c_{\boldsymbol{k}_2 \beta} c^{\dagger}_{\boldsymbol{k}_3 \gamma} \Big[J_{\pm \frac{1}{2}}^{2} \left(S^+ S^- + S^- S^+ \right) \delta_{\beta \gamma} \\ &+ J_z^2 (S^z)^2 \delta_{\beta \gamma} + J_{\pm} J_z \left(S^+ \sigma^-_{\beta \gamma} + S^- \sigma^+_{\beta \gamma} \right) + J_{\pm}^2 S^z \sigma^z_{\beta \gamma} \Big] \,. \end{split}$$

Both terms give a spin-independent contribution. They cancel each other for a symmetric band. The remaining terms have the same spin structure as the original anisotropic Kondo Hamiltonian. They can indeed be written after a change of the summation variables in the form given by (M.1.31). Assuming that the scattered electrons are near the Fermi surface and their energy, measured from the chemical potential, can be neglected compared to the bandwidth we find

$$\delta J_{\pm} = -\frac{\rho \,\delta D}{z - D} J_{\pm} J_z \,, \qquad \delta J_z = -\frac{\rho \,\delta D}{z - D} J_{\pm}^2 \,. \tag{M.1.34}$$

No new couplings are generated apart from the uninteresting potential scattering. The renormalized couplings depend, however, on the energy variable z. Neglecting this energy compared to the cutoff we have

$$\delta J_{\pm} = \frac{\rho \, \delta D}{D} J_{\pm} J_z \,, \qquad \delta J_z = \frac{\rho \, \delta D}{D} J_{\pm}^2 \,. \tag{M.1.35}$$

When they are written in differential form, we have to take into account that the change in the coupling was determined under a change $-\delta D$ of the bandwidth, that is

$$\delta J_i = -\frac{\mathrm{d}J_i}{\mathrm{d}D}\delta D\,.\tag{M.1.36}$$

Therefore the differential form of the scaling equations is

$$\frac{\mathrm{d}J_{\pm}}{\mathrm{d}D} = -\frac{\rho}{D}J_{\pm}J_z\,,\qquad \frac{\mathrm{d}J_z}{\mathrm{d}D} = -\frac{\rho}{D}J_{\pm}^2\,.\tag{M.1.37}$$

It follows from these equations that the isotropic antiferromagnetic Kondo coupling (J > 0 in our notation) is relevant. J scales toward a strongcoupling fixed point as the bandwidth is reduced. This necessitates consideration of higher order corrections to the scaling equations. One can readily draw the third-order diagrams representing one-particle scattering processes, where there is one electron or one hole in the intermediate states. They are displayed in Fig. M.6.



Fig. M.6. Scattering processes contributing to the renormalized Hamiltonian in third order. Heavy lines indicate electrons or holes lying in the range between $D-\delta D$ and D or between -D and $-D + \delta D$

It is no longer true that \mathcal{H}'_{int} only describes one-particle scattering processes. Two possible two-particle scattering processes are displayed in Fig. M.7.



Fig. M.7. Third-order two-particle scattering processes

Moreover, as mentioned earlier, the renormalization of the initial and final states also have to be taken into account as we go to higher orders. We will therefore define the renormalized couplings in agreement with (M.1.10) and (M.1.11) by requiring the invariance of the matrix elements of the *T*-matrix between the initial and final states,

$$|i\rangle = c_{\boldsymbol{k}\alpha}^{\dagger} |\Psi_{\rm FS}\rangle |M\rangle , \qquad |f\rangle = c_{\boldsymbol{k}'\beta}^{\dagger} |\Psi_{\rm FS}\rangle |M'\rangle , \qquad (M.1.38)$$

containing one extra electron added to the Fermi sea right at the Fermi surface. $|M\rangle$ and $|M'\rangle$ denote the state of the impurity spin as the eigenvalue of S^z . The extra electrons and holes can be anywhere in the entire band in the intermediate states. Up to second order in the interaction we have

$$T_{if} = \left[J_{\pm} \left(S_{M'M}^{+} \sigma_{\beta\alpha}^{-} + S_{M'M}^{-} \sigma_{\beta\alpha}^{+} \right) + J_{z} S_{M'M}^{z} \sigma_{\beta\alpha}^{z} \right] - \left[J_{\pm} J_{z} \left(S_{M'M}^{+} \sigma_{\beta\alpha}^{-} + S_{M'M}^{-} \sigma_{\beta\alpha}^{+} \right) + J_{\pm}^{2} S_{M'M}^{z} \sigma_{\beta\alpha}^{z} \right] \rho \ln \frac{z}{D},$$
(M.1.39)

where

$$S_{M'M}^{\pm} = \delta_{M',M\pm 1} \sqrt{S(S+1) - M(M\pm 1)},$$

$$S_{M'M}^{z} = \delta_{M,M'}M,$$
(M.1.40)

and a volume factor has been dropped. The invariance of these matrix elements under a scaling transformation leads to (M.1.37).

When the matrix element is determined in third order, one has to take into account the change in the norm of the initial and final states associated with the polarization of the impurity spin owing to the interaction with the Fermi sea. Figure M.8 shows all processes contributing to the matrix element in third order.



Fig. M.8. Third-order scattering processes

Their contributions give

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$$\Delta T_{if}^{(3)} = \left[\frac{1}{4} \left(J_{\pm} J_{z}^{2} + J_{\pm}^{3} \right) \left(S_{M'M}^{+} \sigma_{\beta\alpha}^{-} + S_{M'M}^{-} \sigma_{\beta\alpha}^{+} \right) \right. \\ \left. + \frac{1}{2} J_{\pm}^{2} J_{z} S_{M'M}^{z} \sigma_{\beta\alpha}^{z} \right] \rho^{2} \ln \frac{z}{D} \\ \left. + \left[\frac{1}{2} \left(J_{\pm} J_{z}^{2} + J_{\pm}^{3} \right) \left(S_{M'M}^{+} \sigma_{\beta\alpha}^{-} + S_{M'M}^{-} \sigma_{\beta\alpha}^{+} \right) \right. \\ \left. + J_{\pm}^{2} J_{z} S_{M'M}^{z} \sigma_{\beta\alpha}^{z} \right] \rho^{2} \ln^{2} \frac{z}{D} .$$

$$(M.1.41)$$

Substituting this expression into (M.1.11) the terms arising from the $\ln^2(z/D)$ corrections to the matrix element (the contributions of the parquet diagrams depicted in the first and second lines in Fig. M.8) drop out indicating the self-consistency of the scaling procedure, and the scaling equations take the form

$$\frac{\mathrm{d}J_{\pm}}{\mathrm{d}D} = -\frac{\rho}{D} \left[J_{\pm}J_z - \frac{1}{4} \left(J_{\pm}J_z^2 + J_{\pm}^3 \right) \rho + \cdots \right], \\ \frac{\mathrm{d}J_z}{\mathrm{d}D} = -\frac{\rho}{D} \left[J_{\pm}^2 - \frac{1}{2} J_{\pm}^2 J_z \rho + \cdots \right].$$
(M.1.42)

The calculation of further corrections becomes increasingly difficult. That is why a nonperturbative approach is necessary to get the true low-temperature behavior.

M.2 Numerical Renormalization Group

The numerical renormalization group (NRG) proposed by K. G. WILSON is ideally suited to solve quantum impurity problems with local interaction between the band electrons and the internal degrees of freedom of the impurity. In contrast to the usual renormalization-group transformations, where the flow of the coupling constants is considered as the bandwidth (more generally the number of degrees of freedom) is gradually reduced, the flow of the low-lying energy levels is studied in the numerical renormalization group as the size of the system increases and more and more degrees of freedom are incorporated in the iterative diagonalization of the Hamiltonian.

The key element in the calculation is the transformation of the Hamiltonian into a hopping model on a semi-infinite chain. The impurity sits at one end of the chain and the most relevant degrees of freedom of the electron system interact with it locally. The hopping amplitude decreases exponentially far from the impurity. The energy spectrum can then be calculated numerically with good precision by adding successively one extra site in each step of the iterative procedure.

The first step is the transformation of the Hamiltonian, which is usually given in three-dimensional k-space representation, into a one-dimensional energy representation. This is particularly simple for a spherical Fermi surface when the Kondo coupling $J_{kk'}$ is independent of k and k'. We first rewrite the interaction part of the Hamiltonian of the Kondo problem,

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$$\mathcal{H} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} + \frac{1}{V} \sum_{\substack{\boldsymbol{k}\boldsymbol{k}'\\\alpha\beta}} J\boldsymbol{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} c_{\boldsymbol{k}'\alpha}^{\dagger} c_{\boldsymbol{k}\beta}$$
(M.2.1)

in terms of the field operator at the position of the impurity as

$$\mathcal{H}_{\mathrm{K}} = J \sum_{\alpha\beta} \boldsymbol{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} \hat{\psi}^{\dagger}_{\alpha}(0) \hat{\psi}_{\beta}(0) , \qquad (\mathrm{M.2.2})$$

where

$$\hat{\psi}_{\alpha}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} c_{\boldsymbol{k}\alpha} \,. \tag{M.2.3}$$

In the continuum limit, where the discreteness of the ${\pmb k}$ vectors can be neglected,

$$\hat{\psi}_{\alpha}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \frac{V}{(2\pi)^3} \int e^{i\boldsymbol{k}\cdot\boldsymbol{r}} c_{\boldsymbol{k}\alpha} \,\mathrm{d}\boldsymbol{k} \,. \tag{M.2.4}$$

On the other hand, if the field operator is given as a Fourier integral,

$$\hat{\psi}_{\alpha}(\boldsymbol{r}) = \frac{1}{(2\pi)^{3/2}} \int \hat{\psi}_{\boldsymbol{k}\alpha} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \,\mathrm{d}\boldsymbol{k} \,. \tag{M.2.5}$$

Comparison of the two expressions shows that the continuum limit of the creation and annihilation operators is defined by

$$\sqrt{\frac{V}{(2\pi)^3}} c_{\boldsymbol{k}\alpha} \to \hat{\psi}_{\boldsymbol{k}\alpha} , \qquad \sqrt{\frac{V}{(2\pi)^3}} c^{\dagger}_{\boldsymbol{k}\alpha} \to \hat{\psi}^{\dagger}_{\boldsymbol{k}\alpha} . \tag{M.2.6}$$

In the continuum limit

$$\frac{V}{(2\pi)^3} \delta_{\boldsymbol{k}\boldsymbol{k}'} \to \delta(\boldsymbol{k} - \boldsymbol{k}'); \qquad (M.2.7)$$

hence, the operators $\hat{\psi}_{\bm{k}\alpha}$ and $\hat{\psi}^{\dagger}_{\bm{k}'\beta}$ satisfy the anticommutation relations

$$\left[\hat{\psi}_{\boldsymbol{k}\alpha}, \hat{\psi}^{\dagger}_{\boldsymbol{k}'\beta}\right]_{+} = \delta_{\alpha,\beta}\delta(\boldsymbol{k} - \boldsymbol{k}'). \qquad (M.2.8)$$

Since only s-waves are scattered by a contact potential, it is convenient to use orbital-momentum eigenstates and to expand the creation and annihilation operators in terms of spherical waves in the form

$$\hat{\psi}_{\boldsymbol{k}\alpha} = \frac{1}{k} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_l^{m*}(\theta_k, \varphi_k) c_{klm\alpha},$$

$$\hat{\psi}_{\boldsymbol{k}\alpha}^{\dagger} = \frac{1}{k} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_l^m(\theta_k, \varphi_k) c_{klm\alpha}^{\dagger}.$$
(M.2.9)

Inverting this transformation yields

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$$c_{klm\alpha} = k \int_{0}^{2\pi} \int_{0}^{\pi} \sin \theta_k \mathrm{d}\theta_k \mathrm{d}\varphi_k Y_l^m(\theta_k, \varphi_k) \hat{\psi}_{\boldsymbol{k}\alpha} ,$$

$$c_{klm\alpha}^{\dagger} = k \int_{0}^{2\pi} \int_{0}^{\pi} \sin \theta_k \mathrm{d}\theta_k \mathrm{d}\varphi_k Y_l^{m*}(\theta_k, \varphi_k) \hat{\psi}_{\boldsymbol{k}\alpha}^{\dagger} ,$$
(M.2.10)

which implies that these operators satisfy the usual fermionic anticommutation relations

$$\left[c_{klm\alpha}, c_{k'l'm'\beta}^{\dagger}\right]_{+} = \delta_{l,l'} \delta_{m,m'} \delta_{\alpha,\beta} \delta(k-k') \,. \tag{M.2.11}$$

The orbital wavefunction of the state created by $c_{klm\alpha}^{\dagger}$,

$$\phi_{klm}(\boldsymbol{r}) = \mathrm{i}^{l} k \left(\frac{2}{\pi}\right)^{1/2} Y_{l}^{m}(\theta_{r},\varphi_{r}) j_{l}(kr) , \qquad (\mathrm{M.2.12})$$

is readily obtained from the relation

$$\int \frac{1}{(2\pi)^{3/2}} e^{-\mathbf{i}\boldsymbol{k}\cdot\boldsymbol{r}} \mathbf{i}^{l} k' \left(\frac{2}{\pi}\right)^{1/2} j_{l}(k'r) Y_{l}^{m}(\theta_{r},\varphi_{r}) \mathrm{d}\boldsymbol{r} = \frac{1}{k} Y_{l}^{m}(\theta_{k},\varphi_{k}) \delta(k-k'),$$
(M.2.13)

which can be derived by expanding the plane wave in spherical harmonics according to (C.4.38) and making use of the orthogonality of the spherical harmonics as well as the relation

$$\int_{0}^{\infty} j_{l}(kr)j_{l}(k'r)r^{2}\mathrm{d}r = \frac{1}{2}\frac{\pi}{k^{2}}\delta(k-k')$$
(M.2.14)

between the spherical Bessel functions. The functions $\phi_{klm}(\mathbf{r})$ form a complete orthonormal set.

It is crucial for the further calculations to realize that the local interaction with the impurity involves only the l = 0, m = 0 s-waves, since

$$\hat{\psi}_{\alpha}(0) = \frac{1}{(2\pi)^{3/2}} \int \hat{\psi}_{\boldsymbol{k}\alpha} \, \mathrm{d}\boldsymbol{k} = \sqrt{\frac{4\pi}{(2\pi)^3}} \int k \mathrm{d}k \, c_{k00\alpha} \,. \tag{M.2.15}$$

Since the natural variable is the energy measured from the Fermi energy and not the wave number, we express the operators in energy variables by introducing

$$c_{\alpha}(\varepsilon) = \left[\frac{\mathrm{d}\varepsilon_k}{\mathrm{d}k}\right]^{-1/2} c_{k00\alpha} \qquad (\mathrm{M.2.16})$$

with $\varepsilon = \varepsilon_k$. These operators satisfy the anticommutation relation

$$\left[c_{\alpha}(\varepsilon), c_{\beta}^{\dagger}(\varepsilon')\right]_{+} = \delta_{\alpha,\beta} \left[\frac{\mathrm{d}\varepsilon_{k}}{\mathrm{d}k}\right]^{-1} \delta(k-k') = \delta_{\alpha,\beta} \delta(\varepsilon-\varepsilon'). \qquad (M.2.17)$$

Using these operators,

$$\hat{\psi}_{\alpha}(0) = \sqrt{\frac{1}{2\pi^2}} \int k \mathrm{d}k \, \left[\frac{\mathrm{d}\varepsilon_k}{\mathrm{d}k}\right]^{1/2} c_{\alpha}(\varepsilon) = \int \mathrm{d}\varepsilon \left[\rho_{\sigma}(\varepsilon)\right]^{1/2} c_{\alpha}(\varepsilon) \,, \quad (\mathrm{M.2.18})$$

where

$$\rho_{\sigma}(\varepsilon) = \frac{1}{V} \sum_{k} \delta(\varepsilon - \varepsilon_{k}) = \frac{1}{2\pi^{2}} k^{2} \left(\frac{\mathrm{d}\varepsilon_{k}}{\mathrm{d}k}\right)^{-1}$$
(M.2.19)

is the density of states per spin. Assuming a finite band of width 2D situated symmetrically around the Fermi energy and taking a constant density of states $\rho_{\sigma}(0)$,

$$\hat{\psi}_{\alpha}(0) = \left[\rho_{\sigma}(0)\right]^{1/2} \int_{-D}^{D} \mathrm{d}\varepsilon \, c_{\alpha}(\varepsilon) \,. \tag{M.2.20}$$

It is convenient to use D as the energy unit and to work in terms of the dimensionless variable $\tilde{\varepsilon} = \varepsilon/D$. If the operators are rescaled as $c_{\sigma}(\tilde{\varepsilon}) = \sqrt{D}c_{\sigma}(\varepsilon)$ to satisfy the anticommutator

$$\left[c_{\sigma}(\tilde{\varepsilon}), c_{\sigma'}^{\dagger}(\tilde{\varepsilon}')\right]_{+} = \delta_{\sigma,\sigma'}\delta(\tilde{\varepsilon} - \tilde{\varepsilon}'), \qquad (M.2.21)$$

we have

$$\hat{\psi}_{\alpha}(0) = \left[D\rho_{\sigma}(0)\right]^{1/2} \int_{-1}^{1} \mathrm{d}\tilde{\varepsilon} \, c_{\alpha}(\tilde{\varepsilon}) \equiv \left[2D\rho_{\sigma}(0)\right]^{1/2} f_{0,\alpha} \,, \tag{M.2.22}$$

where the fermionic operator $f_{0,\alpha}$ and its adjoint are defined by

$$f_{0,\alpha} = \frac{1}{\sqrt{2}} \int_{-1}^{1} \mathrm{d}\tilde{\varepsilon} \, c_{\alpha}(\tilde{\varepsilon}) \,, \qquad f_{0,\alpha}^{\dagger} = \frac{1}{\sqrt{2}} \int_{-1}^{1} \mathrm{d}\tilde{\varepsilon} \, c_{\alpha}^{\dagger}(\tilde{\varepsilon}) \,. \tag{M.2.23}$$

The interaction Hamiltonian then takes the form

$$\mathcal{H}_{\mathrm{K}} = D J \rho \sum_{\alpha\beta} \boldsymbol{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} f_{0,\alpha}^{\dagger} f_{0,\beta} , \qquad (\mathrm{M.2.24})$$

where ρ is the full density of states.

The kinetic energy of the band electrons can be transformed similarly. For an isotropic dispersion relation, when $\varepsilon_{\mathbf{k}}$ depends only on $k = |\mathbf{k}|$, the kinetic energy is

$$\mathcal{H}_{0} = \sum_{\boldsymbol{k}\sigma} \varepsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma} = \frac{V}{(2\pi)^{3}} \sum_{\sigma} \int d\boldsymbol{k} \, \varepsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^{\dagger} c_{\boldsymbol{k}\sigma}$$
$$= \sum_{\sigma} \int d\boldsymbol{k} \, \varepsilon_{\boldsymbol{k}} \hat{\psi}_{\boldsymbol{k}\sigma}^{\dagger} \hat{\psi}_{\boldsymbol{k}\sigma} = \sum_{lm\sigma} \int d\boldsymbol{k} \, \varepsilon_{\boldsymbol{k}} c_{klm\sigma}^{\dagger} c_{klm\sigma}.$$
(M.2.25)

Keeping again only the l = 0 partial waves and working in the energy representation, for a band of width 2D we find

$$\mathcal{H}_{0} = \sum_{\sigma} \int \mathrm{d}k \,\varepsilon_{k} c_{k00\sigma}^{\dagger} c_{k00\sigma} = \sum_{\sigma} \int_{-D}^{D} \mathrm{d}\varepsilon \,\varepsilon c_{\sigma}^{\dagger}(\varepsilon) c_{\sigma}(\varepsilon) \,, \qquad (M.2.26)$$

while in terms of the scaled energy variables we have

$$\mathcal{H}_{0} = D \sum_{\sigma} \int_{-1}^{1} \mathrm{d}\tilde{\varepsilon} \,\tilde{\varepsilon} c_{\sigma}^{\dagger}(\tilde{\varepsilon}) c_{\sigma}(\tilde{\varepsilon}) \,. \tag{M.2.27}$$

In what follows, the notation ε will be used instead of $\tilde{\varepsilon}$.

The next step is the reduction of the continuous energy spectrum to a discrete set of states in a special way to properly account for the logarithmic nature of the perturbative corrections. The energy range [-1, 1] is divided into an infinite set of intervals at the points $\pm \Lambda^{-n}$, $n = 0, 1, 2, \ldots$, as shown in Fig. M.9, with a discretization parameter $\Lambda > 1$.



Fig. M.9. Logarithmic discretization of the conduction band. The Fermi energy is in the middle of the band

Each interval still has an infinite number of states in the continuum limit. A complete set of states can be introduced in each interval by the definition

$$\psi_{np}^{\pm}(\varepsilon) = \begin{cases} \frac{\Lambda^{n/2}}{(1-\Lambda^{-1})^{1/2}} e^{\pm i\omega_n p\varepsilon} & \text{for } \Lambda^{-(n+1)} < \pm \varepsilon < \Lambda^{-n}, \\ 0 & \text{outside this interval,} \end{cases}$$
(M.2.28)

with $\omega_n = 2\pi/(\Lambda^{-n} - \Lambda^{-(n+1)})$ and p takes all integer values between $-\infty$ and $+\infty$. The electron operators can be expanded in the basis

$$c_{\sigma}(\varepsilon) = \sum_{np} \left[a_{np\sigma} \psi_{np}^{+}(\varepsilon) + b_{np\sigma} \psi_{np}^{-}(\varepsilon) \right], \qquad (M.2.29)$$

where the operators $a_{np\sigma}$ and $b_{np\sigma}$ obey the standard fermionic anticommutation relations. The operator $f_{0\sigma}^{\dagger}$ introduced in (M.2.23), which couples to the impurity, is

$$\frac{1}{\sqrt{2}} \int_{-1}^{1} \mathrm{d}\varepsilon \, c_{\sigma}(\varepsilon) = \frac{1}{\sqrt{2}} (1 - \Lambda^{-1})^{1/2} \sum_{n} \Lambda^{-n/2} \left(a_{n0\sigma} + b_{n0\sigma} \right). \tag{M.2.30}$$

Since it contains only the p = 0 components, we will only keep these terms in expansion (M.2.29). This is equivalent to taking a single state, an average, in each interval. The kinetic energy then has the form

$$\mathcal{H}_0 = D\frac{1}{2} \left(1 + \Lambda^{-1} \right) \sum_{n\sigma} \Lambda^{-n} \left(a_{n0\sigma}^{\dagger} a_{n0\sigma} - b_{n0\sigma}^{\dagger} b_{n0\sigma} \right).$$
(M.2.31)

The third step is the conversion of the full Hamiltonian to a hopping form on a semi-infinite chain. This is achieved by a Lanczos tridiagonalization.¹ Since the state created by the operator $f_{0,\sigma}^{\dagger}$ from the vacuum,

$$|0,\sigma\rangle = f_{0,\sigma}^{\dagger}|0\rangle, \qquad (M.2.32)$$

is not an eigenstate of the kinetic energy \mathcal{H}_0 , we define a state $|1, \sigma\rangle$ using the Gram–Schmidt orthogonalization procedure via

$$|1,\sigma\rangle = \frac{1}{\gamma_0} \Big[\mathcal{H}_0|0,\sigma\rangle - |0,\sigma\rangle\langle 0,\sigma|\mathcal{H}_0|0,\sigma\rangle \Big], \qquad (M.2.33)$$

where γ_0 is a normalization factor. It is also the matrix element of the Hamiltonian between $|0, \sigma\rangle$ and $|1, \sigma\rangle$. A new component,

$$|2,\sigma\rangle = \frac{1}{\gamma_1} \Big[\mathcal{H}_0 |1,\sigma\rangle - |1,\sigma\rangle \langle 1,\sigma|\mathcal{H}_0 |1,\sigma\rangle - |0,\sigma\rangle \langle 0,\sigma|\mathcal{H}_0 |1,\sigma\rangle \Big] \,, \quad (M.2.34)$$

which is orthogonal to both $|0, \sigma\rangle$ and $|1, \sigma\rangle$, appears when the Hamiltonian acts on $|1, \sigma\rangle$. Repetition of this procedure leads us in the *n*th step to a state

$$|n,\sigma\rangle = \frac{1}{\gamma_{n-1}} \Big[\mathcal{H}_0 | n-1,\sigma\rangle - |n-1,\sigma\rangle \langle n-1,\sigma|\mathcal{H}_0 | n-1,\sigma\rangle - |n-2,\sigma\rangle \langle n-2,\sigma|\mathcal{H}_0 | n-1,\sigma\rangle \Big].$$
(M.2.35)

It follows from this construction that \mathcal{H}_0 has nonvanishing nondiagonal matrix elements only between neighboring sites. The kinetic energy can be written in second quantization in the form

$$\mathcal{H}_0 = \sum_{n\sigma} \varepsilon_n f_{n,\sigma}^{\dagger} f_{n,\sigma} + \sum_{n\sigma} \left(\gamma_n f_{n,\sigma}^{\dagger} f_{n+1,\sigma} + \gamma_n^* f_{n+1,\sigma}^{\dagger} f_{n,\sigma} \right), \qquad (M.2.36)$$

where $f_{n,\sigma}^{\dagger}$ creates the state $|n,\sigma\rangle$ from the vacuum. This is indeed the Hamiltonian of electrons hopping between nearest neighbors along a semi-infinite chain, the index *n* being the site index. The parameters, the site energy ε_n and the hopping amplitude γ_n , can be calculated from the dispersion relation of the conduction electrons. Taking a constant density of states one finds

$$\varepsilon_n = 0, \qquad \gamma_n \approx \frac{1 + \Lambda^{-1}}{2\Lambda^{n/2}}.$$
 (M.2.37)

¹ C. Lanczos, 1950.
The diagonal elements vanish because $|n, \sigma\rangle$ is an equal mixture of positiveand negative energy states with energy zero. Taking into account the interaction with the impurity, the Kondo model is finally mapped onto a tight-binding model on a semi-infinite chain with the impurity sitting at site n = 0,

$$\mathcal{H}/D = C \sum_{n,\sigma} \Lambda^{-n/2} \left[f_{n,\sigma}^{\dagger} f_{n+1,\sigma} + f_{n+1,\sigma}^{\dagger} f_{n,\sigma} \right] + J\rho \sum_{\alpha\beta} \mathbf{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} f_{0,\alpha}^{\dagger} f_{0,\beta}, \qquad (M.2.38)$$

with $C = (1 + \Lambda^{-1})/2$. The electrons hop between nearest-neighbor sites. If, eventually, they hop to the impurity site, they interact with the spin of the impurity. The impurity spin and the electron spin can be flipped simultaneously.

In the fourth step the physically interesting low-energy part of the spectrum is calculated by an iterative diagonalization. Assume that we know the spectrum for a chain of N sites $(N \gg 1)$ described by the Hamiltonian

$$\mathcal{H}_N/D = C \sum_{n=0}^{N-1} \sum_{\sigma} \Lambda^{-n/2} \left[f_{n,\sigma}^{\dagger} f_{n+1,\sigma} + f_{n+1,\sigma}^{\dagger} f_{n,\sigma} \right] + J\rho \sum_{\alpha\beta} \mathbf{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} f_{0,\alpha}^{\dagger} f_{0,\beta} \,.$$
(M.2.39)

The renormalization-group transformation consists of (a) adding one extra site of the chain in each step of the iterative scheme, (b) diagonalizing the new Hamiltonian with N + 1 sites, and (c) studying the flow of the energy levels. Since the hopping amplitude decreases as $\Lambda^{-n/2}$ the splitting of the energy levels diminishes gradually as we proceed. Therefore a scale factor $\Lambda^{(N-1)/2}$ is introduced and the renormalization-group transformation is performed on

$$\overline{\mathcal{H}}_{N} = \Lambda^{(N-1)/2} \left\{ \sum_{n=0}^{N-1} \sum_{\sigma} \Lambda^{-n/2} \left[f_{n,\sigma}^{\dagger} f_{n+1,\sigma} + f_{n+1,\sigma}^{\dagger} f_{n,\sigma} \right] + \tilde{J} \sum_{\alpha\beta} \mathbf{S} \cdot \boldsymbol{\sigma}_{\alpha\beta} f_{0,\alpha}^{\dagger} f_{0,\beta} \right\}$$
(M.2.40)

with $\tilde{J} = 2J\rho/(1 + \Lambda^{-1})$, where the smallest term is of order unity and the recursion relation is

$$\overline{\mathcal{H}}_{N+1} = \Lambda^{1/2} \overline{\mathcal{H}}_N + \sum_{\sigma} \left[f_{N,\sigma}^{\dagger} f_{N+1,\sigma} + f_{N+1,\sigma}^{\dagger} f_{N,\sigma} \right].$$
(M.2.41)

The original Hamiltonian is obtained via

$$\mathcal{H}/D = \lim_{N \to \infty} C \Lambda^{-(N-1)/2} \overline{\mathcal{H}}_N \,. \tag{M.2.42}$$

The number of states increases exponentially as new sites are added. This is avoided by a truncation procedure. A fixed number of low-lying levels (typically of the order 10^3) are kept in each step of the iterative diagonalization. The higher lying levels are discarded before a new site is added to the chain. The splitting of the levels is evaluated numerically and the flow of the lowlying part of the energy spectrum is studied as the chain length increases.

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Name	Symbol	Value
Bohr magneton	$\mu_{\rm B} = e\hbar/2m_{\rm e}$	$9.274009 \times 10^{-24}\mathrm{JT^{-1}}$
Bohr radius	$a_0 = 4\pi\epsilon_0 \hbar^2/m_e e^2$	$0.529177 \times 10^{-10}\mathrm{m}$
Boltzmann constant	$k_{\rm B}$	$1.380650 imes 10^{-23}\mathrm{JK^{-1}}$
Conductance quantum	$G_0 = 2e^2/h$	$7.748092 imes 10^{-5}\mathrm{S}$
Electron q-factor	$q_{\rm e} = 2\mu_{\rm e}/\mu_{\rm B}$	-2.002319
Electron gyromagnetic ratio	$\gamma_{\rm e} = 2 \mu_{\rm e} /\hbar$	$1.760860 \times 10^{11}\mathrm{s}^{-1}\mathrm{T}^{-1}$
	$\gamma_{\rm e}/2\pi$	$28024.9540~{ m MHz}{ m T}^{-1}$
Electron magnetic moment	$\mu_{ m e}$	$-9.284764 \times 10^{-24}\mathrm{JT^{-1}}$ -1.001 160 μ_{B}
Electron mass	$m_{ m e}$	9.109382×10^{-31} kg
Electric constant	$\epsilon_0 = 1/\mu_0 c^2$	$8.854188 \times 10^{-12}\mathrm{Fm^{-1}}$
Elementary charge	e	$1.602176 \times 10^{-19}\mathrm{C}$
Hartree energy	$E_{\rm h} = e^2/4\pi\epsilon_0 a_0$	$4.359744 imes 10^{-18}{ m J}$
in eV		$27.211383\mathrm{eV}$
Josephson constant	$K_{\rm J} = 2e/h$	$483597.9 imes10^9{ m Hz}{ m V}^{-1}$
Magnetic constant	μ_0	$4\pi \times 10^{-7} \mathrm{N}\mathrm{A}^{-2}$
Magnetic flux quantum	$\Phi_0 = h/2e$	$2.067834 \times 10^{-15}\mathrm{Wb}$
Nuclear magneton	$\mu_{ m N} = e\hbar/2m_{ m p}$	$5.050783 imes 10^{-27}\mathrm{JT^{-1}}$
Neutron mass	$m_{\rm n}$	$1.674927 \times 10^{-27}\mathrm{kg}$
Neutron magnetic moment	$\mu_{ m n}$	$-0.966236 \times 10^{-26}\mathrm{J}\mathrm{T}^{-1}$
		$-1.913043\mu_{ m N}$
Neutron g -factor	$g_{\mathrm{n}} = 2\mu_{\mathrm{n}}/\mu_{\mathrm{N}}$	-3.826085
Planck constant	h	$6.626069 imes 10^{-34}\mathrm{Js}$
in eV	$h/\{e\}$	$4.135667 \times 10^{-15}\mathrm{eVs}$
Proton g-factor	$g_{\mathrm{p}} = 2\mu_{\mathrm{p}}/\mu_{\mathrm{N}}$	5.585695
Proton gyromagnetic ratio	$\gamma_{ m p} = 2\mu_{ m p}/\hbar$	$2.675222 \times 10^8 \mathrm{s}^{-1} \mathrm{T}^{-1}$
	$\gamma_{ m p}/2\pi$	$42.577482{ m MHzT^{-1}}$
Proton magnetic moment	$\mu_{ m p}$	$1.410607 imes 10^{-26}\mathrm{JT^{-1}}$
		$2.792847\mu_{ m N}$
Proton mass	$m_{ m p}$	$1.672622 \times 10^{-27}\mathrm{kg}$
Reduced Planck constant	$\hbar = h/2\pi$	$1.054572 \times 10^{-34}\mathrm{Js}$
in eV	$\hbar/\{e\}$	$6.582119 \times 10^{-16}\mathrm{eVs}$
Rydberg constant	$R_{\infty} = \alpha^2 m_{\rm e} c/2h$	$10973731.569\mathrm{m}^{-1}$
Rydberg energy	$Ry = R_{\infty}hc$	$2.179872 \times 10^{-18}\mathrm{J}$
in eV		$13.605692\mathrm{eV}$
Speed of light	С	$299792458{\rm ms^{-1}}$
Von Klitzing constant	$R_{\rm K} = h/e^2$	25812.807572Ω

Fundamental physical constants