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Small Superconducting Particles

Why think about small metal particles?

- Of interest to many fields
 - optical properties
 - catalysis
 - components of future electronics

My focus - electronic properties

Experiments on small particles allow measurements of the discrete "electrons-in-a-box" energy spectrum for the first time.

Result - The levels observed are not well-described by non-interacting electron physics.

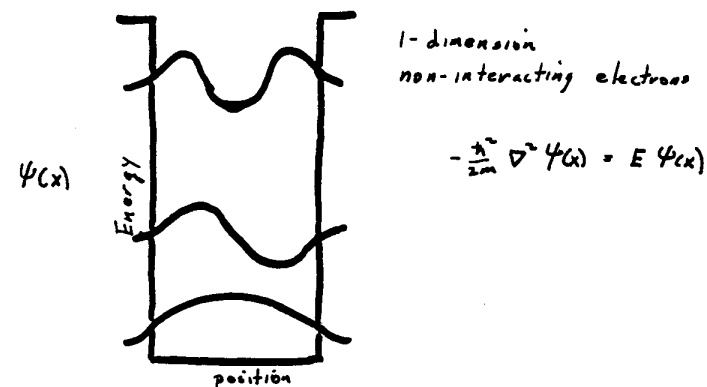
We can use these spectra as a new way of probing interacting-electron systems.

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ELECTRONS IN A BOX

Just as in an atom, the allowed electronic energies in a small metal particle form a discrete spectrum.

Simplest model: Electrons in a box



Complications in a real metal particle:

High quantum numbers -- $N \approx 10,000$

Electronic interactions

Irregular particle shape and scattering from disorder at the particle surface

⇒ No spatial symmetries to give degeneracies (Random matrix theories)

Ralph
Lecture 1

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How small a metal particle is required
in order to resolve individual electronic states?

Need $\delta E > k_B T$.

$$\delta E = \frac{4e_F}{3N} = \frac{2\pi^2 \hbar^2}{mk_F V}$$

$$V = \frac{90 \text{ nm}^3}{\delta E / \text{meV}}$$

Suppose we want $\delta E > k_B (1 \text{ K}) \sim 0.1 \text{ meV}$.

$$\Rightarrow V < (10 \text{ nm})^3.$$

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These lectures:

I. How should we think about interacting electrons?

(Considering small particles provides insights about the general problem.)

- Classifying Interactions
- What is the correct Hamiltonian?
- How good are approximate Hamiltonians?

$$BCS? \quad H_{int} = \sum_{i,j} V_{ij} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow} c_{j\uparrow}$$

↑
same for all states i,j ?

(works for periodic boundary conditions,
what about finite size?)

Stoner Model - Ferromagnetism

$$H_{int} = - \sum_{i,j} J_{ij} (n_{i\uparrow} n_{j\uparrow} + n_{i\downarrow} n_{j\downarrow})$$

$$n_i = c_i^\dagger c_i$$

Is there a unified picture?

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II. Superconductivity in Small Scale Systems

- With a fixed number of electrons,
What is Superconductivity?
- μm -sized samples
- nm-sized samples

III. How a Magnetic Field Destroys Superconductivity

Decreasing
Sample Size
↓

- Meissner Effect
- Orbital Pair-Breaking
- Spin Pair-Breaking in thin Films
- Spin Pair-Breaking in Nanoparticles

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Electron Interactions - The Small Particle View *

This will be a thought calculation - How might we solve the interacting-electron problem exactly? The method will turn out to be wildly impractical for a large number of electrons, but it has the virtue of giving considerable insight.

[We will follow the usual steps for diagonalizing a Hamiltonian

- ① Set up a complete set of states to use as a basis.
- ② Evaluate the matrix elements of the Hamiltonian in this basis
- ③ Diagonalize the Hamiltonian

* Overall picture due to Igor Aleiner and Boris Altshuler

Thanks to Jan van Delft for conversations.

⑦ To form a basis of states for the many-body problem of interacting electrons, we must take into account properly that the total wavefunction must be antisymmetric upon exchange of electrons. This can be accomplished by choosing the many-body basis states to be Slater determinants of non-interacting single-electron states.

Let $\psi_a(r), \psi_b(r), \dots, \psi_n(r)$ be single-electron states, including both spatial and spin degrees of freedom.

A Slater determinant state has the form

$$\Psi_A = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_a(r_1) & \psi_a(r_2) & \dots & \psi_a(r_n) \\ \psi_b(r_1) & & & \psi_b(r_n) \\ \vdots & & & \vdots \\ \psi_n(r_1) & \dots & \dots & \psi_n(r_n) \end{vmatrix} \leftarrow \text{Determinant}$$

If there are N states in the single particle basis and n electrons in the system, then there are $\binom{N}{n}$ Slater determinants in the many-body basis $\Rightarrow$ BIG matrix

If the set of single-particle states is complete for single electrons, then the Slater determinant states will form a complete basis for the many-electron states.

⑧ Alternative Notation (2nd Quantization)

To within a sign, the Slater determinant state is completely determined just by saying what list of single-particle states go into the determinant. This suggests a labelling based on raising operators (meaning $c_i c_i^\dagger + c_i^\dagger c_i = 1$)

$$\Psi_A = c_a^\dagger c_b^\dagger \dots c_n^\dagger |\text{vacuum}\rangle$$

$\nwarrow$ The Same Slater determinant state from the previous page, just written in an alternative notation

In order that the many-body wavefunction change sign upon exchange of electrons, the raising and lowering operators must anticommute

$$c_a^\dagger c_b^\dagger = -c_b^\dagger c_a^\dagger \quad c_a c_b = -c_b c_a, \quad c_a c_b^\dagger + c_b^\dagger c_a = 0 \quad \text{if } a \neq b.$$

The 2nd Quantized notation will make it much easier to evaluate matrix elements of the Hamiltonian (without fooling with factorials, etc.). We will go through the arguments using both notations, for clarity.

② Evaluating matrix elements

Eventually, we will care most about 2-body electron-electron interactions. However, as a warm-up, let's think about a one-body interaction. (For instance, a potential energy term)

$$V_1 = \sum_i V(r_i)$$

↖ The interaction must act on all the electrons the same way, since they are identical.

We will want to know the value of matrix elements $\langle \Phi_A | V_1 | \Phi_B \rangle$ between Slater determinant states.

$$= \frac{1}{n!} \sum_i \int d^3r_1 \dots d^3r_n \begin{vmatrix} \psi_1^+(r_1) & \dots & \psi_n^+(r_1) \\ \vdots & & \vdots \\ \psi_1^+(r_i) & \dots & \psi_n^+(r_i) \end{vmatrix} V(r_i) \begin{vmatrix} \psi_1(r_1) & \dots & \psi_n(r_1) \\ \vdots & & \vdots \\ \psi_1(r_i) & \dots & \psi_n(r_i) \end{vmatrix}$$

Think about expanding the determinants and doing the integrals. For the integrals not involving r_i (the spatial component in $V(r_i)$) the wave functions in Φ_A and Φ_B must all be the same, or there will be an integration over orthogonal single-particle wave functions, giving 0. This means that for the matrix element to be non-zero, Φ_A and Φ_B must be composed of the same single-particle states, with at most one change $\psi_d \rightarrow \psi_p$.

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Working things out:

$$\langle \Phi_A | V_1 | \Phi_B \rangle = \int d^3r_i \psi_p^+(r_i) V(r_i) \psi_d(r_i)$$

(all other integrals, in $n!$ combinations, give 1)

$$= V_{pd} \text{ if } d \neq p$$

If Φ_A and Φ_B are exactly the same, then

$$\langle \Phi_A | V_1 | \Phi_A \rangle = \sum_{a=1}^n V_{aa}$$

These results are easy to express in 2nd Quantized notation.

It turns out that V_1 can be written in the form:

$$V_1 = \sum_{i,j,k} V_{ijk} c_{j\sigma}^\dagger c_{k\sigma}$$

Think scattering



↖ Here I've switched notation to give separate indices for orbit and spin.

This can be verified explicitly with the operator algebra

$$\begin{aligned} \langle \Phi_A | V_1 | \Phi_B \rangle &= \langle \text{vac} | c_1 \dots c_p \dots c_n | \sum_{i,j,k} V_{ijk} c_{j\sigma}^\dagger c_{k\sigma} | c_1^\dagger c_2^\dagger \dots c_d^\dagger \dots c_n^\dagger | \text{vac} \rangle \\ &= \sum_{i,j,k} V_{ijk} \langle \text{vac} | c_1 \dots c_p \dots c_n c_{j\sigma}^\dagger c_{k\sigma} c_1^\dagger \dots c_d^\dagger \dots c_n^\dagger | \text{vac} \rangle \end{aligned}$$

This is non-zero only if $k=d$, $p=j$, and all the other single-particle states are the same in the 2 determinants.

Can eliminate pairs of operators by anticommuting and using $c_\alpha c_\alpha^\dagger = 1 - c_\alpha^\dagger c_\alpha$

$$\begin{aligned} &= \sum_{i,j,k} V_{ijk} \delta_{kd} \delta_{pi} \langle \text{vac} | c_p c_{j\sigma}^\dagger c_k c_d^\dagger | \text{vac} \rangle \\ &= V_{pd} // \end{aligned}$$

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Now let's consider the more important case of 2-body electron-electron interactions:

$$V_{ee} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} V(r_i - r_j)$$

We will think about this as being the residual Coulomb interaction between screened quasiparticles, so V will be short ranged and spin-independent.

$$\langle \Phi_A | V_{ee} | \Phi_B \rangle$$

$$= \frac{1}{n!} \frac{1}{2} \sum_{i,j} \int d^3r_1 \dots d^3r_n \left| \begin{matrix} \psi_{i_1}^*(r_1) & \dots & \psi_{i_n}^*(r_n) \\ \vdots & & \vdots \\ \psi_{j_1}^*(r_1) & \dots & \psi_{j_n}^*(r_n) \end{matrix} \right| V(r_i - r_j) \left| \begin{matrix} \psi_{k_1}(r_1) & \dots & \psi_{k_n}(r_n) \\ \vdots & & \vdots \\ \psi_{l_1}(r_1) & \dots & \psi_{l_n}(r_n) \end{matrix} \right|$$

Now the integrals will be non-zero only if Φ_A and Φ_B are the same except for at most 2 single particle states different

The second-quantized form of the same interaction is

$$V_{ee} = -\frac{1}{2} \sum_{i,j,k,m} V_{ijkl} c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{k\uparrow} c_{m\downarrow}$$

Spin indices written as required for spin conservation

where $V_{ijkl} = \int d^3r_1 d^3r_2 \psi_{i\uparrow}^*(r_1) \psi_{j\downarrow}^*(r_2) V(r_1 - r_2) \psi_{k\uparrow}(r_1) \psi_{l\downarrow}(r_2)$

and $\psi_{i\uparrow}(r) = \psi_i(r) \chi_{\uparrow}$

↑ space part ↑ spin part

matrix element takes the form of overlap integral involving 4 wavefunctions.

Rewriting

$$V_{ee} = -\frac{1}{2} \sum_{i,j,k,m} V_{ijkl} c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{k\uparrow} c_{m\downarrow}$$

$$V_{ijkl} = \int d^3r_1 d^3r_2 \psi_{i\uparrow}^*(r_1) \psi_{j\downarrow}^*(r_2) V(r_1 - r_2) \psi_{k\uparrow}(r_1) \psi_{l\downarrow}(r_2)$$

For electrons in a finite hunk of metal, the states $\{\psi_i(r)\}$ will be rapidly-oscillating (in r) standing waves, and neglecting spin-orbit interactions they may be taken as real. Let's approximate the short-ranged interaction between screened electrons as a δ -function $V(r_1 - r_2) = V \delta(r_1 - r_2)$. [This is not a bad approximation - the actual range will be about λ_F , which is also the fastest oscillation scale of the wave functions, so indeed the wave functions will be approximately constant over the range of interactions.]

WHAT MATRIX ELEMENTS WILL BE BIGGEST?

(and therefore the most important...)

All the $\psi_i(r)$ will be highly oscillatory, both + and -. Most matrix elements will be integrals over random functions with zero mean, so that most matrix elements will be close to zero.

$$V_{ijkl} \approx V \int d^3r \psi_i(r) \psi_j(r) \psi_k(r) \psi_l(r)$$

Exception - If you pick spatial wave functions pairwise, then the integrand has a definite sign, and the matrix elements are much bigger.

3 ways to do this	$i=k, j=m$	Direct
	$i=m, j=k$	Exchange
	$i=j, k=m$	Pairing

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To see this, evaluate the diagonal matrix element

$$\langle \Phi_A | V_{\text{exchange}} | \Phi_A \rangle = \langle \Phi_A | -\frac{1}{2} \sum_{i,j} \sum_s K_{ij} c_{i\bar{s}}^\dagger c_{is} c_{j\bar{s}}^\dagger c_{js} | \Phi_A \rangle$$

For repulsive interactions, $K_{ij} > 0$. The matrix element causes the energy of Φ_A to be lowered if the spins in different orbital states are aligned. This can produce an instability to ferromagnetism.

Instructive exercise

$$\text{Writing } n_i = c_{i\uparrow}^\dagger c_{i\uparrow} + c_{i\downarrow}^\dagger c_{i\downarrow}$$

$$\text{and } \vec{S}_i = \frac{1}{2} \sum_{s,\bar{s}} c_{i\bar{s}}^\dagger \vec{\sigma}_{s\bar{s}} c_{i\bar{s}}$$

It is possible to write

$$V_{\text{Direct}} + V_{\text{Exchange}} = \sum_{i,j} \left[\frac{1}{2} K_{ij} n_i n_j - 2 K_{ij} \vec{S}_i \cdot \vec{S}_j \right]$$

- invariant under rotations in spin space.

solution in I.L. Kurland, I.L. Aleiner, and B.L. Altshuler
cond-mat/0004205

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$\langle V_{\text{Direct}} \quad i=k \quad j=m \quad (\text{Hartree})$

$$V_{\text{Direct}} = -\frac{1}{2} \sum_{i,j} \sum_{s,\bar{s}} \underbrace{V \int d^3r [u_i(r)]^2 [u_j(r)]^2}_{K_{ij}} \underbrace{c_{i\bar{s}}^\dagger c_{j\bar{s}}^\dagger c_{is} c_{js}}_{\text{number operators}}$$

Coulomb interaction between the charge distributions determined by the wavefunctions

Since V_{Direct} contains only number operators, it contributes only to diagonal matrix elements

$$\langle \Phi_A | V_{\text{Direct}} | \Phi_A \rangle$$

$\langle V_{\text{Exchange}} \quad i=m, j=k, i \neq j \quad (\text{Fock})$

$$V_{\text{Exchange}} = -\frac{1}{2} \sum_{i,j} \sum_{s,\bar{s}} \underbrace{V \int d^3r [u_i(r)]^2 [u_j(r)]^2}_{\boxed{\text{same } K_{ij}!}} \underbrace{c_{i\bar{s}}^\dagger c_{j\bar{s}}^\dagger c_{js} c_{is}}_{\text{(for } \delta\text{-function interaction)}} + c_{i\bar{s}}^\dagger c_{i\bar{s}} c_{j\bar{s}}^\dagger c_{js}$$

This contains both contributions to diagonal matrix elements when $s=\bar{s}$ and off-diagonal matrix elements when $s \neq \bar{s}$.

Even though we are assuming that $V(r_1, r_2)$ is a spin independent potential, it is a consequence of having antisymmetric many-body states that V_{exchange} produces spin-dependent forces

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$$V_{\text{pairing}} \quad i=j, k=m \quad i \neq m$$

$$V_{\text{pairing}} = -\frac{1}{2} \sum_{\substack{i, m \\ s, \bar{s}}} K_{im} \underbrace{c_{i\bar{s}}^{\dagger} c_{i\bar{s}}^{\dagger} c_{m\bar{s}} c_{m\bar{s}}}_{- c_{i\bar{s}}^{\dagger} c_{i\bar{s}}^{\dagger} c_{m\bar{s}} c_{m\bar{s}}}$$

This cannot contribute to any diagonal matrix elements, but it gives non-zero off-diagonal elements if $\bar{s} \neq s$

$$V_{\text{pairing}} = \sum_{i \neq m} K_{im} \underbrace{c_{i\uparrow}^{\dagger} c_{i\downarrow}^{\dagger} c_{m\downarrow} c_{m\uparrow}}_{\text{Scattering from one pair state to another}}$$

(BCS Hamiltonian, almost)

$\{i\uparrow \text{ and } i\downarrow\}$ are the time-reversed eigenstates that make up a Cooper pair.

If the e-e interaction is repulsive, then this does not lead to any instability. However, attractive interactions produce superconductivity through this term.

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Aside

In the BCS and Stoner Hamiltonians, it is assumed that K_{ij} is a constant, the same for all eigenstates i and j

$$K_{ij} = V \int d^3r [u_i(r)]^2 [u_j(r)]^2 \stackrel{?}{=} K$$

How good an approximation is this (for δ -function interaction)?

Answer - Very good if the particle size is $\gg \frac{1}{k_F}$.

Then $u_i(r)$ and $u_j(r)$ have many independent oscillations, and to a good approximation

$$K_{ij} = V \int d^3r \langle [u_i(r)]^2 \rangle \langle [u_j(r)]^2 \rangle$$

$$= V \int d^3r \left(\frac{1}{\text{Vol}} \right) \left(\frac{1}{\text{Vol}} \right) \quad \begin{matrix} \uparrow & \uparrow \\ \text{average values} \end{matrix}$$

$$= \frac{V}{\text{Vol}} \quad \text{independent of } i \text{ and } j$$

$$\equiv K$$

(Later - How much does this depend on assuming the interaction term is a δ -function?)

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Summary of Step 2: Matrix Elements.

The Hartree, Fock (Exchange), and Pairing parts of the interaction Hamiltonian all come from the same spin-independent 2-body interaction.

$$V_{ee} = V_{\text{direct}} + V_{\text{exchange}} + V_{\text{pairing}}$$

$$= \sum_{ij} \left[\frac{1}{2} K n_i n_j - 2K \vec{S}_i \cdot \vec{S}_j + K c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow} c_{j\uparrow} \right]$$

(assuming a δ -function interaction)

③ Final Step - Diagonalizing the Hamiltonian

In general, including the off-diagonal matrix elements, the true eigenstates will be complicated linear superpositions of different Slater determinant states $\Rightarrow$ complicated correlations.

Superconductivity is due to the pairing term - explicitly off-diagonal interaction. Superconducting ground state is a superposition of Slater determinants.

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Cartoon Picture of Superconducting Ground State $|\Psi_0\rangle =$

$$a_1 \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{array} + a_2 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{array} + a_3 \begin{array}{c} \text{---} \\ \text{---} \\ \uparrow\downarrow \\ \uparrow\downarrow \\ \text{---} \\ \uparrow\downarrow \end{array} + a_4 \begin{array}{c} \text{---} \\ \uparrow\downarrow \\ \text{---} \\ \uparrow\downarrow \\ \text{---} \\ \uparrow\downarrow \end{array} + a_5 \begin{array}{c} \text{---} \\ \uparrow\downarrow \\ \text{---} \\ \text{---} \\ \text{---} \\ \uparrow\downarrow \end{array} + \dots$$

$$V_{\text{pairing}} = \sum_{i,m} K_{im} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{m\downarrow} c_{m\uparrow}$$

Partial occupation of higher-lying orbital states costs kinetic energy, but this is offset by opening up "phase space" for pair scattering so that

$$\langle \Psi_0 | V_{\text{pairing}} | \Psi_0 \rangle \neq 0$$

Balance of energies produces partial occupation of pair states within about Δ of E_F .

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Although magnetic and superconducting interactions come from the same source and have similar strength, the magnetic (exchange) interactions destabilize the Fermi liquid state only for repulsive interactions, while the pairing terms produce an instability only for attractive interactions.

⇒ Common to include only one term or the other in effective Hamiltonians

(The other term renormalizes to zero...)

Some approximation schemes (Hartree-Fock theory, for example) consider only the diagonal matrix elements and seek to find the lowest-energy Slater determinant state. Not appropriate for superconductivity.

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< What about a more realistic electron-electron interaction?
(Beyond a δ -function?)

This can be calculated (Random Matrix theory, etc.)
cond-mat/0004205, PRL 78, 1956 (1997).

$$V_{ijklm} = \int d^3r_1 d^3r_2 U_i^*(r_1) U_j^*(r_2) V(r_1 - r_2) U_k(r_1) U_m(r_2)$$

The biggest matrix elements still come from choosing the wavefunctions pairwise, but in the realistic case, not all the matrix elements have exactly the same value.

fluctuations $\frac{|SV|}{|V|} \sim \frac{1}{g}$ where g is the dimensionless conductance

$$g = \frac{E_{\text{bandwidth}}}{\delta E} \leftarrow \begin{array}{l} \hbar / (\text{time for electron to diffuse across the sample}) \\ \text{level spacing} \end{array}$$

$$\approx \frac{k_F^2 L \ell}{6\pi^2} \leftarrow \text{mean free path}$$

$$\gg 1 \quad \text{if} \quad L \gg \frac{1}{k_F}$$

So for a realistic sample, fluctuations in the interaction matrix elements can almost always be ignored.

(For an exception, see PRL 78, 1956 (97).)