1. “Rigorous” development of Hartree-Fock approximation.

Consider the general interacting electron system with Hamiltonian \( H = T + V \), where

\[
T = \sum_{\alpha, \beta} T_{\alpha \beta} c_{\alpha}^{\dagger} c_{\beta},
\]

and

\[
V = \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta} V_{\alpha \beta \gamma \delta} c_{\beta}^{\dagger} c_{\alpha}^{\dagger} c_{\gamma} c_{\delta}.
\]

Here the Greek letters \( \alpha, \beta, \) etc, label a set of single-particle basis states. This is a general Hamiltonian with a “two-body” interaction, meaning that the interaction term \( V \) describes scattering of two electrons. Assume \( V_{\alpha \beta \gamma \delta} = V_{\beta \alpha \delta \gamma} \). This symmetry reflects the fact that each term in the potential describes scattering from the two-particle state \( (\gamma, \delta) \) to \( (\alpha, \beta) \). This is clearly the same as scattering from \( (\delta, \gamma) \) to \( (\beta, \alpha) \).

To make the Hartree-Fock approximation, we define a noninteracting effective Hamiltonian \( H^{\text{eff}} = T + V^{\text{eff}} \), where

\[
V^{\text{eff}} = \sum_{\alpha \gamma} V_{\alpha \gamma} c_{\alpha}^{\dagger} c_{\gamma},
\]

and

\[
V_{\alpha \gamma}^{\text{eff}} = \sum_{\beta \delta} (c_{\beta}^{\dagger} c_{\delta}) (V_{\alpha \beta \gamma \delta} - V_{\alpha \beta \delta \gamma}).
\]

where the above expectation value is to be taken in an eigenstate of \( H^{\text{eff}} \), which we shall call \( |\psi_{0}^{\text{eff}}\rangle \) – usually this is taken to be the ground state.

Suppose we change the wavefunction slightly, writing \( |\psi\rangle = |\psi_{0}^{\text{eff}}\rangle + |\delta \psi\rangle \), where \( |\psi\rangle \) is still a Slater determinant wavefunction, but is otherwise arbitrary. It is a crucial point that we only vary the wavefunction within the space of Slater determinant wavefunctions! The variational energy \( E_{\text{var}} = \langle \psi_{0}^{\text{eff}} | H |\psi_{0}^{\text{eff}}\rangle \) is said to be at a stationary point (or to be stationary) if \( \delta E_{\text{var}} = 0 \) to first order in \( |\delta \psi\rangle \). If \( |\psi_{0}^{\text{eff}}\rangle \) minimizes the variational energy, then the stationary condition must be true – however there is no guarantee that finding a \( |\psi_{0}^{\text{eff}}\rangle \) satisfying the stationary condition gives a true minimum of the variational energy!

Below, you will show that \( E_{\text{var}} \) is at a stationary point if and only if \( |\psi_{0}^{\text{eff}}\rangle \) is an eigenstate of \( H^{\text{eff}} \) (it does not actually need to be the ground state).

Note that part (a) below is not part of the proof of this statement – its point is to show that the more abstract treatment of Hartree-Fock given here reduces to what we already did in class, for the electron gas.

(a) Suppose \( H \) is the Hamiltonian for the interacting electron gas, with general interaction potential \( V(r - r') \), and \( c_{\alpha} \to \psi_{\mathbf{k} \sigma} \). What are \( T_{\alpha \beta} \) and \( V_{\alpha \beta \gamma \delta} \) in this case? Show that \( V^{\text{eff}} \) as defined above reduces to the Hartree and exchange terms we wrote down in class.

(b) Let’s consider a state

\[
|\psi_{0}^{\text{eff}}\rangle = c_{1}^{\dagger} \cdots c_{N}^{\dagger} |0\rangle.
\]

Note that there is no loss of generality in making this assumption, since the basis in which we are working is completely arbitrary.

We now consider making a small change of \( |\psi_{0}^{\text{eff}}\rangle \), but we want the new wavefunction to still be a Slater determinant. We write

\[
|\psi\rangle = |\psi_{0}^{\text{eff}}\rangle + |\delta \psi\rangle = b_{1}^{\dagger} \cdots b_{N}^{\dagger} |0\rangle,
\]
where
\[ b^\dagger_\alpha = c^\dagger_\alpha + \sum_{\beta=1}^{\infty} \lambda_{\alpha\beta} c^\dagger_\beta, \] (7)
and the \( \lambda_{\alpha\beta} \) are taken to be infinitesimal parameters – we have made an arbitrary infinitesimal change of basis for the single particle states. The state \( |\psi\rangle \) is a general Slater determinant wavefunction infinitesimally close to \( |\psi_0^{\text{eff}}\rangle \). It is important to note that \( |\psi\rangle \) will not in general be normalized.

The variational energy is
\[ E_{\text{var}} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \langle \psi_0^{\text{eff}} | H | \psi_0^{\text{eff}} \rangle + \delta E_{\text{var}}. \] (8)
Calculate \( \delta E_{\text{var}} \), throwing away all terms of order \( \lambda_{\alpha\beta}^2 \) and higher. If you get stuck trying to find a nice form in which to put the result, part (c) below will give you some guidance.

(c) The stationary condition is that \( \delta E_{\text{var}} = 0 \) for an arbitrary infinitesimal variation. Therefore, the stationary condition is equivalent to the statement that the coefficient of each each \( \lambda_{\alpha\beta} \) vanishes in \( \delta E_{\text{var}} \). Setting these coefficients to zero, show that, for all pairs \( \alpha,\beta \),
\[ \langle \psi_0^{\text{eff}} | H | \psi_{\alpha\beta} \rangle = \langle \psi_0^{\text{eff}} | H | \psi_{\text{eff} 0} \rangle \langle \psi_0^{\text{eff}} | \psi_{\alpha\beta} \rangle, \] (9)
where the state \( |\psi_{\alpha\beta}\rangle \) is defined by
\[ |\psi_{\alpha\beta}\rangle = c^\dagger_\alpha c_\beta |\psi_0^{\text{eff}}\rangle. \] (10)

(d) Show that Eq. (9) is satisfied in the three cases: (1) \( \alpha = \beta \); (2) \( \alpha \leq N \) and \( \alpha \neq \beta \); and (3) \( \beta > N \).

(e) Now consider the case \( \alpha > N \) and \( \beta \leq N \). Show that \( \langle \psi_0^{\text{eff}} | \psi_{\alpha\beta} \rangle = 0 \), which implies
\[ \langle \psi_0^{\text{eff}} | H | \psi_{\alpha\beta} \rangle = 0. \] (11)
Show that
\[ \langle \psi_0^{\text{eff}} | H | \psi_{\alpha\beta} \rangle = H_{\alpha\beta}^{\text{eff}} = T_{\beta\alpha}^{\text{eff}} + V_{\alpha\beta}^{\text{eff}}, \] (12)
where \( V_{\alpha\beta}^{\text{eff}} \) is as defined above. Therefore, for \( \alpha > N \) and \( \beta \leq N \), we must have \( H_{\beta\alpha}^{\text{eff}} = 0 \) for the stationary condition to hold. Further, because \( H^{\text{eff}} \) is Hermitian, \( H_{\alpha\beta}^{\text{eff}} = 0 \) for the same values of \( \alpha \) and \( \beta \).

(f) Suppose that the single particle states \( \alpha \) are the single-particle eigenstates of \( H^{\text{eff}} \). Show that the stationary condition holds.

(g) Suppose the stationary condition holds. The result of part (e) implies that \( H_{\alpha\beta}^{\text{eff}} = H_{\beta\alpha}^{\text{eff}} = 0 \) for \( \alpha > N \) and \( \beta \leq N \). Given this result, show that if \( H_{\alpha\beta}^{\text{eff}} = c_\alpha \delta_{\alpha\beta} \) for \( \alpha, \beta \leq N \), then \( |\psi_0^{\text{eff}}\rangle \) is an eigenstate of \( H^{\text{eff}} \).

However, in general, \( H_{\alpha\beta}^{\text{eff}} \) is still not diagonal for \( \alpha, \beta \leq N \). But this is not a problem! We make a unitary transformation among the states \( \alpha = 1, \ldots, N \):
\[ d^\dagger_\alpha = \begin{cases} \sum_{\beta=1}^{N} D_{\alpha\beta} c^\dagger_\beta, & \alpha \leq N \\ c^\dagger_\alpha, & \alpha > N \end{cases}. \] (13)
Show that this unitary transformation does not change the state \( |\psi_0^{\text{eff}}\rangle \), except perhaps by an unimportant overall phase; that is, show that
\[ d^\dagger_1 \cdots d^\dagger_N |0\rangle = e^{i\phi} |\psi_0^{\text{eff}}\rangle, \] (14)
Furthermore, show that an appropriate choice of unitary transformation will put \( H_{\alpha\beta}^{\text{eff}} \) in the desired form for \( |\psi_0^{\text{eff}}\rangle \) to be an eigenstate.
2. Ashcroft and Mermin 17.5.

The Lindhard response function is just what we called $\chi(q)$ in class.

Some comments on the notation used in the book: The notation $(\psi_{k'}^0, V \psi_k^0)$ is the matrix element of the potential $V(r)$ between the states $\psi_k^0$ and $\psi_{k'}^0$, that is

$$
(\psi_{k'}^0, V \psi_k^0) = \int d^3r [\psi_{k'}^0(r)]^* V(r) \psi_k^0(r).
$$

(15)

The charge density $\rho(r) = -en(r)$ (i.e. it’s the electric charge density, not the number density). The electric potential $\phi(r)$ is related to $V(r)$ by $V(r) = -e\phi(r)$. Also, $f_k = f(\epsilon_k)$ – that is, it’s the Fermi function. Finally, note there is a typo in Eq. (17.80) in the book. It should read:

$$
\rho(r) = -e \sum_k f_k |\psi_k(r)|^2 = \rho^0(r) + \rho_{\text{ind}}(r).
$$

(16)