Chap 2   Mean field theory

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I. MEAN FIELD APPROXIMATION

A Hamiltonian with only quadratic operators is easy to solve. For example,

$$H = \sum_{\alpha\beta} h_{\alpha\beta} a_\alpha^\dagger a_\beta. \tag{1}$$

Then all we need to do is to diagonalize the matrix $h_{\alpha\beta}$,

$$h_{\alpha\beta} = (\mathbf{U}^\dagger \mathbf{E} \mathbf{U})_{\alpha\beta}, \tag{2}$$

where $\mathbf{E}$ is diagonal with diagonal matrix elements $\{\varepsilon_\alpha\}$, and $\mathbf{U}$ is unitary, such that

$$H = \sum_\alpha \varepsilon_\alpha \tilde{a}_\alpha^\dagger \tilde{a}_\alpha, \quad \tilde{a}_\alpha = \sum_\beta U_{\alpha\beta} a_\beta. \tag{3}$$

The eigenvalues of the system are $\sum_{\text{filled }\alpha} \varepsilon_\alpha$, with the corresponding eigenstates,

$$|\Phi\rangle = \prod_{\text{filled }\alpha} \tilde{a}_\alpha^\dagger |0\rangle. \tag{4}$$

A. Distinguishable particles

With the mean field approximation, we can approximate a Hamiltonian with quartic operators with one with quadratic operators. Let's first consider a system with 2 types of particles, a_α, b_α, and assume that the interaction between different types are important, whereas the interaction within the same type are negligible (see Ref. (1)). The Hamiltonian is

$$
\begin{aligned}
H =\ & \sum_\alpha \varepsilon_\alpha^a a_\alpha^\dagger a_\alpha + \sum_\alpha \varepsilon_\alpha^b b_\alpha^\dagger b_\alpha \quad \leftarrow \quad H_0 \\
& + \sum_{\alpha\alpha'\beta\beta'} V_{\alpha\beta\beta'\alpha'} a_\alpha^\dagger b_\beta^\dagger b_{\beta'} a_{\alpha'}.
\end{aligned}
\tag{5}
$$

The quantum average of $a_\alpha^\dagger a_{\alpha'}$ at finite temperature T is

$$\langle a_\alpha^\dagger a_{\alpha'} \rangle_T = \frac{1}{Z} \sum_{\{n\}} e^{-\beta E_{\{n\}}} \langle \{n\}| a_\alpha^\dagger a_{\alpha'} |\{n\}\rangle, \tag{6}$$

where $\{n\}$ is an abbreviation of occupation numbers $(n_1, n_2, \cdots)$, $E_{\{n\}}$ and $|\{n\}\rangle$ are the *exact* manybody eigenenergies and eigenstates of the Hamiltonian H, $\beta \equiv 1/k_B T$, and

$$Z = \sum_{\{n\}} e^{-\beta E_{\{n\}}} \tag{7}$$

is the **partition function**.

Most of the time, we are unable to obtain, either analytically or numerically, the exact manybody eigenenergies and eigenstates of an interacting Hamiltonian. Therefore, the average above cannot be evaluated accurately. In the mean field theory, one first decomposes the operators to two parts,

$$a_\alpha^\dagger a_{\alpha'} = \underbrace{\langle a_\alpha^\dagger a_{\alpha'} \rangle_T}_{\text{mean value}} + \underbrace{a_\alpha^\dagger a_{\alpha'} - \langle a_\alpha^\dagger a_{\alpha'} \rangle_T}_{\text{quantum fluctuation}}, \tag{8}$$

$$b_\beta^\dagger b_{\beta'} = \langle b_\beta^\dagger b_{\beta'} \rangle_T + b_\beta^\dagger b_{\beta'} - \langle b_\beta^\dagger b_{\beta'} \rangle_T. \tag{9}$$

There is no approximation being made so far. Substituting these to the Hamiltonian, one has

$$
\begin{aligned}
a_\alpha^\dagger b_\beta^\dagger b_{\beta'} a_{\alpha'} =\ & \langle a_\alpha^\dagger a_{\alpha'} \rangle_T b_\beta^\dagger b_{\beta'} + a_\alpha^\dagger a_{\alpha'} \langle b_\beta^\dagger b_{\beta'} \rangle_T \\
& - \langle a_\alpha^\dagger a_{\alpha'} \rangle_T \langle b_\beta^\dagger b_{\beta'} \rangle_T \\
& + (\text{fluctuation})^2.
\end{aligned}
\tag{10}
$$

Assuming the fluctuations in Eq. (10) are small compared to the mean values, then we can ignore the (fluctuation)^2 term above. This is called the **mean-field approximation** (MFA).

As a result,

$$
\begin{aligned}
H^{MF} =\ & H_0 - \sum_{\alpha\alpha'\beta\beta'} V_{\alpha\beta\beta'\alpha'} \langle a_\alpha^\dagger a_{\alpha'} \rangle_T \langle b_\beta^\dagger b_{\beta'} \rangle_T \\
& + \sum_{\alpha\alpha'\beta\beta'} V_{\alpha\beta\beta'\alpha'} \left(\langle a_\alpha^\dagger a_{\alpha'} \rangle_T b_\beta^\dagger b_{\beta'} + a_\alpha^\dagger a_{\alpha'} \langle b_\beta^\dagger b_{\beta'} \rangle_T \right).
\end{aligned}
\tag{11}
$$

The mean-field Hamiltonian now has only quadratic operators, similar to a free-particle Hamiltonian, and thus can be easily solved,

$$H^{MF} |\{n\}\rangle = E_{\{n\}}^{MF} |\{n\}\rangle. \tag{12}$$

However, the coefficients $\langle a_\alpha^\dagger a_{\alpha'} \rangle_T$ and $\langle b_\beta^\dagger b_{\beta'} \rangle_T$ in the Hamiltonian H^{MF} are unknown. Their values can be evaluated only after the eigenvalues $E_{\{n\}}^{MF}$ and eigenstates $|\{n\}\rangle$ have been obtained,

$$\langle a_\alpha^\dagger a_{\alpha'} \rangle_T = \frac{1}{Z} \sum_{\{n\}} e^{-\beta E_{\{n\}}^{MF}} \langle \{n\}| a_\alpha^\dagger a_{\alpha'} |\{n\}\rangle, \tag{13}$$

where $Z = \sum_{\{n\}} e^{-\beta E_{\{n\}}^{MF}}$.

If the quantum numbers α, β both range from 1 to N, then the number of unknown mean values $\langle \cdots \rangle_T$ are

$2N^2$. In numerical calculations, it's difficult to explore a parameter space with such a large dimension (say, if $N = 10$). So one often needs to start with an educated guess for rough distributions of $\langle a_\alpha^\dagger a_{\alpha'} \rangle_T$ and $\langle b_\beta^\dagger b_{\beta'} \rangle_T$, and plug them into the H^{MF} in Eq. (12) to get updated eigenvalues and eigenstates. This process is then iterated many times until we get self-consistent solutions of Eq. (12).

Because of Eq. (10) (without fluctuation),

$$\langle a_\alpha^\dagger b_\beta^\dagger b_{\beta'} a_{\alpha'} \rangle_T = \langle a_\alpha^\dagger a_{\alpha'} \rangle_T \langle b_\beta^\dagger b_{\beta'} \rangle_T. \tag{14}$$

That is, a-particle and b-particle are not correlated within the mean field theory. This is no longer true if the two sets of particles are indistinguishable.

B. Identical particles

Let us first consider *non-interacting*, identical particles. In this case, the operators $a_\alpha^\dagger, a_\alpha$ creates or annihilates a particle at state-α, without disturbing the particles at other single-particle states. When the quartic operator $a_\alpha^\dagger a_\beta^\dagger a_{\beta'} a_{\alpha'}$ acts on a manybody state $|n_1, n_2, \cdots\rangle$, it removes the particles at states α', β', then fills two particles at states α, β. For the following expectation value to be nonzero,

$$\langle n_1, n_2, \cdots | a_\alpha^\dagger a_\beta^\dagger a_{\beta'} a_{\alpha'} | n_1, n_2, \cdots \rangle, \tag{15}$$

one must have either $\alpha = \alpha', \beta = \beta'$, or $\alpha = \beta', \beta = \alpha'$. In the first case,

$$a_\alpha^\dagger a_\beta^\dagger a_\beta a_\alpha |n_1, n_2, \cdots\rangle = n_\alpha n_\beta |n_1, n_2, \cdots\rangle. \tag{16}$$

In the second case,

$$a_\alpha^\dagger a_\beta^\dagger a_\alpha a_\beta |n_1, n_2, \cdots\rangle = \pm n_\alpha n_\beta |n_1, n_2, \cdots\rangle. \tag{17}$$

The signs $\pm$ are for bosons/fermions. Therefore, in general,

$$\langle a_\alpha^\dagger a_\beta^\dagger a_{\beta'} a_{\alpha'} \rangle_{\{n\}} \tag{18}$$
$$= \delta_{\alpha\alpha'} \delta_{\beta\beta'} n_\alpha n_\beta \pm \delta_{\alpha\beta'} \delta_{\beta\alpha'} n_\alpha n_\beta$$
$$= \langle a_\alpha^\dagger a_{\alpha'} \rangle_{\{n\}} \langle a_\beta^\dagger a_{\beta'} \rangle_{\{n\}} \pm \langle a_\alpha^\dagger a_{\beta'} \rangle_{\{n\}} \langle a_\beta^\dagger a_{\alpha'} \rangle_{\{n\}},$$

where we have used $\langle \cdots \rangle_{\{n\}}$ to represent the expectation value in Eq. (15).

A remark: If the particles are interacting, the operators $a_\alpha^\dagger, a_\alpha$ would not only create or annihilate a particle at state-α, but also disturb particles at other single-particle states. As a result, after removing a particle from a manybody state $|\Psi\rangle$ with a_α, even if one adds a particle with $a_{\alpha'}^\dagger$ ($\alpha' \neq \alpha$), $a_\alpha^\dagger a_{\alpha'} |\Psi\rangle$ could still be non-zero.

The decomposition for non-interacting particles in Eq. (18) motivates us to consider the following MFA for interacting electrons (compare with Eq. (10); the subscript T is neglected from now on),

$$a_\alpha^\dagger a_\beta^\dagger a_{\beta'} a_{\alpha'} \tag{19}$$
$$\simeq \langle a_\alpha^\dagger a_{\alpha'} \rangle_T a_\beta^\dagger a_{\beta'} + a_\alpha^\dagger a_{\alpha'} \langle a_\beta^\dagger a_{\beta'} \rangle_T - \langle a_\alpha^\dagger a_{\alpha'} \rangle_T \langle a_\beta^\dagger a_{\beta'} \rangle_T$$
$$\pm \langle a_\alpha^\dagger a_{\beta'} \rangle_T a_\beta^\dagger a_{\alpha'} \pm a_\alpha^\dagger a_{\beta'} \langle a_\beta^\dagger a_{\alpha'} \rangle_T \mp \langle a_\alpha^\dagger a_{\beta'} \rangle_T \langle a_\beta^\dagger a_{\alpha'} \rangle_T.$$

After using the mean-field approximation, the Hamiltonian has only quadratic terms. It resembles a non-interacting Hamiltonian, and its eigenstates resemble non-interacting manybody states. Therefore,

$$\langle a_\alpha^\dagger a_{\alpha'} \rangle_T = \delta_{\alpha\alpha'} n_\alpha. \tag{20}$$

As an example, consider the following interaction between fermions,

$$V_{ee} = \frac{1}{2} \sum_{\alpha\alpha'\beta\beta'} V_{\alpha\beta\beta'\alpha'} a_\alpha^\dagger a_\beta^\dagger a_{\beta'} a_{\alpha'}. \tag{21}$$

The matrix elements are,

$$V_{\alpha\beta\beta'\alpha'} = \langle \alpha | \langle \beta | V^{(2)} | \alpha' \rangle | \beta' \rangle \tag{22}$$
$$= \int dv dv' \phi_\alpha^\dagger(\mathbf{r}) \phi_\beta^\dagger(\mathbf{r}') V^{(2)}(\mathbf{r} - \mathbf{r}') \phi_{\beta'}(\mathbf{r}') \phi_{\alpha'}(\mathbf{r}),$$

The single-particle state $\phi_\alpha(\mathbf{r}) = \varphi_{\tilde{\alpha}}(\mathbf{r}) \chi_s$ is composed of an orbital $\varphi_{\tilde{\alpha}}(\mathbf{r})$ and a spinor χ_s. They form a normalized and complete basis:

$$\langle \alpha | \alpha' \rangle = \int dv \, \varphi_{\tilde{\alpha}}^*(\mathbf{r}) \varphi_{\tilde{\alpha}'}(\mathbf{r}) \cdot \chi_s^\dagger \chi_{s'}$$
$$= \delta_{\tilde{\alpha}\tilde{\alpha}'} \delta_{ss'}, \tag{23}$$

and

$$\sum_\alpha \langle \mathbf{r} | \alpha \rangle \langle \alpha | \mathbf{r}' \rangle = \sum_{\tilde{\alpha}} \varphi_{\tilde{\alpha}}(\mathbf{r}) \varphi_{\tilde{\alpha}}^*(\mathbf{r}') \sum_s \chi_s \chi_s^\dagger \tag{24}$$
$$= \delta(\mathbf{r} - \mathbf{r}') \, \mathbf{1}_{2\times 2}.$$

The matrix elements has the following symmetry,

$$V_{\alpha\beta\beta'\alpha'} = V_{\beta\alpha\alpha'\beta'}. \tag{25}$$

With the help of this relation, one can show that the MFA gives (see Eq. (20))

$$V_{ee} \simeq \sum_{\alpha\beta} \left(V_{\alpha\beta\beta\alpha'} a_\alpha^\dagger a_{\alpha'} n_\beta - V_{\alpha\beta\alpha'\beta} a_\alpha^\dagger a_{\alpha'} n_\beta \right)$$
$$- \frac{1}{2} \sum_{\alpha\beta} \left(V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta} \right) n_\alpha n_\beta$$
$$= \sum_\alpha V_{\alpha\alpha'}^{MF} a_\alpha^\dagger a_{\alpha'} + \text{a number}, \tag{26}$$

where

$$V_{\alpha\alpha'}^{MF} \equiv \sum_\beta \left(V_{\alpha\beta\beta\alpha'} - V_{\alpha\beta\alpha'\beta} \right) n_\beta. \tag{27}$$

II. HARTREE-FOCK THEORY

A. HF energy

We now apply the mean-field approximation to electron gas. It is also called the **Hartree-Fock theory**. The single-particle energy is $h_0 = p^2/2m + V^{(1)}$, where $V^{(1)}(\mathbf{r})$ is an external potential. The Hartree-Fock (HF) Hamiltonian is, apart from a constant term,

$$H^{HF} = \sum_\alpha h_\alpha^0 a_\alpha^\dagger a_\alpha + \sum_\alpha \underbrace{\left[\sum_\beta (V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta})n_\beta\right]}_{V_{\alpha\alpha}^{HF}} a_\alpha^\dagger a_\alpha$$

$$= \sum_\alpha \varepsilon_\alpha^{HF} a_\alpha^\dagger a_\alpha, \tag{28}$$

where $h_\alpha^0 = \langle\alpha|h_0|\alpha\rangle$, $V_{\alpha\beta\beta'\alpha'}$ is defined in Eq. (22) with $V^{(2)}(\mathbf{r},\mathbf{r}') = e^2/|\mathbf{r} - \mathbf{r}'|$. We have chosen a basis that diagonalizes $V_{\alpha\alpha'}^{HF}$. The **HF eigenvalues** are,

$$\varepsilon_\alpha^{HF} = h_\alpha^0 + \sum_\beta (V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta})\, n_\beta, \tag{29}$$

which depend on the occupation numbers n_β of other states.

The total energy is a functional of the single-particle states,

$$E^{HF}[\{\phi_\alpha\}] = \sum_\alpha \varepsilon_\alpha^{HF} n_\alpha + \text{a number} \tag{30}$$

$$= \sum_\alpha h_\alpha^0 n_\alpha + \frac{1}{2}\sum_{\alpha\beta}(V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta})\, n_\alpha n_\beta.$$

We have put back the c-number in Eq. (26), so there is a factor of $1/2$ in front of the second summation. For the ground state at $T = 0$, the occupation numbers are either 0 or 1. Thus,

$$E_0^{HF}[\{\phi_\alpha\}] = \sum_{\text{filled }\alpha} h_\alpha^0 + \frac{1}{2}\sum_{\text{filled }\alpha,\beta}(V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta}). \tag{31}$$

B. HF state

The manybody ground state (at $T = 0$) of the HF theory is,

$$|\Psi^{HF}\rangle = \prod_{\text{filled }\alpha} a_\alpha^\dagger |0\rangle. \tag{32}$$

Under the coordinate representation, it is the Slater determinant,

$$\Psi_{\alpha_1,\alpha_2,\cdots}^{HF}(r_1, r_2, \cdots) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{\alpha_1}(r_1) & \phi_{\alpha_1}(r_2) & \cdots \\ \phi_{\alpha_2}(r_1) & \phi_{\alpha_2}(r_2) & \cdots \\ \vdots & & \ddots \end{vmatrix}. \tag{33}$$

1. choose initial $\{\phi_\alpha\}$, calculate $n(\vec{r}) = \sum_\alpha |\phi_\alpha(\vec{r})|^2$
$\downarrow$
2. calculate $V^H(\vec{r})$ and $V_{ss'}^F(\vec{r}, \vec{r}')$
$\downarrow$
3. solve $\left[-\dfrac{\hbar^2}{2m}\nabla^2 + V_{ion}(\vec{r}) + V^H(\vec{r})\right]\phi'_\alpha(\vec{r}) + \sum_{s'}\int dv\, V_{ss'}^F(\vec{r}, \vec{r}')\phi'_\alpha(\vec{r}') = \varepsilon_\alpha \phi'_\alpha(\vec{r})$
$\downarrow$
4. from $\{\phi'_\alpha\}$, calculate $n'(\vec{r}) = \sum_\alpha |\phi'_\alpha(\vec{r})|^2$
$\downarrow$
5. if $|n'(\vec{r}) - n(\vec{r})| < \delta$, then STOP.
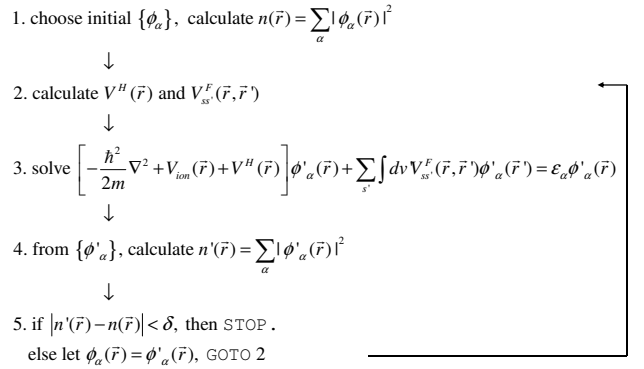   else let $\phi_\alpha(\vec{r}) = \phi'_\alpha(\vec{r})$, GOTO 2

FIG. 1 Self-consistent Hartree-Fock approximation

It has the same form as the determinant of *free fermions* in Chap 1, but the single-particle orbitals ϕ_α here are under the influence of HF potentials (see next sub-sec).

Note that if the HF state is used, then Eq. (18) is an identity, *not* an approximation. That is, the MFA has already been made when we write down the manybody wave function as a Slater determinant. In general, a manybody wave function could be a linear superposition of many Slater determinants.

Given

$$H = \sum_\alpha h_\alpha^0 a_\alpha^\dagger a_\alpha + \frac{1}{2}\sum_{\alpha\beta\beta'\alpha'} V_{\alpha\beta\beta'\alpha'} a_\alpha^\dagger a_\beta^\dagger a_{\beta'} a_{\alpha'}, \tag{34}$$

using the quantum state in either Eq. (32) (easy) or Eq. (33) (hard), one can directly show that,

$$\langle\Psi^{HF}|H|\Psi^{HF}\rangle = \sum_\alpha h_\alpha^0 + \frac{1}{2}\sum_{\alpha\beta}(V_{\alpha\beta\beta\alpha} - V_{\alpha\beta\alpha\beta}). \tag{35}$$

This is the same as the one in Eq. (31) obtained via the route of MFA.

C. HF equation

To evaluate the HF energy, we need to know the single-particle states $\{\phi_\alpha\}$ first, which are determined from the Schrödinger equation. One can get the Schrödinger equation for ϕ_α using the **method of variation**. That is, minimize $E_0^{HF}[\{\phi_\alpha\}]$ with respect to the variation of ϕ_α, while keeping ϕ_α normalized,

$$\delta E_0^{HF}[\{\phi_\alpha\}] = 0, \quad \langle\phi_\alpha|\phi_\alpha\rangle = 1 \text{ for } \forall\alpha. \tag{36}$$

Or,

$$\frac{\delta}{\delta\phi_{\alpha,s}^*}\left(E_0^{HF}[\{\phi_\alpha\}] - \sum_\alpha \lambda_\alpha(\langle\phi_\alpha|\phi_\alpha\rangle - 1)\right) = 0, \tag{37}$$

where λ_α is a **Lagrange multiplier**. It follows that,

$$h_0|\alpha\rangle + \sum_\beta \left(\langle\beta|V^{(2)}|\beta\rangle|\alpha\rangle - \langle\beta|V^{(2)}|\alpha\rangle|\beta\rangle\right) = \lambda_\alpha|\alpha\rangle. \tag{38}$$

This is called the **Hartree-Fock equation**. Basically, one just strip off the bra state $\langle\alpha|$ from the expression of energy in Eq. (35). If $T \neq 0$, then the second term needs to be multiplied by the occupation number n_β.

After multiplying this equation with a bra state $\langle\alpha|$, one can see that the Lagrange multiplier λ_α is nothing but the HF eigenvalue ε_α^{HF} in Eq. (29). This equation determines the HF eigenvalues and eigenstates, but we also need the latter to determine the interaction potential in the HF equation. Therefore, iteration procedure is required to reach self-consistent solutions (see Fig. 2 and below).

In coordinate representation, the HF equation becomes,

$$
\begin{aligned}
h_0\phi_\alpha(\mathbf{r}) &+ \sum_\beta \int dv' V^{(2)}(\mathbf{r}-\mathbf{r}') \underbrace{\phi_\beta^\dagger(\mathbf{r}')\phi_\beta(\mathbf{r}')}_{n_\beta(\mathbf{r}')} \phi_\alpha(\mathbf{r}) \\
&- \sum_\beta \int dv' V^{(2)}(\mathbf{r}-\mathbf{r}')\phi_\beta^\dagger(\mathbf{r}')\phi_\alpha(\mathbf{r}')\phi_\beta(\mathbf{r}) \\
&= \varepsilon_\alpha^{HF}\phi_\alpha(\mathbf{r}).
\end{aligned}
\tag{39}
$$

Recall that $\phi_\alpha(\mathbf{r}) = \varphi_{\tilde{\alpha}}(\mathbf{r})\chi_s$, and

$$
\chi_s^\dagger \chi_{s'} = \delta_{ss'}.
\tag{40}
$$

Define the **Hartree potential** and the **Fock potential** as,

$$
\bar{V}^H(\mathbf{r}) = \sum_\beta \int dv' V^{(2)}(\mathbf{r}-\mathbf{r}')n_\beta(\mathbf{r}'),
\tag{41}
$$

$$
\bar{V}_{ss'}^F(\mathbf{r},\mathbf{r}') = \sum_{\tilde{\beta}} V^{(2)}(\mathbf{r}-\mathbf{r}')\phi_{\tilde{\beta},s'}^\dagger(\mathbf{r}')\phi_{\tilde{\beta},s}(\mathbf{r}).
\tag{42}
$$

Because of Eq. (40), the Fock potential has a factor of $\delta_{ss'}$. Now, the HF equation can be written as

$$
\begin{aligned}
\left[h_0 + \bar{V}^H(\mathbf{r})\right]\phi_{\tilde{\alpha},s}(\mathbf{r}) &- \sum_{s'} \int dv' \bar{V}_{ss'}^F(\mathbf{r},\mathbf{r}')\phi_{\tilde{\alpha},s'}(\mathbf{r}') \\
&= \varepsilon_\alpha^{HF}\phi_{\tilde{\alpha},s}(\mathbf{r}).
\end{aligned}
\tag{43}
$$

The Hartree (or direct) potential is nothing but the classical electrostatic potential. However, the Fock (or exchange) potential does not have a classical counterpart. It is spin-dependent because of the factor $\delta_{ss'}$: *the exchange potential exists only between electrons with parallel spins*. Furthermore, it is non-local, which makes the HF equation difficult to solve.

III. HF THEORY OF UNIFORM ELECTRON GAS

A. HF energy

Let's consider N interacting electrons in a box with volume V_0. There is an uniform positive background charge density in the box, so that the whole box carries no net charges. There is no external potential, so

$V^{(1)} = 0$, and the single-particle states are plane waves $|\alpha\rangle = |\mathbf{k},s\rangle$.

Note: This is not self-evident. But you can check that when $V^{(1)} = 0$, plane waves indeed are self-consistent solutions of the HF equation.

The HF Hamiltonian is,

$$
H^{HF} = \sum_{ks}\left(\frac{\hbar^2 k^2}{2m} + V_{ks,ks}^{HF}\right)a_{ks}^\dagger a_{ks},
\tag{44}
$$

where

$$
\begin{aligned}
V_{ks,ks}^{HF} &= \sum_{k's'}(V_{ks,k's',k's',ks} - V_{ks,k's',ks,k's'})n_{k's}\\
&\equiv V_{ks,ks}^H - V_{ks,ks}^F.
\end{aligned}
\tag{45}
$$

Recall that, for example,

$$
\begin{aligned}
&V_{ks,k's',k's',ks}\\
&= \int dv\, dv'\, \phi_{ks}^\dagger(\mathbf{r})\phi_{k's'}^\dagger(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_{k's'}(\mathbf{r}')\phi_{ks}(\mathbf{r}),
\end{aligned}
\tag{46}
$$

and $\phi_{ks}(\mathbf{r}) = \frac{1}{\sqrt{V_0}}e^{i\mathbf{k}\cdot\mathbf{r}}\chi_s$. Therefore, the Hartree energy of an electron is,

$$
\begin{aligned}
V_{ks,ks}^H &= \sum_{k's'}\frac{1}{V_0^2}\int dv\, dv'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}n_{k's'}\\
&= \int dv\, dv'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\frac{1}{V_0}\frac{N}{V_0}.
\end{aligned}
\tag{47}
$$

This is the electrostatic energy between one negative charge and the other negative charges. The total Hartree energy for all *negative* charges is $V_{ks,ks}^H$ times N, and divided by 2 to avoid double counting.

The *positive* charges also have the same repulsive (positive) self-energy. In addition, there is an attractive (negative) energy between positive and negative charges that would cancel with the two energies above (since it is unnecessary to be divide it by 2 to avoid the double counting). So the classical electrostatic energy of the whole box is zero, as it should be, since the whole box is electrically neutral.

On the other hand, the Fock energy of an electron is,

$$
\begin{aligned}
V_{ks,ks}^F &= \sum_{k's'}\delta_{ss'}\frac{e^2}{V_0^2}\int dv\, dv'\,\frac{e^{i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|}n_{k's'}\\
&= \frac{1}{V_0}\sum_{k'}\underbrace{\frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2}}_{V^{(2)}(\mathbf{k}-\mathbf{k}')}n_{k's},
\end{aligned}
\tag{48}
$$

where $V^{(2)}(\mathbf{k} - \mathbf{k}')$ is the Fourier transform of the Coulomb potential energy $V^{(2)}(\mathbf{r} - \mathbf{r}')$. For the ground state at $T = 0$, which is a Fermi sphere with radius k_F, $n_{k's}$ is $1/0$ inside/outside of the sphere. So the energy for an electron is

$$
\varepsilon_{ks} = \frac{\hbar^2 k^2}{2m} - \int_{k'\leq k_F}\frac{d^3k'}{(2\pi)^3}\frac{4\pi e^2}{|\mathbf{k}-\mathbf{k}'|^2}.
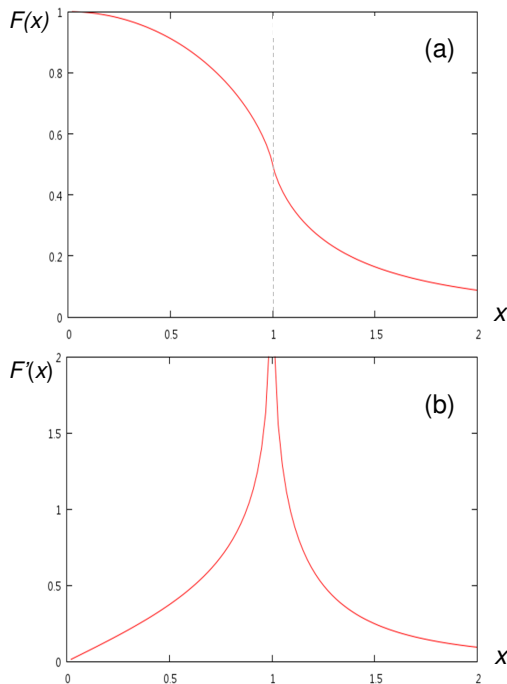\tag{49}
$$

FIG. 2 (a) The Lindhard function $F(x)$. (b) Derivative of the Lindhard function, $F'(x)$, shows a logarithmic divergence at $x = 1$.
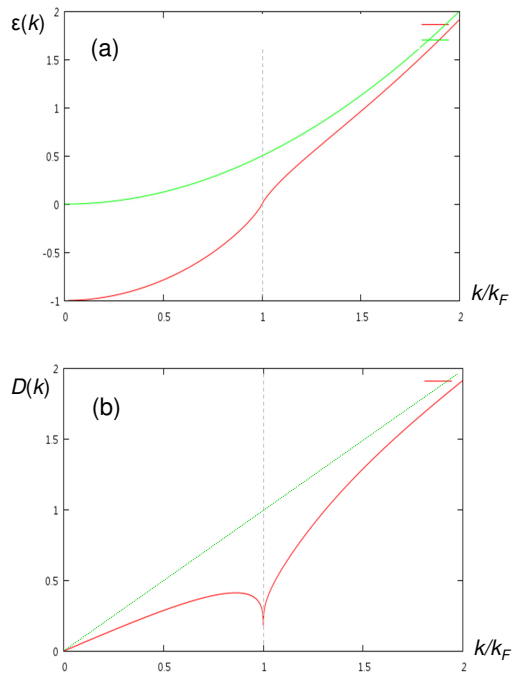

FIG. 3 (a) Free-particle energy (green) vs Hartree-Fock energy (red) of an electron. (b) Density of states for a free electron (green) and a Hartree-Fock electron (red).

The integral can be evaluated as,

$$
\int_{k \leq k_F} \frac{d^3 k}{(2\pi)^3} \frac{4\pi e^2}{|\mathbf{k} - \mathbf{k}'|^2}
$$

$$
= \frac{e^2}{\pi} \int_0^{k_F} \int_{-1}^1 \frac{k'^2 dk' d\cos\theta}{k^2 + k'^2 - 2kk'\cos\theta}
$$

$$
= -\frac{e^2}{k\pi} \int_0^{k_F} k' dk' \left(\ln|k - k'| - \ln|k + k'| \right),
$$

$$
= -\frac{2e^2}{\pi} k_F F(k/k_F), \tag{50}
$$

where

$$
F(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln\left| \frac{1 + x}{1 - x} \right| \tag{51}
$$

is called the **Lindhard function** (see Fig. 2). Thus,

$$
\varepsilon_{ks} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F F\left(\frac{k}{k_F} \right). \tag{52}
$$

The energy of an electron is shown in Fig. 3.

The total energy is,

$$
E^{HF} = \sum_{ks} \frac{\hbar^2 k^2}{2m} n_{ks} + \frac{1}{2} \sum_{ks} V_{ks,ks}^{HF} n_{ks}
$$

$$
= \sum_{ks} \frac{\hbar^2 k^2}{2m} n_{ks} - \frac{1}{2} \frac{e^2}{V_0} \sum_{kqs} \frac{4\pi}{q^2} n_{ks} n_{k+q,s}. \tag{53}
$$

For the ground state at $T = 0$, it can be shown that (e.g., see p. 91 of Ref. (3)),

$$
\frac{E^{HF}}{V_0} = \frac{1}{5\pi^2} \frac{\hbar^2 k_F^5}{2m} - \frac{e^2}{2} \frac{k_F^4}{2\pi^3}, \tag{54}
$$

in which we have used

$$
2 \frac{\frac{4}{3}\pi k_F^3}{(2\pi)^3} = \frac{N}{V_0}. \tag{55}
$$

Define the inter-particle distance r_0 via

$$
\frac{4}{3}\pi r_0^3 N = V_0, \text{ and } r_s \equiv r_0/a_0, \tag{56}
$$

$a_0 = \hbar^2/me^2$ is the Bohr radius, and

$$
1 \text{ Ry} \equiv \frac{e^2}{2a_0} \simeq 13.6 \text{ eV}. \tag{57}
$$

In these units, the energy can be written as,

$$
\frac{E^{HF}}{N} = \frac{e^2}{2a_0} \left[\frac{3}{5}(k_F a_0)^2 - \frac{3}{2\pi}(k_F a_0) \right]
$$

$$
\simeq \frac{2.21}{r_s^2} - \frac{0.961}{r_s} \text{ (in units of Ry).} \tag{58}
$$

The total energy is positive if $r_s \lesssim 2$, which means that the electron gas is unstable. It becomes negative at larger spacing, thanks to the Fock energy.

Some comments are in order:

1. At high density, the kinetic energy is more important

than the interaction energy. On the contrary, at lower density, the interaction energy is more important than the kinetic energy. This is opposite to the intuition based on a gas of classical charges.

2. For alkali metals Li, Na, K, the inter-particle spacing $r_s \simeq 3.25, 3.93, 4.86$. In this range, the second term is larger than the first term. This means that the higher order interaction terms being neglected in the MFA could be important.

3. In 1957, Gell-mann and Brueckner used perturbation theory to find out higher order terms,

$$\frac{E^{HF}}{N} \simeq \frac{2.21}{r_s^2} - \frac{0.961}{r_s} + \underbrace{0.062 \ln r_s - 0.096 + O(r_s)}_{\text{correlation energy}}. \quad (59)$$

The correction to the HF energy is called the **correlation energy**, or "stupidity energy" in Feynman's language, since its magnitude is proportional to our own stupidity.

B. Density of states

The density of states (DOS) $D(\varepsilon)$ is defined as,

$$D(\varepsilon) = 2 \int \frac{d^3 k}{(2\pi)^3} \delta(\varepsilon - \varepsilon_k). \quad (60)$$

Using the spherical coordinate, $d^3 k = 4\pi k^2 dk$, we have

$$\begin{aligned} D(\varepsilon) &= \frac{1}{\pi^2} \int k^2 \delta(\varepsilon - \varepsilon_k) \frac{dk}{d\varepsilon} d\varepsilon \\ &= \frac{1}{\pi^2} \frac{k^2}{d\varepsilon_k/dk}. \end{aligned} \quad (61)$$

In Fig. 3 (b), we plot the DOS as a function of k (instead of ε). Note that in the HF theory, $d\varepsilon_k/dk$ diverges at $k = k_F$, because of the singularity in Fig. 2 (b). As a result, the DOS vanishes at $k = k_F$ (or Fermi energy), which does not fit reality.

Quantities such as electric conductivity and specific heat are proportional to the DOS at Fermi energy. Thus, HFA gives erroneous result regarding these quantities.

C. Pair distribution function

The density operator for particles with spin-s is (see Sec IV.A of Chap 1),

$$\rho_s(\mathbf{r}) = \sum_i \delta(\mathbf{r}_i - \mathbf{r}) \delta_{s_i s}, \quad (62)$$

and the particle density $n_s(\mathbf{r}) = \langle \Psi | \rho_s(\mathbf{r}) | \Psi \rangle$. The **pair distribution function** gives the conditional probability of finding an electron with spin s' at $\mathbf{r}'$, when there is already an electron with spin s at $\mathbf{r}$. It is defined as,

$$g_{ss'}(\mathbf{r}, \mathbf{r}') = \frac{\langle \Psi | \sum_{i,j;i \neq j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \delta_{s_i s} \delta_{s_j s'} | \Psi \rangle}{n_s(\mathbf{r}) n_{s'}(\mathbf{r}')}. \quad (63)$$

The summation in the numerator can also be written as,

$$\sum_{i,j;i \neq j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \delta_{s_i s} \delta_{s_j s'}$$
$$= \rho_s(\mathbf{r}) \rho_{s'}(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') \delta_{ss'} \rho_s(\mathbf{r}). \quad (64)$$

At large separation $|\mathbf{r} - \mathbf{r}'|$, the numerator approaches $n_s(\mathbf{r}) n_{s'}(\mathbf{r}')$, and $g_{ss'}(\mathbf{r}, \mathbf{r}')$ is normalized such that it approaches one at large separation.

Note: In the discussion here, we only consider cases with $T = 0$. If $T \neq 0$, then the pair distribution function needs be defined in terms of density matrix.

In the language of second quantization, the particle-density operator is,

$$\rho_s(\mathbf{r}) = \psi_s^\dagger(\mathbf{r}) \psi_s(\mathbf{r}), \quad (65)$$

and (see Sec IV.B of Chap 1)

$$\rho_s(\mathbf{r}) \rho_{s'}(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') \delta_{ss'} \rho_s(\mathbf{r}) = \psi_s^\dagger(\mathbf{r}) \psi_{s'}^\dagger(\mathbf{r}') \psi_{s'}(\mathbf{r}') \psi_s(\mathbf{r}). \quad (66)$$

Therefore, the pair distribution function can also be written as,

$$g_{ss'}(\mathbf{r}, \mathbf{r}') = \frac{\langle \Psi | \psi_s^\dagger(\mathbf{r}) \psi_{s'}^\dagger(\mathbf{r}') \psi_{s'}(\mathbf{r}') \psi_s(\mathbf{r}) | \Psi \rangle}{n_s(\mathbf{r}) n_{s'}(\mathbf{r}')}. \quad (67)$$

To calculate it, first expand

$$\psi_s(\mathbf{r}) = \sum_{\tilde{\alpha}} \varphi_{\tilde{\alpha}}(\mathbf{r}) a_{\tilde{\alpha} s}. \quad (68)$$

The Fermi sea is filled by electrons in states $(\tilde{\alpha}, s)$. With the help of

$$\langle \Psi^{HF} | a_{\tilde{\alpha}_1 s}^\dagger a_{\tilde{\alpha}_2 s'}^\dagger a_{\tilde{\alpha}_3 s'} a_{\tilde{\alpha}_4 s} | \Psi^{HF} \rangle$$
$$= \delta_{\tilde{\alpha}_1 \tilde{\alpha}_4} \delta_{\tilde{\alpha}_2 \tilde{\alpha}_3} - \delta_{\tilde{\alpha}_1 \tilde{\alpha}_3} \delta_{\tilde{\alpha}_2 \tilde{\alpha}_4} \delta_{ss'}, \quad (69)$$

in which states $\tilde{\alpha}_1, \tilde{\alpha}_2$ need be filled, it follows that,

$$\begin{aligned} &g_{ss'}^{HF}(\mathbf{r}, \mathbf{r}') \\ &= \frac{\sum_{\text{filled } \tilde{\alpha} \tilde{\alpha}'} [n_{\tilde{\alpha} s}(\mathbf{r}) n_{\tilde{\alpha}' s'}(\mathbf{r}') - \delta_{ss'} \varphi_{\tilde{\alpha}}^*(\mathbf{r}) \varphi_{\tilde{\alpha}'}^*(\mathbf{r}') \varphi_{\tilde{\alpha}}(\mathbf{r}') \varphi_{\tilde{\alpha}'}(\mathbf{r})]}{n_s(\mathbf{r}) n_{s'}(\mathbf{r}')} \\ &= 1 - \delta_{ss'} \frac{\left| \sum_{\text{filled } \tilde{\alpha}} \varphi_{\tilde{\alpha}}^*(\mathbf{r}) \varphi_{\tilde{\alpha}}(\mathbf{r}') \right|^2}{n_s(\mathbf{r}) n_{s'}(\mathbf{r}')}, \end{aligned} \quad (70)$$

in which $n_s(\mathbf{r}) = \sum_{\tilde{\alpha}} n_{\tilde{\alpha} s}(\mathbf{r})$.

For the uniform electron gas, $\varphi_{\tilde{\alpha}}(\mathbf{r}) = \frac{1}{\sqrt{V_0}} e^{i\mathbf{k} \cdot \mathbf{r}}$, and the pair distribution function for anti-parallel spins is,

$$g_{\uparrow\downarrow}^{HF}(\mathbf{r}, \mathbf{r}') = 1. \quad (71)$$

For parallel spins, it becomes ($n_s = N/2V_0$)

$$\begin{aligned} g_{\uparrow\uparrow}^{HF}(\mathbf{r}, \mathbf{r}') &= 1 - \left| \frac{2}{N} \sum_{k \leq k_F} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \right|^2 \\ &= 1 - \left[3 \frac{\sin(k_F R) - k_F R \cos(k_F R)}{k_F^3 R^3} \right]^2 \quad (72) \\ \text{or} &= 1 - \left[\frac{3}{k_F R} j_1(k_F R) \right]^2, \quad (73) \end{aligned}$$
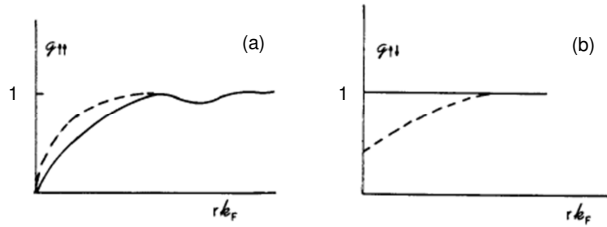
FIG. 4 Pair distribution functions for two electrons with same spin (a) and opposite spins (b). If the effect of correlation is included, then we'll get the dashed lines.

where $R \equiv |\mathbf{r} - \mathbf{r}'|$, and $j_\mu(x) = \sqrt{\frac{\pi}{2x}} J_{\mu+1/2}(x)$ is the spherical Bessel function. Qualitative plot of the pair distribution function can be found in Fig. 4. The hole near $R = 0$ is called an exchange hole, or an **exchange-correlation** (xc) **hole** if the correlation has been included.

It is left as an exercise to show that the $g_{ss'}^{HF}$ for an uniform electron gas in 2D and 1D are,

$$2D \quad g_{ss'}^{HF}(R) = 1 - \delta_{ss'}\left[2\frac{J_1(k_F R)}{k_F R}\right]^2, \quad (74)$$

$$1D \quad g_{ss'}^{HF}(R) = 1 - \delta_{ss'}\left[\frac{\sin(k_F R)}{k_F R}\right]^2, \quad (75)$$

in which J_1 is the Bessel function. See App. 4 of Ref. (2) for more details.

D. Exchange energy

In terms of the Hartree potential and the Fock potential in Eqs. (41),(42), the Hartree-Fock potential energy in Eq. (30) can be written as,

$$
\begin{aligned}
V^{HF} &= \frac{1}{2}\sum_\alpha \int dv \bar{V}^H(\mathbf{r}) n_\alpha(\mathbf{r}) \\
&\quad - \frac{1}{2}\sum_{\tilde{\alpha}ss'} \int dv dv' \bar{V}_{ss'}^F(\mathbf{r},\mathbf{r}')\phi_{\tilde{\alpha}s}^*(\mathbf{r})\phi_{\tilde{\alpha}s'}(\mathbf{r}') \quad (76) \\
&= \frac{e^2}{2}\int dv dv' \sum_{ss'} \frac{n_{s'}(\mathbf{r}')n_s(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}g_{ss'}^{HF}(\mathbf{r},\mathbf{r}'), \quad (77)
\end{aligned}
$$

in which $g_{ss'}^{HF}$ is given in Eq. (70). The connection between HF potential energy and pair distribution function becomes apparent when one writes

$$V^{HF} = \quad (78)$$
$$\frac{e^2}{2}\int dv dv' \sum_{ss'} \frac{\langle \Psi^{HF}|\psi_s^\dagger(\mathbf{r})\psi_{s'}^\dagger(\mathbf{r}')\psi_{s'}(\mathbf{r}')\psi_s(\mathbf{r})|\Psi^{HF}\rangle}{|\mathbf{r}-\mathbf{r}'|},$$

and uses Eq. (67).

Define spin-averaged distribution $g^{HF}(r) = (g_{\uparrow\downarrow}^{HF} + g_{\uparrow\uparrow}^{HF})/2$. With the help of the identity (G+R, 5th ed.

p. 715),

$$\int_0^\infty J_\mu^2(\alpha x)x^{-\nu}dx, \text{ with } 2\mu+1 > \nu > 0, \alpha > 0$$

$$= \frac{\alpha^{\nu-1}\Gamma(\nu)\Gamma\left(\mu - \frac{\nu}{2} + \frac{1}{2}\right)}{2^\nu \Gamma\left(\frac{\nu+1}{2}\right)\Gamma\left(\mu + \frac{\nu+1}{2}\right)\Gamma\left(\frac{\nu+1}{2}\right)}, \quad (79)$$

one can show that,

$$\int dv[1 - g^{HF}(r)] = \frac{V_0}{N}. \quad (80)$$

That is, the volume of an exchange hole equals the average volume of one electron. Furthermore, the Coulomb energy of an exchange hole is actually equal to the exchange energy in Eq. (58),

$$\frac{E_{ex}}{N} = \frac{1}{2}\int dv \frac{e\left[1 - g^{HF}(r)\right]}{r}\left(\frac{-e}{V_0}\right) \quad (81)$$

$$= -\frac{3e^2}{4\pi}k_F. \quad (82)$$

IV. VALIDITY OF THE MEAN FIELD RESULT

The result from a mean-field theory, even if self-consistent, could still be totally wrong. In the calculation above, we start from plane waves, which are self-consistent solutions to the HF equation (you're welcomed to check this). However, in reality, within certain range of parameters, the uniform electron gas could spontaneously develop charge density wave (CDW) or spin density wave (SDW), if one of them has lower ground state energy. In a more complete investigation, one can consider such possibilities, start with non-plane waves, and calculate the ground state energies in the CDW phase and SDW phase. The phase with the lowest energy is more likely to be the actual phase. But there is no guarantee, since there could be other possibilities not considered (such as the Wigner crystal phase). Despite this drawback, the mean-field theory could be very useful when the mean-field phase is close to the phase in reality.

Exercise:
1. The Hartree-Fock energy of an electron gas is,

$$E^{HF} = \sum_\alpha \left(T_\alpha^{(1)} + \frac{1}{2}V_{\alpha\alpha}^{HF}\right)n_\alpha. \quad (83)$$

(a) Show that it takes energy ε_γ to add an electron to a $|\gamma\rangle$-state outside the Fermi sphere (assuming the other electrons are *not* affected), where ε_γ is the HF eigenvalue. (b) Show that it takes energy ε_δ to remove an electron from a $|\delta\rangle$-state inside the Fermi sea (assuming the other

electrons are not affected).

(c) To create an electron-hole pair, one needs

$$\Delta E^{HF} = \varepsilon_\gamma - \varepsilon_\delta - \Delta_{\gamma\delta}. \tag{84}$$

Show that $\Delta_{\gamma\delta} = V_{\gamma\delta\delta\gamma} - V_{\gamma\delta\gamma\delta}$. The HF solution is stable if ΔE^{HF} is positive.

Note: In reality, the other electrons could be affected by the addition or removal of one electron, especially for small systems.

2. Calculate the pair distribution functions in 3D, 2D, and 1D (Eqs. (73), (74), and (75)).

3. Instead of using $|\Psi^{HF}\rangle = \prod_{\mathbf{k}s} a^\dagger_{\mathbf{k}s}|0\rangle$, one can use a mean-field state with spin density wave (Overhauser, 1962). Its one-particle state is,

$$\phi_\alpha(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V_0}} \begin{pmatrix} \cos\frac{\theta_{\mathbf{k}}}{2} \\ \sin\frac{\theta_{\mathbf{k}}}{2} e^{i\mathbf{Q}\cdot\mathbf{r}} \end{pmatrix}, \tag{85}$$

in which $\theta_{\mathbf{k}}$ is independent of $\mathbf{r}$, and $\mathbf{Q}$ is a constant vector.

(a) Find out the orientation of spin $\langle\boldsymbol{\sigma}\rangle$ using the one-particle state. Describe and draw (qualitatively) the spin configuration in space.

(b) In the language of second quantization, the many-body HF state becomes,

$$|\Psi^{HF}_{\mathbf{Q}}\rangle = \prod_{\text{filled } \mathbf{k}} \left(\cos\frac{\theta_{\mathbf{k}}}{2} a^\dagger_{\mathbf{k}\uparrow} + \sin\frac{\theta_{\mathbf{k}}}{2} a^\dagger_{\mathbf{k}+\mathbf{Q}\downarrow} \right)|0\rangle. \tag{86}$$

Starting from

$$\begin{aligned}
H &= \sum_{\mathbf{k}s} \frac{\hbar^2 k^2}{2m} a^\dagger_{\mathbf{k}s} a_{\mathbf{k}s} \\
&+ \frac{1}{2V_0} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} \sum_{ss'} V(\mathbf{q}) a^\dagger_{\mathbf{k}+\mathbf{q}s} a^\dagger_{\mathbf{k}'-\mathbf{q}s'} a_{\mathbf{k}'s'} a_{\mathbf{k}s}, \tag{87}
\end{aligned}$$

one can get its mean-field Hamiltonian,

$$\begin{aligned}
H &= \sum_{\mathbf{k}} \left(\frac{\hbar^2 k^2}{2m} - h_1(\mathbf{k}) \right) a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}\uparrow} \\
&+ \sum_{\mathbf{k}} \left(\frac{\hbar^2 |\mathbf{k}+\mathbf{Q}|^2}{2m} - h_2(\mathbf{k}) \right) a^\dagger_{\mathbf{k}+\mathbf{Q}\downarrow} a_{\mathbf{k}+\mathbf{Q}\downarrow} \\
&- \sum_{\mathbf{k}} g(\mathbf{k}) a^\dagger_{\mathbf{k}+\mathbf{Q}\downarrow} a_{\mathbf{k}\uparrow} - \sum_{\mathbf{k}} g(\mathbf{k}) a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}+\mathbf{Q}\downarrow}. \tag{88}
\end{aligned}$$

Find out the functions $h_1(\mathbf{k}), h_2(\mathbf{k})$ and $g(\mathbf{k})$.

References

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