Hartree-Fock Approximation

Hamiltonian for interacting electrons in a solid can be written in second quantized for as

$$\hat{H}_e = \sum_{\nu,\lambda} \langle \nu | \hat{H}_1 | \lambda \rangle a_\nu^\dagger a_\lambda + \frac{1}{2} \sum_{\nu\lambda\alpha\beta} \langle \nu\ \lambda | \frac{e^2}{r_1 - r_2} |\alpha\ \beta\rangle\ a_\nu^\dagger a_\lambda^\dagger a_\beta a_\alpha \tag{1}$$

Where, $\hat{H}_1 = \frac{\hat{p}_1^2}{2m} + \hat{v}(r_1)$ and $\alpha, \beta, \nu, \lambda$ denote single-particle orbitals. The first term of equation (1) represent one body problem which cab be solved by one creation annihilation operator pair, and the second term represent two-body problem which can be solved by using two creation and two annihilation operator pair.

Noninteracting Limit

In the noninteracting electron problem, all the momentum states up to Fermi level are doubly occupied. Therefore we can represent the ground-state wave function for the filled Fermi sea as

$$|\psi_0\rangle = |p_0 \uparrow, p_0 \downarrow, \cdots, p_F \uparrow, p_F \downarrow\rangle = a_{p_0\uparrow}^\dagger a_{p_0\downarrow}^\dagger \cdots a_{p_F\uparrow}^\dagger a_{p_F\downarrow}^\dagger |0\rangle \tag{2}$$

We can compute the occupancy in the p^{th} level by acting on the ground-state wave function with the number operator $\hat{n}_{p\sigma}$ for a momentum state p:

$$\hat{n}_{p\sigma} |\psi_0\rangle = n_{p\sigma} |\psi_0\rangle \tag{3}$$

The expectation value of kinetic energy is given by

$$\langle \hat{T} \rangle = \langle \psi_0 | \sum_{p,\sigma} \frac{p^2}{2m} \hat{n}_{p\sigma} |\psi_0\rangle$$

$$= \langle \psi_0 | \hat{n}_{p\sigma} |\psi_0\rangle \sum_{p=0}^{p_F} \frac{p^2}{2m}$$

$$\langle \hat{T} \rangle = 2 \sum_{p=0}^{p_F} \frac{p^2}{2m} \tag{4}$$

$$\sum_{p=0}^{p_F} \to \frac{V}{(2\pi)^3} \frac{1}{\hbar^3} \int_0^{p_F} 4\pi p^2\, dp$$

Therefore,

$$\langle \hat{T} \rangle = 2 \frac{V}{(2\pi)^3} \frac{1}{\hbar^3} \int_0^{p_F} 4\pi p^2\, dp\, \frac{p^2}{2m} = 2 \frac{V}{(2\pi)^3} \frac{1}{\hbar^3} 4\pi \frac{1}{2m} \int_0^{p_F} p^4\, dp$$

$$= 2 \frac{V}{(2\pi)^3} \frac{1}{\hbar^3} 4\pi \frac{1}{2m} \frac{p_F^5}{5}$$

$$= \frac{3}{5} \frac{p_F^2}{2m} N$$

$$\boxed{\langle \hat{T} \rangle = \frac{3}{5}\frac{p_F^2}{2m}N} \tag{5}$$

where

$$N = \frac{V}{3\pi^2}\frac{p_F^3}{\hbar^3} = \frac{V}{3\pi^2}k_F^3$$

The expectation value of the potential energy due to nuclei (ions) is evaluated by the expression of the form

$$\langle \psi_0 | a^\dagger_{p\sigma} a_{p'\sigma} | \psi_0 \rangle$$

Since all the state with $p < p_F$ are full,

$$a^\dagger_{p\sigma} |\psi_0\rangle = 0; \text{ for } p < p_F$$

Similarly,

$$a_{p'\sigma} |\psi_0\rangle = 0; \text{ for } p' > p_F$$

When $a^\dagger_{p\sigma} a_{p'\sigma}$ acts on $|\psi_0\rangle$, a new state is created that differs from ψ_0 by at most two states. The overlap of this state with $|\psi_0\rangle$ will be zero because of the orthogonality of the momentum eigenstates unless $p = p'$, $\sigma = \sigma'$ Therefore,

$$\langle \psi_0 | a^\dagger_{p\sigma} a_{p'\sigma} | \psi_0 \rangle = \delta_{pp'} n_{p\sigma} \tag{6}$$

As a consequence,

$$\langle \hat{V}_{ion} \rangle = \sum_{p,\sigma} n_{p\sigma} V_{ion}(0) \tag{7}$$

where,

$$V_{ion}(0) = \frac{1}{V}\int V_{ion}(r)dr \tag{8}$$

And the final result is

$$\langle \hat{H}_1 \rangle = 2\sum_{p<p_F}\left(\frac{p^2}{2m} + V_{ion}(0)\right) \tag{9}$$

In the position space it can be written as,

$$\langle \hat{H}_1 \rangle = \sum_\sigma \int \left[-\frac{\hbar^2}{2m}\psi_\sigma(r)\nabla^2\psi^\dagger_\sigma(r) + \psi^\dagger_\sigma(r)V_{ion}(r)\psi_\sigma(r)\right] dr \tag{10}$$

$$= \sum_\sigma \int \left[-\frac{\hbar^2}{2m}|\nabla\psi_\sigma|^2 + \hat{n}_\sigma(r)V_{ion}(r)\right] dr \tag{11}$$

Homework-04: *Derive equation (5) from equation (4).*
Hint: Use the relation

$$\sum_{p=0}^{p_F} \to \frac{V}{(2\pi)^3}\frac{1}{\hbar^3}\int_0^{p_F} 4\pi p^2\, dp$$

Homework-05: *Derive equation (10) from equation (9).*
Hint: Use the relation

$$a^\dagger_{p_\sigma} = \int \frac{e^{i\, p\cdot r/\hbar}}{\sqrt{V}}\, \psi^\dagger_\sigma(r)\, dr$$