Lecture 1: Hatree - Fock approximation

From this lecture, we begin to study interacting electron systems. The simplest approximation to many-body interactions is just the Hartree-Fock approximation. The Hatree part does not take into account the Fermi antisymmetry of wavefunction which is covered by the Fock part.

We will use a second-quantized form of the Hamiltonian to explain this approximation. We first choose a set of single particle basis $\varphi_{i,\sigma}(r)$ $(i=1,2,\cdots, \sigma=\uparrow,\downarrow)$. The many-body Hamiltonian consists of the "one-particle" and "two-particle" part as follows:

"single particle" part: $H_1 = \sum_{i,\sigma} \left(-\frac{\hbar^2}{2m} \nabla_i^2\right) + U(r_i)]$

second quantization

$$\Rightarrow H_1 = \sum_\sigma \int \psi_\sigma^\dagger(r) \left(-\frac{\hbar^2}{2m} \nabla^2 + U(r)\right) \psi_\sigma(r)\, dr$$

expand using $\psi_\sigma(r) = \sum_{i,\sigma} \varphi_{i,\sigma}(r)\, a_{i,\sigma}$

$$\Rightarrow H_1 = \sum \langle i\sigma | \hat{H}_1 | j\sigma' \rangle a_{i\sigma}^\dagger a_{j\sigma'}, \text{ where } \langle i\sigma | \hat{H}_1 | j\sigma' \rangle = \delta_{\sigma\sigma'} \times$$

$$\int \varphi_i^*(r) \left[-\frac{\hbar^2}{2m} \nabla^2 + U(r)\right] \varphi_j(r)\, dr^3$$

"two particle part"

$$H_2 = \frac{1}{2} \int dr\, dr' \, \frac{\rho(r)\,\rho(r')}{|r-r'|}$$

second quantization $\longrightarrow$

$$H_2 = \frac{e^2}{2} \sum_{\sigma\sigma'} \int dr\, dr' \; \frac{\psi^{\dagger}_{\sigma}(r)\, \psi^{\dagger}_{\sigma'}(r')\; \psi_{\sigma'}(r')\, \psi_{\sigma}(r)}{|r-r'|}$$

$$= \frac{1}{2} \sum_{ijlk} \langle i\sigma_i ; j\sigma_j | \hat{H}_2 | l\sigma_l ; k\sigma_k \rangle \; a^{\dagger}_{i\sigma_i} a^{\dagger}_{j\sigma_j} \; a_{l\sigma_l}\, a_{k\sigma_k}$$

where $\langle i\sigma_i ; j\sigma_j | \hat{H}_2 | l\sigma_l ; k\sigma_k \rangle = \delta_{\sigma_i\sigma_k}\, \delta_{\sigma_j\sigma_l} \cdot e^2 \int dr\, dr' \, \dfrac{\varphi^*_i(r)\, \varphi^*_j(r')\; \varphi_l(r')\, \varphi_k(r)}{|r-r'|}$

thus, we have the second quantization form of Hamiltonian as

$$H = \sum_{ij,\sigma\sigma'} \langle i\sigma | H_1 | j\sigma' \rangle \; a^{\dagger}_{i\sigma} a_{j\sigma'} + \frac{1}{2} \sum_{ijlk} \langle i\sigma_i ; j\sigma_j | \hat{H}_2 | l\sigma_l ; k\sigma_k \rangle \; a^{\dagger}_{i\sigma_i} a^{\dagger}_{j\sigma_j} a_{l\sigma_l} a_{k\sigma_k}.$$

which is valid for any-basis.

We seek a Slater-determinant like Wavefunction and minimize the trial ground state energy:

$$\Psi = a^{\dagger}_{i\sigma_i}\, a^{\dagger}_{j\sigma_j} \cdots a^{\dagger}_{l\sigma_l} |0\rangle, \quad N = \text{tatal number of particles}$$

we minimize $\langle \Psi | H | \Psi \rangle$ under the constraints of each basis is normalized

$$\int \varphi^*_{i\sigma}(r)\, \varphi_{i\sigma}(r) = 1,$$

thus by introducing Langrange multipliers $\lambda_{i\sigma}$, we have

$\langle \Psi | H | \Psi \rangle - \sum_{i\sigma} \lambda_{i\sigma} \int dr\, \varphi^*_{i\sigma}\, \varphi_{i\sigma}$, where

$$E = \langle \Psi | H | \Psi \rangle = \sum_{i\sigma_i} n_{i\sigma} \int dr \left\{ \varphi^*_i(r) \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \varphi_i(r) \right\}$$

$$+ \frac{e^2}{2} \sum_{ij\sigma\sigma'} n_{i\sigma} n_{j\sigma'} \int dr\, dr' \left\{ \frac{|\varphi_i(r)|^2 \, |\varphi_j(r')|^2}{|r-r'|} - \delta_{\sigma\sigma'} \frac{\varphi^*_i(r)\, \varphi^*_j(r')\; \varphi_j(r)\, \varphi_i(r')}{|r-r'|} \right\}$$

a) the first term in the interaction term is the Hatree term, which corresponds to

direct interaction $\quad a^{+}_{i\sigma_i} a^{+}_{j\sigma_j} a_{l\sigma_l} a_{k\sigma_k} \quad (k\sigma_k = i\sigma_i \ \& \ l\sigma_l = j\sigma_j)$

b) the second term in the interaction term is the Fock term corresponding to

exchange interaction $\quad a^{+}_{i\sigma_i} a^{+}_{j\sigma_j} a_{l\sigma_l} a_{k\sigma_k} \quad (k\sigma_k = j\sigma_j \text{ and } i\sigma_i = l\sigma_l)$

☆ For interactions which only dependent on density, the Fock term only exists electrons with the same spin!

Do variation respect to φ or φ^*, and set $n_{i\sigma} = 1$ for all the occupied states.

$$\boxed{\begin{aligned}&\left\{-\frac{\hbar^2}{2m}\nabla^2 + u(r) + \sum_{j\sigma'} n_{j\sigma'} \int dr' \frac{|\varphi_j(r')|^2}{|r-r'|}\right\} \varphi_{i\sigma}(r) \\ &- \sum_{j} n_{j\sigma} \int dr' \frac{\varphi^*_j(r')\varphi_j(r)}{|r-r'|} \varphi_{i,\sigma}(r') = \lambda_{i_\sigma} \varphi_{i_\sigma}(r)\end{aligned}}$$

Hatree - Fock self-consistent equation for the single particle wave functions, $\varphi_{i\sigma_i}(r)$ which enter the Slater determinant.

This set of equations need to be solved self-consistently.

Koopman's theorem: let us try to understand the physical meaning of $\lambda_{i\sigma}$, which equals

$$\lambda_{i\sigma} = \int dr\, \varphi^*_{i\sigma} \left(-\frac{\hbar^2}{2m}\nabla^2 + u(r)\right) \varphi_{i\sigma} + \sum_{j\sigma'} n_{j\sigma'} \int dr dr' \frac{|\varphi_i(r)|^2 |\varphi_j(r')|^2}{|r-r'|}$$

$$- \sum_j n_{j\sigma} \int dr dr' \frac{\varphi^*_i(r)\, \varphi^*_j(r')\, \varphi_j(r)\, \varphi_i(r')}{|r-r'|} .$$

This expression can be obtained by $\boxed{\lambda_{i,\sigma} = \delta E / \delta n_{i,\sigma}}$. Thus $\lambda_{i,\sigma}$ can be considered as the "energy" of the electron in the state (i,σ).

But the ground state energy should not be written as

$$E = \sum_{i\sigma} n_{i\sigma} \lambda_{i,\sigma}, \quad (\text{wrong}).$$

The interaction energy is double counted!

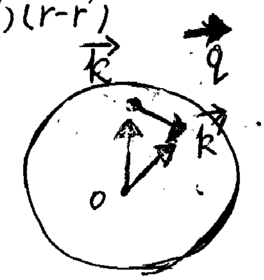
Jellium model Generally, speaking, the HF equation has to solved numerically by iteration. If the external potential (ionic potential) is a constant, it is easy to show that the plane waves are still a solution to HF equation. This correspondes to the case that we averge ionic charge as a uniform positive background to maintain the charge neutrality.

☆ ex: check plane waves are indeed a solution to the HF equation.

let us evaluate the HF energy. for the filled Fermi surface:

The Hartree part cancels with background charge, but the Fock part

$$\mathcal{E}_{HF}(k)_\sigma = \overset{0}{\mathcal{E}}(k) - \frac{1}{V}\sum_{k'} n_{k'\sigma} \cdot \int dr' \frac{e^2}{|r-r'|} e^{i(k-k')(r-r')}$$



$$= \overset{0}{\mathcal{E}}(k) - \frac{1}{V}\sum_{k'} n_{k',\sigma} \frac{4\pi e^2}{|k-k'|^2} \qquad \theta(k'<k_F)$$

$$\delta\mathcal{E}_{HF}(k) = -\frac{1}{V}\sum_{k'} n_{k'\sigma}\frac{4\pi e^2}{|k-k'|^2} = -\frac{1}{(2\pi)^3}\int_0 d\vec{k}' \cdot \frac{4\pi e^2}{|\vec{k}-\vec{k}'|^2}$$

define $\vec{q} = \vec{k}' - \vec{k} \Rightarrow \vec{k}' = \vec{k} + \vec{q} \Rightarrow k'^2 = k^2 + q^2 + 2k\cdot q\cos\theta$

$$\Rightarrow \delta\mathcal{E}_{HF}(k) = -\frac{4\pi e^2}{(2\pi)^3}\cdot 2\pi \int_0^\infty dq \int_{-1}^1 d\cos\theta \;\; \theta_1\left(k_F^2 - (k^2+q^2+2k\cdot q\cos\theta)\right)$$

$$= -\frac{2e^2}{\pi} k_F \frac{1}{2}\int_0^\infty dz \int_{-1}^1 d(\cos\theta)\; \theta\left(1 - (x^2+z^2+2xz\cos\theta)\right)$$

$$= -\frac{2e^2}{\pi} k_F \, F(x), \qquad (z = q/k_F, \; x = k/k_F)$$

$$F(x) = \frac{1}{2}\int_0^\infty f(z)\,dz, \qquad \begin{cases} f(z) = 2 & |x+z|<1 \\ f(z) = \dfrac{1-(x-z)^2}{2x^2} & \text{otherwise} \\ f(z) = 0 & |x-z|>1 \end{cases}$$

★ ex: the evaluation of $F(x)$

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

comments: ① exchange interaction is negative, which only exists between electrons with the same spin.

② $\delta\mathcal{E}_{HF} \sim k_F$, while the $\mathcal{E}_F \sim k_F^2$. thus in the low density region, $\delta\mathcal{E}_{HF}$ could dominate over $\mathcal{E}_{kinetic}$. The naive analysis would give a Ferromagnetic state at low density. But this is a unreliable result.

③ as $k \to k_F$, $\delta\mathcal{E}_{HF}(k) \sim -e^2 (k-k_F)\ln\left[|k-k_F|/k_F\right]$

the velocity shift $v(k) = \hbar^{-1}\, \partial\mathcal{E}/\partial k \Rightarrow v(k) \sim \ln\left(k_F/|k-k_F|\right)$ divergence

This would give a specific heat suppression as $\sim T/\ln(T_F/T)$

This is not correct!

This difficulty lies in the long wavelength part of Coulomb potential $\sim 1/q^2$

$$\sum_q n_{k+q}\frac{1}{q^2} \sim \int q^2 dq\, d\cos\theta\, \frac{1}{q^2}\, \theta_H(\mathcal{E}_k + q v_F \cos\theta < \mathcal{E}_F)$$

$$= \int q^2 dq\, d\cos\theta\, \frac{1}{q^2}\, \theta_H\left[v_F(k_F-k) - q v_F\cos\theta\right]$$

$$\frac{\partial}{\partial k}\left(\sum_q n_{k+q}\frac{1}{q^2}\right) \sim \int q^2 dq\, d\cos\theta\, \frac{1}{q^2}\, \delta\left[(k_F-k) - q\cos\theta\right]$$

$$= \int dq\, \frac{1}{q}\, \theta(|k_F-k| < q) \sim \ln\frac{k_F}{|k-k_F|}.$$

we will see the this difficulty can be removed by taking into account of screening. — the Coulomb potential becomes short ranged!

$\boxed{\text{exchange hole}}$ let us calculate the density correlation function

$$\langle \rho_\sigma(r)\, \rho_{\sigma'}(r')\rangle = \sum_{ij} n_{i\sigma} n_{j\sigma'} \{ |\varphi_i(r)|^2 |\varphi_j(r)|^2 - \delta_{\sigma\sigma'} \varphi_i^*(r) \varphi_j^*(r') \times \varphi_j(r) \varphi_i(r') \}$$

the first term is just $\langle \rho_\sigma(r)\rangle \langle \rho_{\sigma'}(r')\rangle$, thus

$$\langle \rho_\sigma(r)\, \rho_{\sigma'}(r')\rangle - \langle \rho_\sigma(r)\rangle\langle \rho_{\sigma'}(r')\rangle = -\sum_{ij} \delta_{\sigma\sigma'} \varphi_i^*(r) \varphi_j^*(r') \varphi_j(r) \varphi_i(r'),$$

where means nearby an electron it is unlikely to find another electron with the same spin, i.e. the appearance of a hole.

For uniform system, the above express reduces to

$$-\frac{1}{V^2} \sum_{kk'} e^{i(k-k')(r-r')} n_k n_{k'}$$

$$= -\frac{1}{(2\pi)^6} \int d\vec{k}\, d\vec{k}'\, e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}-\vec{r}')} \Theta(k_F - k)\, \Theta(k_F - k')$$

$$= -\left[\frac{1}{(2\pi)^3} \int d\vec{k}\, e^{i(\vec{k})\cdot(\vec{r}-\vec{r}')} \Theta(k_F - k) \right]^2$$

$$\int_0^{k_F} \frac{d\vec{k}}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} = \frac{n}{2} \cdot \int_0^{k_F} dk \cdot k^2 \int_{-1}^{1} dx\, e^{ik|r-r'|x} \Big/ 2\int_0^{k_F} k^2\, dk$$

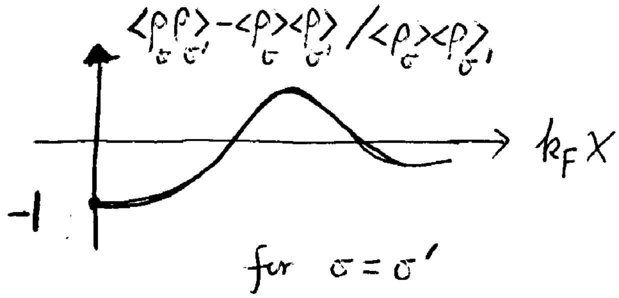
$$\left(\frac{n}{2} = \frac{k_F^3}{6\pi^2}\right)$$

$$= \frac{1}{2\pi^2 |r-r'|} \int_0^{k_F} dk.\, k \sin k|r-r'| = \frac{1}{2\pi^2|r-r'|} \frac{d}{d(|r-r'|)} \int_0^{k_F} \cos k(|r-r'|)\, dk$$

$$= \frac{1}{2\pi^2|r-r'|} \frac{d}{d(|r-r'|)} \left(\frac{\sin k_F(|r-r'|)}{|r-r'|} \right)$$

$$\Rightarrow \langle \rho_\sigma(r)\rho_\sigma(r')\rangle - \langle \rho_\sigma(r)\rangle\langle\rho_\sigma(r')\rangle = -\left(\frac{n}{2}\right)^2 9\left(\frac{x\cos x - \sin x}{x^3}\right)^2$$

with $x \equiv k_F|r-r'|$



For electrons with opposite spin, there are no correlation at HF level

However, this is not ture. Interactions can also bring correlations $\langle\rho_\uparrow(r)\rho_\downarrow(r')\rangle$.

~~In other which can exhibit correlation hole.~~