Lecture 3 Hartree-Fock approximation

We begin to consider electron interactions. The simplest approximation to solve interacting Hamiltonians is the Hartree-Fock approx, which is also often called the mean-field theory. Hartree part is classic, and the Fock part takes into account the effect of Pauli’s exclusion principle, i.e. the many-body wavefunctions of fermions need to be anti-symmetrized.

§1. A quick review of 2nd quantization — quantization of wavefunction.

\[ H_1 = \sum_{i=1}^{N} \hat{h}_i(i), \text{ and } \hat{h}_i(i) = -\frac{\hbar^2}{2m} \nabla_i^2 + U(x_i) \]

In the 1st quantization, the total kinetic and external potential energy of a single body is

we need to fix the particle number \( N \), and the many-body wavefunction is also complicated. If we neglect electron spin for the moment, a \( N \)-body wavefunction typically can be written as a Slater determinant type as:

\[
\Psi(x_1, \ldots x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\
\phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\
\vdots & \vdots & & \vdots \\
\phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N)
\end{vmatrix}
\]
where \( \phi_i (i=1, \ldots, N) \) is a set of orthonormal single-particle states. 

\( \Psi(x, \ldots, x_N) \) describes a \( N \)-particle state in which each single-particle state is filled with one electron. The Slater determinant wavefunction satisfies the anti-symmetric property,

\[
\Psi(r_1, \ldots, r_i, \ldots, r_j, \ldots, r_N) = -\Psi(r_1, \ldots, r_j, \ldots, r_i, \ldots, r_N).
\]

We introduce field operators \( \psi_\alpha^+(\vec{r}) \) and \( \psi_\alpha^-(\vec{r}) \). They anti-commute and satisfy

\[
\{ \psi_\alpha^+(\vec{r}), \psi_\beta^-(\vec{r}') \} = \psi_\alpha^+(\vec{r}) \psi_\beta^-(\vec{r}') + \psi_\beta^-(\vec{r}) \psi_\alpha^+(\vec{r}') = \delta_{\alpha\beta} \delta(\vec{r}-\vec{r}')
\]

\( \alpha, \beta \) are spin indices.

Apply \( \psi_\alpha^+(\vec{r}) \) on the vacuum, we obtain a single-particle state with spin \( \alpha \), and it's a coordinate eigenstate located at \( \vec{r} \), i.e

\[
\langle \vec{r}', \alpha' | \psi_\alpha^+(\vec{r}) | \text{vac} \rangle = \delta(\vec{r}-\vec{r}') \delta_{\alpha\alpha'}.
\]

We define the density operator \( \rho(\vec{r}) = \sum_\alpha \psi_\alpha^+(\vec{r}) \psi_\alpha^-(\vec{r}) \), for a many-body state \( |\Psi\rangle \), \( \langle \Psi | \rho(\vec{r}) | \Psi \rangle \) gives to electron density at \( \vec{r} \).

So, 2nd quantization can be viewed as quantization of wavefunctions \( \rightarrow \) field operators.
using field operator, the single-body operator $H_1$ can be represented as

$$H_1 = \sum_\sigma \int \psi^\dagger_\sigma (r) h_1 (r^2) \psi_\sigma (r) \, dr = \sum_\sigma \int dr \psi^\dagger_\sigma (r) \psi_\sigma (r) \left( -\frac{\hbar^2}{2m} \nabla^2 + \mu (r) \right) \psi_\sigma (r)$$

In many situations, we need to work with different single-particle bases, say, the momentum representation. We expand the field operator in a general basis as

$$\psi_\sigma (r) = \sum_{i, \sigma} \phi_{i, \sigma} (r) a_{i, \sigma}$$

$$\left\{ \psi^\dagger_\sigma (r) = \sum_{i, \sigma} \phi^\ast_{i, \sigma} (r) a_{i, \sigma}^\dagger \right\}$$

where $\{ a_{i, \sigma}, a_{j, \sigma}^\dagger \} = \delta_{ij} \delta_{\sigma\sigma'}$, and $a_{i, \sigma}, a_{i, \sigma}^\dagger$ are creation/annihilation operators for the mode of $\phi_{i, \sigma}$. $N_{i, \sigma} = a_{i, \sigma}^\dagger a_{i, \sigma}$ represent the occupation number of the state $\phi_{i, \sigma}$. Under the basis of $\phi_{i, \sigma} (r)$, we have

$$H_1 = \sum_{ij, \sigma} \langle i \sigma | h_1 | j \sigma' \rangle a_{i, \sigma}^\dagger a_{j, \sigma'}$$

where

$$\langle i \sigma | h_1 | j \sigma' \rangle = \delta_{\sigma\sigma'} \langle i \sigma | h_1 | j \sigma' \rangle = \int \phi_{i, \sigma}^\ast (r) \left( -\frac{\hbar^2}{2m} \nabla^2 + \mu (r) \right) \phi_{j, \sigma'} (r) \, dr$$

if $\mu (r) = 0$, we can use the momentum representation, or, the plane-wave basis: $\varphi_{k, \sigma} (r) = \frac{1}{\sqrt{V}} e^{i \mathbf{k} \cdot \mathbf{r}}$

$$\Rightarrow H_1 = \sum_{k, \sigma} a_{k, \sigma}^\dagger a_{k, \sigma} \frac{\hbar^2 k^2}{2m}$$
two-body operators (interaction).

1st quantization: \[ H_2 = \frac{1}{\alpha} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{\alpha} \sum_{i \neq j} h_2(\vec{r}_i, \vec{r}_j) \]

→ 2nd quantization (using \( \psi_i^+, \psi_i \))

\[ H_2 = \frac{e^2}{\alpha} \sum_{\sigma_0} \int d\vec{r} d\vec{r}' \frac{\psi_i^+(\vec{r}) \psi_i^+(\vec{r}') \psi_i(\vec{r}) \psi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} \]

Please note the sequence of field operators.

→ change to a general basis

\[ H_2 = \frac{1}{\alpha} \sum_{ijeb} \langle i o_i j o_j | h_2 | l e_o, k o_e \rangle a_{i o_i}^+ a_{j o_j}^+ a_{e l} a_{o e} a_{k o} \]

\[ H_2 = \frac{1}{\alpha} \sum_{ijeb} \langle i j o_i | h_2 | e o_e \rangle a_{i o_i}^+ a_{j o_j}^+ a_{e o_e} a_{e o} a_{e o} \]

\[ \langle i o_i j o_j | h_2 | l o_e, k o_e \rangle = \delta_{o_i o_e} \delta_{o_j o_e} \langle i o_i j o_j | h_2 | l o_j, k o_i \rangle \]

\[ \langle i o_j o_j' | h_2 | l o_e, k o_e \rangle = e^2 \int d\vec{r} d\vec{r}' \frac{\Phi_i^*(\vec{r}) \Phi_i^*(\vec{r}') \Phi_i(\vec{r}) \Phi_i(\vec{r}')}{|r - r'|} \]

\[ H = H_1 + H_2 \]

\[ H = \sum_{ij} \langle i j | h_1 | i j \rangle a_{i o}^+ a_{j o} + \frac{1}{\alpha} \sum_{ijeb} \langle i j o_i | h_2 | e o_e \rangle a_{i o_i}^+ a_{j o_j}^+ a_{e o_e} a_{e o} a_{e o} \]

Hamiltonian: interacting electrons (and quantized form!)

Hamitonian: interacting electrons (and quantized form!)
§ Hartree–Fock State

We seek a trial wavefunction of the Slater determinant type

$$\psi = a_{i_0}^+ a_{j_0}^+ \cdots a_{i_0}^+ \Psi$$, \(N = \) total particle number

we minimize \(\langle \psi \mid H \mid \psi \rangle\) under the constraint that each basis is orth-normal, i.e.

$$\int \Phi_i^*(r) \Phi_j(r) \, dr = 1$$. This constraint can be imposed by introducing Lagrangian multiplier \(\lambda_{i_0}\). \

we need to minimize the functional

$$E[\Phi_{i_0}]\langle \psi \mid H \mid \psi \rangle = \sum_{i_0} \lambda_{i_0} \left[ \int dr \left( \Phi_{i_0}^* \Phi_{i_0} \right) - 1 \right]$$.

1. \(\langle \psi \mid H \mid \psi \rangle = \sum_{i,j} \langle i_0 \mid h_{ij} \mid j_0 \rangle \langle \psi \mid a_{i_0}^+ a_{j_0}^+ \psi \rangle\)

we need \(i = j\), otherwise \(\langle \psi \mid a_{i_0}^+ a_{j_0}^+ \psi \rangle = 0 \Rightarrow\)

$$\langle \psi \mid H \mid \psi \rangle = \sum_{i_0} \langle i_0 \mid h_{ii} \rangle \langle \psi \mid a_{i_0}^+ a_{i_0}^+ \psi \rangle$$

$$\quad = \sum_{i_0} n_{i_0} \int dr \, \Phi_{i_0}^* \left[ -\frac{\hbar^2}{2m} \nabla^2 + U(r) \right] \Phi_{i_0}(r)$$

2. \(\langle \psi \mid H \mid \psi \rangle = \frac{1}{2} \sum_{i,j,k} \langle i_0 \mid h_{ij} \mid j_0 \rangle \langle \psi \mid a_{i_0}^+ a_{j_0}^+ a_{i_0} a_{j_0} \psi \rangle\)

Hartree contribution \(j = l, i = k\), but we need to exclude \(i = j = l = k\) and \(\sigma = \sigma'\): \n
$$\langle \psi \mid a_{i_0}^+ a_{j_0}^+ a_{i_0} a_{j_0} \psi \rangle = \hat{\text{Hartree}} \left( n_{i_0} n_{j_0} - n_{i_0} \delta_{ij} \delta_{i_0} \right)$$
Fock contribution \( \sigma = \sigma', i = l, j = k \), but exclude \( i = l = j = k \) & \( \sigma = \sigma' \).

\[
\langle \Psi | a^+_i \alpha_{i\omega} a_{j\sigma} \alpha_{j\sigma'} (\Psi) = - (n_{i\omega} n_{j\sigma} - n_{i\omega} \delta_{ij} \delta_{\sigma\sigma'})
\]

minus sign comes from Fermi statistics

\[
\langle \Psi | H_2 | \Psi \rangle = \frac{1}{2} \sum_{ij, i'j'} \{ \langle i\sigma j\omega | h_2 | j'\sigma' i'\omega \rangle (n_{i\omega} n_{j\sigma} - n_{i\omega} \delta_{ij} \delta_{\sigma\sigma'})
\]

\[- \langle i\sigma j\omega | h_2 | i'\sigma' j'\omega \rangle \delta_{\omega\omega'} (n_{i\omega} n_{j\sigma} - n_{i\omega} \delta_{ij}) \}
\]

\[
= \frac{1}{2} \sum_{ij, i'j'} \{ \langle i\sigma j\omega | h_2 | j'\sigma' i'\omega \rangle - \delta_{\omega\omega'} \langle i\sigma j\omega | h_2 | i'\sigma' j'\omega \rangle \} n_{i\omega} n_{j\sigma}
\]

\[
\text{Hartree} \quad \text{Fock}
\]

Classic electrostatics \quad Quantum statistics

\[
\langle i\sigma j\omega | h_2 | j'\sigma' i'\omega \rangle = \int drdr' \frac{\Phi^*_i(r) \Phi_j^*(r') \Phi_{j'}(r) \Phi_{i'}(r)}{|r - r'|}
\]

\[
\langle i\sigma j\omega | h_2 | i'\sigma' j'\omega \rangle = \int drdr' \frac{\Phi_{i\omega}(r) \Phi_{j\sigma}(r') \Phi_{i\omega}(r') \Phi_{j\sigma}(r)}{|r - r'|}
\]

\[
\mathbb{E}[\Phi^*_i \Phi_j] = \sum_{i\omega} n_{i\omega} \int dr \ \frac{\Phi^*_i(r)}{\Phi_i(r)} \left( -\frac{\hbar^2 \nabla^2}{2m} + u(r) \right) \Phi_i(r) - \sum_{i\omega} \int dr \left( \Phi^*_i \Phi_i - 1 \right)
\]

\[
+ \sum_{i'j', i\omega j'\omega} \left( \int drdr' \frac{\Phi^*_i(r) \Phi^*_j(r') \Phi_{i'}(r') \Phi_{j'}(r)}{|r - r'|} - \delta_{\omega\omega'} \Phi^*_i \Phi_j \right)
\]

\[
\left( \Phi_{i\omega} \Phi_{j\sigma} \Phi_{i'\omega} \Phi_{j'\sigma} \right)
\]
Do variation with respect to \( \psi_{io}^* \), and set \( n_{io}=1 \) for occupied state \( \Rightarrow \)

\[
\left\{ -\frac{\hbar^2}{2m} \nabla^2 + U(r) + \sum_{j \neq i} n_{j0} \int dr' \frac{1}{|r - r'|} \psi_{j0}(r') \psi_{i0}(r) \right\} \psi_{i0}(r)
\]

\[
- \sum_{j} n_{j0} \int dr' \frac{\psi_{i0}^*(r') \psi_{j0}(r')}{|r - r'|} \psi_{j0}(r) = \lambda_{i0} \psi_{i0}(r)
\]

The Hartree potential is local, but Fock-one is not. H-F equation need to be solved self-consistently, and it's often complicated!

\( \star \) If \( U(r) = 0 \), we can use plane-wave \( \psi_{i0}(r) = \frac{1}{\sqrt{V}} e^{ik_{i} \cdot r} \)

\( \Rightarrow \) Hartree part \( \frac{1}{V} \sum_{k_0} \int \psi_{i0}^* \psi_{k_0} \int dr \frac{1}{|r - r'|} = \nabla \cdot U(r \rightarrow 0) \)

\( U(r) = \frac{4\pi e^2}{a^2} \) (Fourier transform of \( \frac{e^2}{r} \)).

Hartree term diverge reflecting long range nature of Coulomb force. We set \( U = \) Hartree to cancel, which is the contribution from positive charge background.

\( \Rightarrow \) Fock \( \frac{1}{V} \sum_{k_j \neq k_i} \int dr' \frac{e^{i(k_{i} \cdot r')}}{\sqrt{V}} \left( \frac{1}{|r - r'|} e^{i(k_{j} \cdot r')} \right) \)

\[
= \left[ \sum_{k_i} \frac{n_{k_i}}{(2\pi)^3} V(k - k_i) \right] \frac{1}{\sqrt{V}} e^{i(k_{i} \cdot r)}
\]

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

$$\lambda_{i,\sigma} = \int dr \, \Phi_{i,\sigma}^* \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \Phi_{i,\sigma} + \sum_{j,\sigma'} \eta_{j,\sigma} \int dr dr' \frac{|\Phi_{j}(r') \Phi_{j}(r) \Phi_{i}(r')|^2}{|r-r'|}$$

$$- \sum_{j} \eta_{j,\sigma} \int dr dr' \frac{\Phi_{i}(r') \Phi_{j}(r) \Phi_{j}(r)}{|r-r'|}.$$

This expression can be obtained by

$$\lambda_{i,\sigma} = \frac{\delta E}{\delta \eta_{i,\sigma}}.$$ 

Thus $\lambda_{i,\sigma}$ can be considered as the "energy" of the electron in the state $(i,\sigma)$.

But the ground state energy should not be written as

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

The interaction energy is double counted!

Jellium model: Generally speaking, the HF equation has to be 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 the HF equation. This corresponds to the case that we average ionic charge as a uniform positive background to maintain 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

\[ \delta E_{HF}(k) = E(k) - \frac{1}{V} \sum_{k'} n_{k',0} \cdot \int d\mathbf{r}' \frac{e^2}{|r-r'|} \theta(k-k')(r-r') \]

\[ = E(k) - \frac{1}{V} \sum_{k'} n_{k',0} \frac{4\pi e^2}{|k-k'|^2} \theta(k-k') \]

\[ \delta E_{HF}(k) = -\frac{1}{V} \sum_{k'} n_{k',0} \frac{4\pi e^2}{|k-k'|^2} = -\frac{1}{(2\pi)^3} \int d\mathbf{k}' \frac{4\pi e^2}{|\mathbf{k}'-\mathbf{k}|^2} \theta(k-k') \]

define \( \mathbf{q} = \mathbf{k}' - \mathbf{k} \Rightarrow \mathbf{k}' = \mathbf{k} + \mathbf{q} \Rightarrow k'^2 = k^2 + q^2 + 2kq \cos \theta \)

\[ \Rightarrow \delta E_{HF}(k) = -\frac{4\pi e^2}{(2\pi)^3} \frac{1}{2\pi} \int dq \int_0^\infty \int d\cos \theta \ \Theta(k_F - (k^2 + q^2 + 2kq \cos \theta)) \]

\[ = -\frac{2e^2}{\pi} k_F \int d\theta d(z^2) \Theta(1-(z^2 + 2z \cos \theta)) \]

\[ = -\frac{2e^2}{\pi} k_F F(z), \quad (z = \frac{q}{k_F}, \ x = \frac{k}{k_F}) \]

\[ F(z) = \frac{1}{2} \int_0^\infty f(z) \ dz, \quad \begin{cases} f(z) = 2, & x = 1 \ \text{otherwise} \\ f(z) = \frac{1-(x-z)^2}{2x^2}, & 0 \leq |x-z| < 1 \\ f(z) = 0, & |x-z| > 1 \end{cases} \]

\[ \text{Ex: the evaluation of } F(x) \]

\[ F(x) = \frac{1}{2} + \left( \frac{1-x^2}{4x} \right) \ln \left| \frac{1+x}{1-x} \right| \]
Comments:

1. Exchange interaction is negative, which only exists between electrons with the same spin.

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

3. As $k \to k_F$, $\delta E_{HF}(k) \sim -e^2 \left( k-k_F \right) \ln \left[ \frac{k-k_F}{k_F} \right]$

   The velocity shift $V(k) = \frac{\hbar}{e} \frac{\partial \delta E}{\partial k} \Rightarrow V(k) \sim \ln \left( \frac{k_F}{k-|k_F|} \right)$

   This would give a specific heat suppression as $\sim \frac{1}{T} \ln \left( \frac{T_F}{T} \right)$

   This is not correct!

This difficulty lies in the long wavelength part of Coulomb potential $\sim \frac{1}{d^2}$

$$\sum_{\mathbf{q}} n_{k+q} \frac{1}{d^2} \sim \int q^2 dq \cos \theta \frac{1}{d^2} \Theta \left( \frac{k_F-q}{d^2} \theta \right)$$

$$= \int q^2 dq \cos \theta \frac{1}{d^2} \Theta \left( \frac{k_F-q}{d^2} \cos \theta \right)$$

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

$$= \int dq \frac{1}{d^2} \Theta \left( |k_F-k| < d \right) \sim \ln \frac{k_F}{|k_F-k|}$$

We will see that this difficulty can be removed by taking into account of screening. --- the Coulomb potential becomes short ranged.
let us calculate the density correlation function

\[ \langle \rho(r) \rho(r') \rangle = \sum_{\sigma \sigma'} n_{\sigma} n_{\sigma'} \left\{ |\psi_{\sigma}(r)|^2 |\psi_{\sigma'}(r')|^2 - \delta_{\sigma \sigma'} \phi_{\sigma}(r) \phi_{\sigma'}^*(r') \times \phi_{\sigma'}(r') \phi_{\sigma}(r) \right\} \]

the first term is just \( \langle \rho(r) \rangle \langle \rho(r') \rangle \), thus

\[ \langle \rho(r) \rho(r') \rangle - \langle \rho(r) \rangle \langle \rho(r') \rangle = -\sum_{ij} \delta_{\sigma \sigma'} \phi_{i}(r) \phi_{i}^*(r') \phi_{j}(r') \phi_{j}(r), \]

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

\[ -\frac{1}{N^2} \sum_{kk'} e^{i(k'k)(r-r')} n_k n_{k'} \]

\[ = -\frac{1}{(2\pi)^6} \int \! dk \, dk' \, e^{i(k-k')(r-r')} \Theta(k_F-k) \Theta(k'_F-k') \]

\[ = -\left[ \frac{1}{(2\pi)^6} \int \! dk \, e^{i(k-k)(r-r')} \Theta(k_F-k) \right]^2 \]

\[ \int_{(2\pi)^3} \! e^{i(k-k')(r-r')} = \frac{n}{2} \cdot \int_{0}^{k_F} \! dk \cdot k^2 \int_{-1}^{1} \! dx \cdot e^{i k |r-r'| x} / 2 \int_{0}^{k_F} \! k^2 \, dk \]

\[ (\frac{n}{2} = \frac{k_F^3}{6\pi^2}) \]

\[ = \frac{1}{2\pi^2 |r-r'|} \int_{0}^{k_F} \! dk \cdot k \sin k |r-r'| = \frac{1}{2\pi^2 |r-r'|} \frac{d}{d(|r-r'|)} \int_{0}^{k_F} \! \cos k |r-r'| \, dk \]

\[ = \frac{1}{2\pi^2 |r-r'|} \frac{d}{d(|r-r'|)} \left( \frac{\sin k_F |r-r'|}{|r-r'|} \right) \]
\[ \Rightarrow \langle \rho_\sigma(r) \rho_\sigma(r') \rangle - \langle \rho_\sigma(r) \rangle \langle \rho_\sigma(r') \rangle = -\left( \frac{\hbar^2}{2m} \right)^2 \frac{q}{x^3} \left( \frac{x \omega s x - \sin x}{x^3} \right)^2 \]

with \( x = k_F |r-r'| \)

\[ \langle \rho\rho \rangle - \langle \rho \rangle \langle \rho \rangle \]

\[ \frac{\langle \rho\rho \rangle - \langle \rho \rangle \langle \rho \rangle}{\langle \rho \rangle \langle \rho \rangle} \]

for \( \sigma = \sigma' \)

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

However, this is not true. Interactions can also bring correlations \( \langle \rho^\uparrow(r) \rho^\downarrow(r') \rangle \)

In this way which can exhibit correlation hole.