Lect 6: Density functional theory and LDA

— for non-uniform interacting electrons

§ Hohenberg – Kohn theorem:

Consider a many-body Hamiltonian $H = \hat{T} + \hat{V} + \hat{U}$, where

$$\hat{T} = \int dr\, \psi_\sigma^\dagger \left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi_\sigma, \quad \hat{V} = \int V(r)\,\psi_\sigma^\dagger(r)\,\psi_\sigma(r), \quad \hat{U} = \frac{e^2}{2}\int dr\,dr'\, \frac{\psi_\sigma^\dagger(r)\psi_{\sigma'}^\dagger(r')\,\psi_{\sigma'}(r')\psi_\sigma(r)}{|\vec{r}-\vec{r}'|}.$$

For a fixed external potential $V(r)$, the Hamiltonian is determined,

In field theory language, $V(r)$ is a source term, H is a functional of $V(r)$, and it's ground state $|\Psi_G\rangle$ and density $\underline{\rho(r)}$ are also
ground state
functionals of $V(r)$.

$$\boxed{V(r) \longrightarrow |\psi_G\rangle, \text{ or } \psi_G(r_1,\cdots r_N) \longrightarrow \rho(r) = \langle \psi_G | \psi_\sigma^\dagger(r)\,\psi_\sigma(r) | \psi_G\rangle}$$

In the $\hat{V}$-term, $V(r)$ couples to $\rho(r)$, $\Rightarrow$ $V(r)$ and $\rho(r)$ are conjugate variables. We could also formulate the theory in terms of $\rho(r)$ as characteristic function, i.e $\rho(r) \longrightarrow |\psi_G\rangle \longrightarrow V(r)$.

This is like the Legendre transformation:

$$\boxed{\begin{aligned} &\text{C.f. } dE = pdV + Tds + m\,dB \\ &\to G = E - TS - Bm \Rightarrow dG = pdV - sdT - B\,dm \end{aligned}}$$

Basically, we need to prove differen $V(r)$ gives diffent $\rho(r)$. i.e. if we have two different potentials $V(r)$ and $V'(r)$ ($V(r) \neq V(r')$ + constant),

they give $\rho(r) \neq \rho(r')$.

First, the ground state of $T+U+V'$, denoted as $\Psi'(r_1 \cdots r_n)$, should be different from that of $T+U+V$, denoted as $\Psi(r_1 \cdots r_n)$.

Otherwise
$$(T + U + V)\,\Psi(r_1 \cdots r_n) = E\,\psi(r_1 \cdots r_n)$$
$$(T + U + V')\,\Psi(r_1 \cdots r_n) = E'\,\psi(r_1 \cdots r_n)$$
$$\Bigg\} \Rightarrow$$

$$(V - V')\,\Psi(r_1 \cdots r_n) = (E' - E)\,\Psi(r_1 \cdots r_n), \Rightarrow V' - V = const, \text{ which means}$$

V and V' are the same potential.

Because Ψ' is different from Ψ, Ψ' is NOT the ground state of $H = T + U + V$ (we assume the GS is non-degenerate). Then

$$\langle \Psi' | H | \psi' \rangle > \langle \Psi | H | \Psi \rangle$$

$$\big\downarrow = \langle \Psi' | H' + V - V' | \Psi' \rangle = \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | V - V' | \Psi' \rangle$$

i.e. $E' + \int dr\, \rho'(r)\,(V - V') > E.$ ①

Similarly, we also have $E + \int dr\, \rho(r)\,(V' - V') > E'.$ ②

① + ② $\Rightarrow \int dr\, [\rho'(r) - \rho(r)]\,(V - V') \ngtr 0$, which means

$\rho'(r) \neq \rho(r).$

So we proved each distribution $\rho(r)$ gives a different $V(r)$, and a different $\Psi(r_1 \cdots r_n).$

Then what's benifit to use $\rho(r)$, rather than $V(r)$?

We define ground state energy functional

$$E_G[\rho(r)] = F[\rho(r)] + \int V(r)\,\rho(r)\,dr$$

where $F[\rho(r)] = \langle \Psi_G | \hat{T} + \hat{u} | \Psi_G \rangle$. $F[\rho(r)]$ contains

correlation effect but not explicitly on $\rho(r)$, thus we can separate

correlation from lattice potention. In other words, $F[\rho(r)]$ is an

intrinsic quantity of interaction electron system. But it may be

complicated, /and/ non-local, etc. We can use local approximation,

such that we use the results from uniform electron gases at different

values of ρ, to approximate the true $F[\rho(r)]$.

§ LDA (local density approximation)

We express $E_G[\rho(r)] = T_0[\rho(r)] + V_H[\rho(r)] + E_{xc}[\rho(r)] + \int d^3r\, V(r)\,\rho(r)$

And approximate the ground state as a slater determinant made by

a set of basis $\phi_{i\sigma}(r)$, which is also determined by $\rho(r)$.

① $T_0[\rho] = \sum_{i\sigma} \int d^3\, \phi_{i\sigma}^*(\vec{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \phi_{i\sigma}(\vec{r})$.

This is not the true kinetic energy functional. The true ground

state $|\psi_G\rangle$ can be significantly disturbed from Slater-determinant by interaction. And thus $T[\rho]$ could be very different from $T_0[\rho]$.

② $V_H[\rho] = \frac{1}{2} \int dr\, dr'\, \rho(r) \frac{e^2}{|r-r'|} \rho(r')$, the Hartree-part

Then what's left is exchange-correlation energy functional

$$E_{xc}[\rho] = F[\rho] - T_0[\rho] - V_H[\rho].$$

exchange correlation $\begin{cases} T[\rho] - T_0[\rho] \\ \text{and interaction energy beyond H.F.} \end{cases}$

We approximate that $E_{xc}[\rho(r)]$ is a function of ρ, in a local way, , i.e. no dependence on $\nabla\rho(r)$.   And we express

$\rho(r) = \sum_\sigma \phi^*_{i,\sigma}(r)\, \phi_{i,\sigma}(r)$.   We minimize the energy functional

subject to the constraint of $\int dr\, \phi^*_{i\sigma} \phi_{i\sigma} = 1$.

$$E_G[\rho(r)] = \sum_{i\sigma} \int d^3r\, \phi^*_{i\sigma}(\vec{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right) \phi_{i\sigma}(\vec{r}) + V_H(\rho)$$

$$+ \int d^3r\, E_{xc}[\rho(r)] - \sum_{i\sigma} \int dr\, \lambda_{i\sigma}(\phi^*_{i\sigma}(r)\, \phi_{i\sigma}(r) - 1)$$

Do variation with respect to $\phi^*_{i\sigma}(\vec{r})$. →

The density of E_{xc}

$$\left\{\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right) + \underbrace{\int d^3r' \frac{e^2}{|r-r'|}\rho(r)}_{V'(r)} + \underbrace{\frac{\delta \mathcal{E}_{xc}(\rho(r))}{\delta\rho(r)}}_{}\right\}\phi_{io}(\vec{r}) = \lambda_{io}\phi_{io}(\vec{r})$$

$\underset{\uparrow \text{Hartree}}{V'(r)}$ exchange + correlation

If the form of $\mathcal{E}_{xc}(\rho(r))$ is known, this equation is local. It's very similar to the usual single particle Schrödinger equation. In other words, we can model the many-body effect through a renormalized lattice potential

$$V_{eff}(r) = V(r) + V'(r) + \frac{\delta\mathcal{E}_{xc}(\rho(r))}{\delta\rho(r)}.$$

We need to assume an initial density distribution $\rho(r)$, then we have V_{eff}, and we can solve the band structure and obtain a revised $\rho(r)$. This process can be iterated until convergence is achieved. Nice thing is that $\frac{\delta\mathcal{E}_{xc}}{\delta\rho}$ only depend under LDA, on ρ. The unknown $\frac{\delta\mathcal{E}_{xc}(\rho)}{\delta\rho}$ can be obtained through homogenous electron gas at density ρ. Thus we separate the effect of lattice potential from correlation. — a strategy of "divide & conquer".

Let's solve the exchange part of $\varepsilon_{xc}(\rho)$.

In Lect 3, we solve the exchange energy for electron with $k < k_F$ is

$$\varepsilon_{Fock}(k) = -\frac{2e^2}{\pi} k_F F(x), \quad \text{where } \begin{cases} F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right| \\ x = k/k_F \end{cases}$$

$\Rightarrow$ the total exchange energy

$$\sum_k \varepsilon_{Fock}(k) = \frac{V}{(2\pi)^3}\int d^3k\, F(x) \cdot \left(-\frac{2e^2}{\pi} k_F\right) = \frac{V k_F^4}{(2\pi)^3} \cdot 4\pi\left(\frac{-2e^2}{\pi}\right)\int_0^1 x^2 F(x)\, dx$$

$$= -N\left(\frac{3e^2}{4\pi}\right) k_F \quad \leftarrow \text{ we used } \begin{cases} \int_0^1 x^2 F(x)\, dx = \frac{1}{4} \\ k_f^3 = \frac{3\pi^2 N}{V} = 3\pi^2 \rho \end{cases}$$

$\Rightarrow$ useing the definition

$$\rho \frac{4\pi}{3}(r_s a_0)^3 = 1 \quad \text{with } a_0 = \frac{\hbar^2}{me^2} \text{ the Bohr radius.}$$

we have $k_F = \left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s a_0}$, and $r_s = \left(\frac{3\rho}{4\pi}\right)^{1/3}\frac{1}{a_0}$.

$$\Rightarrow \frac{E_x}{N} = -\frac{e^2}{2a_0}\left[\frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3}\right]\frac{1}{r_s} \approx -R_y\frac{0.916}{r_s}$$

where $R_y = \frac{e^2}{2a_0} = 13.6 ev$

From this we have $\varepsilon_x = \frac{E_x}{V} = \rho\left(\frac{E_x}{N}\right) = -\frac{e^2}{2a_0}\left[\frac{3^{4/3}}{2\pi^{1/3}}\right]\rho^{4/3} a_0$

$$\Rightarrow \boxed{V_x = \frac{d\varepsilon_x}{d\rho} = -R_y\, 2\left(\frac{3\rho a_0^3}{\pi}\right)^{1/3}}$$

The correlation energy beyond HF

what used!

$$\mathcal{E}_c(r_s) = \frac{E_c}{N} = \begin{cases} -0.2846/(1+1.0529\sqrt{r_s} +0.3334) & r_s \gg 1 \\[2mm] -0.096 + 0.0622 \ln r_s - 0.0232 r_s + 0.0040 \, r_s \ln r_s & \\[1mm] & r_s \ll 1 \end{cases}$$

Fitted by QMC.

RPA at $r_s \ll 1$ $\Rightarrow$ $\mathcal{E}_c = -0.094 + 0.0622 \ln r_s + O(r_s, r_s \ln r_s)$

Wigner crystal $r_s \gg 1$ $\quad \mathcal{E}_c = \dfrac{-0.88}{r_s + 7.8}$

§ Thomas - Fermi approximation

$$E[\rho(r)] \clubsuit = \int d^3r \; T[\rho] + \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d^3r \, d^3r'$$

Constraint of total particle number

$$+ \int d^3r \; \mathcal{E}_{xc}(\rho) + \int V(r)\rho(r) d^3r \; - \; \mu \left[\int dr \, \rho(r) - N \right]$$

$$\to \int \delta\rho(r) \left[\frac{\delta T(\rho)}{\delta \rho} + V(r) + e^2 \int \frac{\rho(r')}{|r-r'|} + \frac{\delta \mathcal{E}_{xc}(\rho)}{\delta \rho} \underbrace{\quad}_{-\mu} \right] d^3r = 0$$

$$\int d^3r \; T[\rho] = \int d^3r \; \rho(r) \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} = \frac{3}{10} \frac{\hbar^2}{m} (3\pi^2)^{2/3} \int \rho(r)^{5/3} d^3r$$

$$\frac{\delta T(\rho)}{\delta \rho} = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3} \quad , \quad \text{if we neglect } \mathcal{E}_{xc}, \Rightarrow$$

$$\Rightarrow \quad \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3} + V(r) + V_i(r) = \mu$$

$$\boxed{\begin{array}{l} \text{or} \;\; \rho(r) = \frac{1}{3\pi^2} \left[\frac{2m}{\hbar^2}(\mu - V(r) - V_i(r)) \right]^{3/2} , \\[2mm] \left\{ \; \nabla^2 V_i(r) = -4\pi e \rho(r) \right. \end{array}} \text{ where } V_i(r) = \int \frac{e\rho(r')}{|r-r'|} d^3r'$$

$$\text{or} \quad \nabla^2 V_i(r) = -\frac{2^{2/2}}{3\pi}(\mu - V(r) - V_i(r))^{3/2} \frac{1}{e^2 a_0^{3/2}}$$

Ex: derive Thomas- Fermi Screening