

— 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 its ground state  $|\Psi_G\rangle$  and density  $\rho(r)$  are also functionals of  $V(r)$ .

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

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:

$$\text{C.f. } dE = pdV + Tds + m dB$$

$$\rightarrow G = E - TS - Bm \Rightarrow dG = pdV - sdT - Bdm$$

⑦

Basically, we need to prove different  $V(r)$  gives different  $\rho(r)$ , i.e.

if we have two different potentials  $V(r)$  and  $V'(r)$  ( $V(r) \neq V'(r) + \text{constant}$ ), they give  $\rho(r) \neq \rho'(r)$ .

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

$$\text{Otherwise } \left. \begin{aligned} (T+U+V)\Psi(r_1 \dots r_n) &= E\Psi(r_1 \dots r_n) \\ (T+U+V')\Psi(r_1 \dots r_n) &= E'\Psi(r_1 \dots r_n) \end{aligned} \right\} \Rightarrow$$

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

$V$  and  $V'$  are the same potential.

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

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

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

$$\text{i.e. } E' + \int dr \rho'(r) (V - V') > E. \quad \textcircled{1}$$

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

$$\textcircled{1} + \textcircled{2} \Rightarrow \int dr [\rho'(r) - \rho(r)] (V - V') > 0, \text{ which means}$$

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

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

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

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

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

state  $|\psi_G\rangle$  can be significantly distorted 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

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

Exchange correlation  $\left\{ \begin{array}{l} T[\rho] - T_0[\rho] \\ \text{and interaction energy beyond HF.} \end{array} \right.$

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

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

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  $\phi_{i\sigma}^*(\vec{r}) \rightarrow$

The density of Exc

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$$\left\{ \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) + \underbrace{\int dr' \frac{e^2}{|r-r'|} \rho(r')}_{V'(r)} + \underbrace{\frac{\delta E_{xc}(\rho(r))}{\delta \rho(r)}}_{\text{exchange + correlation}} \right\} \phi_{i\sigma}(\vec{r}) = \lambda_{i\sigma} \phi_{i\sigma}(\vec{r})$$

↑ Hartree

If the form of  $E_{xc}(\rho(r))$  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

$$V_{eff}(r) = V(r) + V'(r) + \frac{\delta E_{xc}(\rho(r))}{\delta \rho(r)}$$

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  $\frac{\delta E_{xc}}{\delta \rho}$  only depend on  $\rho$ . The unknown  $\frac{\delta E_{xc}(\rho)}{\delta \rho}$  can be obtained through homogenous electron gas at density  $\rho$ . Thus we separate the effect of lattice potential from correlation. — a strategy of "divide & conquer".

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

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

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

⇒ the total exchange energy

$$\sum_{\mathbf{k}} \mathcal{E}_{\text{Fock}}(k) = \frac{V}{(2\pi)^3} \int d^3k F(x) \cdot \left(-\frac{2e^2}{\pi} k_F\right) = \frac{V k_F^4}{(2\pi)^3} \cdot 4\pi \left(\frac{-2e^2}{\pi}\right) \int_0^1 x^2 F(x) dx$$

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

⇒

using the definition

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

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

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

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

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

$$\Rightarrow V_x = \frac{d\mathcal{E}_x}{d\rho} = -R_y 2 \left(\frac{3\rho a_0^3}{\pi}\right)^{1/3}$$

The correlation energy beyond HF

$$E_c(r_s) = \frac{E_c}{N} = \begin{cases} -0.2846 / (1 + 1.0529\sqrt{r_s} + 0.3334) & r_s \gg 1 \\ -0.096 + 0.0622 \ln r_s - 0.0232 r_s + 0.0040 r_s \ln r_s & r_s \ll 1 \end{cases}$$

Fitted by QMC.

RPA at  $r_s \ll 1 \Rightarrow E_c = -0.094 + 0.0622 \ln r_s + O(r_s, r_s \ln r_s)$

Wigner crystal  $r_s \gg 1 \quad E_c = \frac{-0.88}{r_s + 7.8}$

What used!

## § Thomas - Fermi approximation

$$E[\rho(r)] = \int d^3r T[\rho] + \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' \quad \left\{ \begin{array}{l} \text{Constraint} \\ \text{of total particle} \\ \text{number} \end{array} \right.$$

$$+ \int d^3r E_{xc}(\rho) + \int V(r)\rho(r) d^3r - \mu \left( \int dr \rho(r) - N \right)$$

$$\rightarrow \int \delta\rho(r) \left[ \frac{\delta T(\rho)}{\delta\rho} + V(r) + e^2 \int \frac{\rho(r')}{|r-r'|} + \frac{\delta E_{xc}(\rho)}{\delta\rho} \right] d^3r = 0$$

$\underbrace{\hspace{10em}}_{-\mu}$

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

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

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

$$\text{or } \rho(r) = \frac{1}{3\pi^2} \left[ \frac{2m}{\hbar^2} (\mu - V(r) - V_i(r)) \right]^{3/2}, \quad \text{where } V_i(r) = \int \frac{e\rho(r')}{|r-r'|} d^3r'$$

$$\left\{ \begin{array}{l} \nabla^2 V_i(r) = -4\pi e \rho(r) \end{array} \right.$$

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

Ex: derive Thomas - Fermi Screening