

## First Principle 2017-Fall Homework 2 Solution

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1. We start with Hartree-Fock hamiltonian for N electrons:

$$\begin{aligned}\hat{H}_{HF} &= \sum_{n=1}^N \hat{h}_n + \sum_{n,m,n < m}^N \frac{1}{|r_n - r_m|} \\ &= \sum_{n=1}^N \hat{h}_n + \sum_{n,m,n < m}^N \hat{V}_{nm}\end{aligned}$$

Consider the many-electrons wave function  $\Psi(x_1, x_2, \dots)$  which can be represented as Slater determinant:

$$\Psi(q_1, q_2, \dots) = \begin{vmatrix} \phi_1(q_1) & \phi_2(q_1) & \phi_3(q_1) & \dots & \phi_N(q_1) \\ \phi_1(q_2) & \phi_2(q_2) & \phi_3(q_2) & \dots & \phi_N(q_2) \\ \phi_1(q_3) & \phi_2(q_3) & \phi_3(q_3) & \dots & \phi_N(q_3) \\ \dots & \dots & \dots & \dots & \dots \\ \phi_1(q_N) & \phi_2(q_N) & \phi_3(q_N) & \dots & \phi_N(q_N) \end{vmatrix}$$

where the one-site term  $\hat{h}_n$  is non-zero only when acting on the single site.

$$\langle \Psi | \sum_n \hat{h}_n | \Psi \rangle = \sum_n T_n = \sum_n \langle \phi_n | \hat{h}_n | \phi_n \rangle$$

and the total energy is :

$$E_{HF} = \sum_n \langle \phi_n | \hat{h}_n | \phi_n \rangle + \frac{1}{2} \sum_{n,m} \langle \phi_n \phi_m | \hat{V}_{nm} | \phi_n \phi_m \rangle - \langle \phi_m \phi_n | \hat{V}_{nm} | \phi_n \phi_m \rangle$$

To derive the Koopmans' theorem we first extract the energy in orbital with wave vector  $k$  by variation optimize it with representation of Lagrangian multipliers  $\lambda_{nm}$ :

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$$\begin{aligned}
\delta \langle \Psi | \hat{F} | \Psi \rangle &= \delta \left[ \langle \Psi | \hat{H}_{HF} | \Psi \rangle - \sum_{n,m} \lambda_{nm} (\langle \phi_n | \phi_m \rangle - \delta_{nm}) \right] \\
&= \langle \delta \phi_k | \hat{h}_k | \phi_k \rangle + \langle \delta \phi_k | \hat{h}_k | \phi_k \rangle^* - \langle \delta \phi_k \phi_n | \hat{V}_{kn} | \phi_i \phi_k \rangle - \langle \delta \phi_k \phi_i | \hat{V}_{kn} | \phi_i \phi_k \rangle^* \\
&+ \sum_n \langle \phi_n \delta \phi_k | \hat{V}_{nk} | \phi_n \phi_k \rangle + \langle \phi_n \delta \phi_k | \hat{V}_{nk} | \phi_n \phi_k \rangle^* - \lambda_{kn} \langle \delta \phi_k | \phi_n \rangle - \lambda_{nk} \langle \delta \phi_k | \phi_n \rangle^* \\
&= 0
\end{aligned}$$

which we can further re-arrange into:

$$\begin{aligned}
\hat{h} \phi_k(q_1) + \sum_n \int \phi_n^*(q_2) \hat{V} [\phi_n(q_2) \phi_k(q_1) - \phi_n(q_1) \phi_k(q_2)] dq_2 &= \sum_n \lambda_{kn} \phi_n \\
&= \epsilon_k \phi_k(q_1)
\end{aligned}$$

in a sense the  $\epsilon_k$  is the representation of lagrangian multiplier that can be interpret as the energy in orbit  $k$ .

The energy difference to remove one-electron is :

$$\begin{aligned}
\Delta E &= -\langle \phi_k | \hat{h} | \phi_k \rangle + \frac{1}{2} \sum_{n,m \neq k} V_{nm} - \frac{1}{2} \sum_{n,m} V_{nm} \\
&= -\langle \phi_k | \hat{h} | \phi_k \rangle - \frac{1}{2} \sum_m \left[ \langle \phi_m \phi_k | \hat{V}_{mk} | \phi_m \phi_k \rangle - \langle \phi_k \phi_m | \hat{V}_{mk} | \phi_m \phi_k \rangle \right] \\
&\quad - \frac{1}{2} \sum_n \left[ \langle \phi_n \phi_k | \hat{V}_{nk} | \phi_n \phi_k \rangle - \langle \phi_k \phi_n | \hat{V}_{nk} | \phi_n \phi_k \rangle \right] \\
&= -\langle \phi_k | \hat{h} | \phi_k \rangle - \sum_m \left[ \langle \phi_m \phi_k | \hat{V}_{mk} | \phi_m \phi_k \rangle - \langle \phi_k \phi_m | \hat{V}_{mk} | \phi_m \phi_k \rangle \right] \\
&= -\epsilon_k \#
\end{aligned}$$

2. We first unify  $r_s$  in the unit of bohr radius  $a_0$  as  $r_s/a_0 \rightarrow r_s$  appears in energy  $E^{HF}$ ,  $E^{es}$  and  $E^{Wig}$ .

$$\begin{aligned}
\Delta E &= E^{HF} + E^{es} - E^{Wig} \\
&= \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - \frac{6}{5r_s} + \frac{3}{r_s} - \frac{3}{r_s^{3/2}} \\
&= \frac{0.884}{r_s} \left( 1 + \frac{2.21}{0.884r_s} - \frac{3}{0.884r_s^{0.5}} \right) \\
&\approx 0.884(r_s + 3.394)^{-1}
\end{aligned}$$

which is compatible with the correlation energy of Wigner crystal in Table.

3. We first unify the unit of energy  $E$  as  $(Ry)$  and  $r_s/a_0 \rightarrow r_s$ , and represent energies in terms of density  $n$ :

$$\begin{aligned} n &= \frac{N}{\Omega} = \frac{3}{4\pi} r_s^{-3} \\ E^X &= -N \frac{0.916}{r_s} = -N 0.916 \left( \frac{4\pi n}{3} \right)^{1/3} \equiv -N \chi n^{1/3} \\ E^{kin} &= N \frac{3}{5} (3\pi^2 n)^{2/3} \equiv N \gamma n^{2/3} \end{aligned}$$

To calculate the bulk modulus, we make use of energy derivation:

$$\begin{aligned} E_{tot} &= E^X + E^{kin} \\ B &= \Omega \frac{\partial^2 E_{tot}}{\partial \Omega^2} \\ &= \left[ \frac{2n^2}{N} \frac{\partial}{\partial n} - \frac{n^3}{N} \frac{\partial^2}{\partial n^2} \right] E_{tot} \end{aligned}$$

In the sense the derivation is represent in terms of density  $n$ . Using the following relations :

$$\begin{aligned} \frac{\partial E^X}{\partial n} &= N \chi \frac{1}{3} n^{-2/3} = \frac{1}{3} E^X n^{-1} \\ \frac{\partial^2 E^X}{\partial n^2} &= N \chi \frac{-2}{9} n^{-5/3} = -\frac{2}{9} E^X n^{-2} \\ \frac{\partial E^{kin}}{\partial n} &= N \gamma \frac{2}{3} n^{-1/3} = \frac{2}{3} E^{kin} n^{-1} \\ \frac{\partial^2 E^{kin}}{\partial n^2} &= N \gamma \frac{-2}{9} n^{-4/3} = -\frac{2}{9} E^{kin} n^{-2} \end{aligned}$$

We can derive the bulk modulus  $B$ :

$$\begin{aligned} B &= \frac{2n^2}{N} \left[ \frac{E^X}{3} n^{-1} + \frac{2}{3} E^{kin} n^{-1} \right] + \frac{n^3}{N} \left[ -\frac{2}{9} E^X n^{-2} - \frac{2}{9} E^{kin} n^{-2} \right] \\ &= \frac{4}{9} \frac{E^X}{N} n + \frac{10}{9} \frac{E^{kin}}{N} n \\ &= \frac{1}{6\pi r_s^3} \left[ 5 \frac{E^{kin}}{N} + 2 \frac{E^X}{N} \right]_{\#} \end{aligned}$$

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