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 $\Psi(x_1, x_2...)$ which can be represented as slater determinant:

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

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

$$\langle\Psi| \sum_{n}^{N} \hat{h}_n |\Psi\rangle = \sum_{n}^{N} T_n = \sum_{n}^{N} \langle\phi_n| \hat{h}_n |\phi_n\rangle$$

and the total energy is :

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

To derive the Koopermans' theorem we fist extract the energy in orbital with wave vector k by variation optimize it with representation of Lagrangian multipliers λ_{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:

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

in a sense the ϵ_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 :

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

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

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

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

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

$$
\begin{aligned}
n &= \frac{N}{\Omega} = \frac{3}{4\pi} r_s^{-3} \\
E^X &= -N\frac{0.916}{r_s} = -N0.916\left(\frac{4\pi n}{3}\right)^{1/3} \equiv -N\chi n^{1/3} \\
E^{kin} &= N\frac{3}{5}(3\pi^2 n)^{2/3} \equiv N\gamma n^{2/3}
\end{aligned}
$$

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 :

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

We can derive the bulk modulus B:

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

4. To derive the TF equation, we can variational optimization the total energy with Lagrangian multipliers :

$$
\delta\left(E - \mu N\right) = 0
$$

which can gives the density n in equilibration. since:

$$\begin{aligned}\delta\left(E-\mu N\right) &= \delta\left[\int \frac{3}{10}(3\pi^2)^{2/3}n^{2/3}ndr + \int Vndr - \mu\int ndr\right] \\ &= \int\left[\frac{1}{2}(3\pi^2)^{2/3}n^{2/3} + V - \mu\right]\delta(n)dr \\ &= 0\end{aligned}$$

We thus derived the TF equation :

$$\frac{1}{2}(3\pi^2)^{2/3}n^{2/3} + V - \mu = 0 \quad \#$$