8.511 Problem Set 10

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1 Second Quantization

1.1 Part (a)

A Hartree-Fock ket occupying states $\phi_{\alpha_1}, \phi_{\alpha_2}, \cdots, \phi_{\alpha_N}$ is described in second quantization by

$$\Psi = \prod_i c_i^\dagger |0\rangle$$

Since $\{c_{\alpha_i}^\dagger, c_{\alpha_j}^\dagger\} = 0$ for any two creation operators, exchanging two creation operators changes the sign of $|\Psi\rangle$. This means that $|\Psi\rangle$ is antisymmetrized. Let $\hat{A}$ be the antisymmetrization operator, then

$$\Psi = \hat{A}|\phi_{\alpha_1}\rangle|\phi_{\alpha_2}\rangle\cdots|\phi_{\alpha_N}\rangle$$

Therefore, in the representation of position and spin, the Hartree-Fock wavefunction is

$$\begin{aligned}\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \cdots, \mathbf{r}_N\sigma_N) &= \langle \mathbf{r}_1\sigma_1|\langle \mathbf{r}_2\sigma_2|\cdots\langle \mathbf{r}_N\sigma_N|\Psi\rangle \\ &= \hat{A}\phi_{\alpha_1}(\mathbf{r}_1\sigma_1)\phi_{\alpha_2}(\mathbf{r}_2\sigma_2)\cdots\phi_{\alpha_N}(\mathbf{r}_N\sigma_N)\end{aligned}$$

The antisymmetrization operator $\hat{A}$ explores all permutations of $1, 2, \cdots, N$ including the signs, giving exactly the following Slater determinant.

$$\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \cdots, \mathbf{r}_N\sigma_N) = \begin{vmatrix} \phi_{\alpha_1}(\mathbf{r}_1\sigma_1) & \phi_{\alpha_2}(\mathbf{r}_1\sigma_1) & \cdots & \phi_{\alpha_N}(\mathbf{r}_1\sigma_1) \\ \phi_{\alpha_1}(\mathbf{r}_2\sigma_2) & \phi_{\alpha_2}(\mathbf{r}_2\sigma_2) & \cdots & \phi_{\alpha_N}(\mathbf{r}_2\sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{\alpha_1}(\mathbf{r}_N\sigma_N) & \phi_{\alpha_2}(\mathbf{r}_N\sigma_N) & \cdots & \phi_{\alpha_N}(\mathbf{r}_N\sigma_N) \end{vmatrix}$$

1.2 Part (b)

Notice that for all i,

$$c_i^\dagger|\Psi\rangle = (-1)^{P_i} c_i^\dagger c_i^\dagger \prod_{j\neq i} c_j^\dagger|0\rangle = 0$$

where P_i is the number of swaps to move c_i to the beginning of all other creation operators, and the identity $c_i^\dagger c_i^\dagger = 0$ is used. Therefore,

$$\begin{aligned}\langle\Psi|H_0|\Psi\rangle &= \sum_{ij} f_{ij}\langle\Psi|c_i^\dagger c_j|\Psi\rangle \\ &= \sum_{ij} f_{ij}\langle\Psi|(\delta_{ij} - c_j c_i^\dagger)|\Psi\rangle \\ &= \sum_i f_{ii}\langle\Psi|\Psi\rangle - \sum_{ij} f_{ij}\langle\Psi|c_j c_i^\dagger|\Psi\rangle \\ &= \sum_i f_{ii}\end{aligned}$$

Moreover,

$$\begin{aligned}
\langle\Psi|H_1|\Psi\rangle &= \sum_{ijkl} V_{ijkl}\langle\Psi|c_i^\dagger c_j^\dagger c_k c_l|\Psi\rangle \\
&= \sum_{ijkl} V_{ijkl}\langle\Psi|c_i^\dagger(\delta_{jk} - c_k c_j^\dagger)c_l|\Psi\rangle \\
&= \sum_{ijkl} V_{ijkl}\langle\Psi|\delta_{jk}(\delta_{il} - c_l c_i^\dagger) - (\delta_{ik} - c_k c_i^\dagger)(\delta_{jl} - c_l c_j^\dagger)|\Psi\rangle \\
&= \sum_{ijkl} V_{ijkl}\langle\Psi|\delta_{il}\delta_{jk} - \delta_{jk}c_l c_i^\dagger - \delta_{ik}\delta_{jl} + \delta_{jl}c_k c_i^\dagger + \delta_{ik}c_l c_j^\dagger - c_k c_i^\dagger c_l c_j^\dagger|\Psi\rangle \\
&= \sum_{ijkl} V_{ijkl}\langle\Psi|\delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}|\Psi\rangle \\
&= \sum_{ij} V_{ijji} - \sum_{ij} V_{ijij} \\
&= \sum_{i\neq j} V_{ijji} - \sum_{i\neq j} V_{ijij} \\
&= \sum_{i\neq j} v_{ijji}\langle\chi_i|\chi_i\rangle\langle\chi_j|\chi_j\rangle - \sum_{i\neq j} v_{ijij}\langle\chi_i|\chi_j\rangle\langle\chi_j|\chi_i\rangle \\
&= \sum_{i\neq j} v_{ijji} - \sum_{i\neq j,\text{spin}\parallel} v_{ijij}
\end{aligned}$$

Therefore,

$$\langle\Psi|H|\Psi\rangle = \langle\Psi|H_0|\Psi\rangle + \langle\Psi|H_1|\Psi\rangle = \sum_i f_{ii} + \sum_{i\neq j} v_{ijji} - \sum_{i\neq j,\text{spin}\parallel} v_{ijij}$$

Write in first quantization language,

$$\begin{aligned}
\langle\Psi|H_0|\Psi\rangle &= \sum_i f_{ii} \\
&= \sum_i \int d\mathbf{r}_1 u_i^*(1)\left(\frac{\hbar^2\nabla_1^2}{2m} + \frac{Ze^2}{r_1}\right)u_i(1)\langle\chi_i|\chi_i\rangle \\
&= \sum_i \int d\mathbf{r}_1 u_i^*(1)h(1)u_i(1)
\end{aligned}$$

where $h(1)$ is the one body operator of kinetic energy and external potential.

$$\begin{aligned}
\langle\Psi|H_1|\Psi\rangle &= \sum_{i\neq j} v_{ijji} - \sum_{i\neq j,\text{spin}\parallel} v_{ijij} \\
&= \frac{1}{2}\int d\mathbf{r}_1 u_i^*(1)\left(\sum_{j,j\neq i}\int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}}u_j(2)\right)u_i(1) - \frac{1}{2}\int d\mathbf{r}_1 u_i^*(1)\sum_{j,j\neq i,\text{spin}\parallel}\int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}}u_i(2)u_j(1) \\
&= \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)V_H(1)u_i(1) + \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)\hat{V}_{ex}(1)u_i(1)
\end{aligned}$$

Therefore,

$$\begin{aligned}\langle\Psi|H|\Psi\rangle &= \langle\Psi|H_0|\Psi\rangle + \langle\Psi|H_1|\Psi\rangle \\ &= \sum_i \int d\mathbf{r}_1 u_i^*(1)h(1)u_i(1) + \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)V_H(1)u_i(1) + \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)\hat{V}_{ex}(1)u_i(1) \\ &= \sum_i \int d\mathbf{r}_1 u_i^*(1)(h(1)+V_H(1)+\hat{V}_{ex}(1))u_i(1) - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)V_H(1)u_i(1) - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)\hat{V}_{ex}(1)u_i(1) \\ &= \sum_i \varepsilon_i - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)V_H(1)u_i(1) - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)\hat{V}_{ex}(1)u_i(1)\end{aligned}$$

which gives exactly what we have obtained using first quantization.

2 Local Density Approximation

2.1 Part (a)

The Hohenberg-Kohn energy functional is

$$E^{HK}[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

where $T[n(\mathbf{r})]$ is the kinetic energy, $V_{ee}[n(\mathbf{r})]$ the electron-electron interactions, and $V_{ext}(\mathbf{r})$ the external potential. Imagine a non-interacting electron system with the same density $n(\mathbf{r})$, which can be decomposed as $n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})$. Rewrite the energy functional as

$$\begin{aligned}E^{HK}[n(\mathbf{r})] &= T_0[n(\mathbf{r})] + V_H[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{xc}[n(\mathbf{r})] \\ &= \sum_i \int \psi_i^*(\mathbf{r})\left(-\frac{\hbar^2\nabla^2}{2m} + V_{ext}\right)\psi_i(\mathbf{r})d\mathbf{r} + \frac{1}{2}\sum_{ij}\int \psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_i(\mathbf{r})\psi_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})]\end{aligned}$$

where $E_{xc}[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] - T_0[n(\mathbf{r})] - V_H[n(\mathbf{r})]$.

Define Lagrange multipliers ε_{ij}. We want to make the variation of $E^{HK}[n(\mathbf{r})] - \varepsilon_{ij}(\int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} - 1)$ vanish. Treat $\psi_i(\mathbf{r})$ and $\psi_i^*(\mathbf{r})$ as independent, and pick orthogonal orbitals such that $\varepsilon_{ij} = \varepsilon_i\delta_{ij}$. Therefore,

$$\int \delta\psi_i^*(\mathbf{r})\left(-\frac{\hbar^2\nabla^2}{2m} + V_{ext}\right)\psi_i(\mathbf{r})d\mathbf{r} + \sum_j \int \delta\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi_i(\mathbf{r})\psi_j(\mathbf{r}')d\mathbf{r}d\mathbf{r}' + \int V_{xc}[n(\mathbf{r})]\delta\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})d\mathbf{r}$$

$$= \varepsilon_i \int \delta\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})d\mathbf{r}$$

where $V_{xc}[n(\mathbf{r})]$ is the functional derivative of $E_{xc}[n(\mathbf{r})]$. In Local Density Approximation, $E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{xc}(n(\mathbf{r}))d\mathbf{r}$, and $V_{xc}(n(\mathbf{r})) = \mu_{xc}(n(\mathbf{r})) = d(n\varepsilon_{xc})/dn$.

Since $\delta\psi_i^*(\mathbf{r})$ is arbitrary, it follows that

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V_{ext} + \int \frac{n(\mathbf{r}')e^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \mu_{xc}(n(\mathbf{r}))\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Therefore,

$$\begin{aligned}\sum_i \varepsilon_i &= \left(\sum_i \int \psi_i^*(\mathbf{r})\left(-\frac{\hbar^2\nabla^2}{2m}\right)\psi_i^*(\mathbf{r})d\mathbf{r}\right) + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int \frac{n(\mathbf{r})n(\mathbf{r}')e^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int \mu_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r} \\ &= T_0 + 2V_H + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int \mu_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}\end{aligned}$$

Comparing with the expression for E^{HK},

$$\begin{aligned} E^{LDA} &= \sum_i \varepsilon_i - V_H + E_{xc} - \int \mu_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r} \\ &= \sum_i \varepsilon_i - \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')e^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r})(\varepsilon_{xc}(n(\mathbf{r})) - \mu_{xc}(n(\mathbf{r})))d\mathbf{r} \end{aligned}$$

2.2 Part (b)

Use the exchange energy in the previous problem set as $E_{xc}[n(\mathbf{r})]$. Then

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{xc}(n(\mathbf{r}))d\mathbf{r} = -\frac{3}{4}N\frac{e^2k_F}{\pi}$$

Therefore, $\varepsilon_{xc} = -3e^2k_F/4\pi$. And $\mu_{xc} = d(n\varepsilon_{xc})/dn = \varepsilon_{xc}$. Also notice that the external potential cancels the Hartree term. Therefore, we have

$$\left(-\frac{\hbar^2\nabla^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

The eigenstates can be taken as plane waves. Then the eigenvalues are

$$\varepsilon_i^{LDA} = \frac{\hbar^2k_i^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}$$

They are different from the Hartree-Fock eigenvalues

$$\varepsilon_i^{HF} = \frac{\hbar^2k_i^2}{2m} - \frac{2e^2k_F}{\pi}F(k_i/k_F)$$

where

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|$$

Both approximations have the same Fermi velocity, but different bandwidths.

$$\begin{aligned} \Delta\varepsilon^{LDA} &= \frac{\hbar^2k_F^2}{2m} \\ \Delta\varepsilon^{HF} &= \frac{\hbar^2k_F^2}{2m} - \frac{2e^2k_F}{\pi}(F(1)-F(0)) = \frac{\hbar^2k_F^2}{2m} + \frac{e^2k_F}{\pi} \end{aligned}$$

Finally, from part (a) (including the repulsion between positive charges),

$$\begin{aligned} E_{tot}^{LDA} &= \sum_i \varepsilon_i^{LDA} + V_{nucl} - \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')e^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r})(\varepsilon_{xc}(n(\mathbf{r})) - \mu_{xc}(n(\mathbf{r})))d\mathbf{r} \\ &= \sum_i \varepsilon_i^{LDA} \\ &= \sum_i \left(\frac{\hbar^2k_i^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right) \\ &= N\left(\frac{3}{5}\frac{\hbar^2k_F^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right) \end{aligned}$$

This result agrees with the Hartree-Fock answer in the previous problem set.

$$E_{tot}^{HF} = N\left(\frac{3}{5}\frac{\hbar^2k_F^2}{2m} - \frac{3}{4}\frac{e^2k_F}{\pi}\right)$$