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,

$$\langle \Psi | H_1 | \Psi \rangle = \sum_{ijkl} V_{ijkl} \langle \Psi | c_i^\dagger c_j^\dagger c_k c_l | \Psi \rangle$$

$$= \sum_{ijkl} V_{ijkl} \langle \Psi | c_i^\dagger (\delta_{jk} - c_k c_j^\dagger) c_l | \Psi \rangle$$

$$= \sum_{ijkl} V_{ijkl} \langle \Psi | \delta_{jk} (\delta_{il} - c_l c_i^\dagger) - (\delta_{ik} - c_k c_i^\dagger)(\delta_{jl} - c_l c_j^\dagger) | \Psi \rangle$$

$$= \sum_{ijkl} V_{ijkl} \langle \Psi | \delta_{il}\delta_{jk} - \delta_{jk} c_l c_i^\dagger - \delta_{ik}\delta_{jl} + \delta_{jl} c_k c_i^\dagger + \delta_{ik} c_l c_j^\dagger - c_k c_i^\dagger c_l c_j^\dagger | \Psi \rangle$$

$$= \sum_{ijkl} V_{ijkl} \langle \Psi | \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl} | \Psi \rangle$$

$$= \sum_{ij} V_{ijji} - \sum_{ij} V_{ijij}$$

$$= \sum_{i \neq j} V_{ijji} - \sum_{i \neq j} V_{ijij}$$

$$= \sum_{i \neq j} v_{ijji} \langle \chi_i | \chi_i \rangle \langle \chi_j | \chi_j \rangle - \sum_{i \neq j} v_{ijij} \langle \chi_i | \chi_j \rangle \langle \chi_j | \chi_i \rangle$$

$$= \sum_{i \neq j} v_{ijji} - \sum_{i \neq j, \mathrm{spin}\parallel} v_{ijij}$$

Therefore,

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

Write in first quantization language,

$$\langle \Psi | H_0 | \Psi \rangle = \sum_i f_{ii}$$

$$= \sum_i \int d\mathbf{r}_1 u_i^*(1) \left(\frac{\hbar^2 \nabla_1^2}{2m} + \frac{Ze^2}{r_1} \right) u_i(1) \langle \chi_i | \chi_i \rangle$$

$$= \sum_i \int d\mathbf{r}_1 u_i^*(1) h(1) u_i(1)$$

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

$$\langle \Psi | H_1 | \Psi \rangle = \sum_{i \neq j} v_{ijji} - \sum_{i \neq j, \mathrm{spin}\parallel} v_{ijij}$$

$$= \frac{1}{2} \int d\mathbf{r}_1 u_i^*(1) \left(\sum_{j, j \neq i} \int d\mathbf{r}_2 u_j^*(2) \frac{e^2}{r_{12}} u_j(2) \right) u_i(1) - \frac{1}{2} \int d\mathbf{r}_1 u_i^*(1) \sum_{j, j \neq i, \mathrm{spin}\parallel} \int d\mathbf{r}_2 u_j^*(2) \frac{e^2}{r_{12}} u_i(2) u_j(1)$$

$$= \frac{1}{2} \sum_i \int d\mathbf{r}_1 u_i^*(1) V_H(1) u_i(1) + \frac{1}{2} \sum_i \int d\mathbf{r}_1 u_i^*(1) \hat{V}_{ex}(1) u_i(1)$$

Therefore,

$$\langle\Psi|H|\Psi\rangle = \langle\Psi|H_0|\Psi\rangle + \langle\Psi|H_1|\Psi\rangle$$

$$= \sum_i \int d\mathbf{r}_1 u_i^*(1)h(1)u_i(1) + \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)V_H(1)u_i(1) + \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)\hat{V}_{ex}(1)u_i(1)$$

$$= \sum_i \int d\mathbf{r}_1 u_i^*(1)(h(1) + V_H(1) + \hat{V}_{ex}(1))u_i(1) - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)V_H(1)u_i(1) - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)\hat{V}_{ex}(1)u_i(1)$$

$$= \sum_i \varepsilon_i - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)V_H(1)u_i(1) - \frac{1}{2}\sum_i \int d\mathbf{r}_1 u_i^*(1)\hat{V}_{ex}(1)u_i(1)$$

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

$$E^{(HK)}[n(\mathbf{r})] = T_0[n(\mathbf{r})] + V_H[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{xc}[n(\mathbf{r})]$$

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

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

Defining 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,

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

$$= T_0 + 2V_H + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int \mu_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

Comparing with the expression for $E^{(HK)}$,

$$E^{(HK)} = \sum_i \varepsilon_i - V_H + E_{xc} - \int \mu_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

$$= \sum_i \varepsilon_i - \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')e^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int (\varepsilon_{xc}(n(\mathbf{r})) - \mu_{xc}(n(\mathbf{r})))n(\mathbf{r})d\mathbf{r}$$

2.2   Part (b)