8.511 Problem Set 8

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1 Hartree-Fock

Define one-body Hamiltonian

$$H_1 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}$$

I use J_i instead of V_H to denote the Hartree potential. Then the Hartree-Fock equation is written as

$$H_1 u_i(1) + J_i u_i(1) - \sum_{j\neq i,\text{spin}\|} \int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}} u_j(1) u_i(2) = \varepsilon_i u_i(1)$$

The parallel-spin constraint in the exchange summation can be removed, for the integral vanishes whenever i and j have anti-parallel spins.

The Hartree potential is

$$\begin{aligned}
J_i &= \sum_{j\neq i} \int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}} u_j(2) \\
&= \left(\sum_j \int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}} u_j(2)\right) - \int d\mathbf{r}_2 u_i^*(2)\frac{e^2}{r_{12}} u_i(2) \\
&= J' - \Delta J
\end{aligned}$$

where

$$\begin{aligned}
J' &= \sum_j \int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}} u_j(2) \\
\Delta J &= \int d\mathbf{r}_2 u_i^*(2)\frac{e^2}{r_{12}} u_i(2)
\end{aligned}$$

The exchange term is (the spin constraint removed)

$$\begin{aligned}
\hat{K}_i u_i(1) &= \sum_{j\neq i} \int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}} u_j(1) u_i(2) \\
&= \left(\sum_j \int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}} u_j(1) u_i(2)\right) - \int d\mathbf{r}_2 u_i^*(2)\frac{e^2}{r_{12}} u_i(1) u_i(2) \\
&= \hat{K}' u_i(1) - \Delta\hat{K} u_i(1)
\end{aligned}$$

where

$$\begin{aligned}
\hat{K}' u_i(1) &= \sum_j \int d\mathbf{r}_2 u_j^*(2)\frac{e^2}{r_{12}} u_j(1) u_i(2) \\
\Delta\hat{K} u_i(1) &= \int d\mathbf{r}_2 u_i^*(2)\frac{e^2}{r_{12}} u_i(1) u_i(2)
\end{aligned}$$

Notice that

$$\Delta J u_i(1) = \Delta \hat{K} u_i(1)$$

Therefore, the Hartree-Fock equation can be written as

$$H_1 u_i(1) + J' u_i(1) - \hat{K}' u_i(1) = \varepsilon_i u_i(1)$$

Taking dot product with $u_k(1)$, we get

$$\int d\mathbf{r}_1 u_k^*(1)(H_1 + J')u_i(1) - \sum_j \iint d\mathbf{r}_1 d\mathbf{r}_2 u_k^*(1) u_j^*(2) \frac{e^2}{r_{12}} u_j(1) u_i(2) = \varepsilon_i \int d\mathbf{r}_1 u_k^*(1) u_i(1) \tag{1}$$

Exchange i and k, then take Hermitian conjugate. Notice that H_1 and J' are both Hermitian. Therefore,

$$\int d\mathbf{r}_1 u_k^*(1)(H_1 + J')u_i(1) - \sum_j \iint d\mathbf{r}_1 d\mathbf{r}_2 u_k^*(2) u_j^*(1) \frac{e^2}{r_{12}} u_j(2) u_i(1) = \varepsilon_k^* \int d\mathbf{r}_1 u_k^*(1) u_i(1) \tag{2}$$

Subtracting equation (2) from equation (1), we have

$$\sum_j \iint d\mathbf{r}_1 d\mathbf{r}_2 u_k^*(2) u_j^*(1) \frac{e^2}{r_{12}} u_j(2) u_i(1) - \sum_j \iint d\mathbf{r}_1 d\mathbf{r}_2 u_k^*(1) u_j^*(2) \frac{e^2}{r_{12}} u_j(1) u_i(2) = (\varepsilon_i - \varepsilon_k^*) \int d\mathbf{r}_1 u_k^*(1) u_i(1)$$

The difference between the first term and the second term is a swap of arguments. Since $r_{12} = r_{21}$, we can exchange 1 and 2 in the first term, making it identical to the second. Therefore, the left hand side vanishes.

$$(\varepsilon_i - \varepsilon_k^*) \int d\mathbf{r}_1 u_k^*(1) u_i(1) = 0$$

Let $i = k$, then $\varepsilon_i - \varepsilon_i^* = 0$, which means ε_i is real.

Let $i \neq k$. If no degeneracy occurs, $\varepsilon_i \neq \varepsilon_k$, so $\langle u_i | u_k \rangle = 0$. If ε_i and ε_k are degenerate, there is some unitary matrix $\mathbf{T}$ that diagonalizes the degenerate subspace. Later I will prove that this unitary transformation preserves the Hartree-Fock equation. Then there is a way to choose u_i and u_k such that $\langle u_i | u_k \rangle = 0$ even if degeneracy occurs.

Therefore, the solutions are orthonormal: $\langle u_i | u_j \rangle = \delta_{ij}$

Proof of the fact that $\mathbf{T}$ preserves the Hartree-Fock equation:

Let $\tilde{\mathbf{u}} = \mathbf{T}\mathbf{u}$, where $\mathbf{u} = (u_1, u_2, \cdots, u_n)^T$ are the original states, and $\tilde{\mathbf{u}} = (\tilde{u}_1, \tilde{u}_2, \cdots, \tilde{u}_n)^T$ are the diagonalized states. Since H_1 is linear, $H_1(\mathbf{T}\mathbf{u}(1)) = \mathbf{T} H_1 \mathbf{u}(1)$.

The Hartree potential is unaffected by the uniform transformation, i.e. $\tilde{J}'(\mathbf{T}\mathbf{u}(1)) = \mathbf{T} J' \mathbf{u}(1)$, for

$$\begin{aligned}
\tilde{J}'(\mathbf{T}\mathbf{u}(1)) &= \sum_j \int d\mathbf{r}_2 \tilde{u}_j^*(2) \frac{e^2}{r_{12}} \tilde{u}_j(2) \tilde{\mathbf{u}}(1) \\
&= \int d\mathbf{r}_2 \frac{e^2}{r_{12}} (\mathbf{u}^\dagger(2) \mathbf{T}^\dagger)(\mathbf{T}\mathbf{u}(2))(\mathbf{T}\mathbf{u}(1)) \\
&= \int d\mathbf{r}_2 \frac{e^2}{r_{12}} \mathbf{u}^\dagger(2) \mathbf{u}(2) (\mathbf{T}\mathbf{u}(1)) \\
&= \mathbf{T} \sum_j \int d\mathbf{r}_2 u_j^*(2) \frac{e^2}{r_{12}} u_j(2) \mathbf{u}(1) \\
&= \mathbf{T} J' \mathbf{u}(1)
\end{aligned}$$

The exchange operator is also unaffected by the uniform transformation, i.e. $\hat{\tilde{K}}'(\mathbf{Tu}(1)) = \mathbf{T}\hat{K}'\mathbf{u}(1)$, for

$$\begin{aligned}
\hat{\tilde{K}}'(\mathbf{Tu}(1)) &= \sum_j \int d\mathbf{r}_2 \tilde{u}_j^*(2) \frac{e^2}{r_{12}} \tilde{u}_j(1) \tilde{\mathbf{u}}(2) \\
&= \int d\mathbf{r}_2 \frac{e^2}{r_{12}} (\mathbf{u}^\dagger(2)\mathbf{T}^\dagger)(\mathbf{Tu}(1))(\mathbf{Tu}(2)) \\
&= \int d\mathbf{r}_2 \frac{e^2}{r_{12}} \mathbf{u}^\dagger(2)\mathbf{u}(1)(\mathbf{Tu}(2)) \\
&= \mathbf{T} \sum_j \int d\mathbf{r}_2 u_j^*(2) \frac{e^2}{r_{12}} u_j(1)\mathbf{u}(2) \\
&= \mathbf{T}\hat{K}'\mathbf{u}(1)
\end{aligned}$$

Therefore, the uniform transformation preserves the Hartree-Fock equation.

2 Schottky Barrier