8.511 Problem Set 8

Yijun Jiang

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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

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

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

2.1 Part (a)

Before contact, the conduction band E_c of the semiconductor is higher than the chemical potential μ of the metal, and the valance band E_v is lower than μ. The chemical potential of the n-type semiconductor is close to E_c and thus higher than μ. In contact and in equilibrium, the semiconductor chemical potential equals μ, since the electric potential in the metal-semiconductor junction bends E_c and E_v downwards. Close to $z = 0$, in the semiconductor both E_c and E_d are way higher than μ relative to k_BT, which means almost no population of electrons. This leads to a depletion region.

In the depletion region, the charge is dominated by ionized doner cores, whose density is N_d. The ionized electrons move to the metal side. In order to charge neutralize metal-semiconductor junction, these electrons will form a thin negatively charged layer on the metal boundary.

The boundary conditions are $\phi'(z_0) = 0$ and $\phi(z_0) - \phi(0) = E_B/e$. Define the zero point of ϕ at $z = 0$. Then the solution to Poisson's equation has the form

$$\phi(z) = -\frac{2\pi N_d e}{\varepsilon}((z - z_0)^2 - z_0^2)$$

where

$$\phi(z_0) = \frac{2\pi N_d e}{\varepsilon}z_0^2 = \frac{E_B}{e}$$

Therefore,

$$z_0 = \frac{1}{e}\sqrt{\frac{\varepsilon E_B}{2\pi N_d}}$$

Plugging this into the expression for $\phi(z)$,

$$\begin{aligned}
\phi(z) &= -\frac{E_B}{e}\left(\left(\frac{z}{z_0} - 1\right)^2 - 1\right) \\
&= -\left(\sqrt{\frac{2\pi N_d e}{\varepsilon}}z - \sqrt{\frac{E_B}{e}}\right)^2 + \frac{E_B}{e}
\end{aligned}$$

Using the numerical values, we get

$$z_0 \approx 5.76 \times 10^{-7}\ \text{m} = 5.76 \times 10^3\ \text{Å}$$

2.2 Part (b)

The electrons see a potential barrier

$$\begin{aligned} V(z) &= \eta(z)E_B - e\phi(B) \\ &= \begin{cases} 0 & (z < 0 \text{ or } z > z_0) \\ E_B\left(\frac{z}{z_0} - 1\right)^2 & (0 \leqslant z \leqslant z_0) \end{cases} \end{aligned}$$

where $\eta(z) = 1$ if $z \geqslant 0$ and 0 otherwise.

Then

$$\kappa(z) = \frac{\sqrt{2mV(z)}}{\hbar} = \frac{\sqrt{2mE_B}}{\hbar}\left(1 - \frac{z}{z_0}\right)$$

And WKB gives

$$\begin{aligned} P &= \exp\left(-2\int_0^{z_0} \kappa(z)dz\right) \\ &= \exp\left(-\frac{2\sqrt{2mE_B}z_0}{\hbar}\int_0^1 (1-x)dx\right) \\ &= \exp\left(-\frac{\sqrt{2mE_B}z_0}{\hbar}\right) \\ &= \exp\left(-\frac{E_B}{e\hbar}\sqrt{\frac{\varepsilon m}{\pi N_d}}\right) \end{aligned}$$

2.3 Part (c)

Probability for an electron to flow from the metal side to the semiconductor side is $P(m \to s) = (\exp(E_B/kT) + 1)^{-1} \approx \exp(-E_B/kT)$. Probability for an electron to flow from the semiconductor side to the metal side is $P(s \to m) = (\exp((E_B - eV)/kT) + 1)^{-1} \approx \exp((eV - E_B)/kT)$. Therefore, the current is

$$I \propto P(s \to m) - P(m \to s) = \exp(-E_B/kT)(\exp(eV/kT) - 1)$$