Problem 1

Consider a system consisting of G ion cores and N valence electrons, which interact mutually through the electrostatic interaction. The Schrödinger equation for the system is

$$\left[-\frac{\hbar^2}{2}\sum_{\lambda=1}^{G}\frac{1}{M_\lambda}\Delta_\lambda - \frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_i + \mathcal{V}(\boldsymbol{r},\,\boldsymbol{R})\right]\Psi = E_t\Psi, \tag{1}$$

$$\mathcal{V}(\boldsymbol{r},\,\boldsymbol{R}) = \sum_{\lambda>\mu}\frac{Z_\lambda Z_\mu e^2}{|\boldsymbol{R}_\lambda - \boldsymbol{R}_\mu|} - \sum_{\lambda=1}^{G}\sum_{i=1}^{N}\frac{Z_\lambda e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_\lambda|} + \sum_{i>j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{2}$$

where M_λ、$\boldsymbol{R}_\lambda$、$Z_\lambda e$ are the mass, coordinate and charge of the λ-th ion core, and m, the mass of electron, $\boldsymbol{r}_i$, the coordinate of i-th electron. And

$$\Delta_\lambda = \nabla_\lambda^2 = \frac{\partial^2}{\partial X_\lambda^2} + \frac{\partial^2}{\partial Y_\lambda^2} + \frac{\partial^2}{\partial Z_\lambda^2},$$
$$\Delta_i = \nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2},$$
$$\sum_{\lambda>\mu} \equiv \sum_{\lambda}\sum_{\mu} \quad (\text{only for } \lambda>\mu) \quad = \sum_{\lambda=2}^{G}\sum_{\mu=1}^{\lambda-1},$$
$$\sum_{i>j} \equiv \sum_{i}\sum_{j} \quad (\text{only for } i>j) \quad = \sum_{i=2}^{N}\sum_{j=1}^{i-1}.$$

The terms in the brace of (1), Hamiltonian, represent the kinetic energy of ion cores, the kinetic energy of electrons, and the total potential energy. The potential $\mathcal{V}(\boldsymbol{r},\,\boldsymbol{R})$ consists of the Coulomb potential energy between cores, between core and electron, and between electrons. The wave function of the system is

$$\Psi = \Psi(\boldsymbol{r},\,\boldsymbol{R}) = \Psi(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N,\,\boldsymbol{R}_1,\cdots,\boldsymbol{R}_G). \tag{3}$$

The total energy of the system E_t is given by

$$E_t = -\frac{\hbar^2}{2}\sum_{\lambda}\frac{1}{M_\lambda}\int\Psi^*\,\Delta_\lambda\,\Psi\,dV - \frac{\hbar^2}{2m}\sum_{i}\int\Psi^*\,\Delta_i\,\Psi\,dV + \int\Psi^*\,\mathcal{V}\,\Psi\,dV, \tag{4}$$

where $dV \equiv d\boldsymbol{r}_1\cdots d\boldsymbol{r}_N\,d\boldsymbol{R}_1\cdots d\boldsymbol{R}_G$.

Given that the kinetic energy of ion cores is sufficiently small, the equation of motion for electrons is

$$\left[-\frac{\hbar^2}{2m}\sum_{i}\Delta_i + \mathcal{V}(\boldsymbol{r},\,\boldsymbol{R})\right]\psi = E\psi. \tag{5}$$

This equation describes the N-eletron system interacting each other in the electrostatic field due to ion cores fixed in a given distribution. The wave function and energy of the N-electron system

$$\psi = \psi(\boldsymbol{r}_1,\cdots,\boldsymbol{r}_N;\boldsymbol{R}), \quad E = E(\boldsymbol{R}) \tag{6}$$

include the coordinates of ion cores $\boldsymbol{R} = (\boldsymbol{R}_1,\cdots,\boldsymbol{R}_G)$ as parameters.

Assume that (5) is solved, that is, the wave function ψ of N-electron system is known. Use the following trial function for the wave function Ψ of the entire system

$$\Psi(\boldsymbol{r},\,\boldsymbol{R}) = \psi(\boldsymbol{r},\,\boldsymbol{R})\cdot v(\boldsymbol{R}). \tag{7}$$

Show that the equation of motion for cores is

$$\left[-\frac{\hbar^2}{2}\sum_\lambda \frac{1}{M_\lambda}\Delta_\lambda + E(\boldsymbol{R})\right] v = E_t\, v + \delta \mathrm{H}\cdot v, \tag{8}$$

where

$$\delta \mathrm{H}\cdot v = \hbar^2 \sum_\lambda \frac{1}{M_\lambda}(\nabla_\lambda v)\int \psi^*(\nabla_\lambda \psi)\, d\boldsymbol{r} + \frac{\hbar^2}{2}\sum_\lambda \frac{1}{M_\lambda} v \int \psi^*(\Delta_\lambda \psi)\, d\boldsymbol{r}. \tag{9}$$

Problem 2

The Schrödinger equation for N-electron system [Problem 1 (5)] is equivalent to the following variation principle

$$\delta E = \delta\left\{\int \psi^*\, H\, \psi\, d\tau\right\} = 0, \tag{10}$$

$$\int \psi^*\psi\, d\tau = 1. \tag{11}$$

When ψ is given by a Slater determinant

$$\psi(1,\cdots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \vdots & \vdots & & \vdots \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix}, \tag{12}$$

the expectation value of the energy is

$$\begin{aligned} E =& \langle H\rangle = \int \psi^*\, H\, \psi\, d\tau_1 d\tau_2 \cdots d\tau_N \\ =& \sum_i \int \varphi_i^*(1)\, H_1\, \varphi_i(1)\, d\tau_1 + \sum_{i>j}\int \varphi_i^*(1)\varphi_j^*(2)\,\frac{e^2}{r_{12}}\,\varphi_i(1)\varphi_j(2)\, d\tau_1 d\tau_2 \\ & - \sum_{i>j}\int \varphi_i^*(1)\varphi_j^*(2)\,\frac{e^2}{r_{12}}\,\varphi_i(2)\varphi_j(1)\, d\tau_1 d\tau_2, \end{aligned} \tag{13}$$

where

$$H = \sum_i H_i + \sum_{i>j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}, \tag{14}$$

$$H_i = -\frac{\hbar^2}{2m}\Delta_i - \sum_\lambda \frac{Z_\lambda e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_\lambda|}, \tag{15}$$

and variables $1, 2, \cdots$ of one-electron wave function φ represent $\tau_1, \tau_2, \cdots$ being $\tau \equiv \boldsymbol{r}\sigma$, the space and spin coordinates of electron.

In order to give minima of E, $\{\varphi_i\}$ $(i = 1, \ldots, N)$ must meet the following condition for arbitrary φ_i^*;

$$\begin{aligned} \delta E =& \int \delta\varphi_i^*(1)\, H_1\, \varphi_i(1)\, d\tau_1 + \sum_{j(\neq i)}\int \delta\varphi_i^*(1)\varphi_j^*(2)\,\frac{e^2}{r_{12}}\,\varphi_i(1)\varphi_j(2)\, d\tau_1 d\tau_2 \\ & - \sum_{j(\neq i)}\int \delta\varphi_i^*(1)\varphi_j^*(2)\,\frac{e^2}{r_{12}}\,\varphi_i(2)\varphi_j(1)\, d\tau_1 d\tau_2 - \epsilon_i \int \delta\varphi_i(1)\varphi_i(1)\, d\tau_1 = 0. \end{aligned} \tag{16}$$

Thus one obtains the Hartree Fock equation for φ_i:

$$H_1\,\varphi_i(1) + \left[\sum_{j(\neq i)} \int |\varphi_j(2)|^2\,\frac{e^2}{r_{12}}\,d\tau_2\right]\varphi_i(1) - \sum_{j(\neq i)}\left[\int \varphi_j^*(2)\varphi_i(2)\,\frac{e^2}{r_{12}}\,d\tau_2\right]\varphi_j(1) = \epsilon_i\,\varphi_i(1). \tag{17}$$

Show that the wave functions φ_i and φ_j ($\epsilon_i \neq \epsilon_j$) are mutually orthogonal.

Problem 3

Show the orthonormality of the Bloch function

$$\int_\Omega d\boldsymbol{r}\,\phi_k^*(\boldsymbol{r})\phi_{k'}(\boldsymbol{r}) = \delta_{k\,k'}. \tag{18}$$

Here Ω is the volume of the crystal.

Problem 4

When the potential $V(\boldsymbol{r})$ seen by an electron in a crystal is invariant under any lattice translation $\boldsymbol{T}$, the energy of the electron must be periodic in the reciprocal lattice;

$$\epsilon(\boldsymbol{k}) = \epsilon(\boldsymbol{k} + \boldsymbol{G}). \tag{19}$$

Any periodic function in the reciprocal space ($\boldsymbol{k}$-space) can be expanded as a Fourier series with lattice translation vectors;

$$\epsilon(\boldsymbol{k}) = \sum_{\boldsymbol{T}} \epsilon_T\,e^{i\boldsymbol{k}\cdot\boldsymbol{T}}. \tag{20}$$

(a) Show that $\epsilon(\boldsymbol{k})$ has a minimum or maximum at $\boldsymbol{k} = \boldsymbol{G}/2$ and $\boldsymbol{k} = \boldsymbol{G}$, where $\boldsymbol{G}$ is a reciprocal vector.

The effective mass tensor m_{ij}^* is defined by

$$\frac{1}{m_{ij}^*} \equiv \frac{1}{\hbar^2}\,\frac{\partial^2\epsilon(\boldsymbol{k})}{\partial k_i\,\partial k_j}. \tag{21}$$

(b) Calculate m_{ij}^* for the energy given by (20) and show that the effective mass at $\boldsymbol{k} = \boldsymbol{b}_i/2$ has a sign opposite to that at $\boldsymbol{k} = \boldsymbol{0}$. Here $\boldsymbol{b}_i$ is one of the primitive translation vector of the reciprocal lattice ($i = 1,\ 2,\ 3$).