

Chapter 2

2.1 (a) Na in bcc. $n = 2/a^3$ where a is the cube edge.

$$k_F = (3\pi^2 n)^{1/3} = (6\pi^2)^{1/3} / a$$

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} \frac{(6\pi^2)^{1/3}}{a} \sim 10^6 \text{ m/s} \dots \textcircled{1}$$

(b) An estimate of the ionic velocity can be obtained by using

$$\frac{1}{2} M v_I^2 = \frac{3}{2} k_B T$$

At room temperature $T = 300 \text{ K}$, this gives

$$v_I \simeq 42 \text{ m/s} \dots \textcircled{2}$$

(c) From $\textcircled{1}$ and $\textcircled{2}$ we get $\frac{v_I}{v_F} \sim 4.2 \times 10^{-5} \sim \frac{m}{M}$

2.2 Let E_T and ϕ_T be the true ground state energy and wavefunction respectively.

$$H |\phi_T\rangle = E_T |\phi_T\rangle$$

$$\text{or } E_T = \langle \phi_T | H | \phi_T \rangle / \langle \phi_T | \phi_T \rangle$$

$$\begin{aligned} \text{or } E_T \langle \phi_T | \phi_T \rangle &= \langle \phi_T | T_E + T_I + V_{II} + V_{IE} + V_{EE} | \phi_T \rangle \\ &= \langle \phi_T | T_I + V_{II} | \phi_T \rangle + \langle \phi_T | T_E + V_{IE} + V_{EE} | \phi_T \rangle \end{aligned} \dots \textcircled{1}$$

Let ϕ_{BO} and E_{BO} be the BO wavefunction and energy respectively.

$$\phi_{BO} = |\chi_I\rangle |\psi_E\rangle \dots \textcircled{2}$$

$$(T_E + V_{IE} + V_{EE}) |\psi_E\rangle = E_E |\psi_E\rangle \dots \textcircled{3}$$

$$(T_I + V_{II} + E_E) |\chi_I\rangle = E_{BO} |\chi_I\rangle \dots \textcircled{4}$$

From (3) $E_E \langle \Psi_E | \Psi_E \rangle = \langle \Psi_E | T_E + V_{IE} + V_{EE} | \Psi_E \rangle \dots (5)$

Since $|\Psi_E\rangle$ is solution of (5), from the variational principle we get

$$\langle \Psi_E | T_E + V_{IE} + V_{EE} | \Psi_E \rangle \leq \langle \phi_T | T_E + V_{IE} + V_{EE} | \phi_T \rangle \dots (6)$$

Substituting in (1) we get

$$\begin{aligned} E_T \langle \phi_T | \phi_T \rangle &\geq \langle \phi_T | T_I + V_{II} | \phi_T \rangle + \langle \phi_T | E_E | \phi_T \rangle \\ &\geq \langle \phi_T | T_I + V_{II} + E_E | \phi_T \rangle \\ &\geq E_{B0} \langle \phi_T | \phi_T \rangle \end{aligned}$$

or $E_T \geq E_{B0}$

Hence proved

2.3

Hartree equation for ψ_1 in a.u.



$$-\frac{\nabla_1^2}{2} \psi_1(\vec{r}_1) - \frac{2}{r_1} \psi_1(\vec{r}_1) + \int \frac{|\psi_2(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \psi_1(\vec{r}_1) = E_1 \psi_1(\vec{r}_1)$$

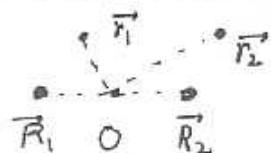
Both electrons are in the lowest energy state $\Rightarrow \psi_2 = \psi_1$.

Also they have opposite spins. This implies that the exchange interaction is zero. Therefore H-F equation reduces to the Hartree equation given above.

2.4

Hydrogen molecule

Hartree eq. for ψ_1 in a.u.



$$-\frac{\nabla_1^2}{2} \psi_1(\vec{r}_1) - \left(\frac{1}{|\vec{r}_1 - \vec{R}_1|} + \frac{1}{|\vec{r}_1 - \vec{R}_2|} \right) \psi_1(\vec{r}_1) + \int \frac{|\psi_2(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d^3r_2 \psi_1(\vec{r}_1) = E_1 \psi_1(\vec{r}_1)$$

In the lowest energy state both electrons have opposite spins. Therefore H-F equation reduces to Hartree equation as in 2.3.

2.5

$$\Psi_{HF}(x_1, x_2, \dots, x_N) = A \sum_P (-1)^P P \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N)$$

where A = Normalization constant and $x \equiv (\vec{r}, s)$

and $\int \psi_i^*(x_i) \psi_j(x_i) dx_i = \delta_{ij} \dots \textcircled{1}$

$$\int \Psi_{HF}^* \Psi_{HF} d\tau = \int \Psi_{HF}^* A \sum_P (-1)^P P \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N) d\tau$$

$$= A \sum_P (-1)^P P \int (P^{-1} \Psi^*) \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N) d\tau$$

$$= A \sum_P \int \Psi^* \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N) d\tau$$

$$= A N! \int \Psi^* \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N) d\tau$$

$$= A^2 N! \quad \text{using } \textcircled{1}$$

$$= 1 \quad \text{or} \quad A = \frac{1}{\sqrt{N!}}$$

2.6

Koopmans' Theorem

The total energy in H-F method is given by (in a.u.)

$$\begin{aligned} E = & \sum_i \psi_i^*(\vec{r}) \left[-\frac{\nabla^2}{2} + V_I(\vec{r}) \right] \psi_i(\vec{r}) d^3r \\ & + \frac{1}{2} \sum_i \sum_j \int \frac{|\psi_i(\vec{r})|^2 |\psi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d^3r d^3r' \\ & - \frac{1}{2} \sum_i \sum_j \int \psi_j^*(\vec{r}') \psi_i(\vec{r}') \psi_j(\vec{r}) \psi_i^*(\vec{r}) d^3r d^3r' \end{aligned}$$

|| spins

Let us now remove $i = k$ electron from the N electron system.

We assume that this does change remaining ψ_i and ϵ_i . Let

E' be the energy of the $(N-1)$ electron system.

$$\begin{aligned} E' = & \sum_{i \neq k} \psi_i^*(\vec{r}) \left[-\frac{\nabla^2}{2} + V_I(\vec{r}) \right] \psi_i(\vec{r}) d^3r \\ & + \frac{1}{2} \sum_{i \neq k} \sum_{j \neq k} \int \frac{|\psi_i(\vec{r})|^2 |\psi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d^3r d^3r' \\ & - \frac{1}{2} \sum_{i \neq k} \sum_{j \neq k} \int \psi_i^*(\vec{r}) \psi_j^*(\vec{r}') \psi_i(\vec{r}') \psi_j(\vec{r}) d^3r d^3r' \end{aligned}$$

|| spins

This gives

$$\begin{aligned}
 E - E' &= \int \psi_k^*(\vec{r}) \left[-\frac{\nabla^2}{2} + V_I(\vec{r}) \right] \psi_k(\vec{r}) d^3r \\
 &+ \sum_{j \neq k} \int \frac{|\psi_k(\vec{r})|^2 |\psi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d^3r d^3r' \\
 &- \sum_{\substack{j \neq k \\ \text{11 spins}}} \int \frac{\psi_k^*(\vec{r}) \psi_j(\vec{r}) \psi_k(\vec{r}') \psi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' \\
 &= E_k
 \end{aligned}$$

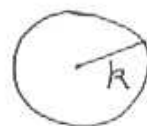
or $E' - E = -E_k =$ energy to remove an electron from k^{th} state.

2.8

In 2D constant energy surface in k -space is a circle.

$$E = \frac{\hbar^2 k^2}{2m}$$

Area of the circle = πk^2



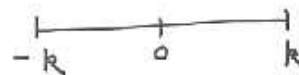
Number of states within the circle = $2 \cdot \frac{\pi k^2}{4\pi^2/A} = N(E)$

where the factor of 2 is due to spin and A is area of the sample.

$$N(E) = \frac{A k^2}{2\pi} = \frac{A 2mE}{\hbar^2 2\pi} = \frac{AmE}{\hbar^2 \pi}$$

$$P(E) = \frac{dN}{dE} = \frac{Am}{\hbar^2 \pi} = \text{constant}$$

In 1D, the k -space is a line. We want to calculate number of states lying between $-k$ and k , of length $2k$.



$$N(E) = 2 \cdot \frac{2k}{2\pi/L} = \frac{2Lk}{\pi} = \frac{2L}{\pi} \left(\frac{2mE}{\hbar^2} \right)^{1/2}$$

where 2 is for spin and L is the length of the sample.

$$P(E) = \frac{dN}{dE} = \frac{L}{\pi} \left(\frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{E^{1/2}}$$

2.9

$$\epsilon_x(\vec{k}) = -\frac{e^2}{\omega \epsilon_0} \sum_{\vec{k}'} \frac{1}{|\vec{k} - \vec{k}'|^2}$$

$$= -\frac{e^2}{\omega \epsilon_0} \frac{\omega}{8\pi^3} \int \frac{d^3 k'}{|\vec{k} - \vec{k}'|^2}$$

Assume k'_z axis along \vec{k} . Then

$$\epsilon_x(\vec{k}) = -\frac{e^2}{8\pi^3 \epsilon_0} \int_0^{k_F} \int_0^{2\pi} \int_0^\pi \frac{k'^2 dk' \sin\theta d\theta d\phi}{[k^2 + k'^2 - 2kk' \cos\theta]}$$

$$= \frac{-e^2 \cdot 2\pi}{8\pi^3 \epsilon_0} \int_0^{k_F} \frac{k'^2 dk'}{2kk'} [\ln|k+k'|^2 - \ln|k-k'|^2]$$

$$= \frac{-e^2}{8\pi^2 k \epsilon_0} \int_{-k_F}^{+k_F} k' dk' \ln|k+k'|^2$$

Integrating by parts we get

$$\epsilon_x(\vec{k}) = -\frac{e^2 k_F}{8\pi^2 \epsilon_0} \left[2 + \frac{k_F^2 - k^2}{k k_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right]$$

2.10

Let E_0 be the exact ground state energy of the system.

The variational principle implies that

$$\langle \phi | H | \phi \rangle \geq E_0$$

where ϕ is the H-F Slater determinant. But the LHS is the H-F energy E_{HF} . Thus

$$E_{HF} \geq E_0 \quad \text{Hence proved.}$$

2.13

For free electron gas in 3D

$$\rho(\epsilon) = \frac{\omega}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}$$

$$N = \frac{\omega}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon_F^{3/2}$$

$$T = \int_0^{\epsilon_F} \epsilon \rho(\epsilon) d\epsilon = \frac{3}{5} \epsilon_F N$$