

PHYS 825 PROBLEM SET III

I. In class*, we obtained the band structure of electrons in the tight binding model as

$$\epsilon_k = A - \sum_l \gamma(R_l) e^{ik \cdot R_l}.$$

This ϵ_k is the energy of an electron that has wave vector k . The constants are

$$A = \int d\mathbf{r} \phi^*(r) H \phi(r)$$

and

$$\gamma(R) = - \int d\mathbf{r} \phi^*(r) H \phi(r - R)$$

where H is the Hamiltonian of the solid and $\phi(r)$ is an atomic wave function of an electron. If we write $H = H_{at} + \Delta U$, where H_{at} is the Hamiltonian of the atom at $R = 0$, then

$$\begin{aligned} A &= \int d\mathbf{r} \phi^*(r) H_{at} \phi(r) + \int d\mathbf{r} \phi^* \Delta U \phi(r) \\ &= \epsilon_{at} - \beta \end{aligned}$$

where ϵ_{at} is the atomic energy of the electron in atomic orbital $\phi(r)$ and β is defined by the second integral.

1. Show that the band structure of a linear lattice, keeping nearest neighbour overlap only, ($R_l = la$) is

$$\epsilon_k = A - 2\gamma \cos(ka)$$

Plot the band structure in first Brillouin zone.

2. The overlap energy $\gamma(R)$ for two hydrogen atoms in 1s states separated a distance R is

$$\gamma(R) = 2\left(1 + \frac{R}{a_0}\right) e^{-\frac{R}{a_0}} \quad \text{Ryd}$$

compare the band width 2γ of a linear lattice of these H atoms at lattice spacing $R = 4a_0$ with ϵ_{at} . Show that the second weakest neighbour $\gamma(2R)$ is much less than $\gamma(R)$.

3. Show that ϵ_k for a 2D square lattice in the x, y plane of spacing a is

$$\epsilon_k = A - 2\gamma [\cos(k_x a) + \cos(k_y a)]$$

4. Show that ϵ_k for the 2D square lattice with an atom in the center of the square is,

$$\epsilon_k = A - 4\gamma \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right)$$

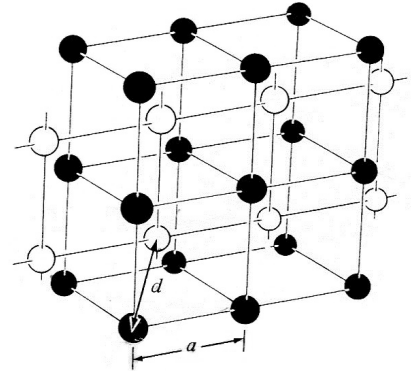
* See Also Chapter 10 Ashcroft & Mermin,

p. 38 Mahan

p. 229 Chapter 9 Kittel.

II. Potential Energy of $CsCl$ - Ewald Sum

$CsCl$ is an inlocking cubic structure of Cs and Cl ions shown opposite.



- Write down the direct lattice vectors
 $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3$
for the $CsCl$ lattice in terms of the lattice spacing a .
- Define the reciprocal lattice \mathbf{G} and write down the reciprocal lattice for $CsCl$.
- There are two atoms per unit cell. Write down the positions $\mathbf{R}_{l\kappa} = \mathbf{T}_l + \mathbf{d}_\kappa$ of the two atoms $\kappa = 1$ and $\kappa = 2$ in the unit cell, e.g.

$$(\mathbf{R}_{l1} = \mathbf{T}_l, \mathbf{R}_{l2} = \mathbf{T}_l + \mathbf{d}_2)$$

and determine d_2 .

- The total electrostatic potential energy (PE) of the ionic crystal is

$$U_T = \frac{1}{2} \sum_{l\kappa} \sum'_{l'\kappa'} V(R_{l\kappa} - R_{l'\kappa'})$$

$$= \frac{1}{2} \sum_{l\kappa} \left[\sum'_{l' \neq l} V(R_{l\kappa} - R_{l'\kappa}) + \sum_{l'=l} V(R_{l\kappa} - R_{l'\kappa'}) \right]$$

where in the first term $\kappa' = \kappa$ and in the second $\kappa' \neq \kappa$. $\sum_{l\kappa} = N_i =$ number of ions. The square bracket in V_T is independent of l and κ so that we may take $l = 0, \kappa = 1$ and replace the sum by N_i . It is usual to express the $P.E.$ as the $P.E.$ per ion pair. $N = N_i/2$ is the number of ion pairs (N is also the number of unit cells in the lattice). We also take the origin at R_{l1} i.e. $R_{l\kappa}(\kappa = 1) = 0$. The PE is

$$U_T = \frac{N_i}{2} \left[\sum_{l' \neq 0} V(|\mathbf{T}_{l'}|) + \sum_{l'=0} V(|\mathbf{T}_{l'} + \mathbf{d}_2|) \right]$$

Including only the electrostatic term $V(R) = +e^2/|R|$ and writing $l' = l$, the *PE* per ion pair $U = U_T/N$ is

$$U = e^2 \left[\sum_{l \neq 0} \frac{1}{T_l} - \sum_{l=0} \frac{1}{|\mathbf{T}_1 + \mathbf{d}_2|} \right],$$

$$\equiv -\frac{e^2}{d_2} \alpha_M, \quad \alpha_M - \text{Madelung constant}$$

As in class, we express $1/r$ in terms of a “reciprocal space” part and a “direct space” part (η is a parameter),

$$\frac{1}{R} = \int \frac{d^3Q}{(2\pi)^3} \cdot \frac{4\pi}{Q^2} e^{-\frac{Q^2}{4\eta}} e^{iQ \cdot R} + \frac{1}{R} [1 - \text{erf}(\sqrt{\eta}R)]$$

where η is a parameter.

(A) Denoting these two terms terms a and b , show that the *PE* per ion pair is (starting with $1/r$ above)

$$U = U_a + U_b$$

$$U_a = e^2 \left[\frac{4\pi}{\Omega_0} \sum_G \frac{1}{G^2} e^{-\frac{G^2}{4\alpha^2}} [1 - e^{i\mathbf{G} \cdot \mathbf{d}_2}] - 2\left(\frac{\eta}{\pi}\right)^{1/2} \right]$$

$$U_b = e^2 \left[\sum_{l \neq 0} \frac{1}{T_l} [1 - \text{erf}(\sqrt{\eta}T_l)] - \sum_{l=0} \frac{1}{|\mathbf{T}_1 + \mathbf{d}_2|} [1 - \text{erf}(\sqrt{\eta}(\mathbf{T}_1 + \mathbf{d}_2))] \right]$$

(B) Choosing $\sqrt{\eta} = \frac{\gamma}{|a|}$, where γ is a dimensionless constant and ($a = T_1 - T_0$) and writing

$$U = U_a + U_b = -\frac{e^2}{d_2} \alpha_M = -\frac{e^2}{d_2} (\alpha_M^a + \alpha_M^b)$$

evaluate the madelung constant α_M using

(a). α_M^a - the 6 nearest (shortest) reciprocal lattice vectors

$$\mathbf{G} = \pm \frac{2\pi}{a} \hat{i}, \pm \frac{2\pi}{a} \hat{j}, \pm \frac{2\pi}{a} \hat{k}$$

- (b). α_M^b - the 8 1^{st} nearest neighbors ($l = 0$) ($\mathbf{T}_1 + \mathbf{d}_2 = \mathbf{d}_2$) and
- the 6 2^{nd} nearest neighbors ($l = 1$) ($\mathbf{T}_1 + 0, l_1 = \pm 1, l_2 = \pm 1, l_3 = \pm 1$)

Use $\gamma = 1$ and $\gamma = 1/2$ to evaluate $\alpha_M^b + \alpha_M^b$. Compare your result with a precise value

$$\alpha_M = 1.7627, \quad (Cs\ Cl\ lattice)$$

5. Add the repulsive term to the potential $U(R)$ to complete the PE per pair for $Cs\ Cl$.