PHYS 825 PROBLEM SET III

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

\[ \epsilon_k = A - \sum_l \gamma(R_l) e^{i k \cdot R_l}. \]

This \( \epsilon_k \) is the energy of an electron that has wave vector \( k \). The constants are

\[ A = \int dr \phi^*(r) H \phi(r) \]

and

\[ \gamma(R) = -\int dr \phi^*(r) H \phi(r-R) \]

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

\[ A = \int dr \phi^*(r) H_{at} \phi(r) + \int dr \phi^* \Delta U \phi(r) \]

\[ = \epsilon_{at} - \beta \]

where \( \epsilon_{at} \) is the atomic energy of the electron in atomic orbital \( \phi(r) \) and \( \beta \) 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 Brillouen zone.

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

\[ \gamma(R) = 2(1 + \frac{R}{a_0}) e^{-\frac{R}{a_0}} \text{ Ryd} \]

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

3. Show that \( \epsilon_k \) for a 2D square lattice in the \( x, y \) plane of spacing \( a \) is

\[ \epsilon_k = A - 2\gamma [\cos(ka) + \cos(ky a)] \]

4. Show that \( \epsilon_k \) for the 2D square lattice with an atom in the center of the square is,

\[ \epsilon_k = A - 4\gamma \cos(\frac{k_x a}{2}) \cos(\frac{k_y a}{2}) \]

* See Also Chapter 10 Ashcroft & Mermin, p. 38 Mahan p. 229 Chapter 9 Kittel.
II. Potential Energy of Cs Cl - Ewald Sum

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

1. Write down the direct lattice vectors
   \( \mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 \)
   for the Cs Cl lattice in terms of the lattice spacing \( a \).

2. Define the reciprocal lattice \( \mathbf{G} \) and write down the reciprocal lattice for Cs Cl.

3. 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.
   \( (\mathbf{R}_{11} = \mathbf{T}_1, \mathbf{R}_{12} = \mathbf{T}_1 + \mathbf{d}_2) \)
   and determine \( d_2 \).

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

   \[
   U_T = \frac{1}{2} \sum_{l \kappa} \sum_{l' \kappa'}' V(\mathbf{R}_{l \kappa} - \mathbf{R}_{l' \kappa'})
   = \frac{1}{2} \sum_{l \kappa} \left[ \sum_{l' \neq l} V(\mathbf{R}_{l \kappa} - \mathbf{R}_{l' \kappa}) + \sum_{l' = l} V(\mathbf{R}_{l \kappa} - \mathbf{R}_{l' \kappa'}) \right]
   \]

   where in the first term \( \kappa' = \kappa \) and in the second \( \kappa' \neq \kappa \). \( \sum_{l \kappa} = N_i = \text{number of ions} \). The square bracket in \( V_T \) is independent of \( l \) and \( \kappa \) 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

   \[
   U_T = \frac{N_i}{2} \left[ \sum_{l' \neq 0} V(|\mathbf{T}_{l'}|) + \sum_{l' = 0} V(|\mathbf{T}_1 + \mathbf{d}_2|) \right]
   \]
Including only the electrostatic term \( V(R) = +e^2/|R| \) and writing \( l' = l \), the PE per ion pair \( U = U_T/N \) is

\[
U = e^2 \left[ \sum_{l \neq 0} \frac{1}{T_l} - \sum_{l=0} \frac{1}{|T_1 + d_2|} \right],
\]

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

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

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

where \( \eta \) 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)

\[
U = U_a + U_b
\]

\[
U_a = e^2 \left[ \frac{4\pi}{\Omega_0} \sum_G \frac{1}{G^2} e^{-\frac{Q^2}{4\pi}} \left[ 1 - e^{iG.d_2} \right] - 2\left( \frac{\eta}{\pi} \right)^{1/2} \right]
\]

\[
U_b = e^2 \left[ \sum_{l \neq 0} \frac{1}{T_l} \left[ 1 - \text{erf}(\sqrt{\eta}T_l) \right] - \sum_{l=0} \frac{1}{|T_1 + d_2|} \left[ 1 - \text{erf}(\sqrt{\eta}(T_1 + d_2)) \right] \right]
\]

(B) Choosing \( \sqrt{\eta} = \frac{\gamma}{|a|} \), where \( \gamma \) 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 \( \alpha_M \) using

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

\[
G = \pm \frac{2\pi}{a} i, \pm \frac{2\pi}{a} j, \pm \frac{2\pi}{a} k
\]
(b) $\alpha^b_M$ - 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 $\alpha^b_M + \alpha^b_M$. Compare your result with a precise value

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

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