

Solution to the Schrödinger equation for periodic solids. Pseudopotential method.

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1 Introduction

The main objective of this assignment is to replicate the band structures calculated by Cohen & Bergstresser in their paper titled "Band Structures and Pseudopotential Form Factors for Fourteen Semiconductors of the Diamond and Zinc-blende Structures" published in 1966 in the *Physical Review* journal. This will be done using a script in Python that implements the pseudopotential method for periodic solids. Included in the appendix, is a solution to the first problem of chapter 8 of *Solid State Physics*, a book by Neil Ashcroft and N. David Mermin.

A direct solution to the Schrödinger equation for the macroscopic crystal cannot be found. But, since solids have periodic symmetry, Bloch's Theorem can be used to simplify the problem significantly by replacing the problem of solving the Schrödinger equation for a periodic solid by that of solving the Schrödinger equation in a unit cell with Born-von Karman boundary conditions.

The band structure of a solid is a feature of the valence electrons of the atoms that constitute the solid. These are the ones that determine the properties of the solid. The pseudopotential method replaces the Coulomb potential of the atoms and the core electrons with a pseudopotential that captures the interaction between these and the valence electrons.

2 Three-dimensional crystals

As an introduction, we will consider solids which are described by crystals in which the atomic nuclei are ordered in a periodic lattice called *Bravais lattice*. The lattice sites, or lattice vectors, \mathbf{R} can be expressed as a linear combination with integer coefficients of three primitive vectors, \mathbf{a}_i , such that

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \quad n_i \in \mathbb{Z} \quad (1)$$

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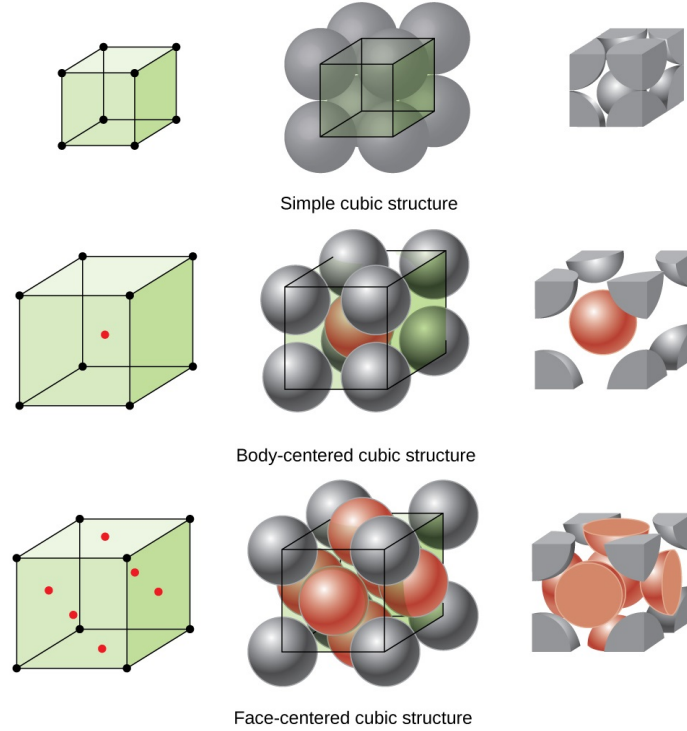


Figure 1: Three common lattice structures. Adapted from *Chemistry*², Chapter 10, section 6 by OpenStax. OpenStax CNX. Jun 20, 2016. Adapted under the creative commons license.

These primitive vectors form a basis for the Bravais lattice and are, in general, linearly independent but not necessarily orthogonal.

The nuclei can be found at all sites $\mathbf{x} + \mathbf{R}$, where \mathbf{x} runs on all atoms in the unit cell. If a cell contains more than one nuclei, the lattice is called a Bravais lattice with a basis. The periodicity implies that the arrangement of these nuclei must be the same within each cell of the lattice. Three common lattice structures, the simple cubic (sc), body-centered cubic (bcc) and face-centered cubic (fcc) structures can be seen in Figure 1.

It is assumed that Born-von Karman boundary conditions can be imposed as follows:

$$\psi(\mathbf{r} + N_1\mathbf{a}_1 + N_2\mathbf{a}_2 + N_3\mathbf{a}_3) = \psi(\mathbf{r}) \quad (2)$$

where $N_1N_2N_3 = N$ is the number of unit cells. Then, the volume of the crystal is $V = N\Omega$, where

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (3)$$

is the volume of the unit cell.

A function that is periodic on a Bravais lattice admits a Fourier decomposition with wave vectors \mathbf{K} such that

$$\mathbf{R} \cdot \mathbf{K} = 2\pi p, \quad p \in \mathbb{Z} \quad (4)$$

²Download for free at <http://cnx.org/contents/85abf193-2bd2-4908-8563-90b8a7ac8df6@9.311>.

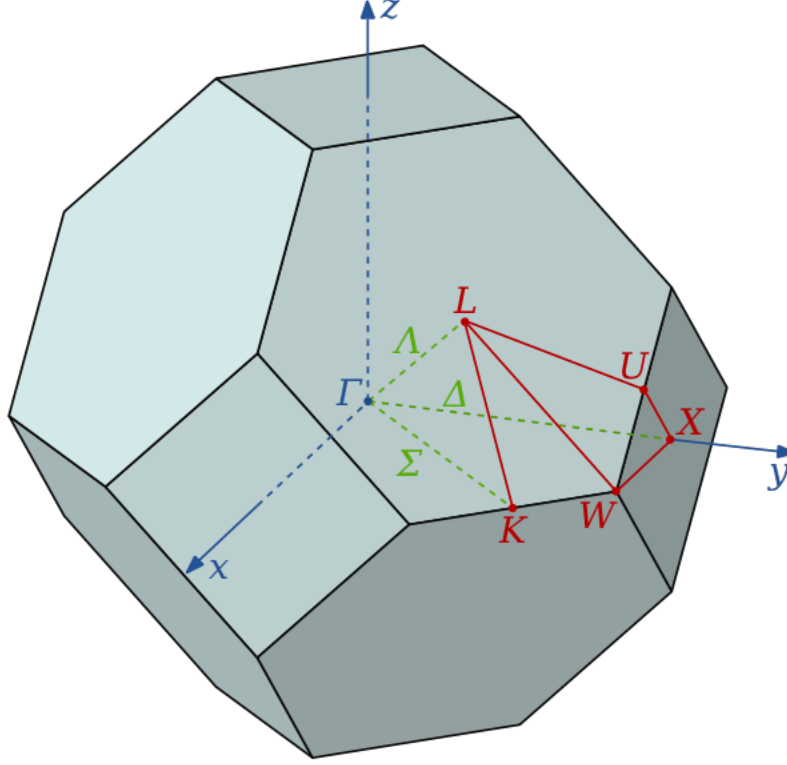


Figure 2: First Brillouin zone of FCC lattice. Labels indicate points and lines that present high symmetry.

These vectors \mathbf{K} form a Bravais lattice, called the *reciprocal lattice*. It can be shown that

$$\mathbf{K} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3, \quad m_i \in \mathbb{Z} \quad (5)$$

for three vectors \mathbf{b}_i that satisfy

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad \text{and} \quad \mathbf{b}_i = 2\pi \varepsilon_{ijk} \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = \frac{2\pi}{\Omega} \varepsilon_{ijk} (\mathbf{a}_j \times \mathbf{a}_k) \quad (6)$$

where ε_{ijk} is the Levi-Civita tensor. These vectors form a basis for the reciprocal lattice.

In the reciprocal lattice, the *first Brillouin zone* is defined as the volume consisting of the points that are closer to the origin than to any other reciprocal lattice point. For example, the first Brillouin zone of the face-centered cubic can be seen in Figure 2.

A general wave vector \mathbf{q} can be written as the sum of a vector \mathbf{k} of the first Brillouin zone and a vector \mathbf{K} of the reciprocal lattice. That is:

$$\mathbf{q} = \mathbf{k} + \mathbf{K} \quad (7)$$

For a finite rectangular lattice, of size $L_x L_y L_z$, the allowed values of \mathbf{q} are restricted by the periodic boundary conditions. In this case, vectors in reciprocal space run over the following values:

$$\mathbf{q} = 2\pi \left(\frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right), \quad n_x, n_y, n_z \in \mathbb{N} \quad (8)$$

2.1 Bloch's Theorem and Periodic Boundary Conditions

So, the Schrödinger equation will be of the form:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r}) \quad (9)$$

where the potential $U(\mathbf{r})$ has the periodicity of the underlying Bravais lattice. That is, for all lattice vectors \mathbf{R} of the form (1):

$$U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \quad (10)$$

Bloch's Theorem states that eigenstates of (9) are the same in the lattice cells located at \mathbf{R}_i and \mathbf{R}_j up to a phase factor. So, for some reciprocal lattice vector \mathbf{k} of the form (5):

$$\psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}_i) = e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}_j) \quad (11)$$

where n denotes the band index.

If we take \mathbf{R}_j to be the null vector, and ignore the index for \mathbf{R}_i , we get that for all lattice vectors \mathbf{R} :

$$\psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r}) \quad (12)$$

Thus, $\psi_{n,\mathbf{k}}$ can be chosen to be the product of a plane wave and a function with the periodicity of the Bravais lattice:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}), \quad u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{r}) \quad (13)$$

all lattice vectors \mathbf{R} . It can be verified that this expression for $\psi_{n,\mathbf{k}}$ is consistent with the previous one.

Now, if we impose Born-von Karman boundary conditions, given by (2), and apply Bloch's Theorem we get:

$$\psi_{n,\mathbf{k}}(\mathbf{r} + N_i \mathbf{a}_i) = e^{iN_i \mathbf{k} \cdot \mathbf{a}_i} \psi_{n,\mathbf{k}}(\mathbf{r}) = \psi_{n,\mathbf{k}}(\mathbf{r}), \quad i = 1, 2, 3 \quad (14)$$

This implies that:

$$e^{iN_i \mathbf{k} \cdot \mathbf{a}_i} = e^{iN_i m_i 2\pi} = 1 \implies N_i m_i = x_i, \quad x_i \in \mathbb{Z}, \quad i = 1, 2, 3 \quad (15)$$

Which means that \mathbf{k} is real, and its values are restricted. Then, the general form for allowed Bloch wave vectors is:

$$\mathbf{k} = \frac{x_1}{N_1} \mathbf{b}_1 + \frac{x_2}{N_2} \mathbf{b}_2 + \frac{x_3}{N_3} \mathbf{b}_3, \quad x_1, x_2, x_3 \in \mathbb{Z} \quad (16)$$

With this expression for \mathbf{k} , we can see that the volume $\Delta \mathbf{k}$ of k -space per allowed value of k is

$$\Delta \mathbf{k} = \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3} \right) = \frac{1}{N} \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) \quad (17)$$

Thus, since $\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$ is the volume of a primitive cell of the reciprocal lattice, the number of allowed wave vectors in a primitive cell of the reciprocal lattice is equal to the number of sites in the crystal.

Now, the volume of a reciprocal lattice primitive cell is

$$\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \Omega^{(r)} = \frac{(2\pi)^3}{v}, \quad v = \frac{\Omega}{N} \quad (18)$$

where Ω is, as mentioned previously, the volume of a primitive cell of the direct lattice. So, we can write:

$$\Delta \mathbf{k} = \frac{(2\pi)^3}{\Omega} \quad (19)$$

2.2 Proof of Bloch's Theorem

This proof will be used to ease the transition into pseudopotentials.

If ψ satisfies the Born-von Karman boundary condition (2), it can be expanded into the set of all plane waves that satisfy (2). So:

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \quad (20)$$

where the sum is taken over all vectors allowed by the boundary condition.

As stated before, the potential $U(\mathbf{r})$ has the periodicity of the underlying Bravais lattice. Therefore, it's plane wave expansion will only contain plane waves with this same periodicity and, as a consequence, with wave vectors that are vectors of the reciprocal lattice:

$$U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}}, \quad U_{\mathbf{K}} = \frac{1}{v} \int_{cell} U(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r} \quad (21)$$

Since potential energy is undetermined to within an additive constant, we fix this constant by setting:

$$U_0 = \frac{1}{v} \int_{cell} U(\mathbf{r}) d\mathbf{r} = 0 \quad (22)$$

Since $U(\mathbf{r})$ is real, it follows that $U_{-\mathbf{K}} = U_{\mathbf{K}}^*$. Also, $U_{\mathbf{K}}$ will be real if the crystal has inversion symmetry ($U(-\mathbf{r}) = U(\mathbf{r})$). In this case, we have:

$$U_{-\mathbf{K}} = U_{\mathbf{K}}^* = U_{\mathbf{K}} \quad (23)$$

With all of this in mind, and some algebra, the Schrödinger equation becomes:

$$\sum_{\mathbf{q}} \left[\left(\frac{\hbar^2}{2m} q^2 - \varepsilon \right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} \right] e^{i\mathbf{q} \cdot \mathbf{r}} = 0 \quad (24)$$

Since the plane waves satisfying (2) are orthogonal, the expression within brackets must vanish for all allowed \mathbf{q} .

If we set $\mathbf{q} = \mathbf{k} - \mathbf{K}$, where \mathbf{K} is a reciprocal lattice vector and \mathbf{k} lies in the first Brillouin zone, and then make the change of variables $\mathbf{K}' \rightarrow \mathbf{K}' - \mathbf{K}$, we arrive at:

$$\left(\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \varepsilon \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} = 0 \quad (25)$$

Now, for a fixed \mathbf{k} in the first Brillouin zone, this set of equations for all reciprocal lattice vectors \mathbf{K} only couples coefficients whose wave vectors differ from \mathbf{k} by a reciprocal lattice vector. That is, in a particular equation, only $c_{\mathbf{k}}, c_{\mathbf{k}+\mathbf{K}_1}, c_{\mathbf{k}+\mathbf{K}_2}, c_{\mathbf{k}+\mathbf{K}_3}, \dots$ are involved.

So, we now have N independent problems, one for each \mathbf{k} in the first Brillouin zone. Each of these problems has solutions that are superpositions of plane waves containing only the wave vector \mathbf{k} and wave vectors that differ from \mathbf{k} by a reciprocal lattice vector.

And thus, looking at (20), we see that \mathbf{q} can only assume the values $\mathbf{k}, \mathbf{k} + \mathbf{K}_1, \mathbf{k} + \mathbf{K}_2, \mathbf{k} + \mathbf{K}_3, \dots$. So, the wave function will be of the form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K}) \cdot \mathbf{r}} \quad (26)$$

And so, we arrive at the expression stated by Bloch's theorem:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K} \cdot \mathbf{r}} \quad (27)$$

3 Pseudopotentials

First, we need to distinguish between core electrons and valence electrons. The core wave functions are well localized about the lattice sites. The valence electrons can be found with appreciable probability in the interstitial regions, where their wave function could be well approximated by a very small number of plane waves. Superscripts c or v will be used to indicate whether wave functions describe core electrons or valence electrons, respectively.

We will define the orthogonalized plane wave $\phi_{\mathbf{k}}$, which we require to be orthogonal to every core level, in the following way:

$$\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} + \sum_c b_c \psi_{\mathbf{k}}^c(\mathbf{r}), \quad \int \psi_{\mathbf{k}}^{c*}(\mathbf{r}) \phi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r} = 0 \quad (28)$$

where the sum is over all core levels with Bloch wave vector \mathbf{k} . If we assume that every core level is normalized we can calculate the coefficients b_c as follows:

$$b_c = - \int \psi_{\mathbf{k}}^{c*}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \quad (29)$$

Now, suppose that we write the exact wave function for a valence level as a linear combination of orthogonalized wave functions:

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} \left[e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}} - \sum_c \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}'} d\mathbf{r}' \right) \psi_{\mathbf{k}}^c(\mathbf{r}) \right] \quad (30)$$

If we define

$$\phi_{\mathbf{k}}^v(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}} \quad (31)$$

we can write:

$$\psi_{\mathbf{k}}^v(\mathbf{r}) = \phi_{\mathbf{k}}^v(\mathbf{r}) - \sum_c \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') d\mathbf{r}' \right) \psi_{\mathbf{k}}^c(\mathbf{r}) \quad (32)$$

Since $\psi_{\mathbf{k}}^v$ is an exact valence wave function, it satisfies $\hat{H}\psi_{\mathbf{k}}^v = \varepsilon_{\mathbf{k}}^v \psi_{\mathbf{k}}^v$. A simple substitution yields:

$$\hat{H}\phi_{\mathbf{k}}^v - \sum_c \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') d\mathbf{r}' \right) \hat{H}\psi_{\mathbf{k}}^c = \varepsilon_{\mathbf{k}}^v \left[\phi_{\mathbf{k}}^v - \sum_c \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') d\mathbf{r}' \right) \psi_{\mathbf{k}}^c \right] \quad (33)$$

Now, $\psi_{\mathbf{k}}^c$ satisfies $\hat{H}\psi_{\mathbf{k}}^c = \varepsilon_{\mathbf{k}}^c \psi_{\mathbf{k}}^c$. So:

$$\hat{H}\phi_{\mathbf{k}}^v - \sum_c \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') d\mathbf{r}' \right) \varepsilon_{\mathbf{k}}^c \psi_{\mathbf{k}}^c = \varepsilon_{\mathbf{k}}^v \phi_{\mathbf{k}}^v - \sum_c \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') d\mathbf{r}' \right) \varepsilon_{\mathbf{k}}^c \psi_{\mathbf{k}}^c \quad (34)$$

We can rearrange this in the following way:

$$\hat{H}\phi_{\mathbf{k}}^v + \sum_c (\varepsilon_{\mathbf{k}}^v - \varepsilon_{\mathbf{k}}^c) \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \phi_{\mathbf{k}}^v(\mathbf{r}') d\mathbf{r}' \right) \psi_{\mathbf{k}}^c = \varepsilon_{\mathbf{k}}^v \phi_{\mathbf{k}}^v \quad (35)$$

If we define the following operator

$$\hat{V}^{\mathbf{R}}\Psi = \sum_c (\varepsilon_{\mathbf{k}}^v - \varepsilon_{\mathbf{k}}^c) \left(\int \psi_{\mathbf{k}}^{c*}(\mathbf{r}') \Psi(\mathbf{r}') d\mathbf{r}' \right) \psi_{\mathbf{k}}^c \quad (36)$$

we can write a sort of Schrödinger equation for $\phi_{\mathbf{k}}^v$:

$$(\hat{H} + \hat{V}^{\mathbf{R}})\phi_{\mathbf{k}}^v = \varepsilon_{\mathbf{k}}^v \phi_{\mathbf{k}}^v \quad (37)$$

The *pseudopotential* is defined as the sum of $\hat{V}^{\mathbf{R}}$ and the periodic potential \hat{U} :

$$\hat{H} + \hat{V}^{\mathbf{R}} = \frac{\hat{P}^2}{2m} + \hat{U} + \hat{V}^{\mathbf{R}} = \frac{\hat{P}^2}{2m} + \hat{V}^{pseudo} \quad (38)$$

And thus:

$$\left(\frac{\hat{P}^2}{2m} + \hat{V}^{pseudo} \right) \phi_{\mathbf{k}}^v = \varepsilon_{\mathbf{k}}^v \phi_{\mathbf{k}}^v \quad (39)$$

It must be stated that the pseudopotential depends on the energy level being sought, $\varepsilon_{\mathbf{k}}^v$. Since the valence levels have more energy than the core levels, the hope is that some cancellation will occur between \hat{U} and $\hat{V}^{\mathbf{R}}$ and the pseudopotential will be weak.

3.1 Pseudopotentials for the diamond and zinc-blende crystal structures

For the diamond and zinc-blende crystal structures, we have a face-centered cubic lattice with two atoms in the unit cell. The difference between the two is that for the diamond structure these atoms are the same, while they are different for the zinc-blende structure.

We take the origin of the coordinate system to be the middle point between these two atoms. Then, the primitive vectors for the lattice are:

$$\mathbf{a}_1 = \frac{a_0}{2}(1, 1, 0), \quad \mathbf{a}_2 = \frac{a_0}{2}(1, 0, 1), \quad \mathbf{a}_3 = \frac{a_0}{2}(0, 1, 1) \quad (40)$$

where a_0 is the lattice parameter. Lattice parameters can be seen in Table 1.

Crystal	Si	Ge	Sn	GaAs	ZnS	CdTe
$a_0[\text{\AA}]$	5.43	5.66	6.49	5.64	5.41	6.41

Table 1: Lattice parameters. Taken from the Cohen Bergstresser paper.

The two atoms are located at:

$$\mathbf{x}_1 = \frac{a_0}{8}(1, 1, 1) \quad \text{and} \quad \mathbf{x}_2 = -\frac{a_0}{8}(1, 1, 1) \quad (41)$$

The reciprocal lattice will be a body-centered cubic lattice with primitive vectors:

$$\mathbf{b}_1 = \frac{2\pi}{a_0}(1, 1, -1), \quad \mathbf{b}_2 = \frac{2\pi}{a_0}(1, -1, 1), \quad \mathbf{b}_3 = \frac{2\pi}{a_0}(-1, 1, 1) \quad (42)$$

Also:

$$\Omega = \frac{(a_0)^3}{4} \quad \text{and} \quad \Omega_{BZ} = 4 \frac{(2\pi)^3}{(a_0)^3} \quad (43)$$

As mentioned previously, we will expand the valence wave function in the following way:

$$\phi_{\mathbf{k}}^v(\mathbf{r}) = \psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} = \sum_{\mathbf{K}} \tilde{c}_{\mathbf{K}} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} = \sum_{\mathbf{K}} \tilde{c}_{\mathbf{K}} \xi_{n,\mathbf{k}+\mathbf{K}}(\mathbf{r}) \quad (44)$$

Where $V = N\Omega$ is the volume of the crystal. To get a finite basis, we will introduce an upper bound on the kinetic energy:

$$\frac{\hbar^2(\mathbf{k} + \mathbf{K})^2}{2m} \leq E_{upper} \quad (45)$$

For the pseudopotential, we will assume it to be a linear superposition of spherically symmetric atomic potentials:

$$V^{pseudo}(\mathbf{r}) = \sum_{\mathbf{R}, \mathbf{x}} V_a(|\mathbf{r} - \mathbf{R} - \mathbf{x}|) \quad (46)$$

where \mathbf{R} are lattice vectors and \mathbf{x} are the atomic positions. Using the reciprocal lattice vector, this can be rewritten as:

$$V^{pseudo}(\mathbf{r}) = \sum_{\mathbf{K}} V_{a,\mathbf{K}} S(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}} \quad (47)$$

where the sum is over the allowed values of \mathbf{K} . Also, $V_{a,\mathbf{K}}$ is the atomic form factor and $S(\mathbf{K})$ is the structure factor. They are given by:

$$V_{a,\mathbf{K}} = \frac{1}{\Omega} \int_{cell} V_a(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r}, \quad S(\mathbf{K}) = \frac{1}{N_a} \sum_{\mathbf{d}} e^{-i\mathbf{K} \cdot \mathbf{d}} \quad (48)$$

We can split $V_{a,\mathbf{K}} S(\mathbf{K})$ into a symmetric and an antisymmetric form:

$$V^{pseudo}(\mathbf{r}) = \sum_{\mathbf{K}} [V_{a,\mathbf{K}}^S S^S(\mathbf{K}) + i V_{a,\mathbf{K}}^A S^A(\mathbf{K})] e^{i\mathbf{K} \cdot \mathbf{r}} \quad (49)$$

We should note that, for the diamond structure, $V_{a,\mathbf{K}}^A = 0$ since both atoms are the same. Now, for the diamond and zinc-blende structures, we can find expressions for S^S and S^A . Noting that $N_a = 2$ and using (40), (42) and (41), we can show that:

$$S^S(\mathbf{K}) = \cos(\mathbf{K} \cdot \mathbf{x}_1), \quad S^A(\mathbf{K}) = \sin(\mathbf{K} \cdot \mathbf{x}_1) \quad (50)$$

And so, we arrive at:

$$V^{pseudo}(\mathbf{r}) = \sum_{\mathbf{K}} [V_{a,\mathbf{K}}^S \cos(\mathbf{K} \cdot \mathbf{x}_1) + i V_{a,\mathbf{K}}^A \sin(\mathbf{K} \cdot \mathbf{x}_1)] e^{i\mathbf{K} \cdot \mathbf{r}} \quad (51)$$

4 Algorithm and Implementation

First of all, Rydberg atomic units will be used, so that

$$\hbar = 2m = 1 \quad (52)$$

where m is the mass of the electron. We will use the variational method to calculate the valence bands of the crystals mentioned in Table 1. As mentioned previously, we will use the following plane wave basis:

$$\xi_{n,\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}} \quad (53)$$

The upper bound for the kinetic energy, now in Ry , will be:

$$(\mathbf{k} + \mathbf{K})^2 \leq E_{upper} \quad (54)$$

Thus, the matrix elements for the Hamiltonian $\hat{H}^{pseudo} = \hat{P}^2 + \hat{V}^{pseudo}$ will be:

$$\langle \xi_{n,\mathbf{k}+\mathbf{K}} | \hat{P}^2 | \xi_{n,\mathbf{k}+\mathbf{K}'} \rangle = -\frac{1}{V} \int e^{-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} \nabla^2 e^{i(\mathbf{k}+\mathbf{K}')\cdot\mathbf{r}} d\mathbf{r} = \frac{(\mathbf{k}+\mathbf{K})^2}{V} \delta_{\mathbf{K},\mathbf{K}'} V \quad (55)$$

$$\langle \xi_{n,\mathbf{k}+\mathbf{K}} | \hat{P}^2 | \xi_{n,\mathbf{k}+\mathbf{K}'} \rangle = (\mathbf{k}+\mathbf{K})^2 \delta_{\mathbf{K},\mathbf{K}'} \quad (56)$$

$$\langle \xi_{n,\mathbf{k}+\mathbf{K}} | \hat{V}^{pseudo} | \xi_{n,\mathbf{k}+\mathbf{K}'} \rangle = \frac{1}{V} \int e^{-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} \left(\sum_{\tilde{\mathbf{K}}} [V_{a,\tilde{\mathbf{K}}}^S S^S(\tilde{\mathbf{K}}) + iV_{a,\tilde{\mathbf{K}}}^A S^A(\tilde{\mathbf{K}})] e^{i\tilde{\mathbf{K}}\cdot\mathbf{r}} \right) e^{i(\mathbf{k}+\mathbf{K}')\cdot\mathbf{r}} d\mathbf{r} \quad (57)$$

This gives:

$$\langle \xi_{n,\mathbf{k}+\mathbf{K}} | \hat{V}^{pseudo} | \xi_{n,\mathbf{k}+\mathbf{K}'} \rangle = V_{a,\mathbf{K}-\mathbf{K}'}^S \cos([\mathbf{K}-\mathbf{K}'] \cdot \mathbf{x}_1) + iV_{a,\mathbf{K}-\mathbf{K}'}^A \sin([\mathbf{K}-\mathbf{K}'] \cdot \mathbf{x}_1) \quad (58)$$

And so:

$$[\hat{H}]_{\mathbf{K},\mathbf{K}'} = (\mathbf{k}+\mathbf{K})^2 \delta_{\mathbf{K},\mathbf{K}'} + V_{a,\mathbf{K}-\mathbf{K}'}^S \cos([\mathbf{K}-\mathbf{K}'] \cdot \mathbf{x}_1) + iV_{a,\mathbf{K}-\mathbf{K}'}^A \sin([\mathbf{K}-\mathbf{K}'] \cdot \mathbf{x}_1) \quad (59)$$

For the structures we are working with, the smallest allowed modules squared of $\mathbf{K}-\mathbf{K}'$ are 3, 4, 8 and 11, in units of $(2\pi/a_0)^2$. These are the only allowed values to have a non zero potential. We take $V_{a,0} = 0$. The symmetric structure factor is zero for $|\mathbf{K}-\mathbf{K}'|^2 = 4$, in units of $(2\pi/a_0)^2$, while the antisymmetric structure factor is zero for $|\mathbf{K}-\mathbf{K}'|^2 = 8$, in units of $(2\pi/a_0)^2$. The atomic form factors for these, as presented by Cohen & Bergstresser, can be seen in Table 2, where the subscript in the atomic form factor indicates the value of $|\mathbf{K}-\mathbf{K}'|^2$, in units of $(2\pi/a_0)^2$.

Crystal	V_3^S [Ry]	V_8^S [Ry]	V_{11}^S [Ry]	V_3^A [Ry]	V_4^A [Ry]	V_{11}^A [Ry]
Si	-0.21	0.04	0.08	0	0	0
Ge	-0.23	0.01	0.06	0	0	0
Sn	-0.20	0.00	0.04	0	0	0
GaAs	-0.23	0.01	0.06	0.07	0.05	0.01
ZnS	-0.22	0.03	0.07	0.24	0.14	0.04
CdTe	-0.20	0.00	0.04	0.15	0.09	0.04

Table 2: Atomic form factors to within 0.01Ry. Taken from the Cohen & Bergstresser paper.

With all of these in mind, we should apply the variational method to (59), for different values of \mathbf{k} along symmetry lines of the first Brillouin zone. A collection of points connecting such lines can be seen in Figure 3. We will follow the lines taken by Cohen & Bergstresser

$$L \rightarrow \Gamma \rightarrow X \rightarrow U, \quad K \rightarrow \Gamma \quad (60)$$

where:

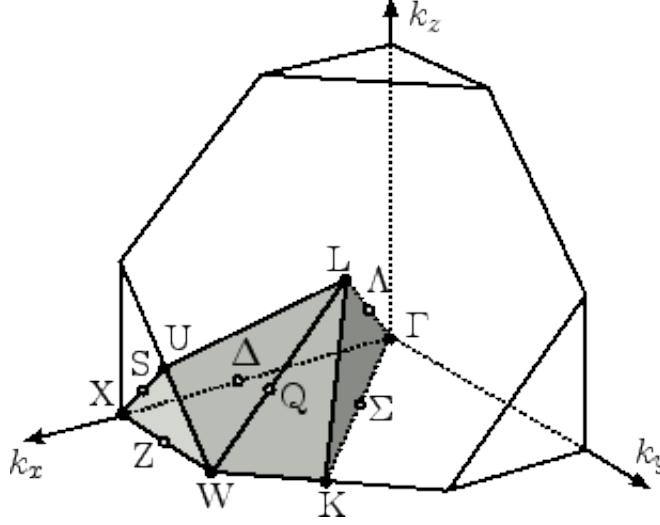


Figure 3: First Brillouin zone of FCC lattice along with locations of certain symmetry points and symmetry lines.

$$\begin{aligned}
 L &= \frac{2\pi}{a_0} \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right), & \Gamma &= \frac{2\pi}{a_0} (0, 0, 0), & X &= \frac{2\pi}{a_0} (1, 0, 0), \\
 U &= \frac{2\pi}{a_0} \left(1, \frac{1}{4}, \frac{1}{4} \right), & K &= \frac{2\pi}{a_0} \left(\frac{3}{4}, \frac{3}{4}, 0 \right)
 \end{aligned} \tag{61}$$

The points U and K can be interchanged, since they are equivalent in the reciprocal space. Thus, the path taken is $\Lambda \cup \Delta \cup S \cup \Sigma$. Excluding named points, 9 samples were taken for Λ and Δ , 3 samples for S and 12 for Σ . Both K and U were used in calculations, so that their equivalence can be explicitly seen.

5 Results and Discussion

Results obtained can be seen in Figures 4 through 9. The value of E_{upper} for which convergence was achieved can be seen as well. To get similar graphs to the ones in the Cohen & Bergstresser paper one would have to set the value of the band in light blue at Γ at zero (Fermi energy).

The band structures obtained for Si, Ge and GeAs are quite similar to those obtained by Cohen & Bergstresser. The ones for ZnS and CdTe not quite, but are somewhat similar. This could be because they considered a contribution from vectors \mathbf{K} such that $E_{upper} < (\mathbf{k} + \mathbf{K})^2$.

The band structure obtained for Sn looks odd. The same structure was obtained for $E_{upper} = 5, 10, 20$. This could indicate that something could be wrong. Parameters in the code were double checked and the other structures gave acceptable results. In particular, CdTe has somewhat similar parameters and the overall shape of the band structure resembles the others.

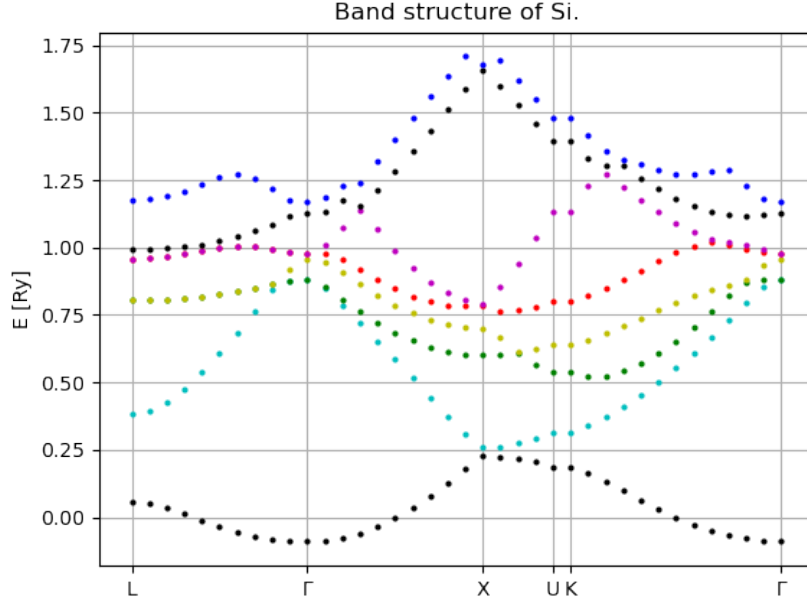


Figure 4: Band structure of Si. $E_{upper} = 12$.

As a possible correction, Cohen & Bergstresser suggest adding an energy dependence to the atomic form factors. This is clearly the case, as per (36). They also suggest taking more non zero atomic form factors, but also mention that doing so didn't improve results.

Another thing to consider is getting better estimates for both the atomic form factors and the lattice parameters. Given that Cohen & Bergstresser published their paper in the sixties, better estimates are bound to exist.

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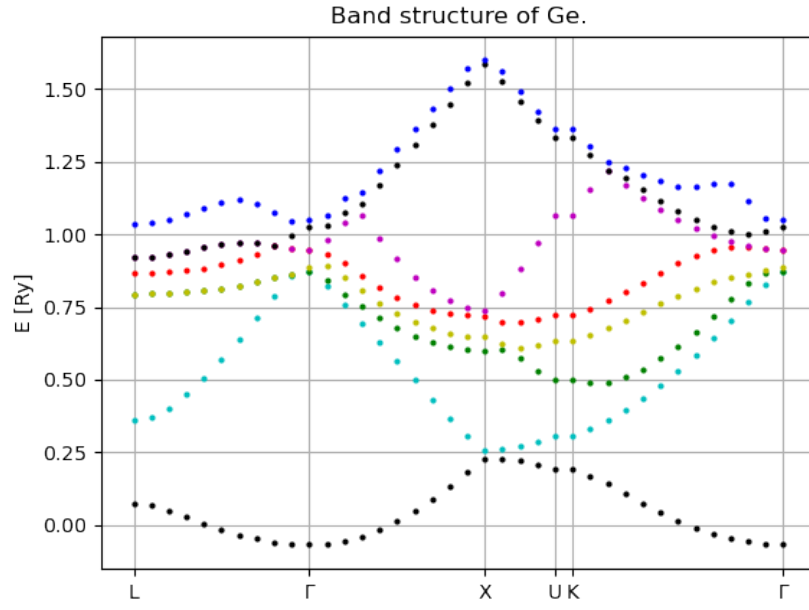


Figure 5: Band structure of Ge. $E_{upper} = 12$.

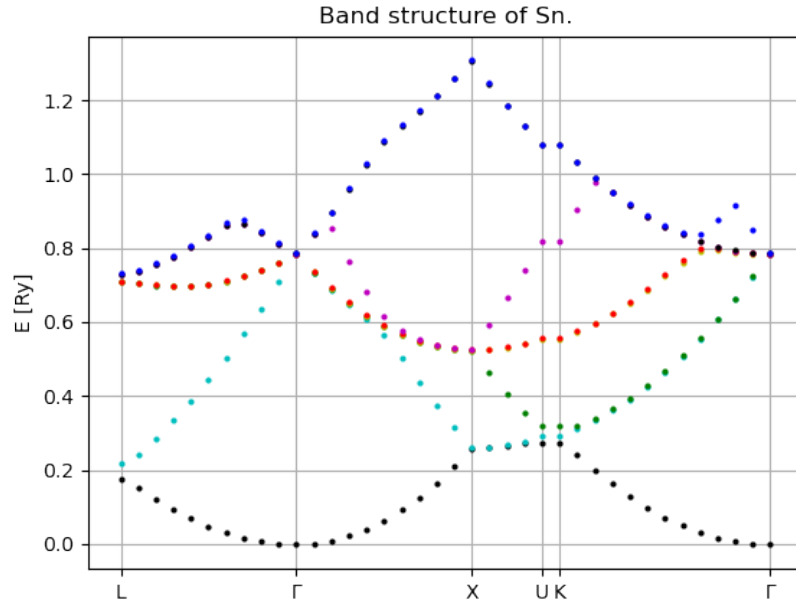


Figure 6: Band structure of Sn.

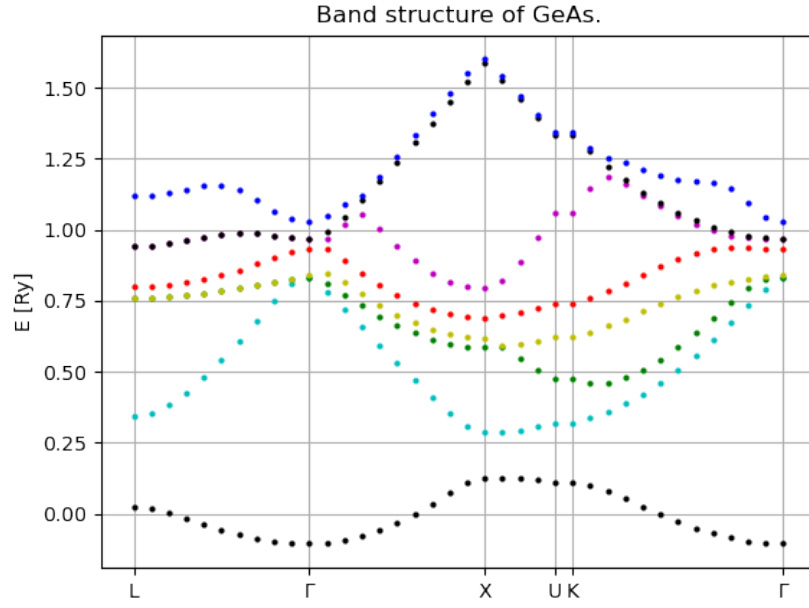


Figure 7: Band structure of GeAs. $E_{upper} = 11$.

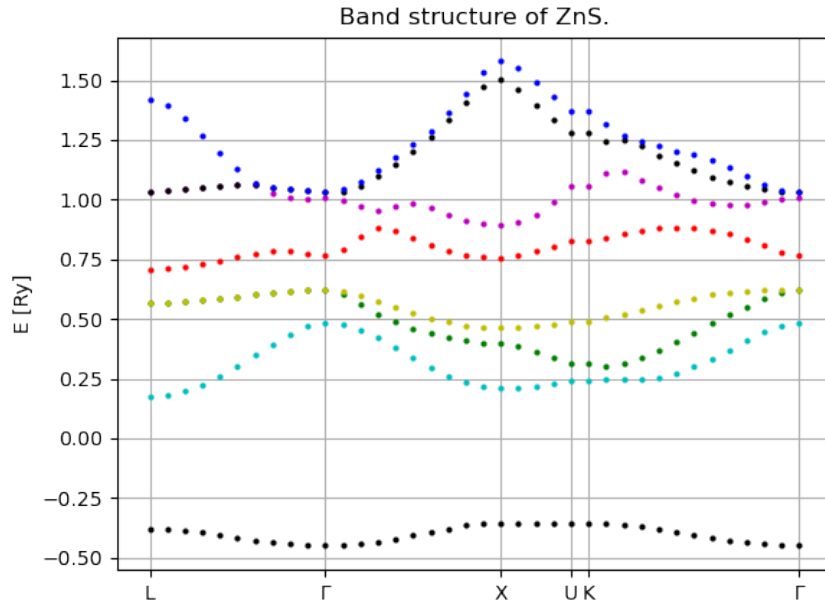


Figure 8: Band structure of ZnS. $E_{upper} = 13$.

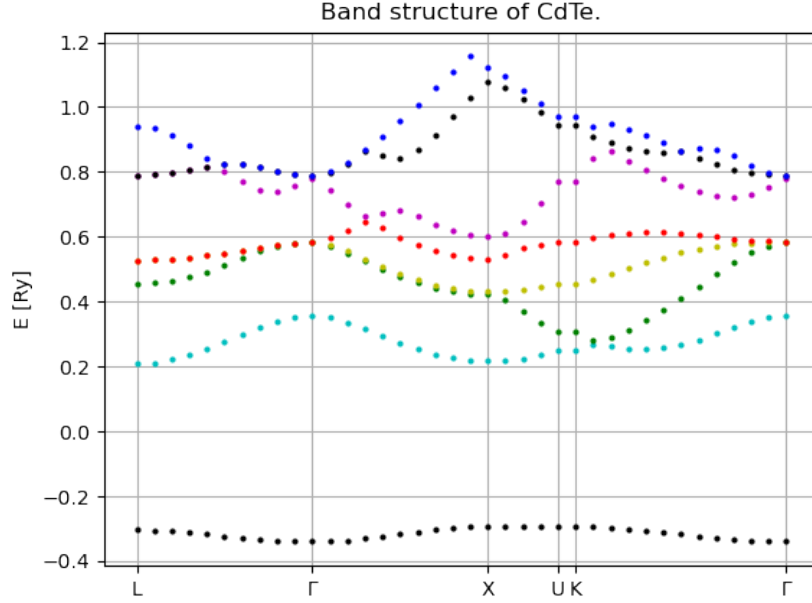


Figure 9: Band structure of CdTe. $E_{upper} = 13$.

A Solution to Problem 1, Chapter 8 of *Solid State Physics*.

Here I present a solution to problem 1 of *Solid State Physics*'s chapter 8.

We consider a one-dimensional periodic potential $U(x)$. It's minima are at zero. We express it as a superposition of potential barriers $v(x)$ of width a , centered at $x = \pm na$:

$$U(x) = \sum_{n=-\infty}^{\infty} v(x - na) \quad (62)$$

We assume $v(x)$ is even. Also note that $v(x) = 0$ for $|x| \geq a/2$. So, for $|x| \geq a/2$, the wave function of an electron with energy

$$\varepsilon = \frac{\hbar^2 K^2}{2m} \quad (63)$$

that's incident from the left on the potential barrier $v(x)$ has the form

$$\psi_l(x) = \begin{cases} e^{iKx} + re^{-iKx} & \text{if } x \leq -\frac{a}{2} \\ te^{iKx} & \text{if } x \geq \frac{a}{2} \end{cases} \quad (64)$$

where t and r are the transmission and reflection coefficients, respectively. If it's incident from the right, it's wave function is

$$\psi_r(x) = \begin{cases} te^{-iKx} & \text{if } x \leq -\frac{a}{2} \\ e^{-iKx} + re^{iKx} & \text{if } x \geq \frac{a}{2} \end{cases} \quad (65)$$

Since $\psi_l(x)$ and $\psi_r(x)$ are two linearly independent solutions of the same Schrödinger equation, any solution with energy ε in must be a linear combination of these two:

$$\psi(x) = A\psi_l(x) + B\psi_r(x) \quad (66)$$

Now, Bloch's theorem states that for a suitable wave vector k :

$$\psi(x+a) = e^{ika}\psi(x) \quad (67)$$

Furthermore, differentiating we get

$$\psi'(x+a) = e^{ika}\psi'(x) \quad (68)$$

a) By imposing the conditions (67) and (68) at $x = -a/2$, and using (64), (65) and (66), show that the energy of the electron is related to the wave vector k by:

$$\cos ka = \frac{t^2 - r^2}{2t} e^{iKa} + \frac{1}{2t} e^{-iKa}, \quad K^2 = \frac{2m\varepsilon}{\hbar^2} \quad (69)$$

First we set

$$\psi(x) = A\psi_l(x) + B\psi_r(x) \quad \text{and} \quad \psi'(x) = A\psi'_l(x) + B\psi'_r(x) \quad (70)$$

where

$$\psi'_l(x) = \begin{cases} iKe^{iKx} - iKre^{-iKx} & \text{if } x \leq -\frac{a}{2} \\ iKte^{iKx} & \text{if } x \geq \frac{a}{2} \end{cases} \quad \text{and} \quad \psi'_r(x) = \begin{cases} -iKte^{-iKx} & \text{if } x \leq -\frac{a}{2} \\ -iKe^{-iKx} + iKre^{iKx} & \text{if } x \geq \frac{a}{2} \end{cases} \quad (71)$$

Then, we impose (67) and (68) at $x = -a/2$ to get:

$$\psi\left(\frac{a}{2}\right) = e^{ika}\psi\left(-\frac{a}{2}\right) \quad \text{and} \quad \psi'\left(\frac{a}{2}\right) = e^{ika}\psi'\left(-\frac{a}{2}\right) \quad (72)$$

Using this for $\psi(a/2)$ we get:

$$Ate^{iK\frac{a}{2}} + Be^{-iK\frac{a}{2}} + Bre^{iK\frac{a}{2}} = e^{ika}(Ae^{-iK\frac{a}{2}} + Are^{iK\frac{a}{2}} + Bte^{iK\frac{a}{2}}) \quad (73)$$

$$A[te^{iK\frac{a}{2}} - re^{ika}e^{iK\frac{a}{2}} - e^{ika}e^{-iK\frac{a}{2}}] = B[te^{ik}e^{iK\frac{a}{2}} - e^{-iK\frac{a}{2}} - re^{iK\frac{a}{2}}] \quad (74)$$

Using it for $\psi'(a/2)$ we get

$$A(iKte^{iK\frac{a}{2}}) + B(iK(-e^{-iK\frac{a}{2}} + re^{iK\frac{a}{2}})) = e^{ika}(AiK(e^{-iK\frac{a}{2}} - re^{iK\frac{a}{2}}) - BiKte^{iK\frac{a}{2}}) \quad (75)$$

$$A[te^{iK\frac{a}{2}} - e^{ika}e^{-iK\frac{a}{2}} + re^{ika}e^{iK\frac{a}{2}}] = B[e^{-iK\frac{a}{2}} - re^{iK\frac{a}{2}} - te^{ika}e^{iK\frac{a}{2}}] \quad (76)$$

Now, if we set

$$\tau = iK\frac{a}{2} \quad (77)$$

and take (74) divided by (76) we get:

$$[te^\tau - re^{ika}e^\tau - e^{ika}e^{-\tau}][e^{-\tau} - re^\tau - te^{ika}e^\tau] = [te^{ika}e^\tau - e^{-\tau} - re^\tau][te^{-\tau} - e^{ika}e^{-\tau} + re^{ika}e^\tau] \quad (78)$$

Multiplying through and simplifying we arrive at

$$(r^2 - t^2)e^{2\tau} + 2t \cos ka = e^{-2\tau} \quad (79)$$

which, by replacing 2τ with iKa and rearranging, let's us write

$$\cos ka = \frac{t^2 - r^2}{2t}e^{iKa} + \frac{1}{2t}e^{-iKa} \quad (80)$$

We write t as

$$t = |t|e^{i\delta} \quad (81)$$

where δ is a real number known as the phase shift, since it specifies the change in phase of the transmitted wave relative to the incident one.

By conservation, the probability of transmission plus the probability of reflection must be unity:

$$|t|^2 + |r|^2 = 1 \quad (82)$$

Now, let ϕ_1 and ϕ_2 be any two solutions to the one-barrier Schrödinger equation with the same energy:

$$-\frac{\hbar^2}{2m}\phi_i''(x) + v(x)\phi_i(x) = \frac{\hbar^2 K^2}{2m}\phi_i(x) \quad (83)$$

Define the Wronskian W as:

$$W(\phi_1(x), \phi_2(x)) = \phi_1'(x)\phi_2(x) - \phi_1(x)\phi_2'(x) \quad (84)$$

b) Show that $W(\phi_1(x), \phi_2(x))$ is independent of x by deducing that it's derivative vanishes.

This is a straightforward calculation. For the derivative of W we get:

$$W'(\phi_1(x), \phi_2(x)) = \phi_1''(x)\phi_2(x) - \phi_1(x)\phi_2''(x) \quad (85)$$

If we use the Schrödinger equation to express $\phi_i''(x)$ in terms of $\phi_i(x)$ we arrive at:

$$W'(\phi_1(x), \phi_2(x)) = \frac{2m}{\hbar^2} \left(v(x) - \frac{\hbar^2 K^2}{2m} \right) [\phi_1(x)\phi_2(x) - \phi_2(x)\phi_1(x)] = 0 \quad (86)$$

Thus, W does not depend on x .

Show that

$$|t|^2 + |r|^2 = 1 \quad (87)$$

by evaluating $W(\psi_l(x), \psi_l^*(x))$ for $x \leq -a/2$ and $x \geq -a/2$, noting that, since $v(x)$ is real, $\psi_l^*(x)$ will be a solution to the same Schrödinger equation as $\psi_l(x)$.

So, we have:

$$\psi_l(x) = \begin{cases} e^{iKx} + re^{-iKx} & \text{if } x \leq -\frac{a}{2} \\ te^{iKx} & \text{if } x \geq \frac{a}{2} \end{cases} \quad \text{and} \quad \psi_l^*(x) = \begin{cases} e^{-iKx} + r^*e^{iKx} & \text{if } x \leq -\frac{a}{2} \\ t^*e^{-iKx} & \text{if } x \geq \frac{a}{2} \end{cases} \quad (88)$$

Since W is independent of x , it must be that:

$$W(\psi_l(x), \psi_l^*(x)) \Big|_{a \leq -\frac{a}{2}} = W(\psi_l(x), \psi_l^*(x)) \Big|_{a \geq \frac{a}{2}} \quad (89)$$

By calculating these we get:

$$W(\psi_l(x), \psi_l^*(x)) \Big|_{a \leq -\frac{a}{2}} = 2iK[1 - |r|^2] \quad (90)$$

and:

$$W(\psi_l(x), \psi_l^*(x)) \Big|_{a \geq \frac{a}{2}} = 2iK|t|^2 \quad (91)$$

And so:

$$|t|^2 + |r|^2 = 1 \quad (92)$$

d) By evaluating $W(\psi_l(x), \psi_r^*(x))$, show that rt^* is pure imaginary, so r must be of the form

$$r = \pm i|r|e^{i\delta} \quad (93)$$

where the phase shift δ is the same as in $t = |t|e^{i\delta}$.

So, for $\psi_r^*(x)$ we have:

$$\psi_r^*(x) = \begin{cases} t^*e^{iKx} & \text{if } x \leq -\frac{a}{2} \\ e^{iKx} + r^*e^{-iKx} & \text{if } x \geq \frac{a}{2} \end{cases} \quad (94)$$

Thus:

$$W(\psi_l(x), \psi_r^*(x)) \Big|_{a \leq -\frac{a}{2}} = -2iKrt^* \quad (95)$$

and:

$$W(\psi_l(x), \psi_l^*(x)) \Big|_{a \geq \frac{a}{2}} = 2iKtr^* \quad (96)$$

Since these two must be equal:

$$-rt^* = tr^* \quad (97)$$

Now, since

$$(rt^*)^* = r^*t \quad \text{and} \quad rt^* = -r^*t \quad (98)$$

it must be that rt^* is pure imaginary since it's complex conjugate is it's opposite. So, rt^* must be of the form:

$$rt^* = i\alpha, \quad \text{for} \quad \alpha \in \mathbb{R} \quad (99)$$

Thus:

$$r = \frac{i\alpha}{t^*} = \frac{i\alpha}{|t|e^{-i\delta}} = i\frac{\alpha}{|t|}e^{i\delta} = \pm i\frac{|\alpha|}{|t|}e^{i\delta} \implies r = \pm i|r|e^{i\delta} \quad (100)$$

Which is what we wanted to show.

e) Show that, as a consequence of (69), (87) and (93), the energy and Bloch's wave vector of the electron are related by

$$\frac{\cos(Ka + \delta)}{|t|} = \cos ka, \quad \varepsilon = \frac{\hbar^2 K^2}{2m} \quad (101)$$

Using (87) and (93) in (69), it's straightforward to show that

$$\cos(ka) = \frac{t^2 - r^2}{2t}e^{iKa} + \frac{1}{2t}e^{-iKa} = \frac{e^{2i\delta}e^{iKa} + e^{-iKa}}{2|t|e^{i\delta}} \quad (102)$$

Thus:

$$\cos(ka) = \frac{\cos(Ka + \delta)}{|t|} \quad (103)$$

If the energy ε grows, so does K , and the potential barrier is less effective, so $|t| \rightarrow 1$.

For a given k , the allowed values of K , and of ε , are given by (101). Note that for values of K where $\cos(Ka + \delta)$ is close to 1 we get:

$$\cos(ka) = \frac{\cos(Ka + \delta)}{|t|} > 1 \quad \text{since} \quad |t| \leq 1 \quad (104)$$

Thus, values of K in the neighborhood of those satisfying $Ka + \delta = n\pi$ for $n \in \mathbb{Z}$ are not allowed values, for any k . This gives a region of forbidden energy. If δ is a bounded function of K , then there will be infinitely many regions of forbidden energy as well as infinitely many regions of allowed energy for each value of k .

f) Suppose the barrier is weak ($|t| \approx 1$, $|r| \approx 0$ and $\delta \approx 0$). Show that the energy gaps are very narrow, with the width of the gap containing $K = n\pi/a$ being

$$\Delta \varepsilon_{gap} \approx 2\pi n \frac{\hbar^2}{ma^2} |r| \quad (105)$$

First, we will use a second order Taylor expansion. As a refresher, for a 2-times differentiable function $f(x)$ we have:

$$f(x) \approx f(a) + f'(a)(x - a) + \frac{f''(a)}{2!}(x - a)^2 \quad (106)$$

Since $\delta \approx 0$, we can use the expansion of $\cos(Ka)$ around $n\pi$, which is:

$$\cos(Ka + \delta) \approx \cos(Ka) \approx (-1)^n - \frac{(-1)^n}{2}(Ka - n\pi)^2 \quad (107)$$

Now, since we are considering values of K for which $|\cos(Ka)|$ is near unity, and $|t| \approx 1$, we have that

$$\cos(ka) \approx (-1)^n \quad (108)$$

So, combining these two equations together we get that the values of K for the boundaries of the gap, which we will name K_{max} and K_{min} , are given by:

$$(-1)^n \approx \frac{(-1)^n}{|t|} \left[1 - \frac{1}{2}(K_{min,max}a - n\pi)^2 \right] \quad (109)$$

Solving for $K_{min,max}$ we get that:

$$K_{min,max} \approx \frac{n\pi \pm \sqrt{2(1 - |t|)}}{a} \quad (110)$$

Now, using (87), we can solve for $|t|$, and, since $|r|$ is very small, we can use an expansion to get:

$$|t| = \sqrt{1 - |r|^2} \implies |t| \approx 1 - \frac{1}{2}|r|^2 \implies |r|^2 \approx 2(1 - |t|) \quad (111)$$

So, we get:

$$K_{min,max} \approx \frac{n\pi \pm |r|}{a} \quad (112)$$

Thus:

$$\Delta \varepsilon_{gap} = \varepsilon_{max} - \varepsilon_{min} = \frac{\hbar^2}{2m}(K_{max}^2 - K_{min}^2) \approx \frac{\hbar^2}{2m} \left[\frac{1}{a^2}((n\pi + |r|)^2 - (n\pi - |r|)^2) \right] \quad (113)$$

Simplifying this equation we arrive at:

$$\Delta\varepsilon_{gap} \approx \frac{\hbar^2}{ma^2} 2n\pi|r| \quad (114)$$

Which is what we wanted to show.

g) Now, suppose the barrier is very strong, so that $|t| \approx 0$ and $|r| \approx 1$. Show that the allowed bands of energies are very narrow, with widths

$$\varepsilon_{max} - \varepsilon_{min} = \mathcal{O}(|t|) \quad (115)$$

where $\varepsilon_{min,max}$ are the energy values for the boundaries of the band.

In this case we have that Ka is in the neighborhood of $(2n+1)\pi/2$. This is because, since $|t| \approx 0$, $\cos(Ka)$ must also be around zero. This means that K_{max} will be for $\cos(Ka) \approx 1$ while K_{min} will be for $\cos(Ka) \approx -1$, or vice versa.

If we use a Taylor expansion of $\cos(Ka)$ around $(2n+1)\pi/2$ we get:

$$\cos Ka \approx \sin \left[\left(n + \frac{1}{2} \right) \pi \right] \left(\left(n + \frac{1}{2} \right) \pi - Ka \right) = (-1)^n \left(\left(n + \frac{1}{2} \right) \pi - Ka \right) \quad (116)$$

Thus, for $\cos(ka) = \pm 1$, we get

$$\pm|t| \approx (-1)^n \left(\left(n + \frac{1}{2} \right) \pi - K_{min,max}a \right) \quad (117)$$

which gives

$$K_{min,max} \approx \frac{1}{a} \left[\pi \left(n + \frac{1}{2} \right) \mp (-1)^n |t| \right] \quad (118)$$

Now, we have to consider whether n is even or odd.

If n is even, this means we are considering values of Ka in the neighborhood of the $(n+1)$ -th zero of the cosine function. So, if n is even, the cosine is a decreasing function around this zero. This means that K_{max} has to be for $\cos(ka) = -1$, while K_{min} is for $\cos(ka) = 1$.

If n is odd, the cosine function is an increasing function around the corresponding zero, so K_{max} is for $\cos(ka) = 1$ while K_{min} is for $\cos(ka) = -1$.

Fortunately, as it should be, in either case we get:

$$K_{max} \approx \frac{1}{a} \left[\pi \left(n + \frac{1}{2} \right) + |t| \right], \quad K_{min} \approx \frac{1}{a} \left[\pi \left(n + \frac{1}{2} \right) - |t| \right] \quad (119)$$

Thus:

$$\varepsilon_{max} - \varepsilon_{min} = \frac{\hbar^2}{2m} (K_{max}^2 - K_{min}^2) \approx \frac{\hbar^2}{ma^2} 2\pi \left(n + \frac{1}{2} \right) |t| \quad (120)$$

h) As a concrete example, one often considers the case in which $v(x) = g\delta(x)$, where $\delta(x)$ is the Dirac delta function. Show that, in this case:

$$\cot \delta = -\frac{\hbar^2 K}{mg}, \quad |t| = \cos \delta \quad (121)$$

So, the Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\psi''(x) + g\delta(x)\psi(x) = E\psi(x) \quad (122)$$

Since for $x \neq 0$, $\delta(x) = 0$, it is straightforward to show that

$$\psi(x) = \begin{cases} e^{iKx} + re^{-iKx} & \text{if } x < 0 \\ te^{iKx} & \text{if } x > 0 \end{cases} \quad (123)$$

The condition that $\psi(x)$ must be continuous, specifically at $x = 0$, yields

$$1 + r = t \quad (124)$$

Now, since the potential is a Dirac delta, $\psi'(x)$ must be discontinuous at $x = 0$. We can see this by integrating the Schrödinger equation around zero and taking a limit:

$$-\frac{\hbar^2}{2m} \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \psi''(x) dx + g \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \delta(x)\psi(x) dx = E \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \psi(x) dx \quad (125)$$

This yields:

$$-\frac{\hbar^2}{2m}(\psi'(0^+) - \psi'(0^-)) + g\psi(0) = 0 \quad (126)$$

Thus:

$$-\frac{\hbar^2}{2m}(iKt - iK + riK) + gt = 0 \quad (127)$$

Replacing $r = t - 1$ and solving for t we get:

$$t = \frac{1}{1 + i\frac{mg}{\hbar^2 K}} \implies t = \frac{1}{1 + \left(\frac{mg}{\hbar^2 K}\right)^2} - i\frac{\frac{mg}{\hbar^2 K}}{1 + \left(\frac{mg}{\hbar^2 K}\right)^2} \quad (128)$$

Now, we know that, in exponential form:

$$t = |t|e^{i\delta} \quad \text{where} \quad \delta = \text{Arg}(t) = \arctan \frac{\text{Im}(t)}{\text{Re}(t)} \quad (129)$$

Then:

$$\tan \delta = \frac{\text{Im}(t)}{\text{Re}(t)} \implies \cot \delta = \frac{\text{Re}(t)}{\text{Im}(t)} \quad (130)$$

Thus:

$$\cot \delta = \frac{1}{1 + \left(\frac{mg}{\hbar^2 K}\right)^2} \cdot \frac{1 + \left(\frac{mg}{\hbar^2 K}\right)^2}{-\frac{mg}{\hbar^2 K}} \implies \cot \delta = -\frac{\hbar^2 K}{mg} \quad (131)$$

As for $|t|$, we have:

$$|t|^2 = \left(\frac{1}{1 + \left(\frac{mg}{\hbar^2 K}\right)^2} \right)^2 + \left(\frac{\frac{mg}{\hbar^2 K}}{1 + \left(\frac{mg}{\hbar^2 K}\right)^2} \right)^2 = \frac{1 + \left(\frac{mg}{\hbar^2 K}\right)^2}{\left(1 + \left(\frac{mg}{\hbar^2 K}\right)^2\right)^2} \quad (132)$$

Simplifying, we can write this using the expression we have for $\cot \delta$:

$$|t|^2 = \frac{1}{1 + \tan^2 \delta} = \frac{1}{1 + \frac{\sin^2 \delta}{\cos^2 \delta}} = \frac{\cos^2 \delta}{\cos^2 \delta + \sin^2 \delta} = \cos^2 \delta \quad (133)$$

And so:

$$|t| = \cos \delta \quad (134)$$