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Chapter 1

Periodic Structure of Crystalline Solids

1.1 Condensed matter

To introduce you to condensed matter, we will define some solid structures:

Definition 1.1.1: Solid structures

- Crystalline solids - metals
- Amorphous solids - glass
- Liquid crystals
- Quasi Crystals
- Polymers

1.2 Crystals

Definition 1.2.1: Crystal

A crystal is a lattice and a basis, which in essence is a **periodic arrangement of atoms**.

For now, let's define a lattice as follows:

Definition 1.2.2: Lattice (1)

A lattice is an infinite array of identical points, arranged such that each point sees the other points in an identical way.

We can define a basis in the following way:

Definition 1.2.3: Basis

A basis is a structural unit representation by lattice points. The units in which it can be defined are i.e.:

- Atoms
- Molecules
- Group of atoms

Let's look at some lattices, depicted in figure 1.1. The parameter a is the lattice parameter.

As we can probably see, we can always define a some minimal set of vectors that describe the lattice. That means we can indeed go to each lattice point by taking a linear combination of these vectors. An example is given in figure 1.4. *More examples can be found in the slides.* More on lattice vectors in 1.3.

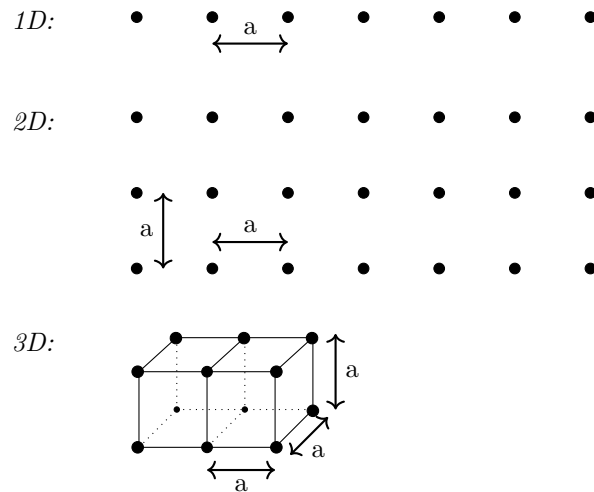


Figure 1.1: Lattices in different dimensions

Example 1.2.1 (Graphene)

To show what a lattice is and what it isn't this example is given, see also figure 1.2. As we know, graphene has a honeycomb lattice. That's why we call it a honeycomb crystal. But the lattice we can define is called a triangular lattice. Why?

By the definition of a lattice, we must have the same surrounding for every lattice point. This is not the case if we take one atom as basis. Therefore we take a set of two atoms to form the basis and define the lattice point as the center. This results in an equivalent surrounding for every basis structure.

Later on we will define a unit cell (section 1.4) and a conventional unit cell (section 1.6) for this lattice.

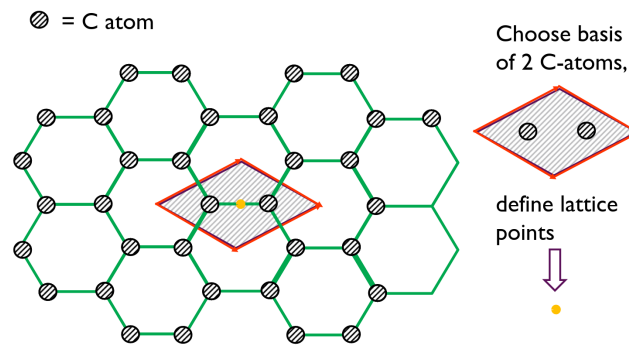


Figure 1.2: The graphene crystal

1.3 Lattice vectors

As already touched upon at section 1.2, we can define a set of lattice vectors. To construct these we first define an origin O :

$$O = \vec{0} \quad (1.1)$$

Then we will define the lattice points in function of the PLV (*Primitive Lattice Vectors*).

$$\vec{a} = PLV \quad (1.2)$$

$$n_i \in \mathbb{Z} \quad (1.3)$$

$$A = [\vec{a}_1, \vec{a}_2, \vec{a}_3]^T \quad (1.4)$$

$$1D : \quad \vec{R} = n_1 \cdot \vec{a} \quad (1.5)$$

$$2D : \quad \vec{R} = [n_1, n_2] \cdot A \quad (1.6)$$

$$3D : \quad \vec{R} = [n_1, n_2, n_3] \cdot A \quad (1.7)$$

We can understand that a lattice must be defined unambiguous, therefore the definition of a lattice can be defined as:

Definition 1.3.1: Lattice (2)

A lattice is a set of points defined by Primitive Lattice Vectors (PLV).

Visually we can represent these vectors as can be seen in figure 1.3 and figure 1.4. We can also conclude that *PLVs* are not unique, one can also show that this is true for 3D. These are indeed *PLVs* because one can reach all lattice points.

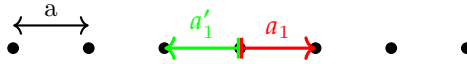


Figure 1.3: An example set of lattice vectors in 1D

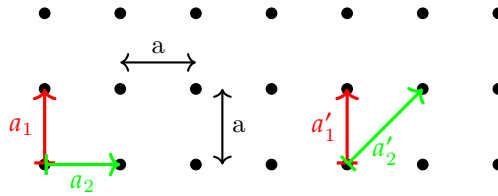


Figure 1.4: An example set of lattice vectors in 2D

1.4 Unit cell

Definition 1.4.1: Unit cell

A unit cell is a region of space such that when translated through the entire space by means of lattice vectors, reproduces the lattice without any overlaps or voids.

The definition of a unit cell is illustrated in figure 1.5

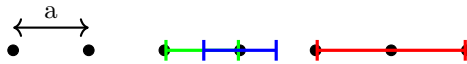


Figure 1.5: Several 1D unit cells

1.5 Primitive unit cell

Definition 1.5.1: Primitive unit cell

A Primitive Unit Cell (PUC) is a unit cell that contains only one lattice parameter. By this is meant that when for example a cube is a primitive unit cell, each point counts as $\frac{1}{8}$, therefore the cube only has 1 lattice point.

We then see that:

- 1D: line spanned by $PLV \vec{a} \Rightarrow$ the line of the $PUC = \|\vec{a}\|$.
- 2D: area spanned by $PLV \vec{a}_1, \vec{a}_2 \Rightarrow$ the area of the $PUC = \|\vec{a}_1 \times \vec{a}_2\|$.
- 3D: volume spanned by $PLV \vec{a}_1, \vec{a}_2, \vec{a}_3 \Rightarrow$ the volume of the $PUC = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$.

1.6 Conventional unit cell

Definition 1.6.1: Conventional unit cell

A conventional unit cell, a.k.a. a convenient unit cell, is a unit cell that contains more than 1 lattice point but has perpendicular axes.

1.7 Weigner-Seitz unit cell

Definition 1.7.1: Weigner-Seitz unit cell

A Weigner-Seitz unit cell is a primitive unit cell that has a region of space around a lattice point such that any point around that lattice point is closer to that lattice point as any other lattice point.

This concept is further elaborated below. The corresponding figure for a 2D example is seen in figure 1.6.

1. Take any lattice point (green in this case).
2. Look for the nearest lattice point and draw a line between them (in gray).
3. Draw the bisecting, perpendicular on this first line (in blue).
4. Do this for all other nearby lattice points (in cyan).

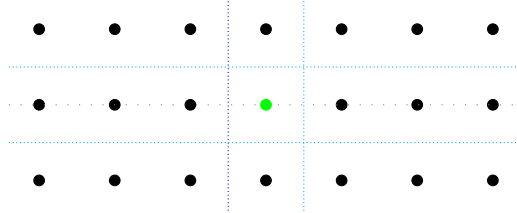


Figure 1.6: 2D example for Weigner-Seitz unit cell

Chapter 2

Periodic Structure of Crystals

2.1 Bravais lattices

Definition 2.1.1: Bravais lattices

There are 14 different lattice types, these are called Bravais lattices. These lattices can be subdivided into 7 different lattice systems, these lattice systems are:

1. Triclinic
2. Monoclinic
3. Orthohombic
4. Tetragonal
5. Cubic
6. Triagonal
7. Hexagonal

The Cubic structure will mostly be studied during this course.

2.2 Cubic lattice systems

Cubic lattice systems come in three flavours, we will define them here. The different systems can be found in figure 2.1.

Definition 2.2.1: Simple cubic lattice

A simple cubic lattice is a conventional unit cell and therefore also a *PUC*. This lattice has a straightforward basis, as can be seen in figure 2.2.

The basis chosen is $\{\vec{a}_1, \vec{a}_2, \vec{a}_3\}$. As we can see (figure 2.2), the basis isn't body centered. Because the body centered atom is a different one as the other 'side' atoms, the smallest possible unit cell (or *PUC*) is the full cube. Whereas if the middle atom is the same, the basis is chosen in the middle, this is the **body centered cubic lattice**.

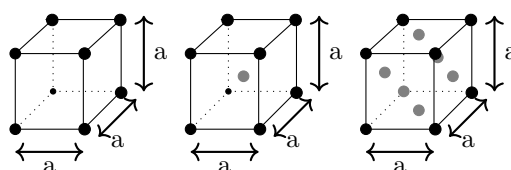


Figure 2.1: The three different cubic lattice systems

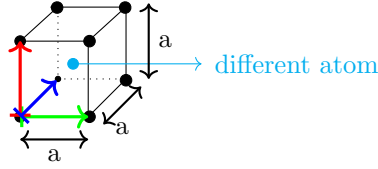


Figure 2.2: The basis for a simple cubic lattice

Definition 2.2.2: Body centered cubic lattice

A Body centered cubic lattice has 1 atom as primitive unit cell, its basis is depicted in figure 2.3. As mentioned before, all atoms are the same and that is why the *PUC* is smaller.

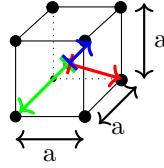


Figure 2.3: The three different cubic lattice systems

Definition 2.2.3: Face centered cubic lattice

If all atoms are the same and the extra atoms position themselves on the middle of every face, one gets the face centered cubic lattice. This is depicted in figure 2.4.

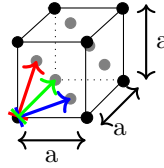


Figure 2.4: The three different cubic lattice systems

2.3 C/Si/Ge - lattice systems

As we know, the lattice systems for C, Si and Ge have a diamond lattice structure. This diamond structure takes the form of a fcc (face centered cubic) lattice. In figure 2.5, one can see the primitive unit cell. The basis vectors are:

$$\vec{a}_1 = \left(\frac{1}{2}, \frac{1}{2}, 0\right) \quad (2.1)$$

$$\vec{a}_2 = \left(0, \frac{1}{2}, \frac{1}{2}\right) \quad (2.2)$$

$$\vec{a}_3 = \left(\frac{1}{2}, 0, \frac{1}{2}\right) \quad (2.3)$$

2.3.1 Translation symmetry

As a tiny intermezzo I'll introduce translation symmetry. This will be important later on for solving the Schrödinger equation.

$$\left\{ -\frac{\hbar}{2m} \nabla^2 + V(\vec{r}) \right\} \phi(\vec{r}) = E \phi(\vec{r}) \quad (2.4)$$

$$\longrightarrow V(\vec{r} + \vec{T}) = V(\vec{r}') = V(\vec{r}) \quad (2.5)$$

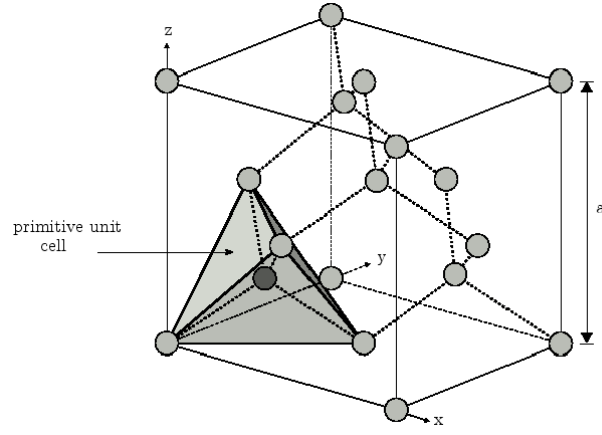


Figure 2.5: The diamond structure and its PUC

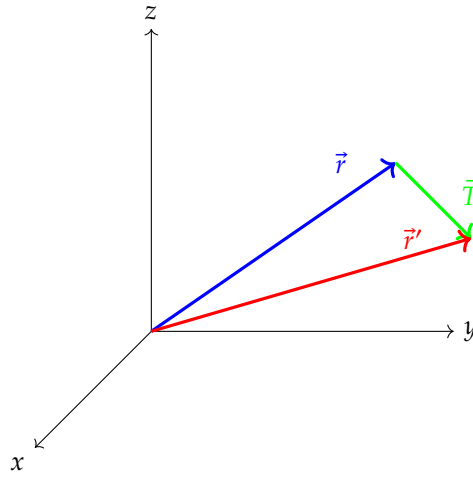


Figure 2.6: Translational symmetry

Because $V(\vec{r})$ is actually a periodic function in a crystal lattice, it becomes $V(\vec{r} + \vec{T})$. This \vec{T} is responsible for the translation in translational symmetry.

Definition 2.3.1: Translational symmetry

Translational symmetry is a symmetry operation for a crystal. This operation leaves the crystal invariant. Meaning that the addition of \vec{T} to \vec{r} returns the same value for $V(\vec{r})$. This is graphically represented in figure 2.6.

2.4 Lattice dimensions

Definition 2.4.1: Lattice dimensions

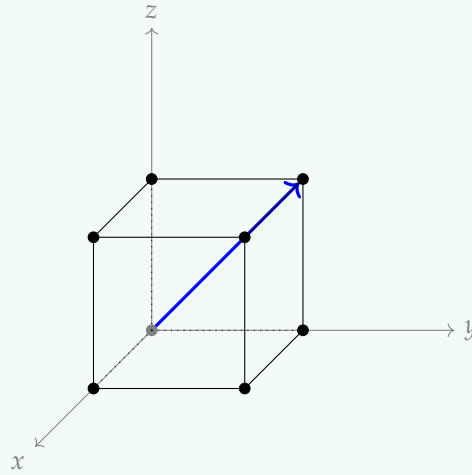
Lattice dimensions are defined by the parameters $[u, v, w]$. These parameters are defined by a vector $\vec{r} = k(u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3)$.

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ are unit cell vectors, k is a common factor in order that $u, v, w \in \mathbb{Z}_{\text{without common factor}}$.

One thing to notice is that if $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are PLVs, $k \in \mathbb{Z}$. Else $k \in \mathbb{Q}$.

Example 2.4.1 (Lattice dimensions)

Take the following vector in the lattice:



Then the vector can be denoted as $[0, 1, 1]$.

As one might, rightly so, notice is that some directions have the same symmetry. What about labeling these directions? First, what do we mean with ‘same directions’?

The concept is demonstrated in figure 2.7, where \vec{a} and \vec{b} have the same symmetry. This is because the red lattice points in this crystal see each surrounding lattice point in exactly the same way, therefore symmetry is the same.

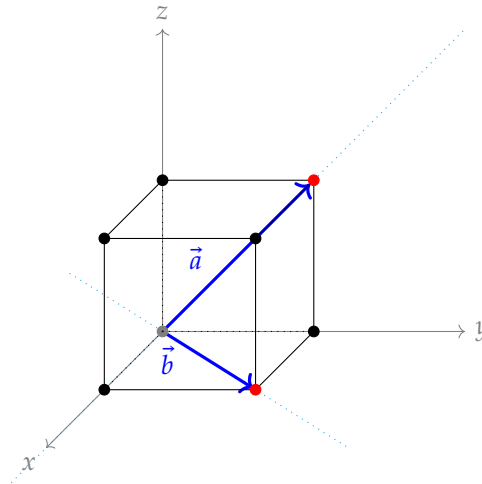


Figure 2.7: Demonstration of vectors with the same symmetry

Note:-

If one of u, v, w is negative, remove the $-$ and add a bar on top, i.e., $-x = \bar{x}$.

These equivalent directions are denoted as $\langle u, v, w \rangle$ where $[u, v, w]$ is the direction of one of these directions that share symmetry.

2.5 Lattice planes

Definition 2.5.1: Lattice planes

Lattice planes are defined by the parameters $[h, k, l]$. These parameters are called **Miller Indices (MI)** and describe a crystal plane that contain at least 3 non colinear lattice points.

Claim 2.5.1 Property of lattice planes

Lattice planes are an infinite set of parallel planes which are equally spaced and contain ALL lattice points.

Question 1: How do we calculate these points?

To calculate h, k, l we:

1. Take a unit cell $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ with its lattice point in the origin.
2. Let the lattice plane intersect the axis along $\vec{a}_1, \vec{a}_2, \vec{a}_3$ in $n \cdot \vec{a}_1, m \cdot \vec{a}_2, p \cdot \vec{a}_3$. $n, m, p \in \mathbb{Q}$.
3. See that the lattice plane does not intersect the origin. Finally take the reciprocal of n, m, p and multiply with the least common multiple γ .

$$h = \frac{1}{n}\gamma \quad (2.6)$$

$$k = \frac{1}{m}\gamma \quad (2.7)$$

$$l = \frac{1}{p}\gamma \quad (2.8)$$

This last step defines a vector perpendicular onto the plane, which is how one defines a plane.

Note:-

We use a 0 for h, k, l if the plane is perpendicular to that direction.

Chapter 3

Reciprocal Space

3.1 Definition and properties

Definition 3.1.1: Direction

The direction in reciprocal space is defined by $[u, v, w]$

Definition 3.1.2: Planes

The reciprocal planes are defined by (h, k, l)

Claim 3.1.1 Properties of reciprocal space

1. There are an infinite amount of lattice planes in a lattice.
2. The set of all lattice planes contains only parallel lattice plains that contain all lattice points.
3. The lattice plane closest to the origin cuts the coordinate axis in $(\frac{1}{h}, \frac{1}{k}, \frac{1}{l})$.
4. There is always a lattice plane going through the origin.

3.2 Reciprocal space

3.2.1 Fourier transform of a periodic function

As we know from section 2.3.1, $V(\vec{r})$ is periodic. That's why we look at the FT of a periodic function.

$$f(x) = f(x + n \cdot a) \quad (3.1)$$

$$= \frac{a_0}{2} + \sum_{n=2}^{\infty} \left\{ a_n \cos \frac{2\pi \cdot nx}{a} + b_n \sin \frac{2\pi \cdot nx}{a} \right\} \quad (3.2)$$

$$= \sum_G F(G) \cdot e^{iGx} \quad (3.3)$$

Assuming for $n = -\infty \rightarrow \infty$

$$G = \frac{2\pi}{a}n \quad (3.4)$$

$$G \cdot a = 2n\pi \quad (3.5)$$

$$\Rightarrow e^{iGa} = e^{2\pi ni} = 1 \quad (3.6)$$

Note:-

For a reciprocal lattice number G: $[G] = \frac{1}{2}$

Furthermore, the solutions for a_n and b_n are give by:

$$a_n = \frac{2}{a_0} \int_0^a dx f(x) \cos \frac{2\pi \cdot nx}{a} \quad (3.7)$$

$$b_n = \frac{2}{a_0} \int_0^a dx f(x) \sin \frac{2\pi \cdot nx}{a} \quad (3.8)$$

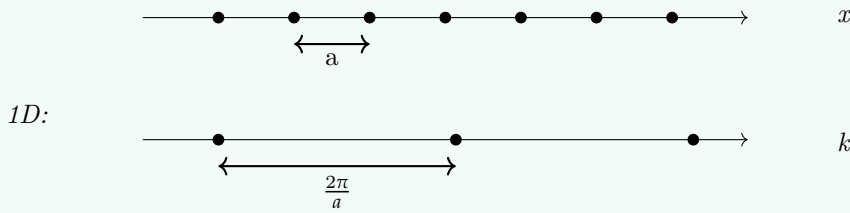
Claim 3.2.1 Property of $F(G)$

For a real sum: $F(-G) = F^*(G)$

Question 2: Using the FT for conversion of the lattice space to the recipocal space

How does this translate to the lattice and potential?

Example 3.2.1 (Using the FT for conversion of the lattice space to the recipocal space)



In lattice space we see that $V(x)$ is periode, $V(x) = V(x + na)$. a is the lattice vector.

3.2.2 Extension to 2D/3D

Now, extending the above principle to 2D and 3D is straightforward but I'll still go over it.

Theorem 3.2.1

$$f(\vec{r}) = f(x, y, z) = f(\vec{r} + \vec{T}) \quad (3.9)$$

$$\Rightarrow e^{i\vec{G} \cdot \vec{T}} = 1 \quad \forall \vec{T} \quad (3.10)$$

We define \vec{r} as a vector in the lattice space and $\vec{T} = n_1 \cdot \vec{a}_1 + n_2 \cdot \vec{a}_2 + n_3 \cdot \vec{a}_3$.

Proof:

$$f(\vec{r}) = \sum_{\vec{G}} F(\vec{G}) e^{i\vec{G} \cdot \vec{r}} \quad (3.11)$$

$$\Rightarrow f(\vec{r} + \vec{T}) = \sum_{\vec{G}} F\vec{G} e^{i\vec{G} \cdot (\vec{r} + \vec{T})} \quad (3.12)$$

$$= \sum_{\vec{G}} F\vec{G} e^{i\vec{G} \cdot \vec{r}} \quad (3.13)$$

$$e^{i\vec{G} \cdot \vec{T}} = 1 \quad (3.14)$$

■

By section 2.3.1 we can do step (3.13) because we know $f(\vec{r}) = f(\vec{r} + \vec{T})$ for a periodic lattice. In general we can say:

$$F(\vec{G}) = \frac{1}{V} \int_V f(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d\vec{r} \quad (3.15)$$

3.3 Finding reciprocal lattice vectors

As we know is \vec{G} the reciprocal lattice vector, but how do we find this vector?
We know that:

$$e^{i\vec{G}\cdot\vec{T}} = 1 \Rightarrow \vec{G} \cdot \vec{T} = 2\pi n \quad (3.16)$$

With

$$\vec{G} = m_1 \cdot \vec{b}_1 + m_2 \cdot \vec{b}_2 + m_3 \cdot \vec{b}_3 \quad (3.17)$$

$$\vec{T} = n_1 \cdot \vec{a}_1 + n_2 \cdot \vec{a}_2 + n_3 \cdot \vec{a}_3 \quad (3.18)$$

$$n \rightarrow \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \quad (3.19)$$

This results in the following definition:

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} \quad (3.20)$$

Note:-

The reason for defining δ_{ij} as either 0 or 1 is to have orthogonal \vec{a}_i and \vec{b}_j .

Then the following vectors \vec{b}_j span the reciprocal space \vec{G} . When satisfying relation (3.20), \vec{b}_j can be described in function of \vec{a}_i :

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{V} (\vec{a}_2 \times \vec{a}_3) \quad (3.21)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)} = \frac{2\pi}{V} (\vec{a}_3 \times \vec{a}_1) \quad (3.22)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)} = \frac{2\pi}{V} (\vec{a}_1 \times \vec{a}_2) \quad (3.23)$$

$$\Rightarrow \vec{G} = m_1 \cdot \vec{b}_1 + m_2 \cdot \vec{b}_2 + m_3 \cdot \vec{b}_3 \quad (3.24)$$

As we see describing \vec{b}_j is a cyclic procedure.

3.4 Properties of reciporcal spaces

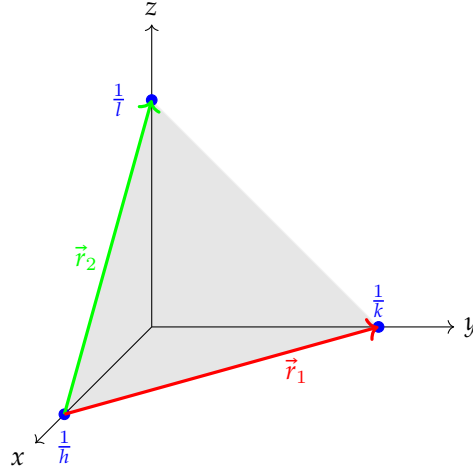
Claim 3.4.1 Property 1

To every lattice plane (h, k, l) there is a reciprocal lattice vector perpendicular to that plane and is given by $\vec{G} = h \cdot \vec{b}_1 + k \cdot \vec{b}_2 + l \cdot \vec{b}_3$.

Proof: It is sufficient to show that the vector \vec{R} , perpendicular to the lattice plan (h, k, l) , is parallel to \vec{G} . In order that:

$$\frac{\vec{R}}{\|\vec{R}\|} = \frac{\vec{G}}{\|\vec{G}\|} \quad (3.25)$$

Then take a lattice plane (h, k, l) :



We define $\vec{r}_1 = \frac{\vec{a}_2}{k} - \frac{\vec{a}_1}{h}$ and $\vec{r}_2 = \frac{\vec{a}_3}{l} - \frac{\vec{a}_1}{h}$. The vector perpendicular to the area spanned (gray) by \vec{r}_1 and \vec{r}_2 is given by $\vec{R} = \vec{r}_1 \times \vec{r}_2$. If we fill in the vectors according to the definitions, we get:

$$\vec{R} = \left\{ \frac{\vec{a}_2}{k} - \frac{\vec{a}_1}{h} \right\} \times \left\{ \frac{\vec{a}_3}{l} - \frac{\vec{a}_1}{h} \right\} \quad (3.26)$$

$$= \frac{\vec{a}_2}{k} \times \left\{ \frac{\vec{a}_3}{l} - \frac{\vec{a}_1}{h} \right\} - \frac{\vec{a}_1}{h} \times \left\{ \frac{\vec{a}_3}{l} - \frac{\vec{a}_1}{h} \right\} \quad (3.27)$$

$$= C \cdot \vec{G} \quad (3.28)$$

$$\sim \vec{G} \quad (3.29)$$

And thus from

$$\frac{\vec{G}}{\|\vec{G}\|} = \frac{\vec{R}}{\|\vec{R}\|} \quad (3.30)$$

$$= \frac{C \cdot \vec{G}}{\|C \cdot \vec{G}\|} \quad (3.31)$$

$$= \frac{C \cdot \vec{G}}{C \cdot \|\vec{G}\|} = \frac{\vec{G}}{\|\vec{G}\|} \quad (3.32)$$

$$\Rightarrow \vec{R} // \vec{G}$$

■

Note:-

If you work out equation 3.27 you get the formulas for \vec{b}_j , see equations 3.21 - 3.23. Keep in mind that $\vec{a} \times -\vec{b} = \vec{b} \times \vec{a}$ and that distributivity is defined for cross products.

Claim 3.4.2 Property 2

The spacing d between the lattice plane closest to the origin and the origin itself is given by:

$$\frac{2\pi}{\|\vec{G}\|} \quad (3.33)$$

$$\Rightarrow \|\vec{G}\| = \frac{2\pi}{d} \quad (3.34)$$

Proof:

d = the distance between the (h, k, l) planes

$$= \frac{\vec{a}_1}{h} \cdot \frac{\vec{G}}{\|\vec{G}\|} \quad (3.35)$$

$$= \frac{1}{h\|\vec{G}\|} h\vec{a}_1 \cdot \vec{b}_1 = \frac{2\pi}{\|\vec{G}\|} \quad (3.36)$$

Step 3.36 uses the fact that \vec{a}_i and \vec{b}_j are perpendicular as per 3.19. ■

Claim 3.4.3 Property 3

The direct lattice is the reciprocal of its own reciprocal lattice. Because switching the vectors in expression 3.16 results in the same expression.

Claim 3.4.4 Property 4

The volume of a primitive unit cell of the reciprocal lattice is given by:

$$V_R = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \quad (3.37)$$

$$= \frac{8\pi^3}{V} \quad (3.38)$$

With $V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$, the volume of the direct lattice *PUC*.

3.5 X-ray diffraction

One way where the 'Von Laue-Bragg' condition can be observed is in x-ray diffraction. The 'Von Laue-Bragg' condition states that an incident electron is or scattered or stays unscattered when colliding with a crystal. This scattering is elastic thus the amplitude of the wave function does not change. This is illustrated in figure 3.1. Because the scattering is elastic we can state the following, define the wave as $e^{i\vec{k} \cdot \vec{r}}$:

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} \quad (3.39)$$

$$= E(\vec{k}') \quad (3.40)$$

$$= \frac{\hbar^2 k'^2}{2m} \quad (3.41)$$

$$\Rightarrow |\vec{k}| = |\vec{k}'| \quad (3.42)$$

One way of figuring out if an electron is scattered is to use the Fermi golden rule.

3.6 Fermi golden rule

Definition 3.6.1: The fermi golden rule

The fermi golden rule states that ($\tau_{\vec{k} \rightarrow \vec{k}'}$ is the mean time to have a diffraction):

$$\frac{1}{\tau_{\vec{k} \rightarrow \vec{k}'}} = \frac{2\pi}{\hbar} |\langle \vec{k} | V(\vec{r}) | \vec{k}' \rangle|^2 \delta(E(\vec{k}) - E(\vec{k}')) \quad (3.43)$$

We will look a bit further into this equation. We know that $V(\vec{r})$ is a periodic potential field of the crystal. Then

$$\langle \vec{k} | V(\vec{r}) | \vec{k}' \rangle = \int_V d\vec{r} \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} V(\vec{r}) \frac{1}{\sqrt{V}} e^{-i\vec{k}' \cdot \vec{r}} \quad (3.44)$$

$$= \frac{1}{V} \sum_{\vec{R}} \int_{\text{unit cell}} d\vec{r} V(\vec{r} + \vec{R}) e^{i(\vec{k} - \vec{k}') \cdot (\vec{r} + \vec{R})} \quad (3.45)$$



Figure 3.1: X-ray diffraction on a lattice

Equation 3.44 has normalization constants $\frac{1}{\sqrt{V}}$. Furthermore, in equation 3.45 we exploit the periodicity of $V(\vec{r})$ and translation symmetry (section 2.3.1). When is this integral in equation 3.45 non-zero?

$$\text{The integral is non-zero} \iff \vec{k} - \vec{k}' = \vec{G} \text{ (the reciprocal lattice vector)} \quad (3.46)$$

Equation 3.46 states the Bragg condition, further elaborated in section 3.7. By symmetry, we can leave \vec{R} out of equation 3.45, we get:

$$\langle \vec{k} | V(\vec{r}) | \vec{k}' \rangle = \frac{1}{V} \sum_{\vec{R}} \int_{\text{unit cell}} d\vec{r} V(\vec{r} + \vec{R}) e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} \quad (3.47)$$

$$\text{where } \int_{\text{unit cell}} d\vec{r} V(\vec{r} + \vec{R}) e^{i\vec{G} \cdot \vec{r}} = \tilde{V}(\vec{G}) \quad (3.48)$$

$$\text{with } V(\vec{r}) = \sum_{\vec{G}} \tilde{V}(\vec{G}) e^{i\vec{G} \cdot \vec{r}} \quad (3.49)$$

$$\iff e^{i\vec{G} \cdot \vec{r}} = 1 \quad (3.50)$$

As we know from section 3.2 if $\vec{G} (= \vec{k} - \vec{k}')$ is not a reciprocal lattice vector, $\tilde{V}(\vec{G}) = 0$. \vec{G} must be a lattice vector. The condition 3.46 is the von Laue condition for constructive scattering.

So if we have elastic scattering, then the wavevectors and wavelengths are the same:

$$|\vec{k}| = |\vec{k}'| \quad (3.51)$$

$$\frac{2\pi}{\lambda} = \frac{2\pi}{\lambda'} \quad (3.52)$$

$$\iff \lambda = \lambda' \quad (3.53)$$

If we have the same wavelength, this scattering introduces extra distance for different incoming waves, we can see that in figure 3.2. The extra distance is defined by:

$$\frac{\vec{R}}{|\vec{k}|} \cdot \vec{k} - \frac{\vec{R}}{|\vec{k}|} \cdot \vec{k}' = n\lambda \quad (3.54)$$

$$\Rightarrow \vec{R}(\vec{k} - \vec{k}') = 2\pi n \quad (3.55)$$

$$\Rightarrow e^{i\vec{R}(\vec{k} - \vec{k}')} = 1 \quad (3.56)$$

This leaves us with the Bragg condition (section 3.7), we can conclude that:

$$\vec{k} - \vec{k}' = \vec{G} \quad (3.57)$$

3.7 Von Laue-Bragg condition

As proven in section 3.6,

$$\vec{k} - \vec{k}' = \vec{G} \quad (3.58)$$

. We will rewrite this equation:

$$\vec{k} - \vec{k}' = \vec{G} \quad (3.59)$$

$$\iff \vec{k}' = \vec{k} - \vec{G} \quad (3.60)$$

$$\text{From eq. 3.51} \rightarrow |\vec{k}'|^2 = |\vec{k}|^2 = k^2 = |\vec{k} - \vec{G}|^2 = k^2 - 2\vec{k} \cdot \vec{G} + G^2 \quad (3.61)$$

$$\Rightarrow 2\vec{k} \cdot \vec{G} = G^2 \quad (3.62)$$

$$\iff \vec{k} \cdot \frac{\vec{G}}{G} = \frac{G}{2} \quad (3.63)$$

$$\iff \vec{k} \cdot \vec{e}_{\vec{G}} = \frac{G}{2} \quad (3.64)$$

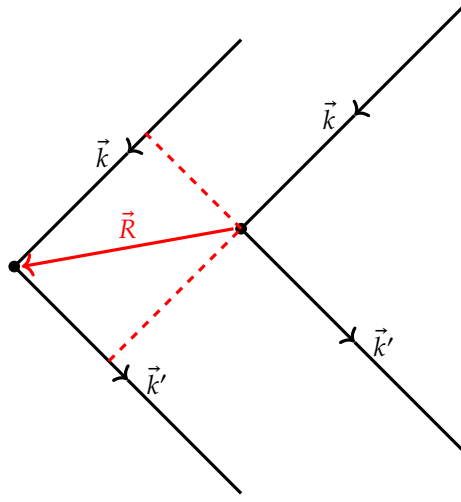


Figure 3.2: Extra distance for different wavevectors

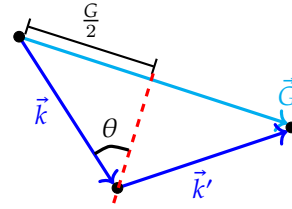


Figure 3.3: Drawing of the physical meaning of the Bragg condition

This means that the component of an incident wave vector along the reciprocal lattice vector direction $G = \frac{|\vec{G}|}{2}$. This is graphically represented in figure 3.3. The dashed red line is a Bragg plane, this is generally defined by:

$$k \sin \theta = \frac{G}{2} \quad (3.65)$$

Furthermore, this bragg plane is derive from equation 3.64. From the properites of reciprocal spaces, we know that (see equation 3.34):

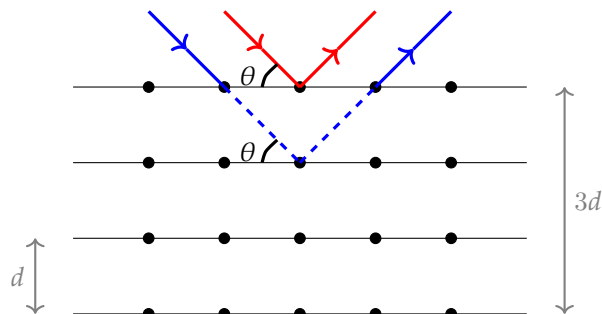
$$d = \frac{2\pi}{G} \quad (3.66)$$

$$\text{with } \vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \quad (3.67)$$

$$\text{where } h, k, l \text{ are Miller indices (section 2.5)} \quad (3.68)$$

Now, form equation 3.34 and equation 3.65 we can derive an interference pattern. As we can see in figure 3.7, for normal scattering waves in a crystal lattice, Von Laue and the Bragg condition are the same. As we further also see, if the extra distance (marked with a dashed line) $d = n\lambda$, then there is no interference.

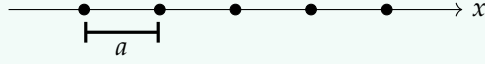
Example 3.7.1 (Von Laue - Bragg condition in 1D)



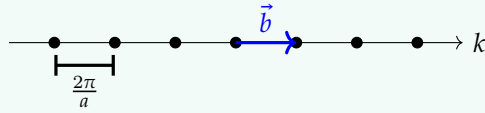
For 1D, we can write the Von Laue condition as:

$$\vec{k} \cdot \vec{G} = \frac{|\vec{G}|^2}{2} \Rightarrow kG = \frac{G^2}{2} \quad (3.69)$$

We take the following 1D lattice:



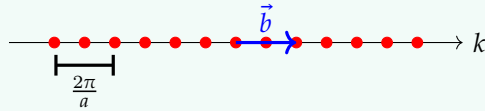
With the following reciprocal 1D lattice and reciprocal vector $\vec{G} = \vec{b}$:



Then if we calculate the Bragg points, we get from equation 3.69:

$$kb = \frac{b^2}{2} \Rightarrow k = \frac{b}{2} \quad (3.70)$$

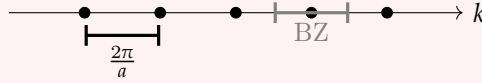
This results in the following Bragg points on the lattice:



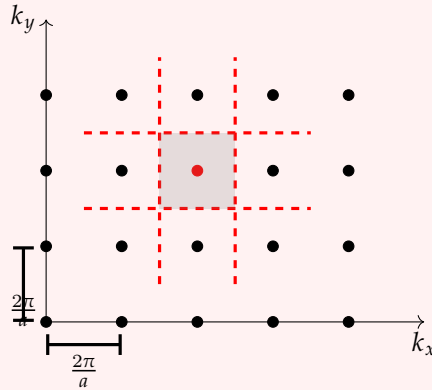
3.8 The Brillouin Zone (BZ)

Definition 3.8.1: The first Brillouin Zone

The first Brillouin Zone is a Weigner-Sietz unit cell (section 1.7) of the reciprocal lattice.
For a 1D lattice, this becomes:



For a 2D lattice, the BZ (in gray) becomes:



If \vec{G} is defined on red dot, then the red dashed lines represent Bragg lines. The BZ is given in gray.

3.8.1 Higher order BZ

These higher order BZ are all the other zones limited by Bragg points (1D) / lines (2D) / planes (3D):

- The first BZ is a set of points that can be reached without crossing other Bragg points / lines / planes.
- The second BZ is a set of points that can be reached by crossing Bragg points / lines / planes once. The second zone does not contain the lower order BZ.
- ...

Chapter 4

Solids

4.1 Defining solids

Question 3: What is a solid?

Solid = nuclei + electrons

For describing solids we define following concepts:

Definition 4.1.1: Core electrons

- Tightly bound to nucleus
- Occupy lower shells
- Do not participate in bonding

Definition 4.1.2: Valence electrons

- Loosely bound to nucleus
- Occupy higher E-shells
- Responsible for bonding

To describe the Hamiltonian for solids for the Schödinger equation we use:

$$H = H_{electron} + H_{electron-electron} + H_{nucleus} + H_{nucleus-nucleus} + H_{electron-nucleus} \quad (4.1)$$

$$H = H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion} \quad (4.2)$$

The following definitions for the H_i are used:

$$H_{electron} = \sum_{i=1}^N -\frac{\hbar^2}{2m_{electron}} \nabla_i^2 \quad (4.3)$$

$$H_{nucleus} = \sum_{i=1}^M -\frac{\hbar^2}{2 * M_i} \nabla_o^2 \quad (4.4)$$

$$H_{electron-electron} = \frac{1}{2} \sum_{i,j;i \neq j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \quad (4.5)$$

$$H_{nucleus-nucleus} = \frac{1}{2} \sum_{i,j;i \neq j} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\vec{R}_i - \vec{R}_j|} \quad (4.6)$$

$$H_{electron-nucleus} = \sum_{i,j} -\frac{Z_j e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_j|} \quad (4.7)$$

Note:-

In equation (1.5) and (1.11) we have $i \neq j$ in order that we do not double count an interaction. Furthermore, in equation (1.8) we have Z_i which is an atomic number

To further describe the solid lattice, one has to describe ions. In essence, ions are just nuclei and core electrons together. In the following equations is $M' = M$ and the amount of valence electrons is N' .

Looking at the hamiltonians of the electron - ion interactions, these become:

$$H_{electron} = \sum_{i=1}^{N'} -\frac{\hbar^2}{2m_{electron}} \nabla_i^2 \quad (4.8)$$

$$H_{ion} = \sum_{i=1}^{M'} -\frac{\hbar^2}{2 * M_i} \nabla_o^2 \quad (4.9)$$

$$H_{electron-electron} = \frac{1}{2} \sum_{i,j;i \neq j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \quad (4.10)$$

$$H_{ion-ion} = \frac{1}{2} \sum_{i,j;i \neq j} V_{ion}(\vec{R}_i - \vec{R}_j) \quad (4.11)$$

$$H_{electron-ion} = \sum_{i,j} V_{electron-ion}(\vec{r}_i - \vec{R}_j) \quad (4.12)$$

We can see the equations for electron - ion interactions are very similar to electron nucleus interactions.

What we eventually want to solve is: $H\Phi = E\Phi$. We will therefore define following vectors:

$\vec{r} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ and $\vec{R} = (\vec{R}_1, \vec{R}_2, \dots, \vec{R}_M)$.

We can now define the probability density function as: $P(\vec{r}, \vec{R}) = |\Phi(\vec{r}, \vec{R})|^2$ Later on, we separate the degrees of freedom of valence electrons from the degrees of freedom of bound electrons, that's why we separated them here already.

4.2 Born-Oppenheimer approximation

This definition comes down to saying electrons move much faster as ions thus ions are immobile.

$$H\Phi(\vec{r}, \vec{R}) = E\Phi(\vec{r}, \vec{R}) \quad (4.13)$$

Claim 4.2.1

$$\Phi(\vec{r}, \vec{R}) \approx \psi(\vec{r}, \vec{R})\phi(\vec{R})$$

$$H\Phi(\vec{r}, \vec{R}) = H\psi(\vec{r}, \vec{R})\phi(\vec{R}) \quad (4.14)$$

$$= (H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) \quad (4.15)$$

$$= (H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) + (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) \quad (4.16)$$

$$= \phi(\vec{R})(H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R}) + \psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R}) \\ + (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) - \psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R}) \quad (4.17)$$

We can move $\phi(\vec{R})$ to the front because there is no differnetial operation acting on it in the hamiltonians. In step 3 we perform a '+ $\psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R})$ ' and '- $\psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R})$ ' operation.

Because $m_{electron} \approx M \cdot 10^{-4}$, $(H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) - \psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R}) \approx 0$. We can now simplify equation (1.5) = $E\psi(\vec{r}, \vec{R})\phi(\vec{R})$ further by dividing with $\psi(\vec{r}, \vec{R})\phi(\vec{R})$. Equation (1.5) now becomes:

$$\frac{(H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R})}{\psi(\vec{r}, \vec{R})} + \frac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})} = E \quad (4.18)$$

Note:-

We cannot divide the leftover function as the numerator still acts on it!

We can now define:

$$E_{el}(\vec{R}) = E - \frac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})} \quad (4.19)$$

As mentioned before already, this makes it possible to separate valence electronic part and the ionic part.

Definition 4.2.1: Formulation of the solid hamiltonians

$$\begin{cases} (H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R}) = E_{el}\psi(\vec{r}, \vec{R}) \\ \frac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})}\psi(\vec{r}, \vec{R}) = (E - E_{el})\psi(\vec{r}, \vec{R}) \end{cases} \quad (4.20)$$

4.3 Static approximation (w.r.t. the lattic)

We know $\vec{R} = (\vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) \Rightarrow \vec{R}_i^{(0)} + \delta\vec{R}_i(t)$ This delta is small and can be ignored.

$$H_{electron-ion} = \sum V_{electron-ion}(\vec{r}_i - \vec{R}_j) \quad (4.21)$$

$$= \sum (V_{electron-ion}(\vec{r}_i - \vec{R}_j^{(0)}) + \delta\vec{R}_j(t) \cdot \vec{\nabla}_j V_{electron-ion}(\vec{r}_i - \vec{R}_j^{(0)})) \quad (4.22)$$

Note:-

- $\delta\vec{R}_j(t) \cdot \vec{\nabla}_j V_{electron-ion}(\vec{r}_i - \vec{R}_j^{(0)})$ is the electron - phonon interaction.
- Why does it only depend on distance? In normal circumstances, most interactions are distance related but sometimes it is (in anisotropic materials) vector dependent, therefore the \parallel is left out here in $H_{electron-ion}$.

Now we simplify equation (1.20), in hope for writing the time dependent Schrödinger equation easier. Namely it becomes a single electron particle operator instead of a complex Hamiltonian.

- $H_{electron}$ stays the same
- $H_{electron-ion}$ stays the same
- $H_{electron-electron} = 1/2 \sum \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} \approx \sum v_i(\vec{r}_i)$

Such that:

$$\sum_i \left\{ -\frac{\hbar^2}{2m_{electron}} \nabla_i^2 + \sum_j \left\{ V_{electron-ion}(\vec{r}_i - \vec{R}_j) + v_i(\vec{r}_i) \right\} \right\} \psi(\vec{r}, \vec{R}) = E_{el}\psi(\vec{r}, \vec{R}) \quad (4.23)$$

$$\Rightarrow \sum h_i(\vec{r}_i)\psi(\vec{r}) = E_{el}\psi(\vec{r}) \quad (4.24)$$

$$\longrightarrow \psi(\vec{r}) = \xi(\vec{r}_1) + \xi(\vec{r}_2) + \dots \quad (4.25)$$

$$\Rightarrow h_i(r_i)\xi(\vec{r}_i) = \epsilon_i\xi(\vec{r}_i) \quad (4.26)$$

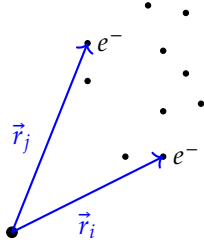
4.4 Hartree approximation**Question 4: What does this approximation mean?**

First of all, the Hartree approximation is an electron - electron interaction approximation. It means that electron number i sees all other electrons as a continous charge distribution. Can be seen in the

figure, too.

$$g_i(\vec{r}) = \sum_{k \neq i} -e |\xi_k(\vec{r})|^2 \quad (4.27)$$

$$\longrightarrow \nabla^2 \Phi_i(\vec{r}) = \frac{g_i(\vec{r})}{\epsilon} \quad (4.28)$$



We can calculate the Potential enegery as follows:

$$v_i(\vec{r}) = -e\Phi \quad (4.29)$$

$$= \sum_{k \neq i} \int_V \frac{e^2 |\xi_k(\vec{r})|^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} d\vec{r}' \quad (4.30)$$

Note:-

Φ is electrostatic potential. Furthermore, \vec{r}_i means it **belongs** to electron i.

Now we can solve the one electron problem by:

$$h(\vec{r})\xi(\vec{r}) = \epsilon\xi(\vec{r}) \quad (4.31)$$

$$\Rightarrow h(\vec{r}) = -\frac{\hbar^2}{2m_e} \nabla^2 + v(\vec{r}) + \sum V_{electron-ion}(\vec{r} - \vec{R}) \quad (4.32)$$

Looking at the last part of h we see that in a lattice, \vec{R} is a lattice vector. Then for a solid, the lattice is infinite and therefore $V_{electron-ion}$ will be periodic. We will call $\sum V_{electron-ion}(\vec{r} - \vec{R})$ a periodic potential: $U(\vec{r}) = U(\vec{r} - \vec{R}_l')$

Corollary 4.4.1 Conclusion

As show above we can now write the Schrödinger equation as a simplified wave function:

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V(\vec{r}) \right) \xi(\vec{r}_i) = \epsilon \xi(\vec{r}_i) \quad (4.33)$$

Chapter 5

Band Theory of Metals

In Chapter 4, we showed how all the contributions of all the valence ions/electrons/..., kinetic energies and interactions between the particles could be written as a one electron Schrödinger equation. Some approximations made to achieve this are: Born-Oppenheimer approximation, Hartree approximation and the static approximation. The one electron Schrödinger equation states:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad (5.1)$$

As we know, this potential is called the crystal potential energy function. It has periodic properties. Now, we can deduce properties, originating from the periodicity of $V(\vec{r})$, of this Schrödinger equation.

5.1 Property 1: Influence of translation operator on the Schrödinger equation

Definition 5.1.1: Translation operator

What is a translation operator:

$$\hat{T}_{\vec{R}} f(\vec{r}) = f(\vec{r} + \vec{R}) \quad (5.2)$$

Note:-

We put a hat (^) on the letter to show that it is a operator.

Applying this on the Schrödinger equation result in:

$$\hat{T}_{\vec{R}} H \psi(\vec{r}) = \hat{T}_{\vec{R}} (H(\vec{r}) \psi(\vec{r})) \quad (5.3)$$

$$= H(\vec{r} + \vec{R}) \psi(\vec{r} + \vec{R}) \quad (5.4)$$

$$= H(\vec{r}) \psi(\vec{r} + \vec{R}) \quad (5.5)$$

$$= H(\vec{r}) \hat{T}_{\vec{R}} \psi(\vec{r}) \quad (5.6)$$

Thus we can conclude that:

$$\hat{T}_{\vec{R}} H \psi = H \hat{T}_{\vec{R}} \psi \quad (5.7)$$

$$\hat{T}_{\vec{R}} H = H \hat{T}_{\vec{R}} \quad (5.8)$$

$$[\hat{T}_{\vec{R}}, H] = 0 \quad (5.9)$$

Claim 5.1.1 Product of translation operators

The product of two translation operators can be defined as:

$$\hat{T}_{\vec{R}} \hat{T}_{\vec{R}'} = \hat{T}_{\vec{R} + \vec{R}'} \quad (5.10)$$

Proof: We can show this by simply working out the operations on a function:

$$\hat{T}_{\vec{R}}\hat{T}_{\vec{R}'}\psi(\vec{r}) = \hat{T}_{\vec{R}}\psi(\vec{r} + \vec{R}') \quad (5.11)$$

$$= \psi(\vec{r} + \vec{R} + \vec{R}') \quad (5.12)$$

$$= \hat{T}_{\vec{R}+\vec{R}'}\psi(\vec{r}) \quad (5.13)$$

■

What is now so interesting about this commutation relation (equation 5.9)? Well, it is linked to a fundamental property of Quantum mechanics.

Theorem 5.1.1 Property of commutators in QM

If $[\hat{T}_{\vec{R}}, H] = 0$ then all eigenstates of H can be chosen to have the same eigenstates as $\hat{T}_{\vec{R}}$. In other words, if H and $\hat{T}_{\vec{R}}$ commute, then they have a common set of eigenstates. We will derive them here. Because the translational operator has the same set of eigenstates the following set of equations are equivalent.

$$\begin{cases} H\psi = E\psi \\ \hat{T}_{\vec{R}}\psi = \lambda(\vec{R})\psi \end{cases} \quad (5.14)$$

We still do not know what these $\lambda(\vec{R})$ eigenvalues belong to it, the energy states are the same. Following from the property from equation 5.10, we can deduce some properties for $\lambda(\vec{R})$:

$$\lambda(\vec{R})\lambda(\vec{R}') = \lambda(\vec{R} + \vec{R}') \quad (5.15)$$

$$\lambda^n(\vec{R}) = \lambda(n\vec{R}) \quad (5.16)$$

A value that satisfies, these two conditions is:

$$\lambda(\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \quad \text{with } \vec{k} \text{ some complex vector.} \quad (5.17)$$

Normalisation requires that:

$$\int_V |\psi|^2 d\vec{r} = 1 \quad (5.18)$$

$$\Rightarrow \int_V |\hat{T}_{\vec{R}}\psi(\vec{r})|^2 d\vec{r} = \int_V |\psi(\vec{r} + \vec{R})|^2 d\vec{r} \quad (5.19)$$

$$= \int_V |\lambda(\vec{R})\psi(\vec{r})|^2 d\vec{r}$$

$$= \int_V |\lambda(\vec{R})|^2 |\psi(\vec{r})|^2 d\vec{r}$$

$$= |\lambda(\vec{R})|^2 \int_V |\psi(\vec{r})|^2 d\vec{r}$$

$$= |\lambda(\vec{R})|^2 \quad (5.20)$$

$$= 1 \quad (5.21)$$

Step 5.20 is possible due to 5.18. The last step (equation 5.21) follows from that is ψ is normalized (equation 5.18), the translation of ψ is still normalized.

Now because of the fact that we have the normalisation (equation 5.19), we can say that \vec{k} can be written as a real vector $k_x\vec{e}_x + k_y\vec{e}_y + k_z\vec{e}_z$ with $k \in \mathbb{R}$.

Now because we have a periodic crystal potential, we can write the following:

$$\hat{T}_{\vec{R}}\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) \quad (5.22)$$

5.2 Bloch's theorem

Definition 5.2.1: Bloch's theorem

The Bloch's theorem states:

$$\psi(\vec{r}) = u(\vec{r})e^{i\vec{k}\cdot\vec{r}} \quad \text{where } u(\vec{r}) \text{ is periodic} \quad (5.23)$$

$e^{i\vec{k}\cdot\vec{r}}$ is a plain wave function.

Example 5.2.1 (How Bloch's theorem works)

$$\hat{T}_{\vec{R}}\psi(\vec{r}) = \hat{T}_{\vec{R}}\left(u(\vec{r})e^{i\vec{k}\cdot\vec{r}}\right) \quad (5.24)$$

$$= u(\vec{r} + \vec{R})e^{i\vec{k}\cdot(\vec{r} + \vec{R})} \quad (5.25)$$

$$\text{(if } u(\vec{r}) \text{ is periodic)} \quad = e^{i\vec{k}\cdot(\vec{r} + \vec{R})}u(\vec{r}) \quad (5.26)$$

$$\text{(using Bloch)} \quad = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) \quad (5.27)$$

$$= \lambda(\vec{R})\psi(\vec{r}) \quad (5.28)$$

$$= \hat{T}_{\vec{R}}\psi(\vec{r}) \quad (5.29)$$

Furthermore, you can the eigenstates of the translation operator (equation 5.22), too:

$$\hat{T}_{\vec{R}}\psi(\vec{r}) = \psi(\vec{r} + \vec{R}) = u(\vec{r} + \vec{R})e^{i\vec{k}\cdot(\vec{r} + \vec{R})} = u(\vec{r})e^{i\vec{k}\cdot\vec{r}}e^{i\vec{k}\cdot\vec{R}} = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) \quad (5.30)$$

5.2.1 Closer look at the Schrödinger equation

To identify each wavevector, we will use a \vec{k} subscript referring to the plain wave in Bloch's theorem (section 5.2). As it turns out the function $u(\vec{r})$ will also depend on \vec{k} ($u_{\vec{k}}(\vec{r})$). We now get the following by using Bloch:

$$H\psi = E\psi \quad (5.31)$$

$$H\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\psi_{\vec{k}}(\vec{r}) \quad (5.32)$$

$$\left\{ \frac{\hbar^2}{2m} \left(-i\vec{\nabla} + \vec{k} \right)^2 + V(\vec{r}) \right\} u_{\vec{k}}(\vec{r}) = E(\vec{k})u_{\vec{k}}(\vec{r}) \quad (5.33)$$

We get a Schrödinger equation for the periodic function u . Equation 5.33 is an eigenvalue problem that is confined in a finite volume (the crystal) where u has to obey to its periodic boundary conditions $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$. What are the eigenvalues?

From differential equation analysis and eigenvalue problems we know we get a discrete set of eigenvalues: $E_n(\vec{k})$. This existence of this discrete set is because we impose boundary conditions on the problem. We can now 'update' the Schrödinger equation (5.33):

$$\left\{ \frac{\hbar^2}{2m} \left(-i\vec{\nabla} + \vec{k} \right)^2 + V(\vec{r}) \right\} u_{n,\vec{k}}(\vec{r}) = E(n, \vec{k})u_{n,\vec{k}}(\vec{r}) \quad (5.34)$$

5.3 Properties of the energy eigenvalues of $u_{n,\vec{k}}$

Claim 5.3.1

Both wave function and energy eigenvalues satisfy (for \vec{G} a reciprocal lattice vector):

$$\begin{cases} E_n(\vec{k} + \vec{G}) = E_n(\vec{k}) \\ \psi_{n,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r}) \end{cases} \quad (5.35)$$

Proof: If we substitute the following equation into equation 5.1, we get 5.37.

$$\psi_{n,\vec{k}+\vec{G}}(\vec{r}) = u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \quad (5.36)$$

$$\left\{ \frac{\hbar^2}{2m} \left(-i\vec{\nabla} + \vec{k} \right)^2 + V(\vec{r}) \right\} u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i\vec{G}\cdot\vec{r}} = E_n(\vec{k} + \vec{G})u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i\vec{G}\cdot\vec{r}} \quad (5.37)$$

What we see now is that from 5.34 and 5.37 we expect:

$$u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i\vec{G}\cdot\vec{r}} = u_{n,\vec{k}}(\vec{r}) \quad (5.38)$$

Thereby we can say that:

$$\psi_{n,\vec{k}+\vec{G}}(\vec{r}) = u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i(\vec{k}+\vec{G})\cdot\vec{r}} = u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} = \psi_{n,\vec{k}}(\vec{r}) \quad (5.39)$$

Now we can also show that $E_n(\vec{k} + \vec{G}) = E_n(\vec{k})$. ■

What you might notice now is that \vec{G} can be any vector, instead of being a reciprocal lattice vector. How do we enforce this requirement? Well, because equation 5.34 and equation 5.37 are the same, the wavefunctions must obey the same periodic boundary conditions. That is only true if \vec{G} is a reciprocal lattice vector. We can show this has to be the case by:

$$\hat{T}_{\vec{R}} \left(u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i\vec{G}\cdot\vec{r}} \right) = u_{n,\vec{k}+\vec{G}}(\vec{r} + \vec{R})e^{i\vec{G}\cdot(\vec{r}+\vec{R})} \quad (5.40)$$

$$= u_{n,\vec{k}+\vec{G}}(\vec{r})e^{i\vec{G}\cdot\vec{r}}e^{i\vec{G}\cdot\vec{R}} \quad (5.41)$$

$$\Rightarrow e^{i\vec{G}\cdot\vec{R}} = 1 \quad (5.42)$$

5.4 Property 2: Inversion symmetry

Definition 5.4.1: Inversion symmetry

Inversion symmetry states that

$$E_n(-\vec{k}) = E_n(\vec{k}) \quad (5.43)$$

This has an effect on a property of the wave equation:

$$\psi_{n,\vec{k}}^*(\vec{r} + \vec{R}) = \left(\psi_{n,\vec{k}}(\vec{r} + \vec{R}) \right)^* \quad (5.44)$$

$$\text{(By equation 5.22)} \quad = \left(e^{i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}(\vec{r}) \right)^* \quad (5.45)$$

$$= e^{-i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}^*(\vec{r}) \quad (5.46)$$

The complex conjugate wavefunction still complies with Bloch's theorem, therefore we can say that:

$$\psi_{n,\vec{k}}^*(\vec{r}) = \psi_{n,-\vec{k}}(\vec{r}) \quad (5.47)$$

Now, we proof the property for energy eigenvalues (equation 5.43) by starting from the complex conjugate Schrödinger equation:

$$H^* \psi_{n,\vec{k}}^*(\vec{r}) = H \psi_{n,\vec{k}}^*(\vec{r}) = \left(H \psi_{n,\vec{k}}(\vec{r}) \right)^* \quad (5.48)$$

$$= \left(E_n(\vec{k}) \psi_{n,\vec{k}}(\vec{r}) \right)^* \quad (5.49)$$

$$= E_n \psi_{n,\vec{k}}^*(\vec{r}) \quad (5.50)$$

$$\Rightarrow H \psi_{n,-\vec{k}}(\vec{r}) = E_n(-\vec{k}) \psi_{n,-\vec{k}}(\vec{r}) \quad (5.51)$$

$$= E_n(-\vec{k}) \psi_{n,\vec{k}}^*(\vec{r}) \quad (5.52)$$

$$\Rightarrow E_n(-\vec{k}) = E_n(\vec{k})$$

5.5 Consequences of the properties

As we saw for the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{n,\vec{k}}(\vec{r}) + V(\vec{r})\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n,\vec{k}}(\vec{r}) \quad (5.53)$$

$$\rightarrow V(\vec{r}) = V(\vec{r} + \vec{R}) \quad (5.54)$$

This says something about the energy spectrum, in function of \vec{k} . As we see in figure 5.1, we have energy bands E_i , these all have all eigenvalues and between the bands we have bandgaps, there are no eigenvalues. Now there is also a possibility of overlap of the energy bands.

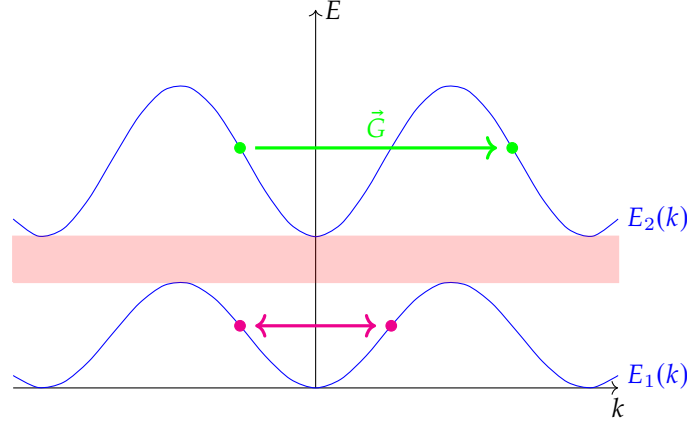


Figure 5.1: Energy band diagram

The wave functions are also periodic in k -space. Thus if we take the green point and translate that on the wave, that point has the same wave, this is translational symmetry (section 5.1). We also notice inversion symmetry, depicted in magenta (section 5.4).

5.6 Empty lattice - 1D

Suppose we take a very trivial example: take $V(x) = 0$, then the Schrödinger equation is very simple to solve. $V(x) = 0$ means we have free electrons.

$$V(x + a) = V(x) = 0 \quad (5.55)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_k(x) = E(k)\psi_k(x) \quad (5.56)$$

$$\psi_k(x) = \frac{1}{\sqrt{L}}e^{ikx} \quad E(k) = \frac{\hbar^2 k^2}{2m} \quad \text{for } \frac{-G}{2} \leq k \leq \frac{G}{2} \quad (5.57)$$

Equation 5.57 gives the wave functions of the Schrödinger equation, the corresponding energies are solutions of the Schrödinger equation, too. Seen in figure 5.2, when we shift our wavefunction and energy with G , we get a periodic energy spectrum. If we plot these extra potentials, we get what we call energy bands on the intersections. For a free particle, this is silly because these bandgaps have 0 width, yet they are labeled with a gray dot.

Note:-

Keep in mind that: $\frac{G}{2} - \frac{-G}{2} = \frac{2\pi}{a}$.

5.7 Nearly free electron-approximation

Now, we include a weak periodic potential. Then the hamiltonian becomes:

$$\hat{H} = \hat{H}_0 + V(\vec{r}) \quad (5.58)$$

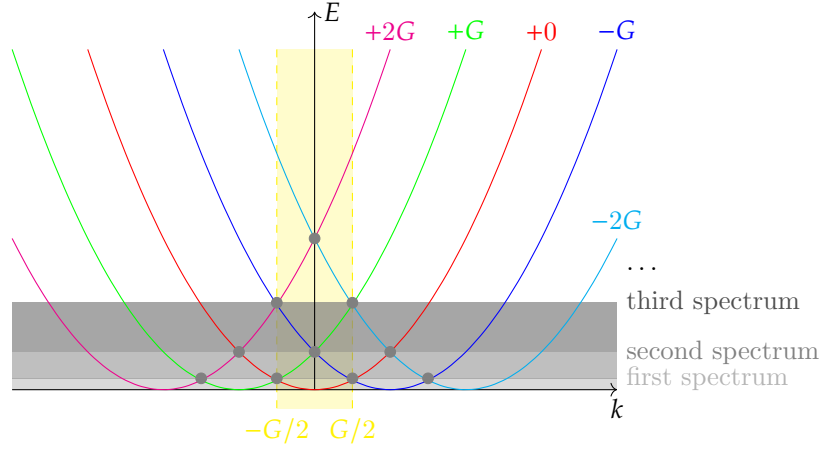


Figure 5.2: Displaced energy bands with different spectra

Where \hat{H} is the free kinetic operator: $-\frac{\hbar^2}{2m}\nabla^2$ and $V(\vec{r})$ is the introduced weak potential. We can solve it by using the perturbation theory for solving this modified Schrödinger equation. First solve Schrödinger for H_0 , this gives:

$$\hat{H}_0\psi_{\vec{k}}^{(0)}(\vec{r}) = E_{\vec{k}}^{(0)}\psi_{\vec{k}}^{(0)}(\vec{r}) \quad (5.59)$$

$$\Rightarrow \begin{cases} \psi_{\vec{k}}^{(0)}(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}} \\ E^{(0)}(\vec{k}) = \frac{\hbar^2 k^2}{2m} \end{cases} \quad (5.60)$$

5.7.1 Perturbation theory

Solving with the weak potential goes as follows:

$$E(\vec{k}) \approx E^{(0)}(\vec{k}) + E^{(1)}(\vec{k}) + E^{(2)}(\vec{k}) \quad (5.61)$$

$$E^{(0)}(\vec{k}) = \text{see equation 5.60} \quad (5.62)$$

$$E^{(1)}(\vec{k}) = \langle \vec{k}^{(0)} | V(\vec{r}) | \vec{k}^{(0)} \rangle = \int_V \frac{1}{\sqrt{V}} e^{-i\vec{k}\cdot\vec{r}} V(\vec{r}) \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} V(\vec{r}) \quad (5.63)$$

$$E^{(2)}(\vec{k}) = \sum_{\vec{k}' \neq \vec{k}} \frac{|\langle \vec{k}^{(0)} | V(\vec{r}) | \vec{k}^{(0)} \rangle|^2}{E^{(0)}(\vec{k}) - E^{(0)}(\vec{k}')} \quad (5.64)$$

Note:-

We use **box normalisation**, thus putting the particle inside a box, then the k space is a sum instead of an integral. Then at the end making it unbox by making the length infinity again, we see that it works. Now, we have a more convenient way for deriving the same thing because we don't have dirac functions anymore.

So let's start calculating the first order approximation:

$$E^{(1)}(\vec{k}) = \frac{1}{V} \int_V V(\vec{r}) d\vec{r} = \tilde{V}(0) = \text{constant} \quad (5.65)$$

$$E^{(2)}(\vec{k}) = \text{see equation 5.64} \quad (5.66)$$

$$\text{with: } \langle \vec{k}' | V(\vec{r}) | \vec{k} \rangle = \frac{1}{V} \int_V e^{-i\vec{k}'\cdot\vec{r}} V(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \quad (5.67)$$

$$= \frac{1}{V} \int_V e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} V(\vec{r}) d\vec{r} = \tilde{V}(\vec{k}-\vec{k}') \delta_{\vec{k}-\vec{k}', \vec{G}} \quad (5.68)$$

We see a fourier transform in equation 5.68, but as we know the potential $V(\vec{r})$ is periodic thus if \vec{k} is not a lattice vector, the integral must be 0. Now we can simplify the second step (equation 5.64):

$$\sum_{\vec{k}' \neq \vec{k}} \frac{|\tilde{V}(\vec{k}-\vec{k}') \delta_{\vec{k}-\vec{k}', \vec{G}}|^2}{E^{(0)}(\vec{k}) - E^{(0)}(\vec{k}')} \quad (5.69)$$

We rewrite this as

$$\sum_{\vec{G}} \frac{|\tilde{V}(\vec{G})|^2}{E^{(0)}(\vec{k}) - E^{(0)}(\vec{k}')} \quad (5.70)$$

by using $\vec{k} - \vec{k}' = \vec{G}$ (this is just a simple substitution using the Bragg condition (section 3.7), the δ -function is in this case 1). Now we can write equation 5.60 in function of the derived values. Using the "normal" symbolic numeric values for the energies, we get:

$$E(\vec{k}) \approx \frac{\hbar^2 k^2}{2m} + \tilde{V}(0) + \frac{2m}{\hbar^2} \sum_{\vec{G}} \frac{|\tilde{V}(\vec{G})|^2}{k^2 - (\vec{k} - \vec{G})^2} \quad (5.71)$$

As we see this gives a problem when the denominator is 0, for $k^2 = (\vec{k} - \vec{G})^2$. This is the Bragg condition (section 3.7)! Let's look more closely at that specific case: $E^{(0)}(\vec{k}) = E^{(0)}(\vec{k} - \vec{G})$:

$$\begin{cases} \psi_{\vec{k},1}^{(0)}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} & \text{with: } E^{(0)}(\vec{k}) = \frac{\hbar^2 k^2}{2m} \\ \psi_{\vec{k},2}^{(0)}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i(\vec{k}-\vec{G}) \cdot \vec{r}} & \text{with: } E^{(0)}(\vec{k}) = \frac{\hbar^2 k^2}{2m} \end{cases} \quad (5.72)$$

As we can expect, this is true for multiple values for k . We have to deal with a degeneracy. When you have a degeneracy, you have to span a new wavefunction into your Hilbert space, by using a linear combination of your other wavefunctions. This is Degenerate perturbation theory, we will go over it in section 5.7.2.

5.7.2 Degenreate pertrubation theory

Note:-

Only if we have a degeneracy, $k^2 = (\vec{k} - \vec{G})^2$, we do this section!

We want to find $\tilde{\psi}(\vec{r}) = c_1 \psi_{\vec{k},1} + c_2 \psi_{\vec{k},2}$, we obtain this solution by by diagonalizing the Hamiltonian in the new subspace:

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \quad (5.73)$$

We will work out H_{11} , the other solutions are given below.

$$H_{11} = \int_V d\vec{r} \psi_{\vec{k},1}^*(\vec{r}) \hat{H} \psi_{\vec{k},1}(\vec{r}) \quad (5.74)$$

$$= \int_V d\vec{r} \frac{1}{\sqrt{V}} e^{-i\vec{k} \cdot \vec{r}} \left(\frac{-\hbar^2}{2m} \nabla^2 \right) \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \quad (5.75)$$

$$\text{where } \left(\frac{-\hbar^2}{2m} \nabla^2 \right) \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \text{ is the free energy of an electron: } E^{(0)}(\vec{k}) \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$

$$= \frac{1}{V} \int_V E^{(0)}(\vec{k}) d\vec{r} + \tilde{V}(0) \quad (5.76)$$

$$= E^{(0)}(\vec{k}) + \tilde{V}(0) \quad (5.77)$$

Because $\tilde{V}(0)$ is just a constant, we will set it to 0. The other hamiltonians are:

$$H_{12} = \tilde{V}(\vec{G}) \quad (5.78)$$

$$H_{21} = \tilde{V}(-\vec{G}) = \tilde{V}^*(-\vec{G}) \quad (5.79)$$

$$H_{22} = E^{(0)}(\vec{k} - \vec{G}) \quad (5.80)$$

Now we solve equation 5.73 by means of a determinant, then we get:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0 \quad (5.81)$$

$$\Rightarrow E_{\pm}(\vec{k}) = \frac{\hbar^2}{2m^2} \left(k^2 + (\vec{k} - \vec{G})^2 \right) \pm \frac{1}{2} \sqrt{\left(\frac{\hbar^2}{2m} \right)^2 \left(k^2 - (\vec{k} - \vec{G})^2 \right)^2 + 4|\tilde{V}(\vec{G})|^2} \quad (5.82)$$

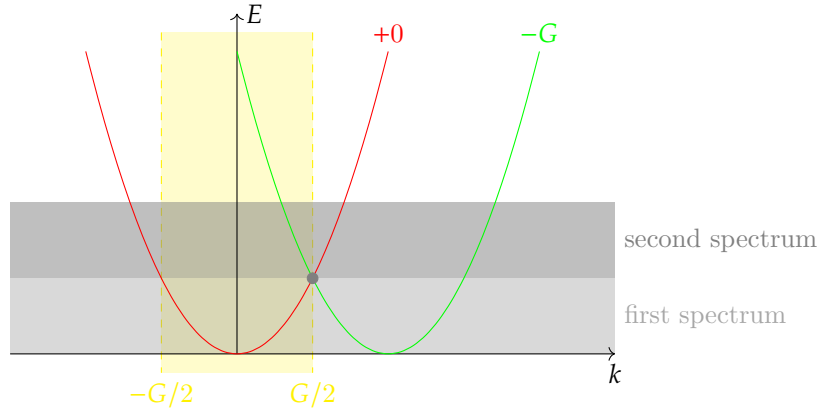


Figure 5.3: The simplified energy diagram

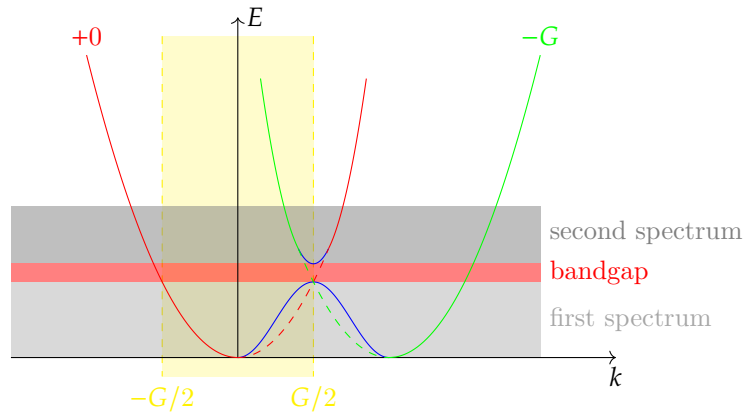


Figure 5.4: The simplified energy diagram with bandgap

If we take $k^2 = (\vec{k} - \vec{G})^2$ we get $E_{\pm}(\vec{k}) = \frac{\hbar^2}{2m}k^2 \pm |\tilde{V}(\vec{G})|$ and we can introduce gaps into our state (it still depends on our fourier transform \tilde{V}). The height of the introduced bandgap is:

$$\Delta E = E_+ - E_- = 2|\tilde{V}(\vec{G})| \quad (5.83)$$

Let's look at this from a more practical standpoint. In figure 5.3, we plot $E^{(0)}(\vec{k})$ and one $E^{(0)}(\vec{k} - \vec{G})$, of course there are more curves but his figure is just for illustration. By having degeneracies, we get a bandgap, taking the bandgap gives into consideration, we get figure 5.4. This bandgap is of course a forbidden zone for electrons. The size of the bandgap is given by equation 5.83.

Now, these degeneracies can be represented in another way. As we might expect, these are repeated (or periodic) over k . Therefore we can stay in the first Brillouin zone (section 3.8), this is the zone contained in $-\frac{G}{2} \leq k \leq \frac{G}{2}$, still given in yellow. This results in a structure as can be seen in figure 5.5. Take $\frac{\pi}{a} = \frac{G}{2}$, as the Bragg point.

Example 5.7.1 (1D example)

Let us use

$$V(x) = V_0 \cos \frac{2\pi x}{a} \Rightarrow \tilde{V}(\pm \frac{2\pi}{a}) = \frac{V_0}{2} \quad (5.84)$$

We can use this formula as it is written here because the delta functions are only defined in $\pm \frac{2\pi}{a}$ therefore we dont see the dirac functions, albeit they are there. Looking at the Bragg points:

$$k_n = \frac{G_n}{2} = \frac{\pi}{2}n \quad (5.85)$$

We can now draw the energy diagram.

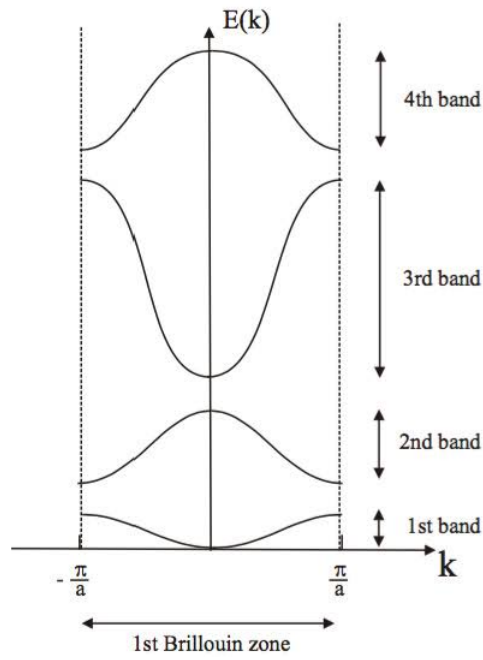
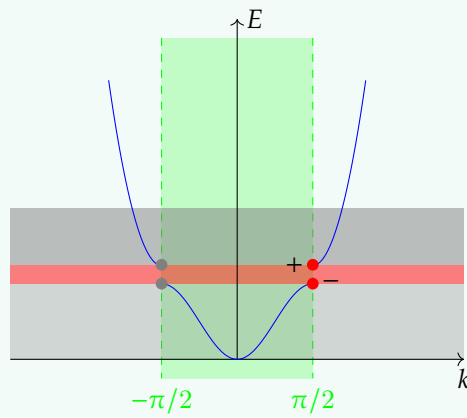


Figure 5.5: Energy band inside the first Brillouin zone



At the bragg points, we see a standing wave: $\psi_{\pm,k} \sim e^{i\pi x/a} \pm e^{-i\pi x/a}$, also shown in the figure in red. The bandgap is V_0 high.

Chapter 6

Crystals

6.1 Crystal momentum

Remember band diagrams derived in previous section 5.7. To introduce the crystal momentum, let's first look at

$$\begin{cases} \hat{H} = \frac{\hat{p}}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \\ \hat{H}\psi_{\vec{k}}(\vec{r}) = E\psi_{\vec{k}}(\vec{r}) \\ \psi_{\vec{k}} = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}} \end{cases} \quad \text{with: } \hat{p} = -\hbar\nabla \quad (6.1)$$

$$[\hat{H}, \hat{p}] = 0 \quad (6.2)$$

$$\text{using de Brogli: } \vec{p} = \hbar\vec{k} \quad (6.3)$$

$$\text{we get: } \hat{p}\psi_{\vec{k}}(\vec{r}) = \hbar\vec{k}\psi_{\vec{k}}(\vec{r}) \quad (6.4)$$

Bloch electrons: $\hat{H} = p^2/2m + V(\vec{r})$, with $\hat{p} = -i\hbar\nabla$. Then now it is clear that these operators $[\hat{H}, \hat{p}] \neq 0$. Then we can derive the following:

$$\hat{H}\psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k})\psi_{n,\vec{k}}(\vec{r}) \quad (6.5)$$

$$\psi_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} \quad (6.6)$$

$$\hat{p}\psi_{n,\vec{k}}(\vec{r}) = -i\hbar\nabla \left[u_{n,\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} \right] \quad \text{using: 6.3 and 6.6} \quad (6.7)$$

$$(6.8)$$

How do we interpret the \vec{k} ? Let's define crystal momentum as follows:

$$\vec{P} = \hbar\vec{k} \quad (6.9)$$

Note:-

Don't confuse \vec{P} with \vec{p} . For a Bloch electron we cannot say that $\vec{p} = \hbar\vec{k}$.

Because real space is infinite, we need some boundary conditions to confine our space.

6.2 Boundary condition

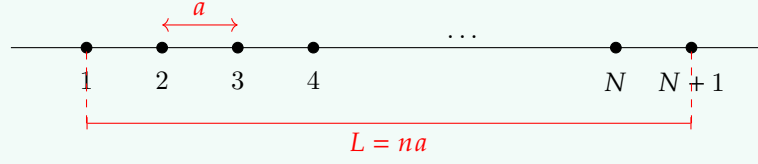
There are two possibilities to impose boundary conditions:

- Dirichlet boundary conditions
- Born-von Kerman (periodic) boundary conditions

We will use periodic boundary conditions to show how energy bands are formed in an atomic crystal. The reason we use periodic boundary conditions is that this makes math easier, you do get the same result when using Dirichlet boundary conditions.

Example 6.2.1 (1D boundary condition)

For the function $\psi(x) = \psi(x + L)$, with L the crystal length.



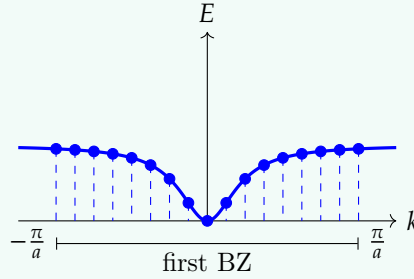
We can use some properties of the bloch functions, now we can deduce the following:

$$\psi(x + L) = e^{ikL}\psi(x) = \psi(x) \quad (6.10)$$

$$\Rightarrow kNa = 2\pi n \quad (6.11)$$

$$\Rightarrow k = \frac{2\pi}{L}n \quad (6.12)$$

We see that the continuous k value has become discrete, therefore we get the following figure. As we might expect, for a bigger lattice, we get a more continuous spectrum (because Δk becomes smaller).



How many lattice points do we have in our first BZ?

$$\frac{\frac{2\pi}{a}}{\Delta k} = \frac{\frac{2\pi}{a}}{\frac{2\pi}{Na}} = N = \text{number of unit cells that build the crystal} \quad (6.13)$$

Can we come to the same conclusion in 3D?

Example 6.2.2 (3D boundary condition)

The full crystal is defined by L_1, L_2, L_3 . For these values, we can say that:

$$\begin{cases} \vec{L}_1 = N_1 \vec{a}_1 \\ \vec{L}_2 = N_2 \vec{a}_2 \\ \vec{L}_3 = N_3 \vec{a}_3 \end{cases} \quad (6.14)$$

We can do the same as we did in the 1D example:

$$\psi(\vec{r} + \vec{L}_j) = \psi(\vec{r}) \quad (6.15)$$

$$= \psi(\vec{r} + N_j \vec{a}_j) \quad (6.16)$$

$$\text{Using Bloch} \quad \Rightarrow \psi(\vec{r}) = e^{i\vec{k}_j \vec{a}_j} \psi(\vec{r}) \quad (6.17)$$

$$\Rightarrow \vec{k} = 2\pi n \cdot (N_j \vec{a}_j)^{-1} \text{ with } n \in \mathbb{Z} \quad (6.18)$$

$$\Rightarrow \vec{k} = \frac{n_1}{N_1} \vec{b}_1 + \frac{n_2}{N_2} \vec{b}_2 + \frac{n_3}{N_3} \vec{b}_3 \quad (6.19)$$

\vec{b}_i are primitive reciprocal lattice vectors.

Now we look at the elemental volume of the unit cell:

$$\Delta \vec{k} = \Delta k^3 = \frac{\vec{b}_1}{N_1} \cdot \left(\frac{\vec{b}_2}{N_2} \frac{\vec{b}_3}{N_3} \right) \quad (6.20)$$

$$= \frac{1}{N} \vec{b}_1 \cdot (\vec{b}_2 \vec{b}_3) \quad (6.21)$$

Where N is the number of unit cells that build the crystal.

We do get the same results, and this has some consequences when we look at the atomic picture of energy bands and how boundary conditions affect them.

1. Even number of electrons in a full shell per unit cell. We get $2N$ = amount of electrons. This gives a semiconductor.
2. Odd number of electrons in a partially filled shell per unit cell. Because there are still states free in the valence band, gives this a metal.

Note:-

This does not mean that a $2N$ amount of electrons gives a semiconductor. Band overlap can still give a metal!

We now link this concept to real atoms.

6.3 Energy bands for the atomic picture

Say, we have N atoms. Then, for each atom we have the states in figure 6.1. Now suppose we have them far apart and bring them closer, then we get figure 6.2. For a semiconductor, we see a bandgap E_g at $d = a$, this is highlighted in red. This just shows how the bands are for the atoms, nothing can be said about momentum,

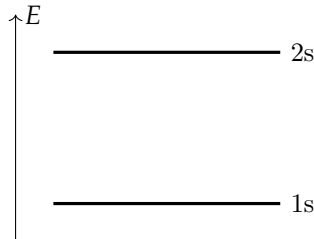
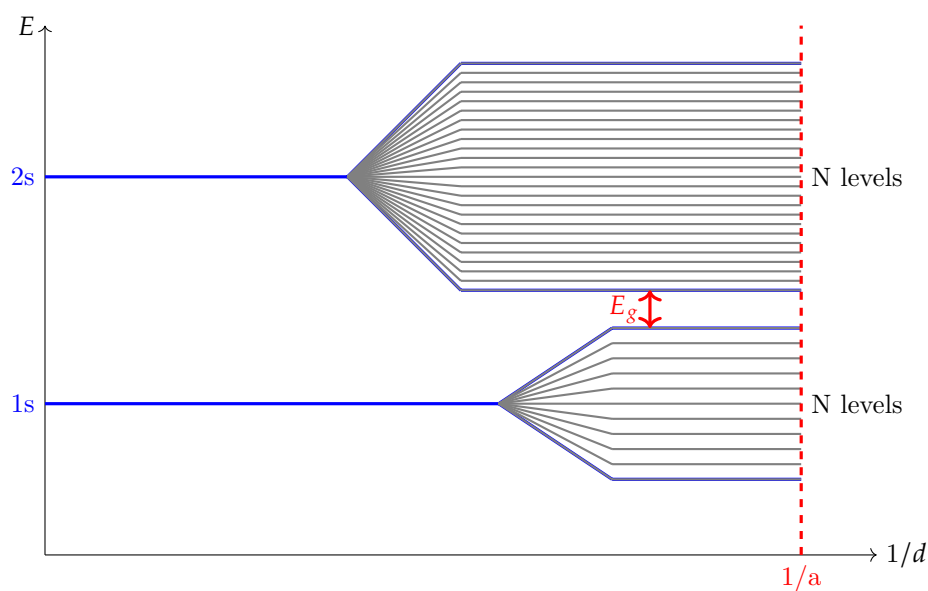


Figure 6.1: The energy state for a fictive single atom

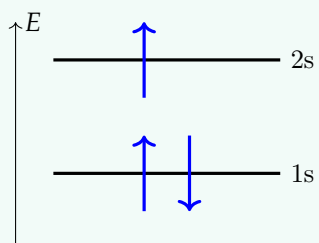
.... What we notice from the picture, too is:

- 2s orbital starts to split sooner, because 2s orbitals overlap more as they are further away from the nucleus.
- We see a smaller band splitting at 1s.

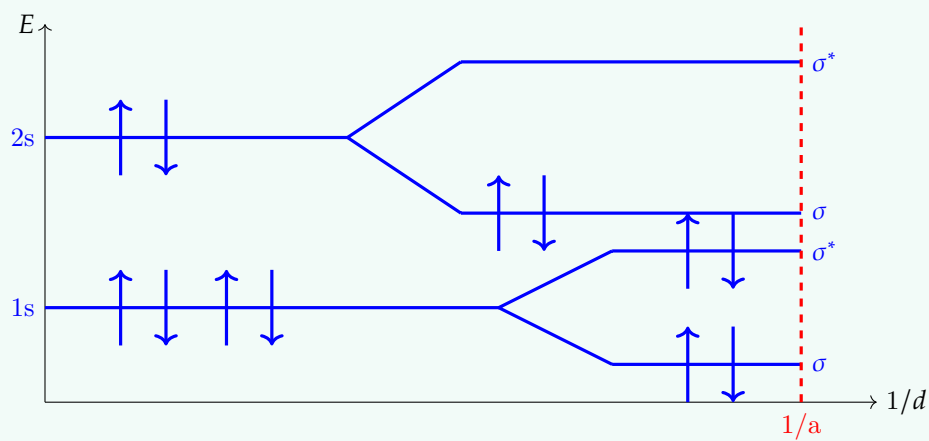
We will now look at some other atoms.

Figure 6.2: Energy band diagram for fictive crystal of N atoms**Example 6.3.1 (Lithium (Li))**

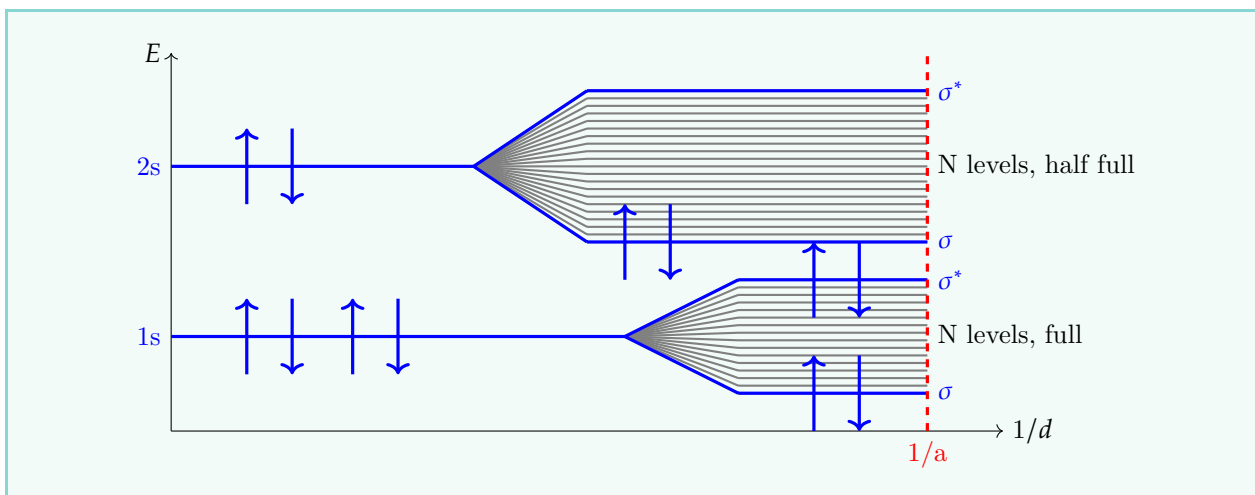
For 1 Li atom we have what can be seen in following figure:



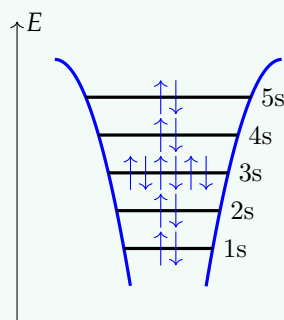
For Li_2 we get:



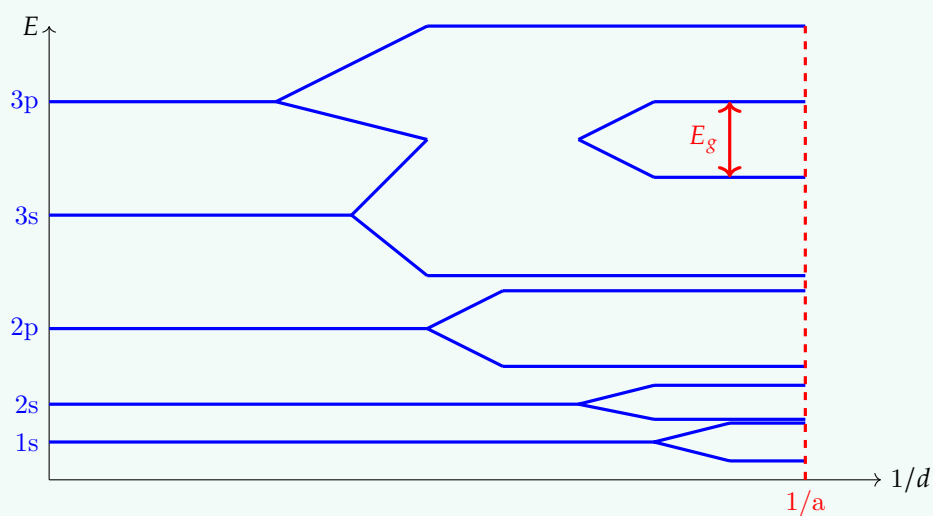
For a crystal Li_N we get:

**Example 6.3.2 (Silicium (Si))**

Si has following configuration: $1s^2 2s^2 2p^6 3s^2 3p^2$. This translates in the following band structure:



For a Si crystal we have N unit cells. Si crystals have a diamond structure with 2 atoms per unit cell. The according band diagram is:



If we now consider that each unit cell has 2 atoms in a silicon lattice, we get the following states for the energy diagram (simplified):

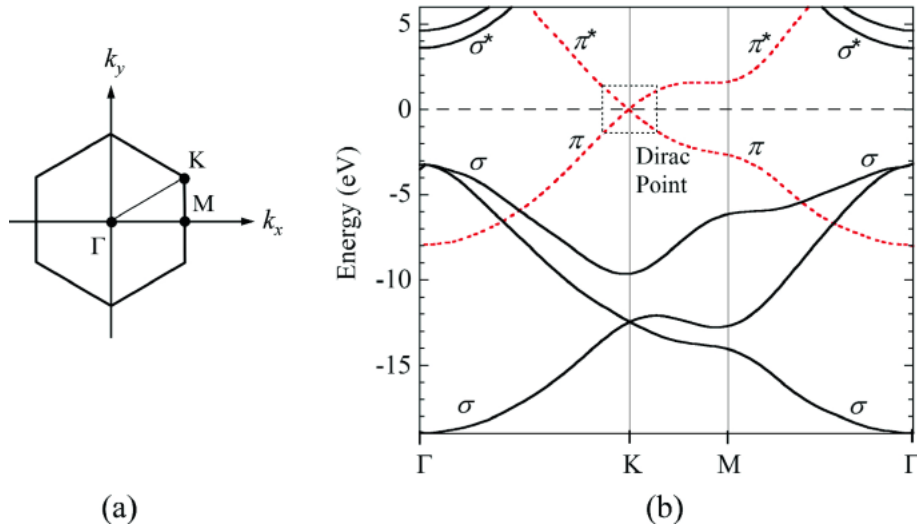
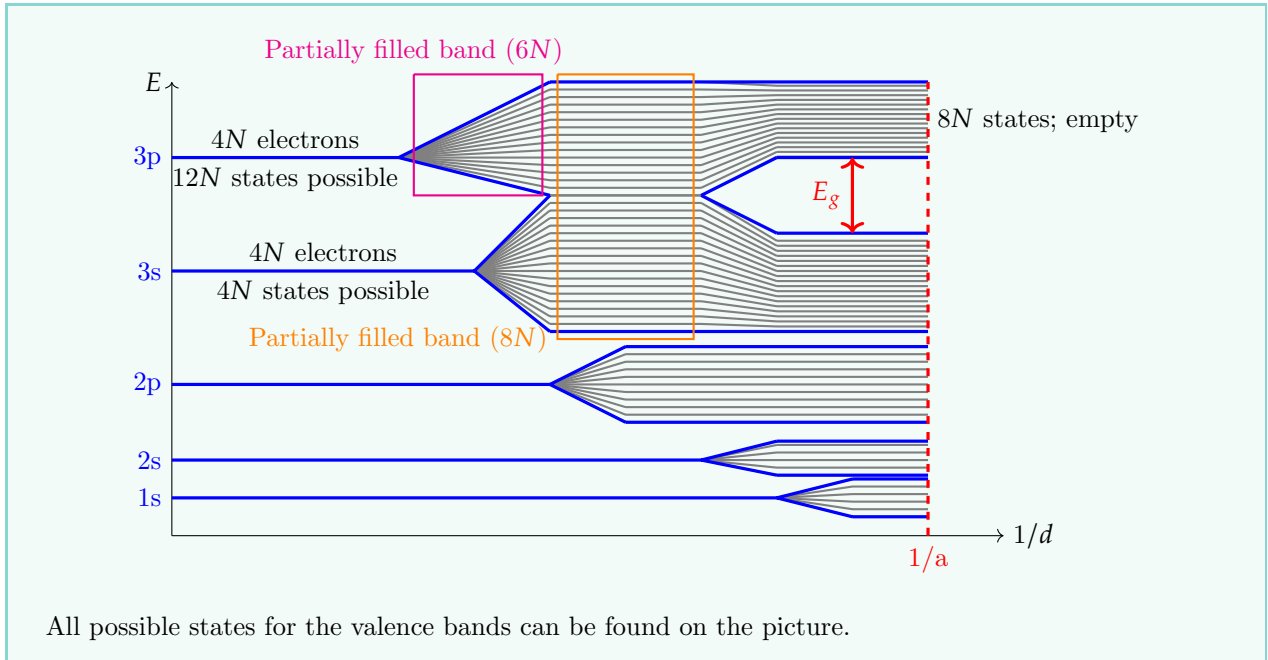


Figure 6.3: 2D banddiagram for silicon



6.3.1 Higher dimension energy band diagrams

We can represent these band configurations in k -space, too, but these plots can get complicated. Luckily, there is a solution for that. This concept is illustrated with picture 6.3. We will travel along the following path: $\Gamma - K - M - \Gamma$. This gives a plot that has enough information about the crystal. Thus plotting $E(\vec{k})$ along the high symmetry points, in the first BZ, is adequate for determining the behaviour of the crystals in higher dimensions. The lines we follow are called **Bragg-lines**. The only thing we want to get to know is what the maximum/minimum of the valence/conduction band are. This is achieved with the Bragg-lines.

6.4 Implications of the periodic boundary condition

Definition 6.4.1: Amount of allowed \vec{k} -states, N

The amount of allowed \vec{k} -states, N , is given by the amount of unit cells that build the crystal. This implicates that in each energy band $E_n(\vec{k})$, where $\vec{k} \in \text{first BZ}$, there are N allowed \vec{k} -states.

There are several cases we can study, we will go over them.

6.4.1 Case 1 - N is odd

Take the amount of valence electrons in each unit cell is odd. If we consider the first BZ we get the energy band structure that is given in figure 6.4. For each \vec{k} -state, we can have two electrons: spin up and spin down. In this picture, the circles depict a hole. Furthermore, the temperature in this figure is 0K, all electrons are in their base state.

Now, the fact that we have an odd number of electrons, we need to have partially filled bands. In this case we have metallic crystals.

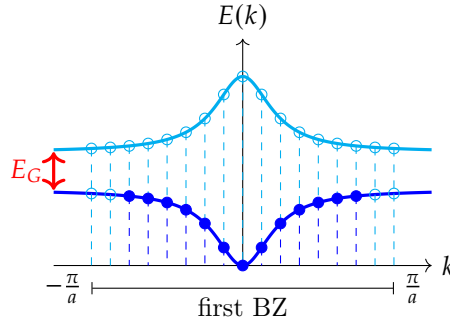


Figure 6.4: Band structure with odd number of electrons

6.4.2 Case 2 - N is even

The amount of electrons in each unit cell is even. Again, we consider the first BZ. We get figure 6.5. Now we speak about a semiconductor (or an insulator if E_G is large).

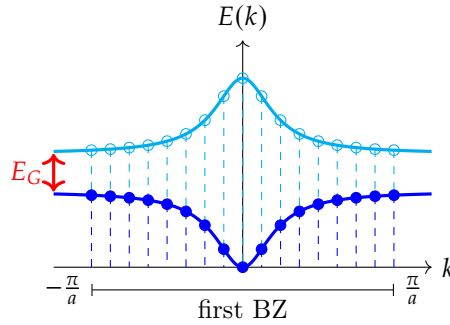


Figure 6.5: Band structure with even number of electrons

6.4.3 Case 3 - N is even + band overlap

The amount of electrons in the crystal is even and we have a band overlap. We now get a figure as figure 6.6. As you might guess, we get a metal again. Because now the electrons can move in their energy band when an electric field is applied.

6.5 Calculating the band structure & solving for the bandstructure

How do we get the bands? By just calculating the Schrödinger equations, of course. Remember we did this for a free electron in section 5.7. There, we solved the equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}(\vec{r}) \quad (6.22)$$

There are also other methods, i.e., the Tight Binding approach. This method is more representative for the band diagrams drawn in section 6.3. In the Tight Binding approximation, one writes the atomic and electronic part separately, which leads to solving the above Schrödinger equation in terms of atomic orbitals. The atomic orbitals are the ones we have drawn in section 6.3.

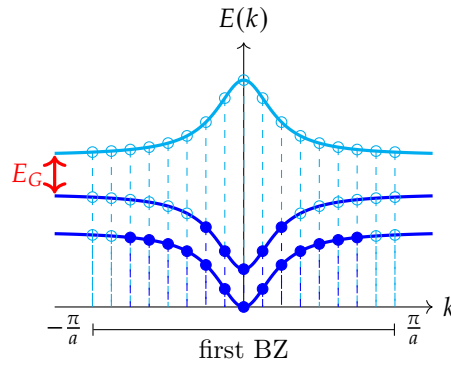


Figure 6.6: Band structure with odd number of electrons

The prediction of the atomic orbitals, as given in section 6.3, cannot be predicted with the nearly free electron approximation. In this approximation, it seems as if all orbitals are s-orbitals. Where both Tight Binding and Nearly Free electron approximation do predict right is the placement of the bandgap, which is at the Bragg-points.

Chapter 7

Band structures of crystals

7.1 Energy band structures at $T = 0K$

As it turns out, as mentioned in the previous chapter (chapter 6), the behaviour of the crystal can be represented by just a few important energy bands. In this section, we start with a simple case: the band structure of a semiconductor/insulator in 1D, see figure 7.1. As it turns out, only the valence band (VB) and conduction band (CB) (in the neighbourhood of the Γ -point) are needed to obtain all information about the behaviour of the electrons.

As we see, the further we go away from the Γ -point (thus increasing/decreasing k), the more the E_g becomes. Meaning thermally exciting electrons is becomes more difficult. That's why the Γ -point is so important. These electrons can be described as quasi-particles, that means free-electrons. As we will see, something will happen to the mass of the electrons.

First, we look at the conduction band. Because we are only interested in the electrons near the Γ -point, we can use a Taylor expansion for the description of the energy:

$$E_{CB}(k) \approx E_{CB}(0) + \left. \frac{dE_{CB}}{dk} \right|_{k=0} k + \frac{1}{2} \left. \frac{d^2E_{CB}}{dk^2} \right|_{k=0} k^2 \quad (7.1)$$

$$= E_{CB}(0) + \frac{1}{2} \left. \frac{d^2E_{CB}}{dk^2} \right|_{k=0} k^2 \quad (7.2)$$

Then for a free electron we know that:

$$E^{(0)}(k) = \frac{\hbar^2 k^2}{2m} \quad (7.3)$$

Then if we use the following substitution:

$$\frac{1}{2} \left. \frac{d^2E_{CB}}{dk^2} \right|_{k=0} = \frac{\hbar^2}{2m^*} \iff m^* = \hbar^2 \left(\left. \frac{d^2E_{CB}}{dk^2} \right|_{k=0} \right)^{-1} \quad (7.4)$$

We get a similar expression to the energy of a free electron:

$$E_{CB}(k) = E_{CB}(0) + \frac{\hbar^2}{2m^*} k^2 \quad (7.5)$$

Except, now the mass is different. This mass is called the effective mass. We can conclude that the electrons in the CB, near the Γ -point, behave as a free electron, albeit they have a different mass.

A similar derivation for the VB can be made, we can just substitute E_{CB} by E_{VB} . As you might notice, the VB and CB don't need to be the same and therefore, the m^* isn't necessary the same.

Note:-

Notice that the effective mass for the VB is smaller than zero. How do we define that? See section 7.3.2

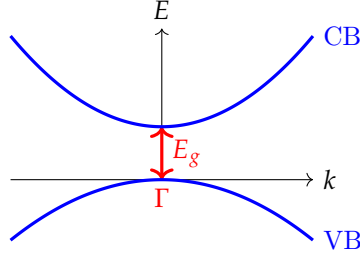


Figure 7.1: A simple 1D semiconductor/insulator band structure

7.1.1 Generalization of the energy band structure at 0K

In general we can say that the energy dispersion is the following:

$$E_n(\vec{k}) \approx E_n(\vec{k}_0) + \frac{1}{2} \sum_{i,j} \left. \frac{\delta^2 E}{\delta k_i \delta k_j} \right|_{\vec{k}=\vec{k}_0} (k_i - k_{i0})(k_j - k_{j0}) \quad \text{for } j, i = 1, 2, 3 \quad (7.6)$$

We then define the effective mass as:

$$\left[m_{i,j}^* \right]^{-1} = \frac{1}{\hbar^2} \left. \frac{\delta^2 E_n(\vec{k})}{\delta k_i \delta k_j} \right|_{\vec{k}=\vec{k}_0} \quad (7.7)$$

The effective mass can be written as a matrix/tensor, this matrix/tensor is symmetric. Furthermore, it is always possible to coordinate transformation k_1, k_2, k_3 to k'_1, k'_2, k'_3 in order that the matrix becomes a diagonal matrix.

After diagonalization, the matrix can be simplified to:

$$\begin{bmatrix} \frac{1}{m_1^*} & 0 & 0 \\ 0 & \frac{1}{m_2^*} & 0 \\ 0 & 0 & \frac{1}{m_3^*} \end{bmatrix} = \begin{bmatrix} \left. \frac{\delta^2 E_n(\vec{k})}{\delta k_1^2} \right|_{\vec{k}=\vec{k}_0} & 0 & 0 \\ 0 & \left. \frac{\delta^2 E_n(\vec{k})}{\delta k_2^2} \right|_{\vec{k}=\vec{k}_0} & 0 \\ 0 & 0 & \left. \frac{\delta^2 E_n(\vec{k})}{\delta k_3^2} \right|_{\vec{k}=\vec{k}_0} \end{bmatrix} \quad (7.8)$$

What we can conclude from this is that if we find the right coordinate transformation then the effective mass of the electron can be different in every direction.

7.1.2 Some examples

Example 7.1.1 (3D example 1)

Suppose you have a semiconductor where the CB minimum is located at the Γ -point. This semiconductor is isotropic, meaning it has $m_x^* = m_y^* = m_z^* = m^*$. In this case take $m^* > 0$.

In this case we can define $E_n(\vec{k})$ as:

$$E_n(\vec{k}) = E_n(\vec{0}) + \frac{\hbar^2}{2} \left[\frac{k_x^2}{2m_x^*} + \frac{k_y^2}{2m_y^*} + \frac{k_z^2}{2m_z^*} \right] = E_n(\vec{0}) + \frac{\hbar^2}{2m^*} k^2 \text{ with } k^2 = k_x^2 + k_y^2 + k_z^2 \quad (7.9)$$

For any value of energy $E > E_n(\vec{0})$, we can define constant energy surfaces that define a sphere with radius

$$R = \sqrt{(E - E_n(\vec{0})) \frac{2m^*}{\hbar^2}} \quad (7.10)$$

When we now look at the VB maximum, we have a problem: $m^* < 0$. This problem is resolved by introducing $m_h^* = -m^*$, this is explain in section 7.3.2.

Example 7.1.2 (Multiple bands)

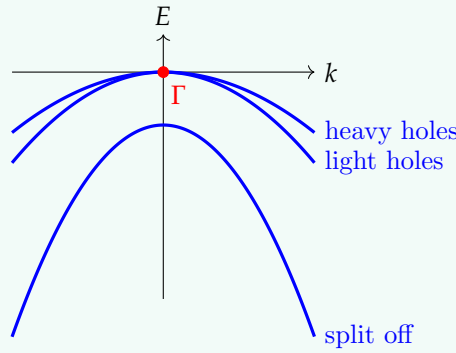
In the picture are the so-called 'split off', 'light holes', 'heavy holes' displayed. Because the curvature determines the effective mass, a wider curve means a heavier hole. Note that we speak about holes and not electrons anymore. The according energy dispersion functions are:

$$E_{heavyhole} = \frac{\hbar^2}{2m_{hh}^*}(k_x^2 + k_y^2 + k_z^2) \quad (7.11)$$

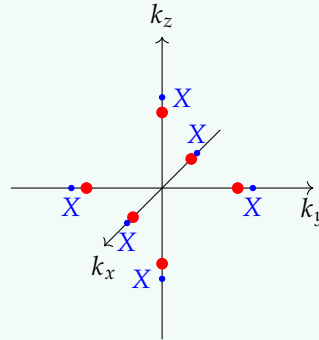
$$E_{lighthole} = \frac{\hbar^2}{2m_{lh}^*}(k_x^2 + k_y^2 + k_z^2) \quad (7.12)$$

$$E_{splitoff} = \frac{\hbar^2}{2m_{so}^*}(k_x^2 + k_y^2 + k_z^2) \quad (7.13)$$

Notice that we introduced the hole effective mass and added a - sign to compensate for the change of variable.

**Example 7.1.3** (Indirect semiconductor)

These semiconductors have, typically, a non-isotropic effective mass tensor. If we take Si for example, we get the following minima for the conduction band (denoted in red on the figure). These points come just before the X-point (like a Γ -point) the first Broullin Zone.



Then the energy dispersion formula will become (in function of $\alpha = 1, 2, 3, 4, 5, 6$, one for each minimum):

$$E_\alpha(\vec{k}) = E_\alpha + \frac{\hbar^2}{2} \left[\frac{(k_x - k_{0,\alpha,x})^2}{m_{\alpha,x}^*} + \frac{(k_y - k_{0,\alpha,y})^2}{m_{\alpha,y}^*} + \frac{(k_z - k_{0,\alpha,z})^2}{m_{\alpha,z}^*} \right] \quad (7.14)$$

We also immediatly see that for the effective inverse mass tensor, alle non-diagonal elements are zero, resulting in:

$$\left[m_{ij}^* \right]^{-1} = \begin{bmatrix} \frac{1}{m_{\alpha,x}^*} & 0 & 0 \\ 0 & \frac{1}{m_{\alpha,y}^*} & 0 \\ 0 & 0 & \frac{1}{m_{\alpha,z}^*} \end{bmatrix} \quad (7.15)$$

As it turns out, there is some symmetry in the effective masses along different axes:
the effective masses along the k_x -axis give: $m_{\alpha,x}^* = m_l^*$ and $m_{\alpha,y}^* = m_{\alpha,z}^* = m_t^*$,
the effective masses along the k_y -axis give: $m_{\alpha,y}^* = m_l^*$ and $m_{\alpha,x}^* = m_{\alpha,z}^* = m_t^*$,

the effective masses along the k_z -axis give: $m_{\alpha,z}^* = m_l^*$ and $m_{\alpha,x}^* = m_{\alpha,y}^* = m_t^*$.

What surfaces do we get now?

The energy dispersion diagram we get for $\alpha = 1$ and $E > E_1(\vec{k}_{0,1})$ is:

$$E_1(\vec{k}) = E_1 + \frac{\hbar^2}{2} \left[\frac{(k_x - k_{0,1,x})^2}{m_l^*} + \frac{(k_y - k_{0,1,y})^2}{m_t^*} + \frac{(k_z - k_{0,1,z})^2}{m_t^*} \right] \quad (7.16)$$

This gives us an ellipsoidal surface. In the 3D space, we will see small elongated ellipsoids along the axes.

Example 7.1.4 (Intermezzo: Ge)

If we now look at Ge, we get the CB minimum at the L -points which are in the $[1\ 1\ 1]$ direction. If we choose a normal axes orientation ($k_x = [1\ 0\ 0]$, etc.). We get ellipsoids along the $[1\ 1\ 1]$ (and the two axes perpendicular to it) axis. This means the effective mass tensor will have a contribution of all elements of the tensor, it will not be a diagonal matrix. Rotate the coordinate system accordingly!

7.2 Energy band structures at $T > 0K$

At a finite temperature there is a chance electrons are excited from the VB to the CB. We can say that there is a probability a certain E-state is occupied. Because particles can be defined in two ways in Quantum mechanics, we will separate them here, too.

7.2.1 Bosons - integer spin

For bosons, any energy state E_i can be occupied by an unlimited amount of particles. The probability distribution is given by the Bose-Einstein distribution:

$$f(E) = \frac{1}{e^{\beta E} - 1} \quad \text{with } \beta = \frac{1}{k_B T} \quad (7.17)$$

We will not further discuss this case.

7.2.2 Fermions - half integer spin

Every energy state can be occupied by at most one particle. this is called the **Pauli exclusion principle**. Still, one has to pay attention to degeneracies. For electrons, one energy state has two degeneracies. The probability distribution is give by the Fermi-Dirac distribution, also given in figure 7.2:

$$f(E) = \frac{1}{1 + e^{\beta(E-\mu)}} \quad \text{with } \beta = \frac{1}{k_B T} \text{ and } \mu = \text{the chemical potential (} E_g \text{ for intrinsic semiconductor)} \quad (7.18)$$

What is the physical significane of this distribution function? Well, $f(E)$ = probability to occupy a state at energy E. Meaning that $1 - f(E)$ = probability that a state E is not occupied. As we know, for $\beta\mu \gg 1$ we can use the Maxwell-Boltzmann distribution.

When graphing the Fermi-Dirac distribution in a band diagram, we get the following graph for different temperatures, see figure 7.3.

Note:-

The reason for having the Fermi-Dirac function going to 1 is that it is an electron is a fermion and only one can occupy a state.

7.3 Electron densities

7.3.1 Electron density in the conduction band

For a 3D semiconductor the energy dispersion relation is:

$$E(\vec{k}) = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2 + k_z^2) + E_{CB}(\vec{0}) \quad (7.19)$$

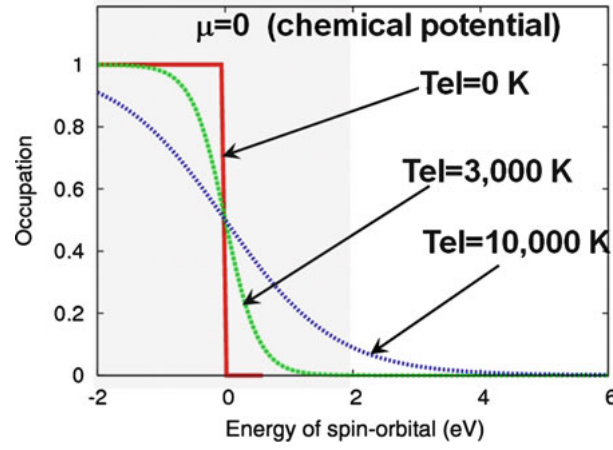


Figure 7.2: The Fermi-Dirac distribution for different temperatures

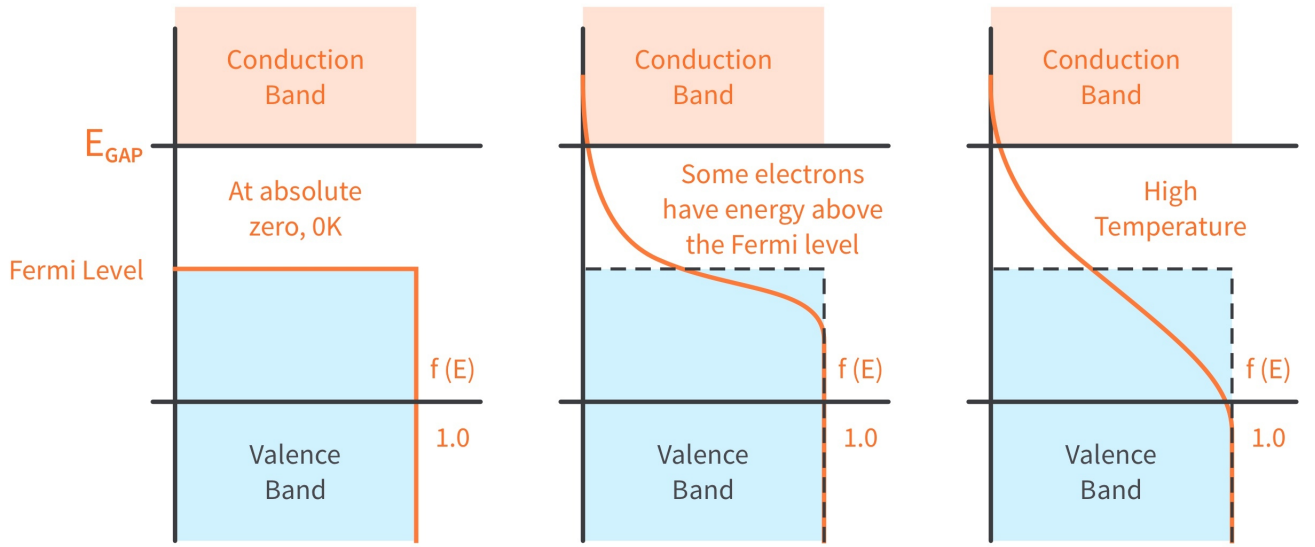


Figure 7.3: The Fermi-Dirac distribution for different temperatures

If we want the electron density at the conduction band, we can use the Fermi-Dirac distribution to know if a state is occupied and we will just sum over all possible \vec{k} values.

$$n = \frac{2}{V} \sum_{\vec{k}} f(E(\vec{k})) \approx \frac{2}{V} \frac{V}{(2\pi)^3} \int d\vec{k} f(E(\vec{k})) \quad (7.20)$$

How can we make this approximation?

As we know from previous chapter, if the volume increases, the amount of k states increases too which gives rise to a Riemann sum that becomes an integral. This is derived in short below:

$$\sum_{k_x} = \dots \quad (7.21)$$

$$= \frac{1}{\Delta k_x} \sum_{k_x} \dots \Delta k_x \quad (7.22)$$

$$\text{with } k_x = \frac{2\pi}{L_x} n_x \approx \frac{1}{\Delta k_x} \int \dots dk_x \quad \text{if } L_x \rightarrow \infty \quad (7.23)$$

$$= \frac{L_x}{2\pi} \int \dots dk_x \quad (7.24)$$

Can we work equation 7.20 further out? If the integral is known, which it is, we can. As a sidenote, this integral can be written in spherical coordinates. Furthermore, normally we work in the first BZ but now, we can without any trouble leave the boundaries at $-\infty$ and ∞ . This is the case because the Fermi-Dirac

distribution becomes 0 at $E = \infty$, see figure 7.3. Thus adding the Jacobian and filling in the boundaries gives:

$$n \approx \frac{2}{V} \frac{V}{(2\pi)^3} \int_{-\infty}^{\infty} d\vec{k} f(E(\vec{k})) \quad (7.25)$$

$$= \frac{2}{(2\pi)^3} \int_0^{\infty} 4\pi k^2 f(E(k)) dk \quad (7.26)$$

Working in energy might be easier than working in k-space. We use the following substitution:

$$dk = \frac{dk}{dE} dE \quad (7.27)$$

$$\frac{dE}{dk} = \frac{d}{dk} \left(\frac{\hbar^2}{2m^*} k^2 + E_{CB}(\vec{0}) \right) = \frac{\hbar^2 k}{m^*} \quad (7.28)$$

$$k = \sqrt{\frac{2m^*}{\hbar^2} (E - E_{CB}(\vec{0}))} \quad (7.29)$$

This then gives a final result for n:

$$n = \frac{2}{(2\pi)^3} \int_{E_{CB}(\vec{0})}^{\infty} 4\pi \frac{2m^*}{\hbar^2} (E - E_{CB}(\vec{0})) f(E(\vec{k})) \frac{m^*}{\hbar^2} \frac{1}{\sqrt{\frac{2m^*}{\hbar^2} (E - E_{CB}(\vec{0}))}} dE \quad (7.30)$$

$$= \frac{2}{(2\pi)^3} 4\pi \frac{m^*}{\hbar^2} \int_{E_{CB}(\vec{0})}^{\infty} \sqrt{\frac{2m^*}{\hbar^2} (E - E_{CB}(\vec{0}))} f(E(\vec{k})) dE \quad (7.31)$$

$$= \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^2} \int_{E_{CB}(\vec{0})}^{\infty} \sqrt{(E - E_{CB}(\vec{0}))} f(E(\vec{k})) dE \quad (7.32)$$

Simplifying the electrons density n

Now, working this integral out even further is difficult. But we can use the well known Fermi-Dirac integral of order 1/2. The Fermi-Dirac integrals is:

$$F_{1/2}(\xi) = \frac{2}{\sqrt{\pi}} \int_{E_{CB}(\vec{0})}^{\infty} \frac{x^{1/2}}{1 + e^{x-\xi}} dx \quad (7.33)$$

If we use the substitute $\xi = \frac{\mu - E_{CB}(\vec{0})}{k_B T}$ we get:

$$n = 2 \left(\frac{m^* k_B T}{2\pi \hbar^2} \right)^{3/2} F_{1/2} \left(\frac{\mu - E_{CB}(\vec{0})}{k_B T} \right) \quad (7.34)$$

$$\text{with } N_C = 2 \left(\frac{m^* k_B T}{2\pi \hbar^2} \right)^{3/2} \quad (7.35)$$

N_C is the effective density of states.

Now, as we know, if μ is sufficiently far away from $E_{CB}(\vec{0})$ (meaning $E_{CB}(\vec{0}) - \mu > 4k_B T$), then the Fermi-Dirac distribution can be approximated by the Maxwell-Boltzmann distribution. This results in:

$$n \approx \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} \int_{E_{CB}(\vec{0})}^{\infty} (E - E_{CB}(\vec{0}))^{1/2} e^{-\frac{1}{k_B T} (E - \mu)} dE \quad (7.36)$$

$$\text{take } x = \frac{E - E_{CB}(\vec{0})}{k_B T} = \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} \sqrt{k_B T} \int_{E_{CB}(\vec{0})}^{\infty} \left(\frac{E - E_{CB}(\vec{0})}{k_B T} \right)^{1/2} e^{-\frac{1}{k_B T} (E - \mu)} dE \quad (7.37)$$

$$= \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} \sqrt{k_B T} e^{-\frac{E_{CB}(\vec{0}) - \mu}{k_B T}} \int_0^{\infty} x^{1/2} e^{-x} dx k_B T \quad (7.38)$$

$$= \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} (k_B T)^{3/2} e^{-\frac{E_{CB}(\vec{0}) - \mu}{k_B T}} \int_0^{\infty} x^{1/2} e^{-x} dx \quad (7.39)$$

The integral in equation 7.39 is a well known Gaussian integral and can be easily calculated to obtain a value of $\frac{\sqrt{\pi}}{2}$. Meaning the final expression for n is:

$$n \approx \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} (k_B T)^{3/2} e^{-\frac{E_{CB}(\vec{0}) - \mu}{k_B T}} \frac{\sqrt{\pi}}{2} = N_C e^{-\frac{E_{CB}(\vec{0}) - \mu}{k_B T}} \quad (7.40)$$

This approximation is true for $E_{CB}(\vec{0}) - \mu > 4k_B T$ which are mostly non-degenerate semiconductors.

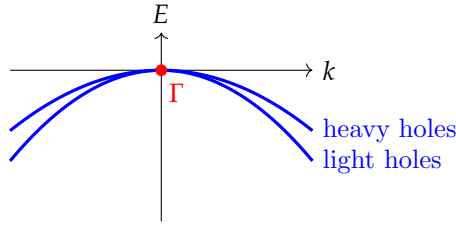


Figure 7.4: Graphical meaning of heavy and light holes in the conduction band

7.3.2 Hole density in the valence band

We will derive the hole densities for both heavy and light holes. The according dispersion relations are:

$$E_{hh} = -\frac{\hbar^2 k^2}{2m_{hh}^*} \quad \text{with } m_{hh}^* = -m_1^* > 0 \quad (7.41)$$

$$E_{lh} = -\frac{\hbar^2 k^2}{2m_{lh}^*} \quad \text{with } m_{lh}^* = -m_2^* > 0 \quad (7.42)$$

Then

$$m_{hh}^* = -\left[\frac{1}{\hbar^2} \frac{\delta^2 E_{hh}}{\delta k_i^2} \right]^{-1} \bigg|_{\vec{k}=\vec{0}} > 0 \quad (7.43)$$

$$m_{lh}^* = -\left[\frac{1}{\hbar^2} \frac{\delta^2 E_{lh}}{\delta k_i^2} \right]^{-1} \bigg|_{\vec{k}=\vec{0}} > 0 \quad (7.44)$$

We immediately see what we mean with heavy and light holes. Because the effective mass is inverse proportional to the second derivative of the energy, we see that $m_{hh}^* > m_{lh}^*$ for every energy. The according bands can be seen in figure 7.4.

What is a hole?

As we know at $T = 0K$, the conduction band is empty and the valence band is completely filled. But at a temperature $T > 0K$, there is a chance that the valence band misses an electron. This chance only gets higher when getting closer to μ . Then the Fermi-Dirac distribution can be defined for the absence of electrons:

$$1 - f(E) = \frac{1}{1 + e^{\beta(\mu - E)}} = f_h(E) \quad (7.45)$$

This will be defined as the Fermi-Dirac distribution of holes, which in their turn are defined by the absence of an electron. Holes can also be treated as quasi-particles (section ??).

Note:-

Note the change of the signs in equation 7.45 compared to equation 7.18

Calculation of the hole density

This part will be practically the same as section 7.3.1, therefore only the differences will be highlighted. Again, we start with:

$$p = \frac{2}{V} \sum_{\vec{k}} f(E_{\alpha}(\vec{k})) \quad \text{with } \alpha = hh, lh \quad (7.46)$$

$$E_{\alpha}(\vec{k}) = -\frac{\hbar^2}{2m_{\alpha}^*} k^2 \quad (7.47)$$

$$(7.48)$$

This results in:

$$p = N_V F_{1/2} \left(\frac{E_{VB}(\vec{0}) - \mu}{k_B T} \right) \quad (7.49)$$

$$N_V = 2 \left(\frac{m_{d,h}^* k_B T}{2\pi \hbar^2} \right)^{3/2} \quad (7.50)$$

$$m_{d,h}^* = \left[(m_{hh}^*)^{3/2} + (m_{lh}^*)^{3/2} \right]^{2/3} \quad (7.51)$$

With $m_{d,h}^*$ the density of states effective mass for holes. Because we worded with two valence bands, we get this somewhat more complex definition for the effective mass. If there is only one valence band the equation simlifies to m_h^* . Notice that there are many similarities between these equation and the ones for electrons.

Simplifying the hole density

For this we can use the following rule: if $\mu - E_{VB}(\vec{0}) > 4k_B T$ we can use the Maxwell-Boltzmann relation. This result in the following equation for the hole density:

$$p = N_V e^{-\frac{E_{VB}(\vec{0}) - \mu}{k_B T}} \quad (7.52)$$

Example 7.3.1 (Try at home)

When using equation 7.50, we can show that $p_{lh} < p_{hh}$. Use the following equation to separate equation 7.50:

$$p = p_{hh} + p_{lh}$$

Why can we show this?

Solution: because

$$\frac{p_{lh}}{p_{hh}} = \frac{N_{V,lh}}{N_{V,hh}} = \left(\frac{m_{lh}^*}{m_{hh}^*} \right)^{3/2} \quad (7.53)$$

where

$$\frac{m_{lh}^*}{m_{hh}^*} < 0 \quad (7.54)$$

7.3.3 An example

Example 7.3.2 (Try at home - Si)

When calculating the electron density for the conduction band for silicon one gets the following:

$$E_\alpha(\vec{k}) = E_{CB}(\vec{0}) + \frac{\hbar^2}{2} \left[\frac{(k_x - k_{0,\alpha,x})^2}{m_l^*} + \frac{(k_y - k_{0,\alpha,y})^2}{m_t^*} + \frac{(k_z - k_{0,\alpha,z})^2}{m_t^*} \right] \quad (7.55)$$

$$n = \frac{2}{V} \sum_{\vec{k}, \alpha} f(E_\alpha(\vec{k})) \quad (7.56)$$

$$= N_C F_{1/2} \left(\frac{\mu - E_{CB}(\vec{0})}{k_B T} \right) \quad (7.57)$$

$$N_C = 2 \left(\frac{m_{d,e}^* k_B T}{2\pi \hbar^2} \right)^{3/2} \quad (7.58)$$

$$m_{d,e}^* = (K^2 m_l^{*2} m_t^*) \quad (7.59)$$

With α between 1 and 6, and K the amount of conduction band minima.

To get to the solution, perform a coordinate transformation which scales the k values according to the relative effective masses.

Figure 7.5: Simple qualitative band diagrams

7.4 Law of mass action

Suppose we restrict ourselves to non-degenerate semiconductors, meaning we can use the Maxwell-Boltzmann equations, and we take the following product:

$$np = N_C N_V e^{\frac{E_V - E_C}{k_B T}} = N_C N_V e^{-\frac{E_g}{k_B T}} \quad (7.60)$$

Thus we can conclude that the product np depends on:

- T
- N_C, N_V ; but not μ
- E_g

For intrinsic semiconductors we will say that

$$np = n_i^2 \quad (7.61)$$

Here, n_i is the intrinsic concentration of the semiconductor. Moreover $n \approx p = n_i$.

Note:-

This is only valid when using Maxwell-Boltzmann!

7.5 Determining the chemical potential μ

Say we have N = the total amount of electrons and we have the following band diagrams for $T = 0K$ and $T > 0K$: We know that the total density n_{tot} is conserved

$$\frac{N}{V} = n_{tot} \Rightarrow n = p \quad (7.62)$$

Because every hole is generated by an electron, and we know no electron is annihilated, we can say that (when using Maxwell-Boltzmann approximations):

$$N_C e^{-\frac{E_C - \mu}{k_B T}} = N_V e^{-\frac{\mu - E_V}{k_B T}} \quad (7.63)$$

$$\iff \mu = \frac{k_B T}{2} \left[\ln \frac{N_V}{N_C} + \frac{E_V + E_C}{k_B T} \right] = \mu(T) \quad (7.64)$$

$$\iff \mu(T) = \frac{E_V + E_C}{2} + \frac{k_B T}{2} \ln \frac{N_V}{N_C} \quad (7.65)$$

We have a temperature dependance for μ meaning that we get two cases:

1. $T = 0K$: $\mu(T = 0) = E_v + \frac{E_g}{2} = E_i$; where E_i is called the intrinsic energy band.
2. $T > 0K$: $\mu(T) = \mu(0) + \frac{k_B T}{2} \ln \frac{N_V}{N_C} = \mu(0) + \Delta\mu(T)$; where, yet again, we have two possibilities:
 - (a) $\Delta\mu(T) > 0$ if $N_v > N_c$
 - (b) $\Delta\mu(T) < 0$ if $N_v < N_c$

We can say that μ will shift towards the band with the lowest effective density states. Yet, this shift is very small, i.e., for Si the $\Delta\mu(T)$ is of the order of $1meV$.

Note:-

For Si at room temperature $n = p = n_i \approx 10^{10} cm^{-3}$.

Chapter 8

Extrinsic semiconductors

In order to increase the electron density n (in CB) or hole density p (in VB), one needs to dope a semiconductor. Meaning impurities get introduced in the semiconductor.

8.1 Doping

If we look at Silicon, a group IV element, we know it has 4 electrons in bonding.

If we now would substitute Si by a group III element (B, Ga, In), which is introducing impurities, we see that there is an electron less in the crystal. This means we introduced a hole in the crystal, and this will be called a p-type doping.

If we now would substitute Si by a group V element (P, As, Sb), which is introducing impurities, we see that there is an extra electron in the crystal. This means we introduced an electron in the crystal, and this will be called a n-type doping.

If we now look at the energy diagrams we notice the following: We notice donor and acceptor levels. At 0K, these states are completely filled with electrons or holes, respectively. Now, at finite temperatures, these electrons or holes jump to the CB or VB (respectively). As we know, an electron that goes away, leaves a hole. Thus when jumping from the E_D to E_C , a hole is left in the donor level. When an electron jumps from the VB to the E_A band, it fills a hole in E_A and leaves a hole behind. Notice the donor/acceptor energy level of the dopant.

The question can now arise: what are these donor and acceptor energies? We know that near the impurity in the silicon lattice, the electron/hole will see a coulomb potential

$$V_{dopant} = \pm \frac{e^2}{4\pi\epsilon_{Si}r} \quad (8.1)$$

which is a hydrogen spectrum. Thus the acceptor and donor energy level is more like a spectrum where the $E_{ionization}$ of the hydrogen model ($13.6eV$) is the difference between E_D and E_C or E_A and E_v . These dopants act like mini-hydrogen atoms. We will come back to this later on.

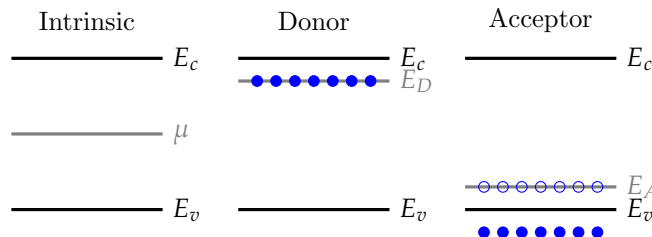


Figure 8.1: Intrinsic, donor and acceptor Si energy diagrams

8.1.1 Donor and acceptor energy levels

Occupation probability of acceptor/donor energy levels

It turns out that the occupation probability for these levels is also given by a Fermi-Dirac distribution:

$$f_D(E_D) = \frac{1}{1 + \frac{1}{g_d} e^{\frac{E_D - \mu}{k_B T}}} \quad (8.2)$$

$$f_A(E_A) = \frac{1}{1 + g_a e^{\frac{E_A - \mu}{k_B T}}} \quad (8.3)$$

$$(8.4)$$

Notice the g_i factor is a degeneration factor for the energy bands, these can be found in tables.

Now we can calculate the chemical potential, because with these donor/acceptor states, the position of the chemical potential will change.

Determining the chemical potential for doped semiconductor

For the intrinsic case, remember we used the fact that $n = p$ to calculate the chemical potential. For the extrinsic case, we will use following rule to obtain charge neutrality

$$\begin{aligned} N_D^* + p &= N_A^- + n \\ \text{Where } N_C^+ &= [1 - f_D(E_D)] N_D \\ N_A^- &= f_A(E_A) N_A \end{aligned} \quad (8.5)$$

Which, after substitution, leads to:

$$\frac{N_D}{1 + g_d e^{\frac{\mu - E_D}{k_B T}}} + N_V F_{1/2} \left(\frac{\mu - E_v}{K_B T} \right) = \frac{N_A}{1 + g_a e^{\frac{E_A - \mu}{k_B T}}} + N_C F_{1/2} \left(\frac{E_c - \mu}{K_B T} \right) \quad (8.6)$$

This way we can determine $\mu(T)$. As we see, there is a temperature dependence of N_D^+ , n and μ . We look at this in the next part.

Temperature dependence of $\frac{n}{N_D}$

We will look at temperatures between 0K and 500K and we suppose there is $N_A = 0$ and $N_D \neq 0 \gg n_i$. As we see in figure 8.2: in the freeze out region, we get an increase of electrons in the conduction band that come from the donor energy levels (the dopants). After a while if all donor electrons are excited, the electrons from the substrate will excite, too.

If we take $T \rightarrow 0$, then we can say

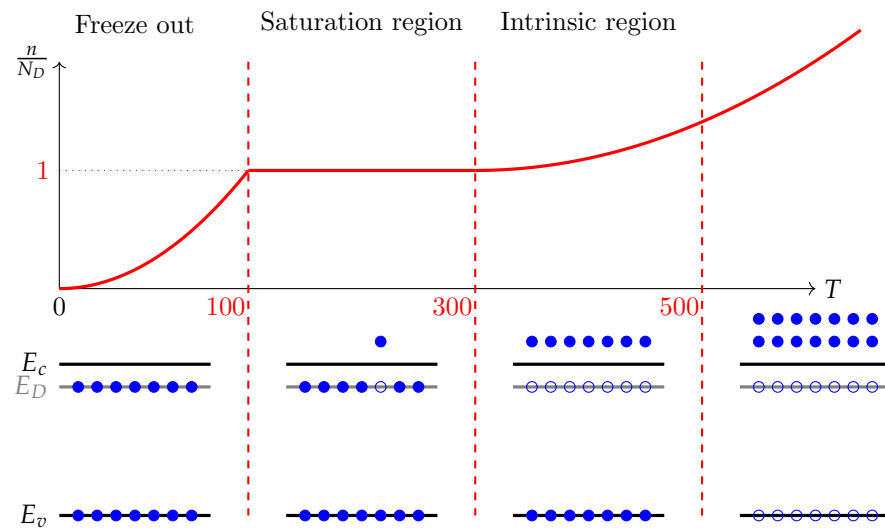
$$\mu = \frac{E_D + E_c}{2} + \frac{k_B T}{2} \ln \frac{N_D}{g_d N_c} \quad (8.7)$$

Note:-

For a acceptor semiconductor ($N_D = 0$, $N_A \neq 0 \gg n_i$), we will get following equation for μ :

$$\mu = \frac{E_A + E_v}{2} + \frac{k_B T}{2} \ln \frac{N_A}{g_a N_v} \quad (8.8)$$

Further information is given in the course book. Part of the exercise session covers deriving the chemical potential at different temperatures.

Figure 8.2: The temperature dependence of $\frac{n}{N_D}$

Chapter 9

Dynamics of charge carriers

9.1 The velocity of an electron

To know what the velocity is, we need to look at quantum mechanics. If we have a Bloch hamiltonian (with periodic $V(\vec{r})$), we can define the velocity operator.

$$\hat{v} = \frac{d\hat{r}}{dt} = \frac{1}{i\hbar} [\hat{r}, \hat{H}] = -\frac{i\hbar}{m} \vec{\nabla} = \frac{\hat{p}}{m} \quad (9.1)$$

What can I say about this velocity operator? Specifically, the expectation value of this velocity:

$$\langle \hat{v} \rangle = \langle \psi | \hat{v} | \psi \rangle = -\frac{i\hbar}{m} \int d^3x \psi^*(\vec{r}) \vec{\nabla} \psi(\vec{r}) \quad (9.2)$$

Because we have a periodic crystal, we can define ψ as

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad (9.3)$$

Then, by using $\int d^3x |u_{\vec{k}}(\vec{r})|^2 = 1$ we can define the expectation value as

$$\langle \hat{v} \rangle = \frac{\hbar \vec{k}}{m} - \frac{i\hbar}{m} \int d^3x u_{\vec{k}}^*(\vec{r}) \vec{\nabla} u_{\vec{k}}(\vec{r}) \quad (9.4)$$

By making use of the Schrödinger equation

$$\left\{ \frac{\hbar^2}{2m} (-\vec{\nabla} + \vec{k})^2 + V(\vec{r}) \right\} u_{\vec{k}}(\vec{r}) = E(\vec{k}) u_{\vec{k}}(\vec{r})$$

it is possible to show that

$$\frac{i\hbar}{m} \int d^3x u_{\vec{k}}^*(\vec{r}) \vec{\nabla} u_{\vec{k}}(\vec{r}) = \frac{\hbar \vec{k}}{m} - \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} E(\vec{k})$$

In order that equation 9.4 becomes

$$\langle \hat{v} \rangle = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} E_n(\vec{k}) \quad (9.5)$$

which is the equation for group velocity, this is the velocity of a wave packet. Say you have an energy dispersion relation and you construct a wave packet representing electrons with different k values, then the maximum this wavepacket is moving is given by the group velocity.

Theorem 9.1.1 Group velocity

Take a 1D Bloch wave function: $\psi_k(x) = u_k(x) e^{ikx}$. Then we can construct a wave packet in the first BZ $(-\pi/a \dots \pi/a)$:

$$\psi(x, t) = \int_{-\pi/a}^{\pi/a} dk A(k) \psi_k(x) e^{-\frac{i}{\hbar} E(k)t}$$

If we fill in the expression for ψ and use a Taylor expansion for the exponential function one gets:

$$\begin{aligned}\psi(x, t) &\approx \int_{-\pi/a}^{\pi/a} dk A(k) u_{k0}(x) e^{i(k_0 x - \frac{E(k_0)t}{\hbar})} e^{i(k-k_0)(x - \frac{dE}{dk}|_{k_0} \frac{t}{\hbar})} \\ &= e^{i(k_0 x - \frac{E(k_0)t}{\hbar})} u_{k0}(x) \int_{-\pi/a}^{\pi/a} dk A(k) e^{i(k-k_0)(x - \frac{dE}{dk}|_{k_0} \frac{t}{\hbar})}\end{aligned}$$

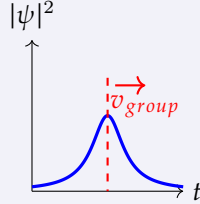
The we can describe the probability density function as:

$$|\psi(x, t)|^2 = P(x, t) = \dots$$

Because we have a very sharp peak around k_0 in the function $A(k)$, this integral will have a stationary phase condition. Meaning we will reach a maximum of our integral if

$$x - \frac{dE}{dk} \Big|_{k=k_0} \frac{t}{\hbar} = 0 \quad x = \frac{dE}{dk} \Big|_{k=k_0} \frac{t}{\hbar}$$

We can represent this in the following way:



This wave moves, with a velocity, the group velocity

$$v = \frac{dx}{dt} = \frac{dE}{dk} \Big|_{k=k_0} \frac{1}{\hbar}$$

Now what is interesting is that this group velocity comes from a wave packet, but we didn't construct a wave packet! When calculating the expectation value of the velocity of the electrons, these electrons in these eigenstates move with a group velocity. This is not a trivial result. The only difference between the two is that the group velocity for a wave packet is only valid nearby this $A(k)$ peak (at k_0), whereas the group velocity here is valid for any \vec{k} .

9.1.1 The acceleration of an electron

This is given by

$$\frac{d}{dt} \langle \vec{v} \rangle = \frac{d}{dt} \left(\frac{1}{\hbar} \vec{\nabla}_{\vec{k}} E(\vec{k}) \right) = 0 = \vec{a} = \langle \vec{a} \rangle \quad (9.6)$$

9.2 The velocity of an electron - with external field

In this case, the hamiltonian becomes

$$\hat{H} = \frac{\hat{p}^2}{2m} + V_C(\vec{r}) + V_{ext}(\vec{r}, t) \quad (9.7)$$

If we want to include these external fields, we need to solve the time dependant Schrödinger equation. This isn't trivial, but there is a trick. By using a "effective" Schrödinger equation defined by the following theorem we can solve this problem easier.

Theorem 9.2.1 Effective mass theorem

It can be shown that

$$\left[\hat{E}_n(-i\vec{\nabla}) + V_{ext}(\vec{r}, t) \right] \psi(\vec{r}, t) = i\hbar \frac{\delta \psi(\vec{r}, t)}{\delta t} \quad (9.8)$$

We obtain this formula by replacing $\vec{k} \rightarrow -i\vec{\nabla}$ in $E_n(\vec{k})$.

Proof:

$$\psi(\vec{r}, t) = \sum_{\vec{k}} c_n(\vec{k}, t) \psi_{\vec{k}}(\vec{r}) \quad \text{with } \psi_{\vec{k}}(\vec{r}) = u_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \quad (9.9)$$

Maybe you can see that equation 9.8 is typically valid for one specific band (see subscript n). this also means that when I do the expansion, we don't want to refer to all the bands. Therefore we make an approximation where we assume that the solution is restricted to a single band. Next, the only electrons we are interested in are the ones in the vicinity of the minimum of the conduction band (or the maxima of the valence band for holes). Then the approximations we make are:

1. Only one band at at time
2. Only \vec{k} -values near band extrema

Thus our wave function will become

$$\psi(\vec{r}, t) = \sum_{\vec{k}} c_{\vec{k}}(t) \psi_{\vec{k}}(\vec{r}) \quad (9.10)$$

$$\text{9.7 in 9.10} \quad \Rightarrow \quad \sum_{\vec{k}} c_{\vec{k}}(t) \left[-\frac{\hbar^2}{2m} \nabla^2 + V_C + V_{ext} \right] \psi_{\vec{k}}(\vec{r}) = i\hbar \frac{\delta \psi}{\delta t} \quad (9.11)$$

If we look at the total hamiltonian acting on the eigenfunction of the Bloch hamiltonian meaning the wavevector is an eigenfunction of the total hamiltonian. Thereby we can replace the hamiltonian by the eigenenergy.

$$\rightarrow \sum_{\vec{k}} c_{\vec{k}}(t) \left[E(\vec{k}) + V_{ext} \right] \psi_{\vec{k}}(\vec{r}) = i\hbar \frac{\delta \psi}{\delta t} \quad (9.12)$$

Because $E(\vec{k})$ is periodic, we can make a fourier expansion in k-space:

$$E(\vec{k}) = \sum_m E_m e^{i\vec{R}_m \cdot \vec{k}} \quad \text{with } \vec{R}_m \text{ a lattice vector} \quad (9.13)$$

substitute $\vec{k} \rightarrow i\vec{\nabla}$

$$\Rightarrow \hat{E}(-i\vec{\nabla}) = \sum_m E_m e^{i\vec{R}_m \cdot \vec{\nabla}} \quad (9.14)$$

When letting the exponential act on a function we get (this can be proved by a taylor expansion of the exponential):

$$e^{i\vec{R}_m \cdot \vec{\nabla}} \psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r} + \vec{R}_m) \quad (9.15)$$

If we now let equation 9.14 act on the Bloch wave function we get the following:

$$\hat{E}(-i\vec{\nabla}) \psi_{\vec{k}}(\vec{r}) = \sum_m E_m e^{i\vec{R}_m \cdot \vec{\nabla}} \psi_{\vec{k}}(\vec{r}) \quad (9.16)$$

$$= \sum_m E_m \psi_{\vec{k}}(\vec{r} + \vec{R}_m) \quad (9.17)$$

$$\text{Using the Bloch wavefunction property} \quad = \sum_m E_m e^{i\vec{R}_m \cdot \vec{k}} \psi_{\vec{k}}(\vec{r}) \quad (9.18)$$

$$= E(\vec{k}) \psi_{\vec{k}}(\vec{r}) \quad (9.19)$$

What we now have showed is that the operator $\hat{E}(-i\vec{\nabla})$ acting on the eigenstates of the Hamiltonian gives as eigenvalues, the eigenenergies of the Hamiltonian. Now we can safely write that $E(\vec{k}) = \hat{E}(-i\vec{\nabla})$.

We can now rewrite equation 9.12 as

$$\sum_{\vec{k}} c_{\vec{k}}(t) \left[E(-i\vec{\nabla}) + V_{ext} \right] \psi_{\vec{k}}(\vec{r}) = i\hbar \frac{\delta \psi}{\delta t} \quad (9.20)$$

$$\left[E(-i\vec{\nabla}) + V_{ext} \right] \sum_{\vec{k}} c_{\vec{k}}(t) \psi_{\vec{k}}(\vec{r}) = i\hbar \frac{\delta \psi}{\delta t} \quad (9.21)$$

$$\left[E(-i\vec{\nabla}) + V_{ext} \right] \psi(\vec{r}, t) = i\hbar \frac{\delta \psi(\vec{r}, t)}{\delta t} \quad (9.22)$$

■

Note:-

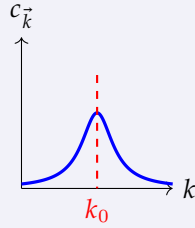
This is only valid if we stick in the conduction or valence band.

9.3 Effective mass equation

Theorem 9.3.1 Effective mass equation

$$\begin{aligned}\psi(\vec{r}, t) &= \sum_{\vec{k}} c_{\vec{k}}(t) \psi_{n, \vec{k}}(\vec{r}) \\ &= \sum_{\vec{k}} c_{\vec{k}}(t) u_{n, \vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}\end{aligned}\quad (9.23)$$

We will restrict the coefficients $c_{\vec{k}}(t)$ to values around \vec{k}_0 , where \vec{k}_0 is located at a band extremum. We get a visualization like



Because they are sharply peaked we can write equation 9.23 as

$$\begin{aligned}\psi(\vec{r}, t) &= \sum_{\vec{k}} c_{\vec{k}}(t) u_{n, \vec{k}_0}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \\ &= \sum_{\vec{k}} c_{\vec{k}}(t) u_{n, \vec{k}_0}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}} e^{-i\vec{k}_0 \cdot \vec{r}} \\ &= \sum_{\vec{k}} c_{\vec{k}}(t) e^{i(\vec{k} - \vec{k}_0) \cdot \vec{r}} \psi_{n, \vec{k}_0}(\vec{r}) \\ &= \psi_{n, \vec{k}_0}(\vec{r}) \sum_{\vec{k}} c_{\vec{k}}(t) e^{i(\vec{k} - \vec{k}_0) \cdot \vec{r}}\end{aligned}\quad (9.24)$$

The function $\sum_{\vec{k}} c_{\vec{k}}(t) e^{i(\vec{k} - \vec{k}_0) \cdot \vec{r}}$ will oscillate if \vec{k} is far away from \vec{k}_0 , which cannot happen. Therefore this function varies slowly in time. This function is called the **envelope wave function**:

$$F(\vec{r}, t) = \sum_{\vec{k}} c_{\vec{k}}(t) e^{i(\vec{k} - \vec{k}_0) \cdot \vec{r}} \quad (9.25)$$

Yet again, we have constructed some kind of wave packet. In particular, it turns out that if we restrict the coefficients around the values k_0 (with some deviation Δk , $\Delta k \ll \frac{2\pi}{a}$). This implies that the uncertainty of the position $\Delta x \gg a$.

This is a result from the Fourier analysis and wave-packets that give a relation $\Delta x \Delta k > 1$, it is the same relation that gives rise to the Heisenberg uncertainty principle.

How does this description of the wavefunction behave when the operator $\hat{E}(-i\vec{\nabla})$ acts on it?

We perform the same principle as in section 9.2

$$\hat{E}(-i\vec{\nabla})\psi(\vec{r}, t) = \hat{E}(-i\vec{\nabla}) \left[\psi_{n, \vec{k}_0}(\vec{r}) F(\vec{r}, t) \right] \quad (9.26)$$

$$= \sum_m E_m e^{\vec{R}_m \cdot \vec{\nabla}} \left[\psi_{n, \vec{k}_0}(\vec{r}) F(\vec{r}, t) \right] \quad (9.27)$$

$$= \sum_m E_m \psi_{n, \vec{k}_0}(\vec{r} + \vec{R}_m) F(\vec{r} + \vec{R}_m, t) \quad (9.28)$$

$$\text{using Bloch} \quad = \sum_m E_m e^{i\vec{R}_m \cdot \vec{k}_0} \psi_{n, \vec{k}_0}(\vec{r}) e^{\vec{R}_m \cdot \vec{\nabla}} F(\vec{r}, t) \quad (9.29)$$

$$= \sum_m E_m \psi_{n, \vec{k}_0}(\vec{r}) e^{i\vec{R}_m \cdot (\vec{k}_0 - i\vec{\nabla})} F(\vec{r}, t) \quad (9.30)$$

$$= \psi_{n, \vec{k}_0}(\vec{r}) \sum_m E_m e^{i\vec{R}_m \cdot (\vec{k}_0 - i\vec{\nabla})} F(\vec{r}, t) \quad (9.31)$$

And this is nothing else as

$$\psi_{n, \vec{k}_0}(\vec{r}) \hat{E}(\vec{k}_0 - i\vec{\nabla}) F(\vec{r}, t) \quad (9.32)$$

As a result, using the effective mass theorem we can become a more general description (i.e. the effective mass equation) by making use of equation 9.24 and equation 9.32:

$$i\hbar \frac{\delta F}{\delta t} = \left[\hat{E}(\vec{k}_0 - i\vec{\nabla}) + V_{ext} \right] F(\vec{r}, t) \quad (9.33)$$

How can we use the effective mass equation? Suppose we look at a CB minimum located at \vec{k}_0 , not located at the Γ -point. We can then say that because we are at a minimum, we can write

$$E_n(\vec{k}) = E_n(\vec{k}_0) + \frac{1}{2} \sum_{i,j} \frac{\delta^2 E_n(\vec{k})}{\delta k_i \delta k_j} \bigg|_{\vec{k}=\vec{k}_0} (k_i - k_{i,0})(k_j - k_{j,0}) \quad (9.34)$$

Then the effective mass equation becomes:

$$i\hbar \frac{\delta F}{\delta t} = \left[\hat{E}(\vec{k}_0 - i\vec{\nabla}) + V_{ext} \right] F(\vec{r}, t) \quad (9.35)$$

$$\text{where } \hat{E}(\vec{k}_0 - i\vec{\nabla}) = E_n(\vec{k}_0) - \frac{1}{2} \sum_{i,j} \frac{\delta^2 E_n(\vec{k})}{\delta k_i \delta k_j} \bigg|_{\vec{k}=\vec{k}_0} \frac{\delta}{\delta r_i} \frac{\delta}{\delta r_j} \quad (9.36)$$

$$\text{using equation 7.7} \Rightarrow i\hbar \frac{\delta F}{\delta t} = \left[\hat{E}_n(\vec{k}_0) - \frac{\hbar^2}{2} \sum_{i,j} \left[m_{i,j}^* \right]^{-1} \frac{\delta}{\delta r_i} \frac{\delta}{\delta r_j} + V_{ext} \right] F \quad (9.37)$$

Example 9.3.1 (Using the effective mass equation - 1D)

Consider a CB minimum at $k = 0$. Then, the conduction band is described by:

$$E_{CB}(k) = E_{CB} + \frac{\hbar^2 k^2}{2m^*} \quad \text{with } m^* > 0$$

Then, we can find the envelope wave function as

$$i\hbar \frac{\delta F}{\delta t} = \left[E_{CB} - \frac{\hbar^2}{2m^*} \frac{d^2}{dx^2} + V_{ext} \right] F$$

Say we take $V_{ext} = 0$, then (after filling in $F(x, t) = \psi(x) e^{-iEt/\hbar}$) we get:

$$-\frac{\hbar^2}{2m^*} \frac{d^2}{dx^2} \psi(x) = (E - E_{CB}) \psi(x)$$

This is just a normal time independent Schrödinger equation.

Remember that earlier was said that when working with acceptors and donors, the energy levels of these acceptors and donors, first of all, were in the energy gap, but also that they had a hydrogen-like energy spectrum. From that spectrum, it is possible to derive the ionization energy for the energy levels of the acceptors and donors.

Example 9.3.2 (E-spectrum of donor impurities in GaAs (III - V))

We will replace Ga by Si. Then what is the V_{ext} introduced by Si? Well what we want to know is the following

$$\begin{aligned} V_{ext}(\vec{r}) &= V_{Si}(\vec{r}) - V_{Ga}(\vec{r}) \\ &= -\frac{(Z_{Ga} + 1)e^2}{4\pi\epsilon|\vec{r}|} + \frac{Z_{Ga}e^2}{4\pi\epsilon|\vec{r}|} \\ &= -\frac{e^2}{4\pi\epsilon|\vec{r}|} \end{aligned}$$

We know that the energy of the conduction band is given by:

$$E(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m^*}$$

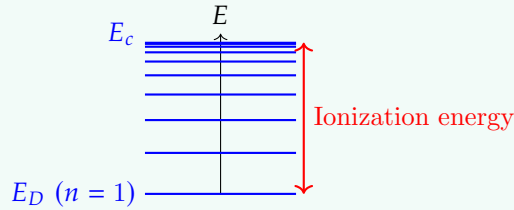
Then the effective mass equation becomes:

$$\begin{aligned} i\hbar \frac{\delta F}{\delta t} &= \left[E_c - \frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\epsilon|\vec{r}|} \right] F(\vec{r}, t) \\ \text{with } F(\vec{r}, t) &= \psi(\vec{r})e^{-i/\hbar Et} \\ \left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\epsilon|\vec{r}|} \right] \psi(\vec{r}) &= (E - E_c)\psi(\vec{r}) \end{aligned}$$

This is just the Schrödinger equation for a hydrogen atom with one electron, instead now with an effective mass m^* . Particularly, we are looking for the **bound states**. For hydrogen we know then that $E - E_c$ must be given by

$$E - E_c = -\frac{e^4 m^*}{2n^2 (4\pi\epsilon\hbar)^2} \quad \text{with } n = 1, 2, \dots$$

Now we have degeneracies and an ionization energy. Once this energy level is passed, electrons can freely move in the conduction band. The result is given in this figure:



Example 9.3.3 (E-spectrum of acceptor impurities in Si)

Now, we will replace Si by an acceptor. We can now define V_{ext} as

$$V_{ext} = \frac{e^2}{4\pi\epsilon|\vec{r}|}$$

Then the energy solution of the valence band becomes (after introduction of $m_h = -m^* > 0$):

$$E(\vec{k}) = -\frac{\hbar^2 k^2}{2m_h}$$

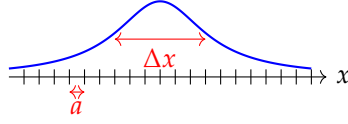


Figure 9.1: Underlying lattice with envelope wave function

Then we can write the effective mass equation as

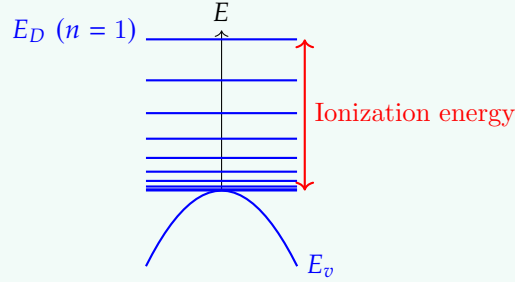
$$i\hbar \frac{\delta F}{\delta t} = \left[\frac{\hbar^2}{2m_h} \nabla^2 + \frac{e^2}{4\pi\epsilon|\vec{r}|} \right] F$$

$$\Rightarrow \left[\frac{\hbar^2}{2m_h} \nabla^2 + \frac{e^2}{4\pi\epsilon|\vec{r}|} \right] \psi(\vec{r}) = E\psi(\vec{r})$$

Now, this is just the hydrogen spectrum, at least if we introduce some minus signs. We get the following:

$$\left[-\frac{\hbar^2}{2m_h} \nabla^2 - \frac{e^2}{4\pi\epsilon|\vec{r}|} \right] \psi(\vec{r}) = -E\psi(\vec{r})$$

If we then take $\tilde{E} = -E$ the 'hydrogen' atom is complete. We get the following figure:



Yet again, if we want to get an electron to the acceptor level we need an energy equal to the "Ionization energy"

9.4 Semi-classical electron (or hole) dynamics

When the external field is time varying, solving the effective mass theorem (equation 9.22) for electrons (or holes) in the VB or CB becomes rather difficult to solve. Now luckily, it turns out one can find a solution (by approximation) for the effective mass theorem. Meaning one can derive semi-classical equation of motion. The effective mass theorem given by equation 9.22 has a wave function

$$\psi(\vec{r}, t) = \sum_{\vec{k}} c_{\vec{k}}(t) \psi_{n,\vec{k}}(\vec{r}) \quad (9.38)$$

$$= \psi_{n,\vec{k}_0} F(\vec{r}, t) \quad (9.39)$$

Because $c_{\vec{k}}(t)$ is sharply peaked around k_0 in the conduction band and valence band, we can write it as equation .

For classical/semi-classical particles/electrons, we know that \vec{p} and \vec{r} is well defined. So how can we define them?

In figure 9.1 we see an underlying lattice and the envelope wave function (because c is sharply peaked we have this). We can decrease Δx , however this way we increase Δp . From fourier analysis, we know that

$$\Delta x \Delta k > 1 \quad \Rightarrow \quad \Delta x \Delta p > \hbar \quad (9.40)$$

So we will need our Bloch electrons to behave with a $\Delta x \ll$ variation of V_{ext} and that $\Delta x \gg a$. Why this last statement? We want the uncertainty on k (Δk) to be within the first BZ.

9.4.1 The semi-classical approach

Instead of using $\hat{H} = \hat{E}(-i\vec{\nabla}) + V_{ext}(\vec{r}, t)$ we use $H = E(\vec{k}) + V_{ext}(\vec{r}, t)$ which is equivalent to $H = E(\frac{\vec{P}_C}{\hbar}) + V_{ext}(\vec{r}, t)$. With \vec{P}_C the crystal momentum.

Now, the hamiltonian equations represent the well known Newton equations of motion:

$$\frac{\delta H}{\delta \vec{r}} = \vec{\nabla}_{\vec{r}} H = -\frac{\delta \vec{P}_C}{\delta t} \quad (9.41)$$

$$\frac{\delta H}{\delta \vec{r}} = \vec{\nabla}_{\vec{P}_C} H = \frac{\delta \vec{x}}{\delta t} \quad (9.42)$$

Then we can derive the semi-classical equation as

$$\text{from equation 9.41} \quad \frac{\delta \vec{P}_C}{\delta t} = \frac{\delta}{\delta t}(\hbar \vec{k}) = -\vec{\nabla}_{\vec{r}} H = \vec{F}_{ext}(\vec{r}, t) \quad (9.43)$$

$$\text{from equation 9.42} \quad \frac{\delta \vec{x}}{\delta t} = \vec{v} = \vec{\nabla}_{\vec{P}_C} H = \vec{\nabla}_{\vec{P}_C} E_n(\frac{\vec{P}_C}{\hbar}) = \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} E_n(\vec{k}) = \vec{v}_g(\vec{k}) \quad (9.44)$$

Example 9.4.1 (Constant F_{ext} - 1D example)

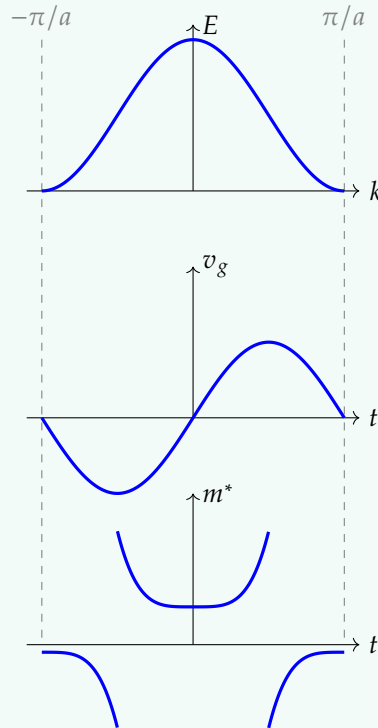
$$\hbar \frac{\delta k}{\delta t} = F_{ext} \Rightarrow k(t) = k(0) + \frac{F_{ext} t}{\hbar} \quad (9.45)$$

$$v = \frac{1}{\hbar} \frac{\delta E}{\delta k} = \frac{1}{\hbar} \frac{\delta E(k(t))}{\delta k} = v_g(k(t)) \quad (9.46)$$

$$a = \frac{F_{ext}}{m^*(k)} \quad (9.47)$$

$$\frac{1}{m^*(k)} = \frac{1}{\hbar^2} \frac{\delta^2 E}{\delta k^2} \quad (9.48)$$

The conduction band is represented in the following figure, along with the group velocity and the effective mass.



If we would let the CB go beyond π/a , we would get an oscillation. This leads to an oscillation of the group velocity, too. These are called **Bloch oscillations**.

How should one interpret these graphs? Well, suppose we start at no external force, then we are at $k = 0$. Once a force is introduced, we see k change. One important thing to extract from the figures, is

that when going away from the CB minimum, the calculations make no sense anymore (just look at m^*).

One thing to note, too, is that the time constant for the Bloch oscillations is much larger than other time constants of the crystal (defects, backscattering, ...), i.e., $\tau_B \gg \tau_{scatt}$ meaning one doesn't see these Bloch oscillations before a full oscillation of the k value.

9.4.2 Importance of holes

Say we have a full VB, then the total crystal momentum is

$$\vec{P}_{C,VB}^{tot} = \vec{0} = \sum_{\vec{k},VB} \hbar \vec{k}$$

Now if we introduce one empty state at \vec{k}_0 , i.e., a hole, we get the following momentum

$$\vec{P}_{C,VB}^{tot} = \sum_{\vec{k},VB} \hbar \vec{k} - \hbar \vec{k}_0 = \vec{0} - \hbar \vec{k}_0 = -\hbar \vec{k}_0$$

Then a hole can be defined to have a crystal momentum of

$$\vec{P}_{C,VB} = -\hbar \vec{k}_0$$

Movement of holes and electrons

If we look at the semi-classical description for the external force acting on the electrons/holes, we see for an electron the following description

$$\hbar \frac{\delta \vec{k}_{electron}}{\delta t} = \vec{F}_{ext} \quad (9.49)$$

$$= -e(\vec{E} + \vec{v} \times \vec{B}) \quad (9.50)$$

Then, if we define $\vec{k}_h = -\vec{k}_{electron}$ for a hole, we get

$$\hbar \frac{\delta(-\vec{k}_{electron})}{\delta t} = -\vec{F}_{ext} \quad (9.51)$$

$$\hbar \frac{\delta \vec{k}_h}{\delta t} = -\vec{F}_{ext,h} \quad (9.52)$$

$$= e(\vec{E} + \vec{v} \times \vec{B}) \quad (9.53)$$

If we would now look at the equivalent Newton equation for electrons, we'd get (from equation 9.49)

$$\vec{a} = \vec{m}^{*-1} \cdot \vec{F}_{ext}$$

To define the one of holes we will introduce (as we did in previous sections) the hole effective mass: $\vec{m}_h^{*-1} = -\vec{m}^{*-1}$. In order that from equation 9.52, we'd get

$$\vec{a} = -\vec{m}_h^{*-1} \cdot \vec{F}_{ext}$$

$$\vec{a} = \vec{m}_h^{*-1} \cdot \vec{F}_{ext,h}$$

Thus the acceleration for holes and electrons is the same (i.e., mass times force), just instead of having negative particles, we have positive particles for holes.

Note:-

$\vec{v} \times \vec{B}$ is the Lorentz force acting on the crystal