

# Semiconductor Physics Lectures

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# Notes

# Contents

# 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 ???. 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 ???. *More examples can be found in the slides.* More on lattice vectors in ???.

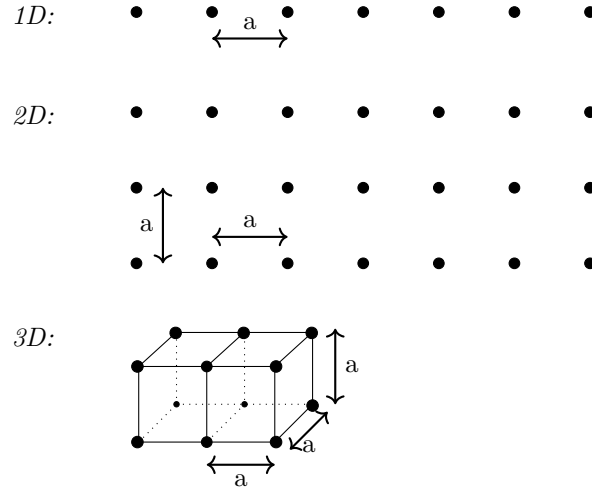


Figure 1.1: Lattices in different dimensions

### Example 1.2.1 (Graphene)

To show what a lattice is and what it isn't this example is given, see also figure ?? . 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 ??) and a conventional unit cell (section ??) for this lattice.

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## 1.3 Lattice vectors

As already touched upon at section ??, 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 ?? and figure ?. 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.

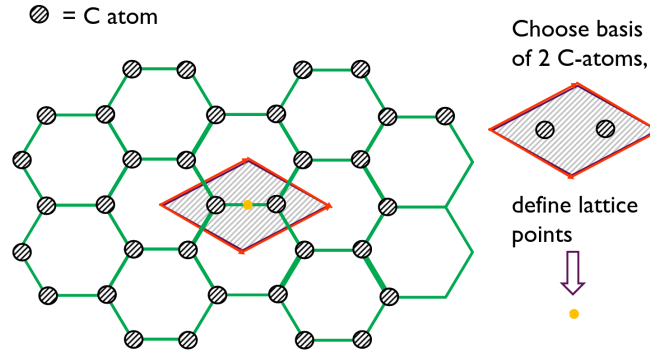


Figure 1.2: The graphene crystal



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

## 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 ??

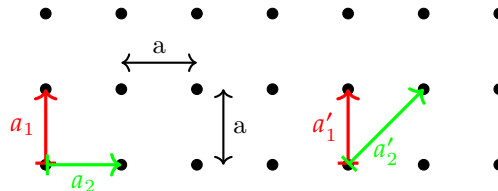


Figure 1.4: An example set of lattice vectors in 2D

## 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. 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).

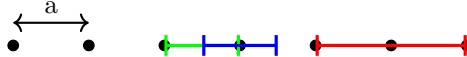


Figure 1.5: Several 1D unit cells

## 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 ??.

#### 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 ??.

The basis chosen is  $\{\vec{a}_1, \vec{a}_2, \vec{a}_3\}$ . As we can see (figure ??), 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**.

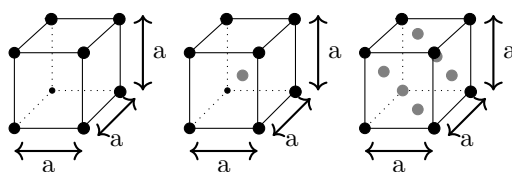


Figure 2.1: The three different cubic lattice systems



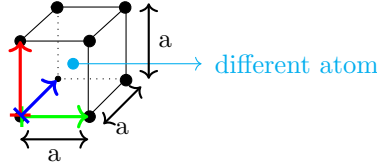


Figure 2.2: The basis for a simple cubic lattice

#### 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 ???. As mentioned before, all atoms are the same and that is why the *PUC* is smaller.

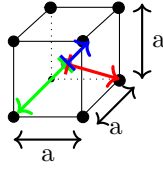


Figure 2.3: The three different cubic lattice systems

#### 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 ??.

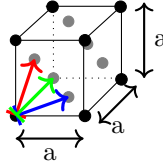


Figure 2.4: The three different cubic lattice systems

## 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 ??, one can see the primitive unit cell. The basis vectors are:

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

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

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

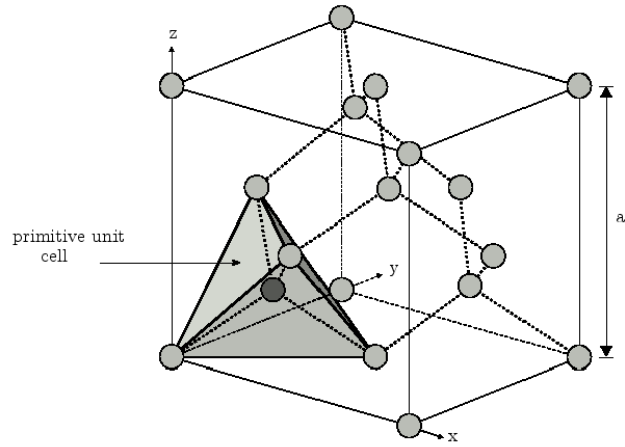


Figure 2.5: The diamond structure and its *PUC*

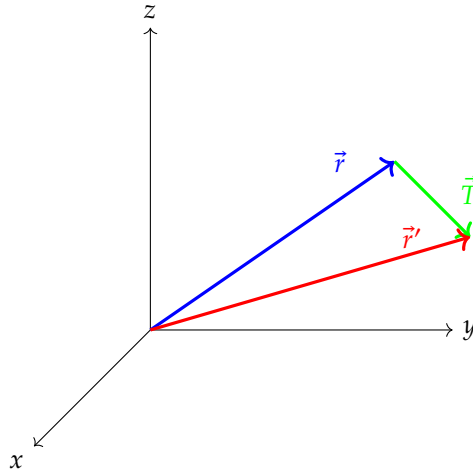


Figure 2.6: Translational symmetry

### 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.

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

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

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 ??.

## 2.4 Lattice dimensions

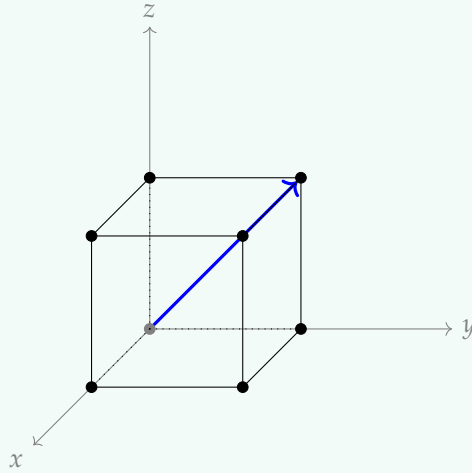
### Definition 2.4.1: Lattice dimensions

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 ??, 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.

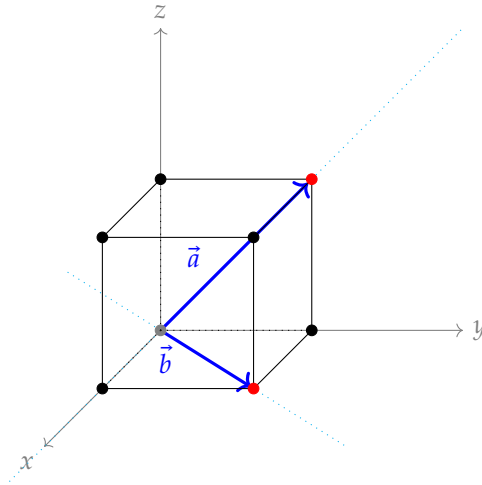


Figure 2.7: Demonstration of vectors with the same symmetry

**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  $\gamma$ .

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

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

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

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 ??,  $V(\vec{r})$  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:

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

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

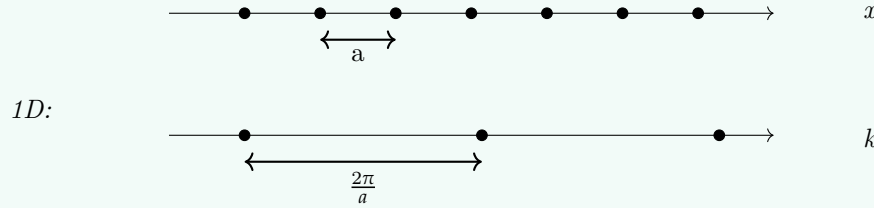
**Claim 3.2.1** Property of  $F(G)$

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

**Question 2: Using the FT for conversion of the lattice space to the reciprocal 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 reciprocal 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 ?? 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  $\delta_{ij}$  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 reciprocal spaces

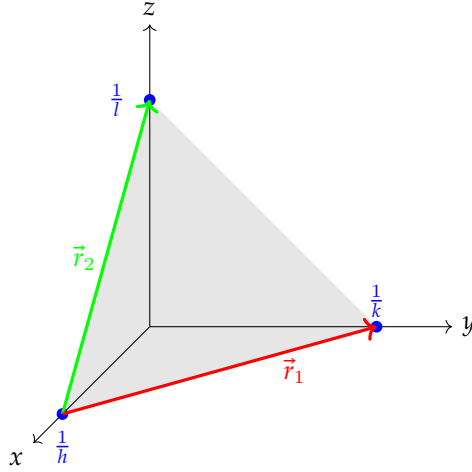
#### Claim 3.4.1 Property 1

To every lattice plane  $(h, k, l)$  there is a reciprocal lattice vector perpendicular to that plan and is give 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 ?? you get the formulas for  $\vec{b}_j$ , see equations ?? - ???. 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 ?? uses the fact that  $\vec{a}_i$  and  $\vec{b}_j$  are perpendicular as per ??.

#### Claim 3.4.3 Property 3

The direct lattice is the reciprocal of its own reciprocal lattice. Because switching the vectors in expression ?? 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 ??. 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.

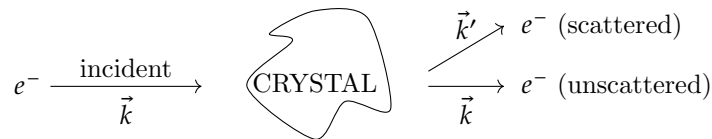


Figure 3.1: X-ray diffraction on a lattice

### 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

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

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

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

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

Equation ?? states the Bragg condition, further elaborated in section ?. By symmetry, we can leave  $\vec{R}$  out of equation ??, 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 ?? 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 ?? 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 ?. 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 ??), we can conclude that:

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

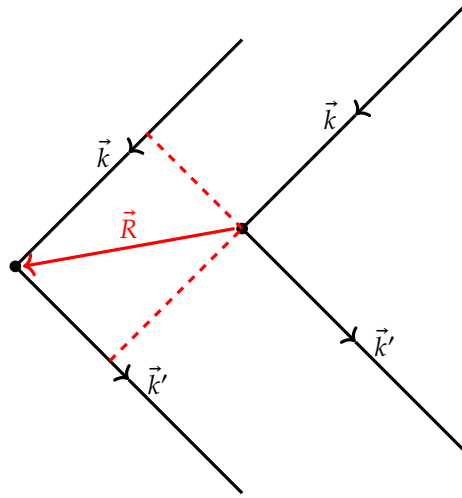


Figure 3.2: Extra distance for different wavevectors

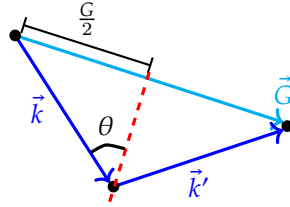


Figure 3.3: Drawing of the physical meaning of the Bragg condition

### 3.7 Von Laue-Bragg condition

As proven in section ??,

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

. We will rewrite this equation:

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

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

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

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

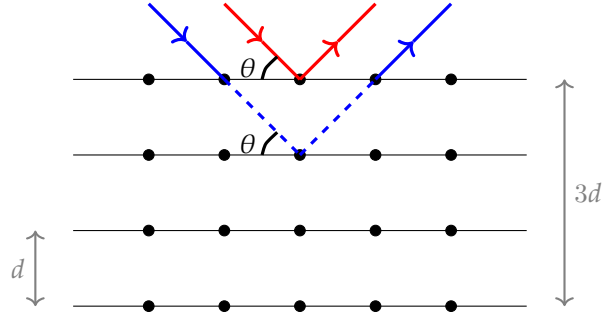
$$\iff \vec{k} \cdot \frac{\vec{G}}{G} = \frac{G}{2} \quad (3.63)$$

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

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 ??. 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 ??. From the properites of reciprocal spaces, we know



that (see equation ??):

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

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

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

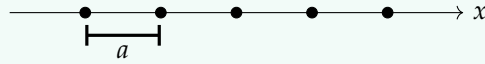
Now, from equation ?? and equation ?? we can derive an interference pattern. As we can see in figure ??, for normal scattering waves in a crystal lattice, Von Laue and the Bragg condition are the same. As we further also see, if the extra distance (marked with a dashed line)  $d = n\lambda$ , then there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

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

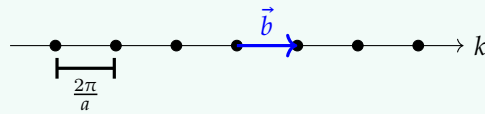
For 1D, we can write the Von Laue condition as:

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

We take the following 1D lattice:



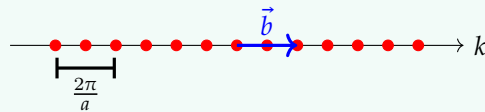
With the following reciprocal 1D lattice and reciprocal vector  $\vec{G} = \vec{b}$ :



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

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

This results in the following Bragg points on the lattice:

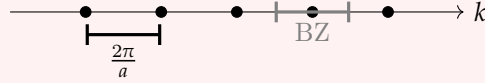


## 3.8 The Brillouin Zone (BZ)

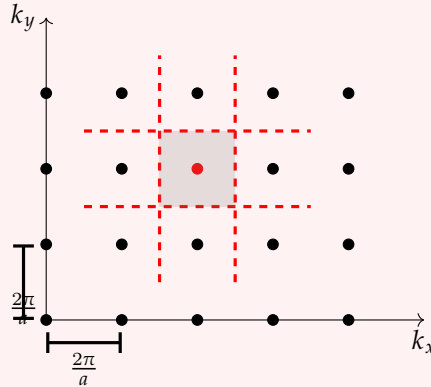
### Definition 3.8.1: The first Brillouin Zone

The first Brillouin Zone is a Weigner-Sietz unit cell (section ??) 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

Redo references to equations with label

### 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 Schrödinger 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**

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

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

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

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

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

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

Because  $m_{\text{electron}} \approx M \cdot 10^{-4}$ ,  $(H_{\text{ion}} + H_{\text{ion-ion}})\psi(\vec{r}, \vec{R})\phi(\vec{R}) - \psi(\vec{r}, \vec{R})(H_{\text{ion}} + H_{\text{ion-ion}})\phi(\vec{R}) \approx 0$ . 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:

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

**Note:-**

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

We can now define:

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

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**

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

**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.

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

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

**Note:-**

- $\delta\vec{R}_j(t) \cdot \vec{\nabla}_j V_{\text{electron-ion}}(\vec{r}_i - \vec{R}_j^{(0)})$  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  $||$  is left out here in  $H_{\text{electron-ion}}$ .

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:

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

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

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

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

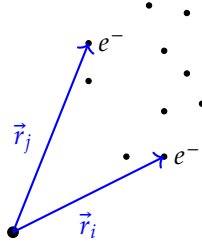
## 4.4 Hartree approximation

### 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 continuous 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:

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

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

### Note:-

$\Phi$  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 ??, 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 an 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 ??)? 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, the energy states are the same. Following from the property from equation ??, 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 ?? is possible due to ??. The last step (equation ??) follows from that  $\psi$  is normalized (equation ??), the translation of  $\psi$  is still normalized.

Now because of the fact that we have the normalisation (equation ??), 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 ??), 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 ??). 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 ?? 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 (??):

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

## 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 ??, we get ??.

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

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

What we see now is that from ?? and ?? 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 ?? and equation ?? 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:

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

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

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

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 ??) 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 ??, we have energy bands  $E_i$ , these all have all eigenvalues and between the bands we have bandgaps, there there are no eigenvalues. Now there is also a possibility of overlap of the energy bands.

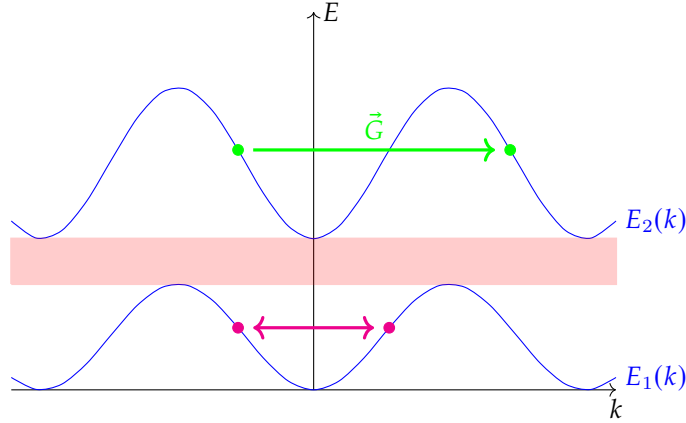


Figure 5.1: Energy band diagram

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 ??). We also notice inversion symmetry, depicted in magenta (section ??).

## 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 ?? gives the wave functions of the Schrödinger equation, the corresponding energies are solutions of the Schrödinger equation, too. Seen in figure ??, 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.

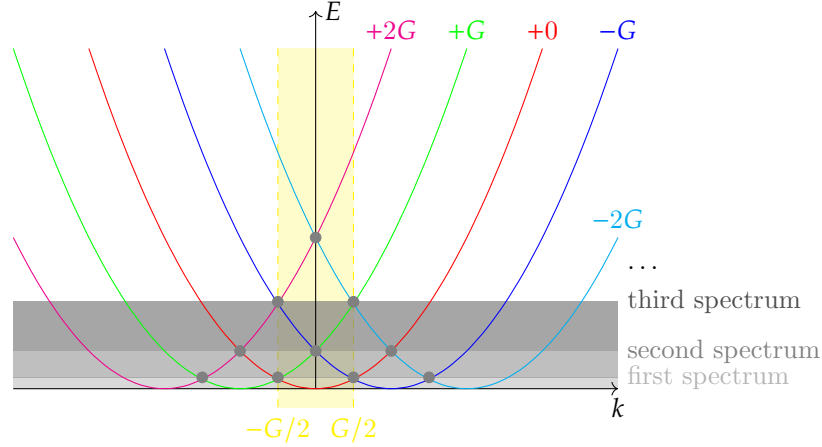


Figure 5.2: Displaced energy bands with different spectra

**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:

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

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:

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

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

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

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



**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:

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

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

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

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

We see a fourier transform in equation ??, 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 ??):

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

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 ??), the  $\delta$ -function is in this case 1). Now we can write equation ?? 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 ??)! 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 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  $\bar{\psi}(\vec{r}) = c_1 \psi_{\vec{k},1} + c_2 \psi_{\vec{k},2}$ , we obtain this solution by diagonalizing the Hamiltonian in the new subspace:

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

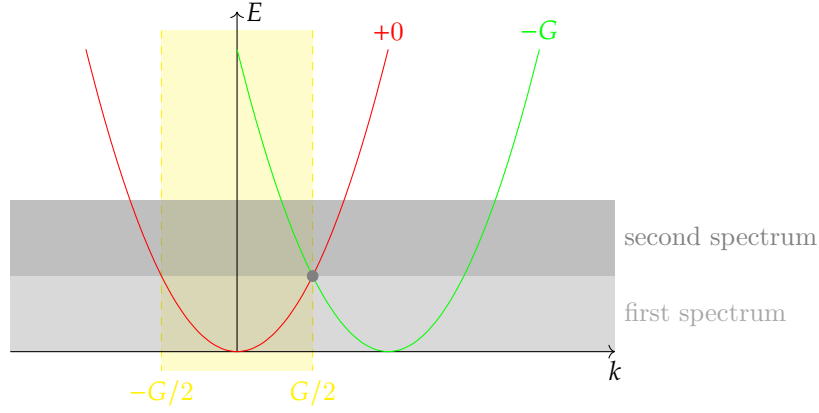


Figure 5.3: The simplified energy diagram

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 ?? by means of a determinant, then we get:

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

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

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 ??, 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 bandgab, taking the bandgap gives into consideration, we get figure ??. This bandgap is of course a forbidden zone for electrons. The size of the bandgap is given by equation ??.

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 ??), 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 ??. Take  $\frac{\pi}{a} = \frac{G}{2}$ , as the Bragg point.

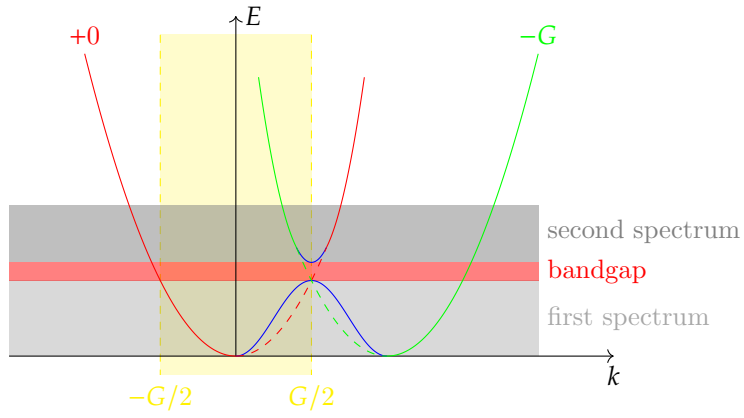


Figure 5.4: The simplified energy diagram with bandgap

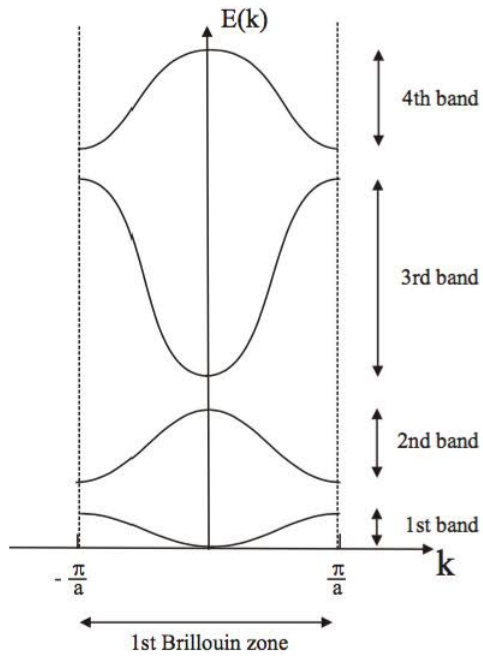


Figure 5.5: Energy band inside the first Brillouin zone

**Example 5.7.1** (1D example)

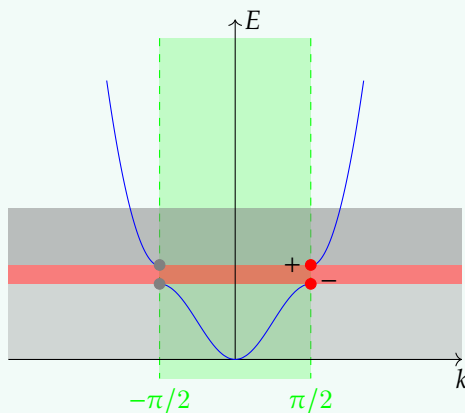
Let us use

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

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 don't 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.



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

## Chapter 7

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