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, lets 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.

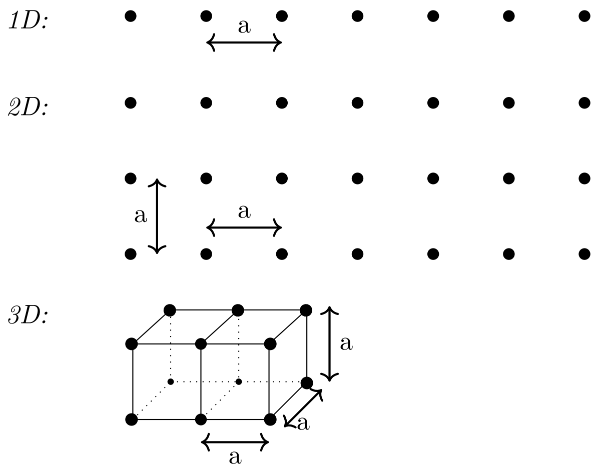

Figure 1.1: Lattices in different dimensions

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 honneycomb 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.

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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:

$$O = \vec{0} \tag{1.1}$$

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

$$\vec{a} = PLV \tag{1.2}$$

$$n_i \in \mathbb{Z} \tag{1.3}$$

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

$$1D: \qquad \vec{R} = n_1 \cdot \vec{a} \tag{1.5}$$

$$2D: \qquad \vec{R} = [n_1, n_2] \cdot A \tag{1.6}$$

$$3D: \qquad \vec{R} = [n_1, n_2, n_3] \cdot A \tag{1.7}$$

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.

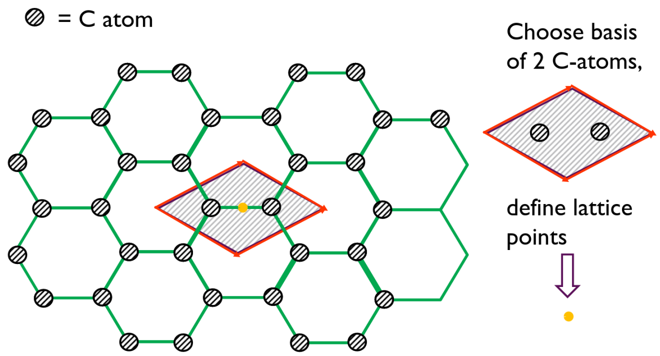


Figure 1.2: The graphene crystal

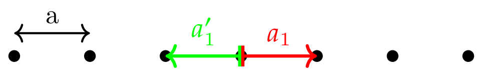


Figure 1.3: An example set of lattice vectors in 1D

1.4 Unit cell

Definition 1.4.1: Unit cell

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

The definition of a unit cell is illustrated in figure 1.5

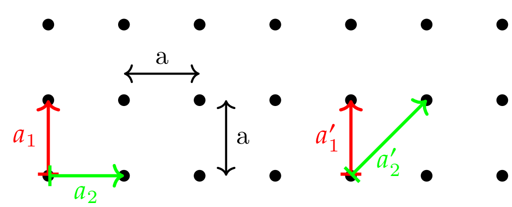


Figure 1.4: An example set of lattice vectors in 2D

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: Convetional unit cell

A convenctional unit cell, a.k.a. a convinient unit cell, is a unit cell that contains mare than 1 lattice point but has perpendicular axis.

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 furhter elaborated below. The correspoding 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 bissecting, perpendicular on this first line (in blue).
4. Do this for all other nearby lattice points (in cyan).

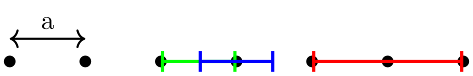


Figure 1.5: Several 1D unit cells

Chapter 2

Periodic Structure of Crystals

2.1 Bravais lattices

Definition 2.1.1: Bravais latticees

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. Orthohombric
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**.

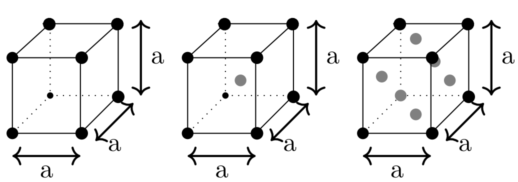


Figure 2.1: The three different cubic lattice systems

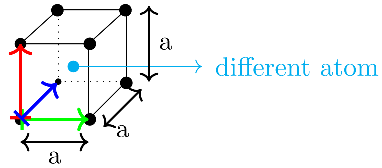


Figure 2.2: The basis for a simple cubic lattice

Definition 2.2.2: Body centered cubic lattice

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

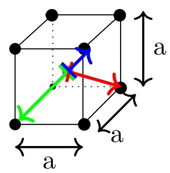


Figure 2.3: The three different cubic lattice systems

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 centere cubic lattice. This is depicted in figure 2.4.

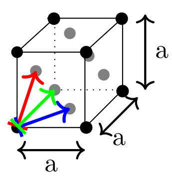


Figure 2.4: The three different cubic lattice systems

2.3 C/Si/Ge - lattice systems

As we know, the lattice systems for C, Si and Ge have a diamond lattice structre. 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:

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

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

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

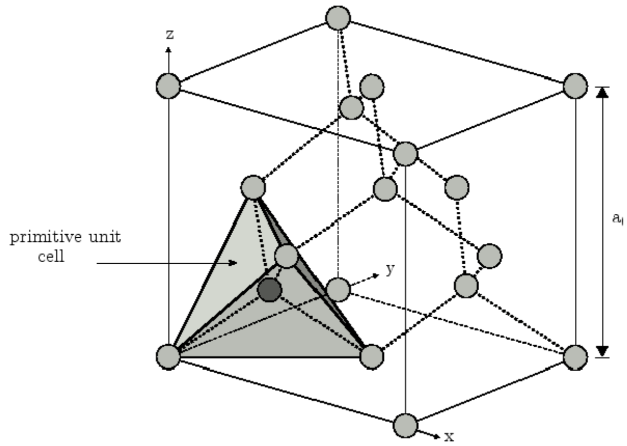


Figure 2.5: The diamond structure and its PUC

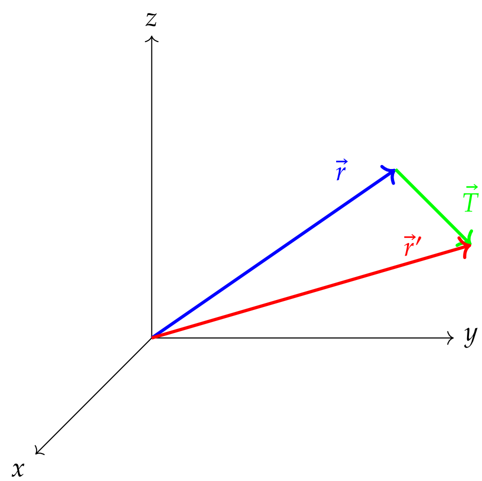


Figure 2.6: Translational symmetry

2.3.1 Translation symmetry

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

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

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

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 2.6.

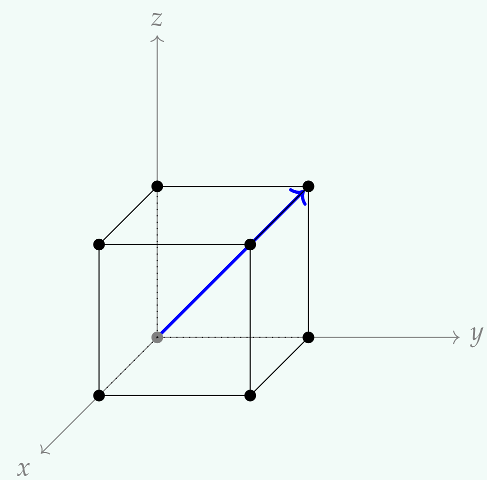
2.4 Lattice dimensions

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 $u, v, w \in \mathbb{Z}_{without\,common\,factor}$.
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 cyrstal see each surrounding lattice point in exactly the same way, therefore symmetry is the same.

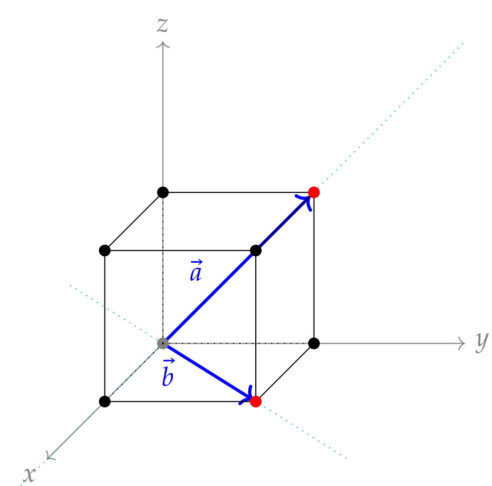


Figure 2.7: Demonstration of vectors with the same symmetry

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 $< u, v, w >$ where $[u, v, w]$ is the dirction 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.

$$h = \frac{1}{n}\gamma \tag{2.6}$$

$$k = \frac{1}{m}\gamma \tag{2.7}$$

$$l = \frac{1}{p}\gamma \tag{2.8}$$

This last step defines a vector perpendicular ont he 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.

$$
\begin{aligned}
f(x) &= f(x + n \cdot a) && (3.1)\\
&= \frac{a_0}{2} + \sum_{n=2}^{\infty} \left\{ a_n \cos \frac{2\pi \cdot nx}{a} + b_n \sin \frac{2\pi \cdot nx}{a} \right\} && (3.2)\\
&= \sum_G F(G) \cdot e^{iGx} && (3.3)
\end{aligned}
$$

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

$$
\begin{aligned}
G &= \frac{2\pi}{a} n && (3.4)\\
G \cdot a &= 2n\pi && (3.5)\\
\Rightarrow e^{iGa} &= e^{2\pi ni} = 1 && (3.6)
\end{aligned}
$$

Note:-

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

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

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

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

Theorem 3.2.1 Property of $F(G)$

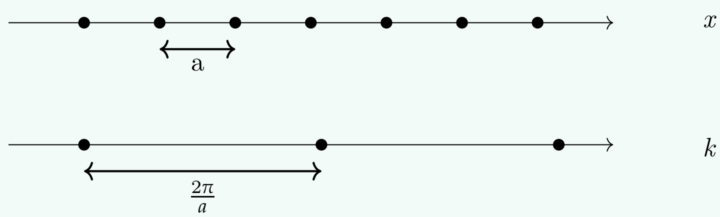
For a real sum: $F(-G) = F^*(G)$

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)

1D:



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 3.2.2

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

$$\Rightarrow e^{i\vec{G}\cdot\vec{T}} = 1 \qquad \forall\vec{T} \tag{3.10}$$

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:

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

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

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

$$e^{i\vec{G}\cdot\vec{T}} = 1 \tag{3.14}$$

■

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:

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

.

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:

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

With

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

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

$$n \longrightarrow \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \tag{3.19}$$

This results in the following definition:

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

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 $\vec{a}_i$:

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

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

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

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

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

3.4 Properties of reciporcal spaces

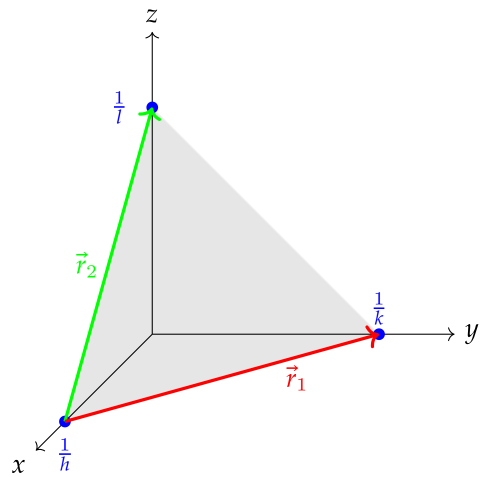
Claim 3.4.1 Property 1

To every lattice plane (h, k, l) there is a reciprocal lattice vector perpendicular to htat 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:

$$\frac{\vec{R}}{\|\vec{R}\|} = \frac{\vec{G}}{\|\vec{G}\|} \tag{3.25}$$

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 perpendiculas 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 definitons, we get:

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

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

$$= C \cdot \vec{G} \tag{3.28}$$

$$\sim \vec{G} \tag{3.29}$$

And thus from

$$\frac{\vec{G}}{\|\vec{G}\|} = \frac{\vec{R}}{\|\vec{R}\|} \tag{3.30}$$

$$= \frac{C \cdot \vec{G}}{\|C \cdot \vec{G}\|} \tag{3.31}$$

$$= \frac{C \cdot \vec{G}}{C \cdot \|\vec{G}\|} = \frac{\vec{G}}{\|\vec{G}\|} \tag{3.32}$$

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

■

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:

$$\frac{2\pi}{\|\vec{G}\|} \tag{3.33}$$

$$\Rightarrow \|\vec{G}\| = \frac{2\pi}{d} \tag{3.34}$$

Proof:

$$
\begin{aligned}
d &= \text{the distance betwee the } (h, k, l) \text{ planes} \\
&= \frac{\vec{a}_1}{h} \cdot \frac{\vec{G}}{\|\vec{G}\|} && (3.35) \\
&= \frac{1}{h\|\vec{G}\|} h\vec{a}_1 \cdot \vec{b}_1 = \frac{2\pi}{\|\vec{G}\|} && (3.36)
\end{aligned}
$$

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:

$$
\begin{aligned}
V_R &= \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) && (3.37) \\
&= \frac{8\pi^3}{V} && (3.38)
\end{aligned}
$$

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

Va laue

3.6 Fermi golder rule

abc

3.6.1 Von Laue-Bragg condition

abc

3.7 Von Laue-Bragg condition

abc

3.8 The Brillaun Zone (BZ)

abc

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:

$$H = H_{electron} + H_{electron-electron} + H_{nucleus} + H_{nucleus-nuclues} + H_{electron-nucleus} \tag{4.1}$$
$$H = H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion} \tag{4.2}$$

The following definitions for the H_i are used:

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

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

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

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

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

Note:-

In equation (1.5) and (1.11) we have $i \neq j$ in order that we do not double count i.
Furthermore, in equation (1.8) and 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:

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

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

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

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

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

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

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

Claim 4.2.1
$\Phi(\vec{r}, \vec{R}) \approx \psi(\vec{r}, \vec{R})\phi(\vec{R})$

$$\begin{aligned}
H\Phi(\vec{r}, \vec{R}) &= H\psi(\vec{r}, \vec{R})\phi(\vec{R}) && (4.14)\\
&= (H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) && (4.15)\\
&= (H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) + (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) && (4.16)\\
&= \phi(\vec{R})(H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R}) + \psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R})\\
&\quad + (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) - \psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R}) && (4.17)
\end{aligned}$$

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:

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

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

We can now define:

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

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

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

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

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

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

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

Note:-

- $\delta\vec{R}_j(t) \cdot \vec{\nabla}_j V_{electrion-ion}(\vec{r}_i - \vec{R}_j^{(0)})$ is the electron - phonon interaction.
- Why does it only depend on distance? In normal curcomstances, most interactions are distance related but sometimes it is (in anisotropic materials) vector dependent, therefore the || 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 signle electron particle operator istead of a complex Hamiltonian.

- $H_{electron}$ stays the same
- $H_{electrion-ion}$ 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:

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

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

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

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

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 continious charge distribution.

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

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

We can calculate the Potential enegery as follows:

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

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

Note:-

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

Now we can solve the one electron problem by:

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

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

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 Conslusion

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

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