Semiconductor Physics Lectures

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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.
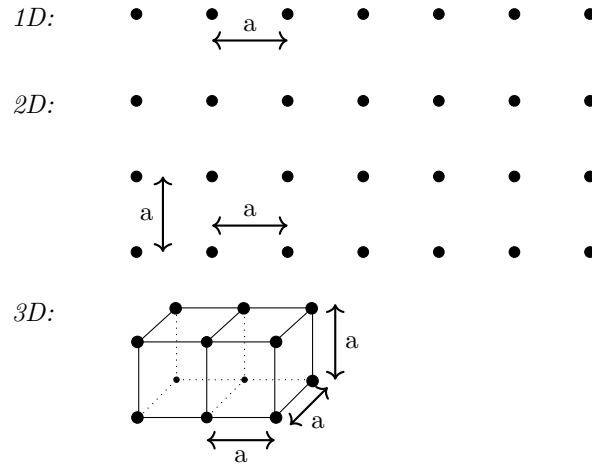
Figure 1.1: Lattices in different dimensions

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.
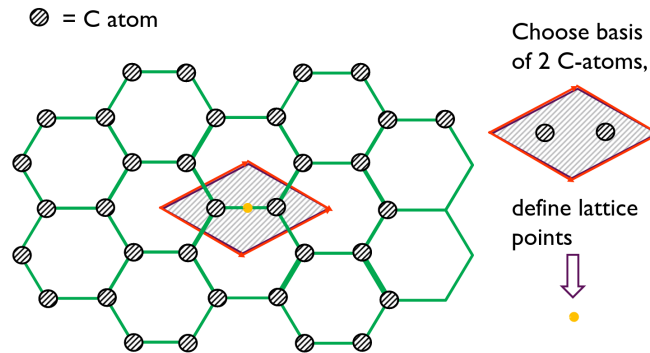

Figure 1.2: The graphene crystal

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:

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

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 *PLV*s are not unique, one can also show that this is true for 3D. These are indeed *PLV*s because one can reach all lattice points.

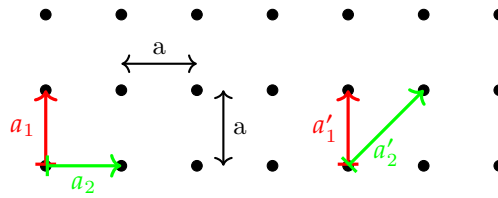Figure 1.3: An example set of lattice vectors in 1D

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 taht when translated through the entire space by means of lattice vecotrs, reproduces the lattice without any overlaps or voids.

This is illustrated in figure 1.5

Figure 1.5: Several 1D unit cells

1.5 Primitive unit cell

b

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

d

Chapter 2

Solids

2.1 Defining solids

Question 1: What is a solid?

Solid = nuclei + electrons

For describing solids we define following concepts:

Definition 2.1.1: Core electrons

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

Definition 2.1.2: 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:

$$H = H_{electron} + H_{electron-electron} + H_{nucleus} + H_{nucleus-nuclues} + H_{electron-nucleus} \tag{2.1}$$

$$H = H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion} \tag{2.2}$$

The following definitions for the H_i are used:

$$H_{electron} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_{electron}} \nabla_i^2 \tag{2.3}$$

$$H_{nucleus} = \sum_{i=1}^{M} -\frac{\hbar^2}{2 * M_i} \nabla_o^2 \tag{2.4}$$

$$H_{electron-electron} = \frac{1}{2} \sum_{i,j;i\neq j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \tag{2.5}$$

$$H_{nucleus-nucleus} = \frac{1}{2} \sum_{i,j;i\neq j} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\vec{R}_i - \vec{R}_j|} \tag{2.6}$$

$$H_{electron-nucleus} = \sum_{i,j} -\frac{Z_j e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_j|} \tag{2.7}$$

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:

$$H_{electron} = \sum_{i=1}^{N'} -\frac{\hbar^2}{2m_{electron}} \nabla_i^2 \tag{2.8}$$

$$H_{ion} = \sum_{i=1}^{M'} -\frac{\hbar^2}{2 * M_i} \nabla_o^2 \tag{2.9}$$

$$H_{electron-electron} = \frac{1}{2} \sum_{i,j;i\neq j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \tag{2.10}$$

$$H_{ion-ion} = \frac{1}{2} \sum_{i,j;i\neq j} V_{ion}(\vec{R}_i - \vec{R}_j) \tag{2.11}$$

$$H_{electron-ion} = \sum_{i,j} V_{electron-ion}(\vec{r}_i - \vec{R}_j) \tag{2.12}$$

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.

2.2 Born-oppenheimer approximation

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

$$H\Phi(\vec{r}, \vec{R}) = E\Phi(\vec{r}, \vec{R}) \tag{2.13}$$

Claim 2.2.1
$\Phi(\vec{r}, \vec{R}) \approx \psi(\vec{r}, \vec{R})\phi(\vec{R})$

$$H\Phi(\vec{r}, \vec{R}) = H\psi(\vec{r}, \vec{R})\phi(\vec{R}) \tag{2.14}$$

$$= (H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) \tag{2.15}$$

$$= (H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) + (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) \tag{2.16}$$

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

$$+ (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) - \psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R}) \tag{2.17}$$

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:

$$\frac{(H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R})}{\psi(\vec{r}, \vec{R})} + \frac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})} = E \qquad (2.18)$$

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

We can now define:

$$E_{el}(\vec{R}) = E - \frac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})} \qquad (2.19)$$

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

> **Definition 2.2.1: Formulation of the solid hamiltonians**
>
> $$\begin{cases} (H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R}) = E_{el}\psi(\vec{r}, \vec{R}) \\ \dfrac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})}\psi(\vec{r}, \vec{R}) = (E - E_{el})\psi(\vec{r}, \vec{R}) \end{cases} \qquad (2.20)$$

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

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

$$H_{electron-ion} = \sum V_{electron-ion}(\vec{r}_i - \vec{R}_j) \qquad (2.21)$$
$$= \sum (V_{electrion-ion}(\vec{r}_i - \vec{R}_j^{(0)}) + \delta\vec{R}_j(t) \cdot \vec{\nabla}_j V_{electron-ion}(\vec{r}_i - \vec{R}_j^{(0)})) \qquad (2.22)$$

> **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:

$$\sum_i \left\{ -\frac{\hbar^2}{2m_{electron}}\nabla_i^2 + \sum_j \left\{ V_{electron-ion}(\vec{r}_i - \vec{R}_j) + v_i(\vec{r}_i) \right\} \right\}\psi(\vec{r}, \vec{R}) = E_{el}\psi(\vec{r}, \vec{R}) \qquad (2.23)$$

$$\Rightarrow \sum h_i(\vec{r}_i)\psi(\vec{r}) = E_{el}\psi(\vec{r}) \qquad (2.24)$$

$$\longrightarrow \psi(\vec{r}) = \xi(\vec{r}_1) + \xi(\vec{r}_2) + \dots \qquad (2.25)$$

$$\Rightarrow h_i(r_i)\xi(\vec{r}_i) = \epsilon_i \xi(\vec{r}_i) \qquad (2.26)$$

2.4 Hartree approximation

Question 2: 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.

$$g_i(\vec{r}) = \sum_{k \neq i} -e|\xi_k(\vec{r})|^2 \tag{2.27}$$

$$\longrightarrow \nabla^2 \Phi_i(\vec{r}) = \frac{g_i(\vec{r})}{\epsilon} \tag{2.28}$$

We can calculate the Potential enegery as follows:

$$v_i(\vec{r}) = -e\Phi \tag{2.29}$$

$$= \sum_{k \neq i} \int_V \frac{e^2|\xi_k(\vec{r})|^2}{4\pi\epsilon_0|\vec{r} - \vec{r'}|} dr' \tag{2.30}$$

Note:-

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

Now we can solve the one electron problem by:

$$h(\vec{r})\xi(\vec{r}) = \epsilon\xi(\vec{r}) \tag{2.31}$$

$$\Rightarrow \quad h(\vec{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + v(\vec{r}) + \sum V_{electron-ion}(\vec{r} - \vec{R}) \tag{2.32}$$

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 2.4.1 Conslusion

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

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V(\vec{r})\right)\xi(\vec{r}_i) = \epsilon\xi(\vec{r}_i) \tag{2.33}$$