Semiconductor Physics Lectures

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Chapter 1

Solids

1.1 Defining solids

Question 1: What is a solid?

Solid = nuclei + electrons

For describing solids we define following concepts:

Definition 1.1.1: Core electrons

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

Definition 1.1.2: 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:

$$H = H_{electron} + H_{electron-electron} + H_{nucleus} + H_{nucleus-nuclues} + H_{electron-nucleus} \tag{1.1}$$

$$H = H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion} \tag{1.2}$$

The following definitions for the H_i are used:

$$H_{electron} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_{electron}}\nabla_i^2 \tag{1.3}$$

$$H_{nucleus} = \sum_{i=1}^{M} -\frac{\hbar^2}{2*M_i}\nabla_o^2 \tag{1.4}$$

$$H_{electron-electron} = \frac{1}{2}\sum_{i,j;i\neq j} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} \tag{1.5}$$

$$H_{nucleus-nucleus} = \frac{1}{2}\sum_{i,j;i\neq j} \frac{Z_iZ_je^2}{4\pi\epsilon_0|\vec{R}_i - \vec{R}_j|} \tag{1.6}$$

$$H_{electron-nucleus} = \sum_{i,j} -\frac{Z_je^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_j|} \tag{1.7}$$

> **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:

$$H_{electron} = \sum_{i=1}^{N'} -\frac{\hbar^2}{2m_{electron}}\nabla_i^2 \tag{1.8}$$

$$H_{ion} = \sum_{i=1}^{M'} -\frac{\hbar^2}{2*M_i}\nabla_o^2 \tag{1.9}$$

$$H_{electron-electron} = \frac{1}{2}\sum_{i,j;i\neq j}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} \tag{1.10}$$

$$H_{ion-ion} = \frac{1}{2}\sum_{i,j;i\neq j} V_{ion}(\vec{R}_i - \vec{R}_j) \tag{1.11}$$

$$H_{electron-ion} = \sum_{i,j} V_{electron-ion}(\vec{r}_i - \vec{R}_j) \tag{1.12}$$

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.

1.2   Born-oppenheimer approximation

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

$$H\Phi(\vec{r}, \vec{R}) = E\Phi(\vec{r}, \vec{R}) \tag{1.13}$$

> **Claim 1.2.1**
> $\Phi(\vec{r}, \vec{R}) \approx \psi(\vec{r}, \vec{R})\phi(\vec{R})$

$$H\Phi(\vec{r}, \vec{R}) = H\psi(\vec{r}, \vec{R})\phi(\vec{R}) \tag{1.14}$$

$$= (H_{electron} + H_{electron-electron} + H_{ion} + H_{ion-ion} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) \tag{1.15}$$

$$= (H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) + (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) \tag{1.16}$$

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

$$+ (H_{ion} + H_{ion-ion})\psi(\vec{r}, \vec{R})\phi(\vec{R}) - \psi(\vec{r}, \vec{R})(H_{ion} + H_{ion-ion})\phi(\vec{R}) \tag{1.17}$$

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:

$$\frac{(H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R})}{\psi(\vec{r}, \vec{R})} + \frac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})} = E \qquad (1.18)$$

Note:-

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

We can now define:

$$E_{el}(\vec{R}) = E - \frac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})} \qquad (1.19)$$

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

Definition 1.2.1: Formulation of the solid hamiltonians

$$\begin{cases} (H_{electron} + H_{electron-electron} + H_{electron-ion})\psi(\vec{r}, \vec{R}) = E_{el}\psi(\vec{r}, \vec{R}) \\ \dfrac{(H_{ion} + H_{ion-ion})\phi(\vec{R})}{\phi(\vec{R})}\psi(\vec{r}, \vec{R}) = (E - E_{el})\psi(\vec{r}, \vec{R}) \end{cases} \qquad (1.20)$$

1.3 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.

$$H_{electron-ion} = \sum V_{electron-ion}(\vec{r}_i - \vec{R}_j) \qquad (1.21)$$

$$= \sum (V_{electrion-ion}(\vec{r}_i - \vec{R}_j^{(0)}) + \delta\vec{R}_j(t) \cdot \vec{\nabla}_j V_{electrion-ion}(\vec{r}_i - \vec{R}_j^{(0)})) \qquad (1.22)$$

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:

$$\sum_i \left\{ -\frac{\hbar^2}{2m_{electron}}\nabla_i^2 + \sum_j \left\{ V_{electron-ion}(\vec{r}_i - \vec{R}_j) + v_i(\vec{r}_i) \right\} \right\}\psi(\vec{r}, \vec{R}) = E_{el}\psi(\vec{r}, \vec{R}) \qquad (1.23)$$

$$\Rightarrow \sum h_i(\vec{r}_i)\psi(\vec{r}) = E_{el}\psi(\vec{r}) \qquad (1.24)$$

$$\longrightarrow \psi(\vec{r}) = \xi(\vec{r}_1) + \xi(\vec{r}_2) + \dots \qquad (1.25)$$

$$\Rightarrow h_i(r_i)\xi(\vec{r}_i) = \epsilon_i\xi(\vec{r}_i) \qquad (1.26)$$

1.4 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 continuous charge distribution.

$$g_i(\vec{r}) = \sum_{k \neq i} -e|\xi_k(\vec{r})|^2 \tag{1.27}$$

$$\longrightarrow \nabla^2 \Phi_i(\vec{r}) = \frac{g_i(\vec{r})}{\epsilon} \tag{1.28}$$

We can calculate the Potential enegery as follows:

$$v_i(\vec{r}) = -e\Phi \tag{1.29}$$

$$= \sum_{k \neq i} \int_V \frac{e^2|\xi_k(\vec{r})|^2}{4\pi\epsilon_0|\vec{r} - \vec{r}'|} dr' \tag{1.30}$$

Note:-

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

Now we can solve the one electron problem by:

$$h(\vec{r})\xi(\vec{r}) = \epsilon\xi(\vec{r}) \tag{1.31}$$

$$\Rightarrow \quad h(\vec{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + v(\vec{r}) + \sum V_{electron-ion}(\vec{r} - \vec{R}) \tag{1.32}$$

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 1.4.1 Conslusion

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

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V(\vec{r})\right)\xi(\vec{r}_i) = \epsilon\xi(\vec{r}_i) \tag{1.33}$$