

## Lecture 13

### Band Diagrams

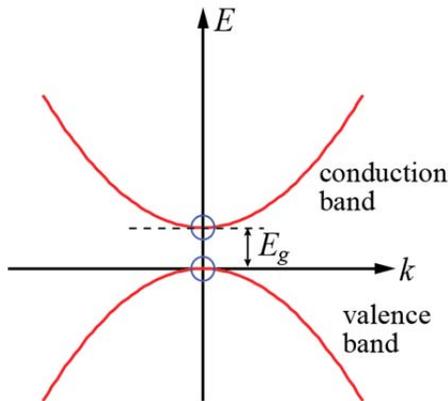
#### Today:

1. Analytical expression for bandgaps
2. Group velocity, density of states
3. Counting the number of states per band: periodic boundary  $\square$  conditions

#### Questions you should be able to answer by the end of today's lecture:

1. How is the group velocity calculated from the Bloch waveform and from the band diagram?
2. How does the group velocity change from mid-band to band edge?
3. How is the effective mass found from the band diagram?
4. How to derive an approximate expression for the effective mass of the  $\square$  electrons and holes?
5. What are periodic boundary conditions?
6. How periodic boundary conditions they lead to discretization of the Bloch wave vector?
7. How many states exist per band?

## What information can we get from the band diagrams?



1. Allowed and forbidden bands.  
Identification of the gap energy.
2. Slope of the bands – group velocity.
3. Curvature of bands – effective mass.

1. **Magnitude of the band gaps:** Larger atoms  $\Rightarrow$  smaller potential  $\Rightarrow$  smaller bandgap.

### 2. Group velocity

Let's examine the form of the energy eigenfunctions:

$$\begin{aligned}
 u_{k,E_{k,n}}(x) &= \dots C_{k-2g} e^{i(k-2g)x} + C_{k-g} e^{i(k-g)x} + C_k e^{ikx} + C_{k+g} e^{i(k+g)x} + C_{k+2g} e^{i(k+2g)x} + \dots \\
 &= \sum_G C_{k-G} e^{i(k-G)x} = e^{ikx} \underbrace{\sum_G C_{k-G} e^{-iGx}}_{f_k(x)}
 \end{aligned}$$

Clearly the energy eigenfunction is not a momentum eigenfunction, which is not surprising as the momentum is not a constant of motion in the periodic potential system:  $[\hat{p}, \hat{H}_{crystal}] \neq 0$

Does an energy eigenfunction (Bloch wave) have an average momentum?

If we were to conduct a momentum measurement we would get any one of the  $\hbar(k-G)$  momentum values (momentum eigenvalues) with a probability of  $|C_{k-G}|^2$ . Therefore we can assign an average value to the momentum of a Bloch state, which is simply:

$$\begin{aligned}
 \langle p_{n,k} \rangle &= \langle u_{n,k}(x) | \hat{p} | u_{n,k}(x) \rangle = \int_{-\infty}^{\infty} u_{n,k}^*(x) \left( -i\hbar \frac{\partial}{\partial x} u_{n,k}(x) \right) dx = \\
 &= \dots + |C_{k-2g}|^2 \hbar(k-2g) + |C_{k-g}|^2 \hbar(k-g) + |C_k|^2 \hbar k + |C_{k+g}|^2 \hbar(k+g) + |C_{k+2g}|^2 \hbar(k+2g) + \dots = \\
 &= \sum_G |C_{k-G}|^2 \hbar(k-G)
 \end{aligned}$$

It turns out that one can show that the average momentum per eigenfunction can be derived directly from the band diagram:

$$\frac{\langle p_{n,k} \rangle}{m} = v_g = \frac{1}{\hbar} \frac{\partial E_n}{\partial k}$$

**Definition – group velocity:**  $\vec{v}_g = \frac{1}{\hbar} \vec{\nabla}_k E_n$

Away from the band edges the electron has a finite and nonzero group velocity as the band edge is approached the group velocity decreases until it is equal to zero. This means that electrons that have Bloch wave eigenfunctions are moving with a constant velocity (in the absence of fields) – a very surprising result given that they are moving in the presence of ions which they could collide with.

### 3. Effective mass

Near the band edge the bands can be expanded in terms of Taylor series:

$$E_{v,c}(k) \approx E_{v,c}(0) + \frac{1}{1!} \frac{\partial E_{v,c}}{\partial k}(0)k + \frac{1}{2!} \frac{\partial^2 E_{v,c}}{\partial k^2}(0)k^2 + \dots, \quad \frac{\partial E_{v,c}}{\partial k}(0) = 0$$

$$E_v(k) = -\frac{1}{2} \frac{\partial^2 E_v}{\partial k^2}(0)k^2$$

$$E_c(k) = E_g + \frac{1}{2} \frac{\partial^2 E_c}{\partial k^2}(0)k^2$$

- Then we can define effective mass as:

$$\frac{1}{m_{v,c}^*} = \frac{1}{\hbar^2} \frac{\partial^2 E_{v,c}}{\partial k^2}$$

- Charge carriers can have larger or smaller effective masses than the mass of an electron depending on the curvature of the bands. For the simple case above we can then write:

$$E_v(k) = -\frac{\hbar^2 k^2}{2m_v^*}$$

$$E_c(k) = E_g + \frac{\hbar^2 k^2}{2m_c^*}$$

The masses  $m_{v,c}^*$  are referred to as electron effective mass  $m_c^* = m_e^*$  and hole effective mass  $m_v^* = m_h^*$ .

**Then the band structure near the band edge can be described by two parameters: the band gap  $E_g$  and the effective masses  $m_{e,h}^*$  of the hole and electron.**

Keep in mind that the exact shape of the curve needs to be calculated by solving the Hamiltonian eigenvalue equation taking the exact form of the potential into account.

### Relation of the effective mass to the magnitude of the bandgap:

Let's take another look at the 2X2 matrix determinant equation that we've used to derive the bandgap:

$$\begin{vmatrix} \frac{\hbar^2}{2m}k^2 - E & V \\ V & \frac{\hbar^2}{2m}(k-g)^2 - E \end{vmatrix} = 0$$

Remember, that we have shifted our  $k$  to have the band edge at zero:  $k \rightarrow k + \frac{g}{2}$ , then:

$$\begin{vmatrix} \frac{\hbar^2}{2m}\left(k + \frac{g}{2}\right)^2 - E & V \\ V & \frac{\hbar^2}{2m}\left(k - \frac{g}{2}\right)^2 - E \end{vmatrix} = 0 \Rightarrow \left(\frac{\hbar^2}{2m}\left(k + \frac{g}{2}\right)^2 - E\right)\left(\frac{\hbar^2}{2m}\left(k - \frac{g}{2}\right)^2 - E\right) - V^2 = 0$$

$$E^2 - \left(\frac{\hbar^2}{2m}\left(k + \frac{g}{2}\right)^2 + \frac{\hbar^2}{2m}\left(k - \frac{g}{2}\right)^2\right)E + \left(\frac{\hbar^2}{2m}\right)^2\left(k^2 - \left(\frac{g}{2}\right)^2\right)^2 - V^2 = 0$$

$$E^2 - 2\frac{\hbar^2}{2m}\left(k^2 + \left(\frac{g}{2}\right)^2\right)E + \left(\frac{\hbar^2}{2m}\right)^2\left(k^2 - \left(\frac{g}{2}\right)^2\right)^2 - V^2 = 0$$

Solving a quadratic equation we find:

$$E_{\pm} = \frac{\hbar^2}{2m}\left(k^2 + \left(\frac{g}{2}\right)^2\right) \pm \sqrt{\left(\frac{\hbar^2}{2m}\right)^2\left(k^2 + \left(\frac{g}{2}\right)^2\right)^2 - \left(\frac{\hbar^2}{2m}\right)^2\left(k^2 - \left(\frac{g}{2}\right)^2\right)^2 + V^2}$$

$$E_{\pm} = \frac{\hbar^2}{2m}\left(k^2 + \left(\frac{g}{2}\right)^2\right) \pm \sqrt{4\left(\frac{\hbar^2}{2m}\right)^2 k^2 \left(\frac{g}{2}\right)^2 + V^2} = \frac{\hbar^2}{2m}\left(k^2 + \left(\frac{g}{2}\right)^2\right) \pm V \sqrt{\frac{4}{V^2}\left(\frac{\hbar^2}{2m}\right)^2 k^2 \left(\frac{g}{2}\right)^2 + 1}$$

If we assume that:  $\frac{4}{V^2}\left(\frac{\hbar^2}{2m}\right)^2 k^2 \left(\frac{g}{2}\right)^2 \ll 1$ , then we can use Taylor series to expand the square root:

$$E_{\pm} = \frac{\hbar^2}{2m} \left( k^2 + \left( \frac{g}{2} \right)^2 \right) \pm V \sqrt{ \frac{4}{V^2} \left( \frac{\hbar^2}{2m} \right)^2 k^2 \left( \frac{g}{2} \right)^2 + 1 } \approx \frac{\hbar^2}{2m} \left( k^2 + \left( \frac{g}{2} \right)^2 \right) \pm V \left( 1 + \frac{1}{2} \frac{4}{V^2} \left( \frac{\hbar^2}{2m} \right)^2 k^2 \left( \frac{g}{2} \right)^2 \right) =$$

$$E_{\pm} \approx \frac{\hbar^2}{2m} \left( k^2 + \left( \frac{g}{2} \right)^2 \right) \pm V \pm \frac{2}{V} \left( \frac{\hbar^2}{2m} \right)^2 k^2 \left( \frac{g}{2} \right)^2 = \frac{\hbar^2}{2m} \left( 1 \pm \frac{2}{V} \frac{\hbar^2}{2m} \left( \frac{g}{2} \right)^2 \right) k^2 + \frac{\hbar^2}{2m} \left( \frac{g}{2} \right)^2 \pm V$$

$$E_{\pm} \approx \frac{\hbar^2}{2m} \left( 1 \pm \frac{2\lambda}{V} \right) k^2 + \lambda \pm V, \quad \lambda = \frac{\hbar^2}{2m} \left( \frac{g}{2} \right)^2$$

Here  $\lambda$  represents the kinetic energy of a free electron having a wavefunction corresponding to the edge of the Brillouin zone.

Then we can find the effective masses for the hole and electron:

$$\frac{1}{m_e^*} = \frac{1}{m_+} = \frac{1}{m} \left( 1 + \frac{2\lambda}{V} \right) \Rightarrow \frac{m_e^*}{m} = \frac{1}{1 + 2\lambda/V}$$

$$\frac{1}{m_h^*} = \frac{1}{m_-} = \frac{1}{m} \left( 1 - \frac{2\lambda}{V} \right) \Rightarrow \frac{m_h^*}{m} = \frac{1}{1 - 2\lambda/V}$$

As you can see the holes are heavier than electrons.

### Comments:

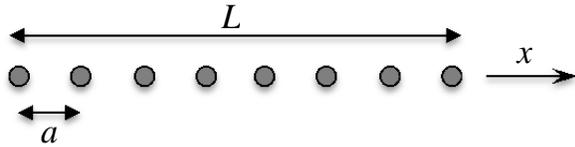
1. The ratio  $\lambda/V$  is approximately equal to the bandwidth divided by the band gap, which can be as large as 10.
2. The effective mass scales with bandgap - small potential small band gap and effective mass.
3. Prediction that holes are heavier than electrons is reflected in the data.

### Effective masses of electrons and holes in direct gap semiconductors

Crystal	Electron $m_e/m$	Heavy hole $m_{hh}/m$	Light hole $m_{lh}/m$	Split-off hole $m_{soh}/m$	Spin-orbit $\Delta, \text{ eV}$
InSb	0.015	0.39	0.021	(0.11)	0.82
InAs	0.026	0.41	0.025	0.08	0.43
InP	0.073	0.4	(0.078)	(0.15)	0.11
GaSb	0.047	0.3	0.06	(0.14)	0.80
GaAs	0.066	0.5	0.082	0.17	0.34
Cu <sub>2</sub> O	0.99	-	0.58	0.69	0.13

**Counting states in a finite crystal via periodic (Born - Von Karman) boundary conditions.**

Consider the following finite 1D crystal:

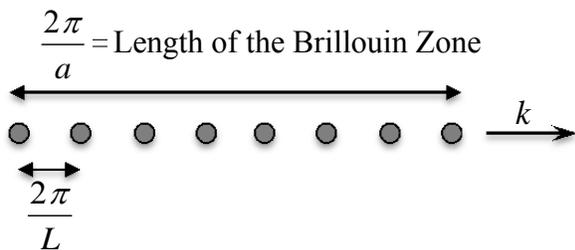


As we saw previously an alternative statement of Bloch's theorem is:  $u_k(x+R) = e^{ikR} u_k(x)$

Let us now consider a specific boundary condition of the form:  $u_k(x+L) = u_k(x)$

Combining the Bloch theorem with the boundary condition yields:  $e^{ikL} = 1 \Rightarrow k = \frac{2\pi}{L} n$

This implies a discretization of  $k$  and enables us to count the number of states:



As you remember the length of the 1D Brillouin zone is:  $k_{\max} - k_{\min} = \frac{\pi}{a} - \left(-\frac{\pi}{a}\right) = \frac{2\pi}{a}$ ,

where  $a$  is a lattice period.

Hence the number of states is:  $2 \cdot \frac{2\pi/a}{2\pi/L} = 2 \cdot \frac{L}{a} = 2 \times \text{number of unit cells}$

Where does the 2 come from? - Spin!

There are approximately  $10^{22}$  unit cells in a cubic centimeter of material, which is also a number of states.

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