## 9. Electrons in Semiconductors
M: - nothing
B&S: p199 – 201
K&K: p353 – 372
H&H: chapters 4.1, 4.2, 5.2, 5.3

### 9.1 Nearly Free Electrons – Energy Bands
Consider a 1D solid. Have a potential $\phi = V$ keeping the electrons confined within an area of length $L$, potential $\phi$.
**(9.1-1)**
Free electron potential: the potential V confines the electrons in the box.

### True potential
**(9.1-2)**
Periodic potential: $V(x) = V(x+a)$

Weak between the ions. The potential can be considered to be weak – only has a big effect on electrons of a particular set of wavelengths – those which satisfy the Bragg Scattering condition.
$$2d\sin\theta = n\lambda$$
For us, $d = a$ and $\theta = 90°$.
**(9.1-3)**
$2a = n\lambda$ → condition for constructive interference.
$\lambda = \dfrac{2a}{n}$, $n = 1, 2, 3,...$ for Bragg diffraction.

The incident wave plus the Bragg reflected wave gives rise to a standing wave.
Incoming wave: $e^{-ikx}$
Reflected wave: $e^{ikx}$
$e^{-ikx} \pm e^{ikx} \rightarrow \cos kx$ or $\sin kx$.
$\lambda = \dfrac{2a}{n}$; $k = \dfrac{2\pi}{\lambda} = \dfrac{n\pi}{a}$, $n = \pm 1, \div 2,...$

For free electrons, the energy $E = \dfrac{\hbar^2 k^2}{2m}$ → dispersion curve for free electrons.

**(9.1-4)**

So the parabola is broken up into different energy bands. Between $-\dfrac{\pi}{a}$ and $\dfrac{\pi}{a}$ is the first energy band. It is separated from the second energy band by a band gap $E_G = E_B - E_A$, where A and B denote the lower and higher energy levels respectively of the jump in the curve.

The effect of the periodic potential is small, except for $k \approx \dfrac{n\pi}{a}$.

Reason for the band gap at $k = \dfrac{\pi}{a}$: $\lambda = 2a$.

**(9.1-5)**
If we look at $\psi_A$, then there is a high probability that the electrons will be near the ion core. This is a low energy state. $\psi_B$, on the other hand, has a high probability of the electrons being in between the ions, which is a high energy state.

Two important comments:

1. Because states at A and B are standing waves, their group velocity is 0.
$$v_g = \frac{d\omega}{dk} = 0 = \frac{1}{\hbar}\frac{d(\hbar\omega)}{dk} = \frac{1}{\hbar}\frac{d\varepsilon}{dk} = 0$$
   Therefore $e(k)$ must have zero slope at A and B.

2. Each energy band contains $2N$ states ($N$ = number of atoms)
   The number of states = the volume of K-space in each band
$$= \frac{\frac{2\pi}{a}}{\frac{2\pi}{L}} \times 2 = \frac{2L}{a} = 2N$$
   where 2 is the spin degeneracy. $\frac{2\pi}{a} = \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk$. $\frac{2\pi}{L}$ is the spacing of states in k-space.

## 9.2 Metals, Insulators and Semiconductors
Consider $T = 0$.
a) Monovalent Materials → N electrons
**(9.2-1)**
The first band is ½ full.
Each band can contain up to $2N$ electrons. N electrons have to be put into the band for a Monovalent material. Electrons at $\varepsilon_f$ have empty states nearby in energy, therefore can create an electric current.

   a) Monovalent material
   More electrons traveling to the right than to the left → current . Therefore Monovalent atom → metallic solid.
   b) Divalent material → 2N electrons
   First band – valence band – completely full. Most energetic electrons are in states most affected by lattice (ion core) potential, therefore very non-free-electron-like.
   No nearby energy states to move into. Therefore no conduction. Therefore insulator. (but divalent metals do exist, e.g. Mg – need to think in 3D to explain how this happens → overlapping bands.)
   c) Trivalent material → $3N$ electrons.
   Actually fill first band and half, not 2 ½ bands.
   1 - ½ bands full → metal.
   In a pure semiconductor at $T = 0$ has a completely full band (the valence band). The next band above is completely empty. Therefore at $T = 0$ it is an insulator. However the band gap $E_G$ is sufficiently small to allow thermal excitation of electrons from the KB to the CB at finite T. e.g. Silica
   $E_G = 0.6eV$. At room temperature, $\sim \frac{1}{40} eV$.

## 9.3 Pure (Intrinsic) Semiconductor
$$\varepsilon = E_G + \frac{\hbar^2}{2m_e}(k - k_0)^2$$

valid near minimum of conduction band because $\dfrac{d\varepsilon}{dk} = 0$ .

$\varepsilon = -\dfrac{\hbar}{2m_k}\left(k - k_0\right)^2$  - valid near max of VB.

Conventional to shift zero of energy to top of the VB.

NB: $m_e$ and $m_k$ are determined by the band structure – can be very different to bare electron mass.

## 9.3.1 Density of States for Electrons and Holes

NB:

Band width: few eV

Band gaps: ~ 1eV

$k_B T$ at room temp $\sim \dfrac{1}{40}\, eV$

Usually only interested in states within $k_B T$ of band edge, therefore above dispersion relations adequate.

Below 0:

$$\dfrac{V}{2\pi^2}\left(\dfrac{2m_k}{\hbar^2}\right)^{3/2}\left(-\varepsilon\right)^{1/2}$$

Above $E_G$ :

$$\dfrac{V}{2\pi^2}\left(\dfrac{2m_e}{\hbar^2}\right)^{3/2}\left(\varepsilon - E_G\right)^{1/2}$$

Proof: suppose min. of CB occurs at $\underline{k} = \underline{k_0}$ .

Draw a spherical shell radius $\underline{k'}$ thickness $\underline{dk}$ centered on $\underline{k_0}$ .

Contain $V\dfrac{k'^2}{2\pi^2}dk'$ states.

These states have energy $\varepsilon \rightarrow \varepsilon + d\varepsilon$ where $\varepsilon = E_G + \dfrac{\hbar^2}{2m_e}\left(\underline{k} - \underline{k_0}\right)^2 = \left(E_G + \dfrac{\hbar^2 k'^2}{2m_e}\right)$

$d\varepsilon = \dfrac{2}{2m_e}\hbar^2 k' dk'$

Number of electron states between $\varepsilon$ and $\varepsilon + d\varepsilon$ :

$$= 2\dfrac{V}{2\pi^2}k'k'dk'$$

where the first 2 comes from spin degeneracy.

$$= 2\dfrac{V}{2\pi^2}\left[\left(\varepsilon - \varepsilon_G\right)\dfrac{2m_e}{\hbar^2}\right]^{1/2} m_e \dfrac{d\varepsilon}{\hbar^2}$$

$$= \dfrac{V}{2\pi^2}\left(\dfrac{2m_e}{\hbar^2}\right)^{3/2}\left(\varepsilon - E_G\right)^{1/2} d\varepsilon$$

→ similar arguament for VB. $\varepsilon = -\dfrac{\hbar^2 k'^2}{2m_k}$

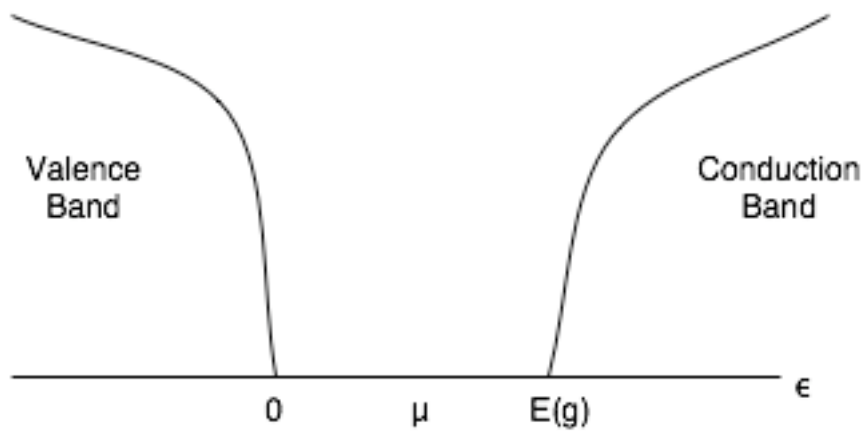$$\rightarrow \frac{V}{2\pi^2}\left(\frac{2m_k}{\hbar^2}\right)^{3/2}(-\varepsilon)^{-1/2}d\varepsilon$$

NB: the minimum of the CB and the max of the VB need not be at the same point in k-space. If they are → direct band-gap semiconductor. If they are not → indirect band-gap semiconductor.

## 9.3.2 Number of Electrons in the Conduction Band

The average number of electrons in a state of energy $\varepsilon$ when we have the chemical potential $\mu$ is:

$$\varepsilon = f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)\beta}+1}$$

$g(\varepsilon)$:



The number of electrons in the conduction band / volume:

$$n = \frac{1}{V}\int_{E_G}^{\infty}f(\varepsilon)g(\varepsilon)d\varepsilon = \frac{1}{V}\int_{E_G}^{\infty}\frac{1}{e^{(\varepsilon-\mu)\beta}+1}\frac{V}{2\pi^2}\left[\frac{2m_e}{\hbar^2}\right]^{3/2}(\varepsilon-E_G)^{1/2}d\varepsilon$$

Remember that $m_e$ is the effective mass of the electron.

Usually $(\varepsilon-\mu)\beta \gg 1$, i.e. small number of electrons in the conduction band. Then:

$$\frac{1}{e^{(\varepsilon-\mu)\beta}+1} \approx e^{-(\varepsilon-\mu)\beta}$$

This is the classical Boltzmann Distribution. The electrons in the conduction band of a semi-conductor often behave like a classic gas of particles of mass $m_e$.

$$n = \frac{1}{2\pi^2}\left[\frac{2m_e}{\hbar^2}\right]^{3/2}e^{\mu\beta}\int_{E_G}^{\infty}e^{-\varepsilon\beta}(\varepsilon-E_G)^{1/2}d\varepsilon$$

Substitute:

$$\varepsilon - E_G\beta = x^2$$

$$d\varepsilon = \frac{2x}{\beta}dx$$

$$n = \frac{1}{2\pi^2}\left[\frac{2m_e}{\hbar^2}\right]^{3/2}e^{\mu\beta}e^{-E_G\beta}\left(\frac{1}{\beta}\right)^{3/2}\times 2\underbrace{\int_{0}^{\infty}e^{-x^2}x^2dx}_{\frac{1}{4}\pi^{1/2}}$$

$$= N_c e^{(\mu-E_G)\beta}$$

where $N_c = 2\left(\dfrac{2\pi m_e}{\beta h^2}\right)^{3/2} = \dfrac{2}{\lambda_{T_e}{}^3}$

$\lambda_{T_e}$ is the thermal de Broglie wavelength for the electrons.

$e^{-(E_G - \mu)\beta}$ is the Boltzmann factor for $\varepsilon = E_G$

$N_c$ is the effective number of states for electrons in the conduction band if all the electrons are at the band-edge.

Above calculation does not make any assumptions about the purity of the semiconductor. It is valid also for doped semiconductors.

### 9.3.3 Number of Empty States (holes) in the Valence band

The number of holes in the state of energy $\varepsilon$ is

$$1 - f(\varepsilon) = 1 - \frac{1}{e^{(\varepsilon - \mu)\beta} + 1} = \frac{e^{(\varepsilon - \mu)\beta}}{e^{(\varepsilon - \mu)\beta} + 1} = \frac{1}{1 + e^{(\mu - \varepsilon)\beta}}$$

Therefore the total number of holes / volume:

$$p = \frac{1}{V}\int_{-\infty}^{0}\left(1 - f(\varepsilon)\right)g(\varepsilon)d\varepsilon$$

The lower limit does not matter as $1 - f(\varepsilon) \to 0$ cuts off the integral.

Usually $(\mu - \varepsilon)\beta \gg 1$ → small number of holes in the valence band.

Then $\dfrac{1}{1 + e^{(\mu - \varepsilon)\beta}} \approx e^{-(\mu - \varepsilon)\beta}$

$$1 = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} e^{-\mu\beta} \int_{-\infty}^{0} e^{\varepsilon\beta}(-\varepsilon)^{1/2}\, d\varepsilon$$

where $m_h$ is the mass of the hole.

Make a substitution $-\varepsilon\beta = k^2$

$$p = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} e^{-\mu\beta} \left(\frac{1}{\beta}\right)^{3/2} \underbrace{\int_{0}^{\infty} e^{-x^2} 2x^2 dx}_{\frac{\pi^{1/2}}{2}}$$

$$p = N_v e^{-\mu\beta}$$

$$N_v = 2\left(\frac{2\pi m_h}{h^2\beta}\right)^{3/2} = \frac{2}{\lambda_{T_h}{}^3}$$

$\lambda_{T_h}$ is the thermal de Broglie wavelength of the valance band holes.

$N_v$ can be thought of as the effective number of states for holes in the valance band if all are sitting at the band edge.

The above results are valid for both pure and impure semiconductors.

Question: how is the number of holes related to the number of electrons in the conduction band?

Answer: $n = p$, i.e. the electrons in the conduction band are the electrons excited out of the valance band. This is only true for pure semiconductors.

So for pure semiconductors:

$$N_c e^{(\mu - E_G)\beta} = N_v e^{-\mu\beta}$$

We can solve this for $\mu$:

$$\left(2\mu - E_G\right)\beta = \ln\left(\frac{N_V}{N_e}\right) = \frac{3}{2}\ln\left(\frac{m_h}{m_e}\right)$$

So $\mu = \dfrac{E_G}{2} + \dfrac{3}{4\beta}\ln\dfrac{m_h}{m_e}$

Therefore at $T = 0$, $\mu$ is in the middle of the band gap. Small shift only at room temperature.