ELEC4705 − Fall 2009

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LECTURE 8
Electronic Structure

Contents

8.1. Number of States in a Band

The $E(k)$ relationship tells us where allowable electronic states are, we also need to know how many there are. A crystal of size L is a finite potential well or *"Box"* for a *"free electron"*. Earlier we saw electrons in a crystal could move between the walls like free electrons. Consider figure 1, note that $L = Ma$ where M is the number of atoms in crystal and a is the atomic spacing.
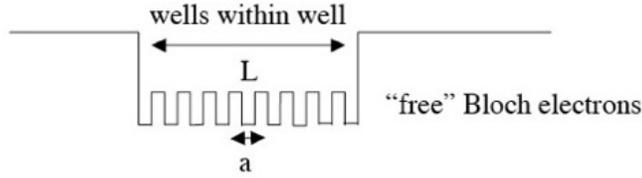

Figure 1. A Crystal as a Well

To account for the fact that the crystal has finite size, we need to impose the following boundary condition on the wave function Ψ as in equation 8.1.

$$\Psi(x) = \Psi(x + L) = 0 \tag{8.1}$$

This results in only certain discrete values of k being allowed. It can easily be verified that the previous B.C. leads to k values as below (apply this B.C. to the free electron solution):

$$k = n\frac{2\pi}{L} \tag{8.2}$$

which indicates that $\Delta k = \frac{2\pi}{L}$ for 1 dimension (x).

In multiple space dimensions we have a distribution in k space with a uniform spacing of states. This is shown in figure 2 for a $2D$ structure. Since the spacing between allowed k values is $\frac{2\pi}{L}$ in all dimensions due to finite crystal size $L \times L \times L$, so a region of k-space of volume Ω will contain for three dimensions:

$$\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{8\pi^3}$$

allowed values of k. Dividing by the volume Ω we obtain a density of states per unit volume.

The number of k values per unit volume of k-space (density of k states) is given by:
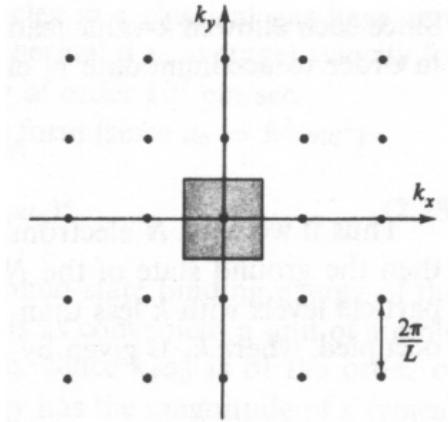
$$\Delta n_k = V/8\pi^3 \tag{8.3}$$

Figure 2. 2D k-space

Where V is the volume of the crystal, L^3.

We generally work in one dimension and the density of k states in k-space is just $L/2\pi$ as we have one state every $2\pi/L$.

We therefore have two constraints on the values of k for an electron in a crystal:

(a) We know from previous lectures that for a crystal electron we have $-\pi/a < k < \pi/a$

(b) We also know due the size of the crystal we have a discrete number of k states equals to the length in k space $(2\pi/a)$ times the density of states $(L/2\pi)$ for a given energy band.

We can therefore calculate the total number of states in each branch (band) of the dispersion relationship,

$$2\pi/a \cdot L/2\pi = L/a = M$$

allowed Bloch wave functions or states in each band.

One complication is that the Pauli exclusion principle says we can place 2 electrons in each Bloch state (2 because electrons have 2 possible spins). We therefore have $2M$ electron states in each band and each atom will provide 2 electron states to each band. Consider figure 3.

As M is very large the band is quasi continuous and size of crystal affects the state density. We can make the effective crystal very small and have only a few states per band. This is used for band gap engineering with thin layers or small structures.
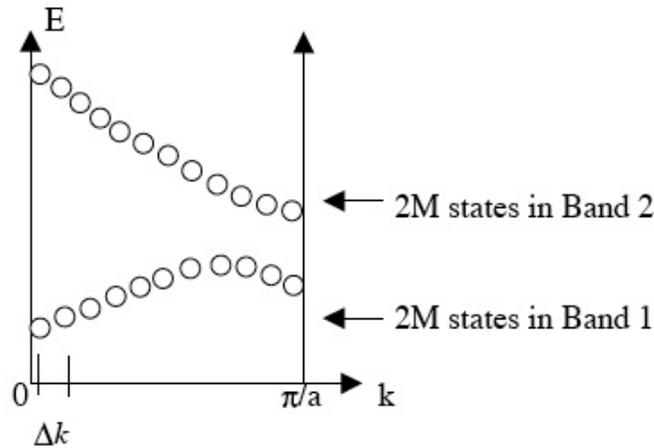
Figure 3. Discrete states separated by $\Delta k = 2\pi/Ma, Ma = L$

8.2. Insulators, Metals and Semiconductors

- The electronic structure of a crystal consists of infinite number of energy bands, separated by band gaps in which there are no allowed energies.
- Each band can hold $2M$ electrons (M is the number of atoms in a crystal)
- Bands fill up from bottom (lowest energy)
- Each atom has N electrons:
  - If N is even then $N/2$ bands are completely full and the material is most likely an insulator.
  - If N is odd, the top band is half full, and $(N-1)/2$ bands are completely full and the material is a conductor.

8.2.1. Energy Band Structure for Carbon

Consider carbon in the form of a diamond fcc crystal (16 electrons), where the band structure depends on atomic spacing and therefore the crystal structure. See figure 4 for the energy band structure (we only show the top two bands). For carbon the band gap between the first empty band and the last filled band is 5.4 eV.

Carbon has just enough electrons to fill the valence band (electrons tend to occupy lowest available levels) and seven lower bands, and the conduction band is empty. We have assumed that all electrons go to the lowest available E level. However, heat (temperature) is kinetic energy and some electrons will be raised to higher E states for $T > 0k$ (absolute 0).
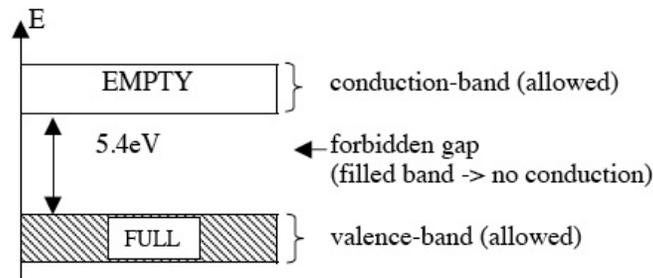
Figure 4. Energy Band Structure for Carbon

At room temperature, $kT \approx 0.0259$ eV which is the average kinetic energy of electrons (k is Boltzmann's constant $= 1.38 \times 10^{-23} J/K$). Electron energies are described by an energy distribution function that is a function of T. The larger T the hotter (more energetic) the electrons are. As for Carbon at room temperature kT$<< E_g$, we know that it is almost impossible for electron to acquire enough thermal (kinetic) energy to be activated into the conduction band and so carbon is an insulator.

8.2.2. Energy Band Structure for Silicon

Now consider silicon with 14 electrons. It has the same crystal structure as carbon, but smaller band gap, see figure 5
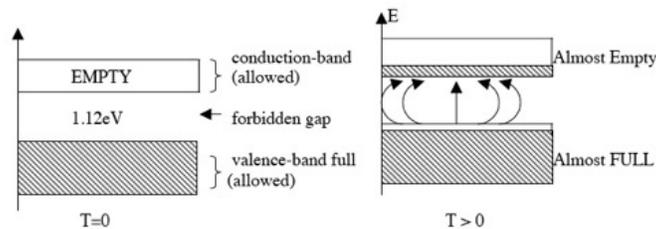

Figure 5. Energy Band Structure for Silicon

Now there is a small (but finite) chance for a few electrons to be thermally excited from valence band to conduction band.

8.2.3. Energy Band Structure for a Metal

Finally consider an alkali metal in figure 6
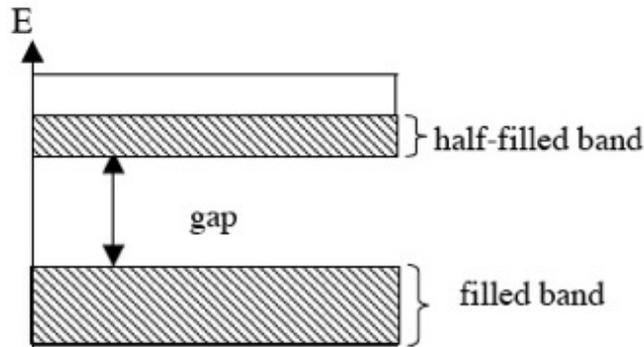
- Odd number of electrons

Figure 6. Energy Band Structure for Metal

- 1/2 filled band

We see that there are electrons in the conduction band so metals are conductors.

8.3. The Conduction Band

We know that conduction is the movement, i.e, acceleration of an electron. To be accelerated an electron must gain energy and change its state/momentum.

If a band is completely filled an electron can not change state as all states are filled (grid lock!) So a band must be partially empty for conduction to occur.

Electrons in the conduction band are free to move through crystal in response to electric field ε as the conduction band is mostly empty. We need to find how nearly free electrons move in the conduction band.

8.4. Effective Mass

Consider electron moving under influence of crystal potential $V(x)$, and externally applied electric field ε, see figure 7. Where ϕ is the electro static potential and $\varepsilon = -d\phi/dx$.

We model the electron as a wavepacket of Bloch waves (free electrons almost) centered around wave vector k. We expect an external
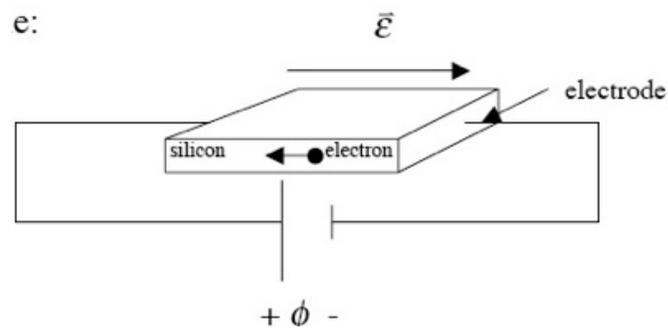
Figure 7. Electron in presence of potential and electric field

field to accelerate the electron, increasing E and k and change the electron's state. Note figure 8 and follow the equations below.
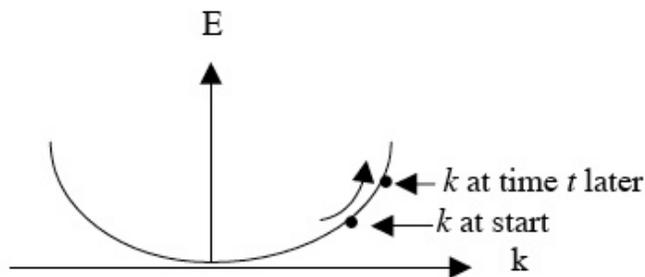

Figure 8. E-k relation for an electron in presence of a potential and external electric field

The potential energy is given by

$$E = -q\phi \tag{8.4}$$

$$\tag{8.5}$$

taking the time derivative:

$$\frac{dE}{dt} = -q\frac{d\phi}{dt} \tag{8.6}$$

$$\tag{8.7}$$

and the group velocity is defined as:

$$V_g = \frac{dx}{dt} = \frac{dw}{dk} \tag{8.8}$$

By re-writing we have:

$$\frac{dE}{dt} = -q\frac{d\phi}{dt}\frac{dx}{dt}\frac{dt}{dx} = -q\frac{d\phi}{dx}.V_g \tag{8.9}$$

$$\tag{8.10}$$

we also have:

$$V_g = \frac{dw}{dk} = \frac{1}{\hbar}\frac{dE}{dk} \tag{8.11}$$

$$\tag{8.12}$$

and can obtain.

$$\frac{dE}{dt}\frac{1}{V_g} = \frac{d(\hbar\omega)}{dt}\frac{1}{V_g} = -q\frac{d\phi}{dx} \tag{8.13}$$

$$\frac{d\hbar\omega}{dt}\frac{dk}{d\omega} = -q\frac{d\phi}{dx} \tag{8.14}$$

$$\frac{d\hbar k}{dt} = -q\frac{d\phi}{dx} \tag{8.15}$$

and noting that $p = \hbar k$ for free or "nearly free" electrons is the momentum:

$$\frac{dp}{dt} = \frac{d}{dt}(\hbar k) = -q\frac{d\phi}{dx} = -q\varepsilon = F \tag{8.16}$$

$$\tag{8.17}$$

where F is the electric force. Therefore for an electron in a periodic potential we identify $\hbar k$ as the *"crystal momentum"* which changes in response to external forces.

Now we can also derive:

$$\frac{dV_g}{dt} = \frac{d}{dt}(\frac{1}{\hbar}\frac{dE}{dk}) \tag{8.18}$$

$$= \frac{1}{\hbar}\frac{d}{dk}(\frac{dE}{dt}) \tag{8.19}$$

$$= \frac{1}{\hbar}\frac{d}{dk}(\frac{dE}{dk})(\frac{dk}{dt}) \tag{8.20}$$

$$= \frac{1}{\hbar}\frac{d^2E}{dk^2}(\frac{dk}{dt}) \tag{8.21}$$

On the other hand:

$$a \quad = \quad \frac{dV_g}{dt} \tag{8.22}$$

$$= \quad (\frac{1}{\hbar^2}\frac{d^2E}{dk^2})\frac{d}{dt}\hbar k \tag{8.23}$$

$$= \quad (\frac{1}{\hbar^2}\frac{d^2E}{dk^2})(-q\varepsilon) \tag{8.24}$$

This has the form $a = F/m^*$ where m^* is the effective mass and is given by equation 8.25.

$$m^* = (\frac{1}{\hbar^2}\frac{d^2E}{dk^2})^{-1} \tag{8.25}$$

Electrons in a crystal are accelerated in response to an external force just as though they were free electrons with effective mass m*. Note m* need not be equal to free electron mass m_o and usually, $m^* < m_o$.

Equation 8.25 relates the curvature of the band to mobility and to effective mass, see figure 9. We can show that a free electron band gives an effective mass equal to the rest mass of an electron.
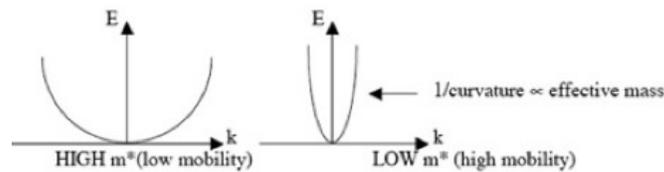

Figure 9. E-k curves for different mobilities

Now consider figure 10.

It seems that the electrons have negative mass and move backwards in response to force!

However we interpret this as a +ve mass particle with a +ve charge which is called a hole.

8.4.1. Electron and Holes

The energy band structure of real semiconductors can be very complex. However to understand many properties it is often enough to consider a band structure as shown in figure 11. We might regard this band representation as being typical for a semiconductor.
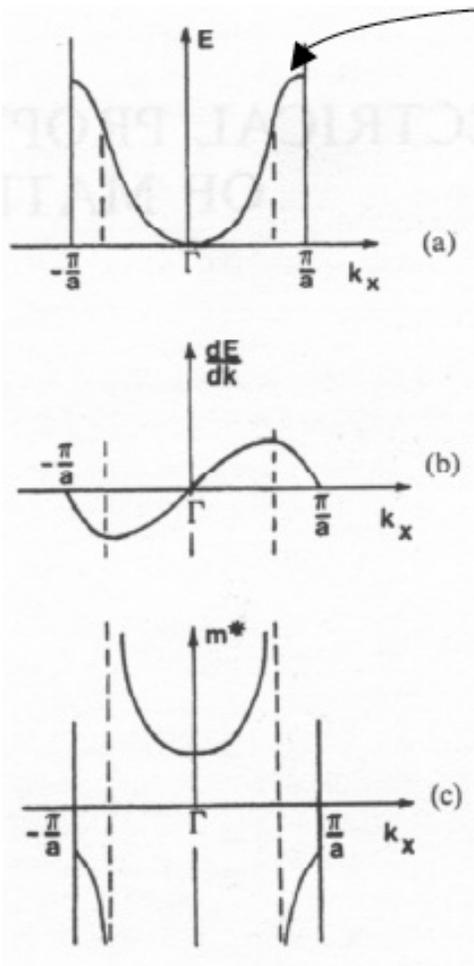
Figure 10. Negative electron mass

At $0K$ in a pure material, conduction band is completely empty, valence band completely filled, and no conduction (insulation).

At $300K$, a few electrons are promoted to the conduction band, leaving a few empty states near the top of the valence band.

At $T \neq 0K$ the charge carriers in a solid are in constant thermal motion. In the absence of external fields this motion is quite random resulting from carriers scattered by collisions. As the motion is random there is no net displacement of charge in any direction and no net current flow ($I = 0$).
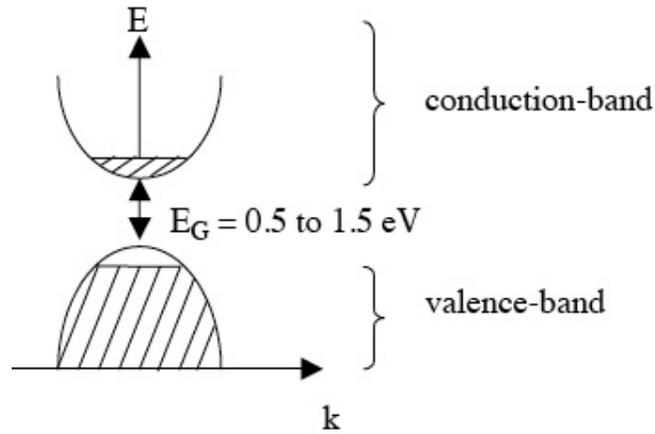
Figure 11. Band Structure for Semiconductors

Clearly, with a field the electrons excited into the conduction band can contribute to current flow. How do the empty states in the valence band contribute to current flow?

As there are now empty states in the valence band, the electrons in this band can also respond to an applied field and contribute to the current flow.

For the electrons occupying the vacant states we have

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} < 0$$

and so the electrons will move in same direction as electric field (wrong way!). Therefore the electrons contribute to current as though they were positively charged, positive effective mass particles. It is therefore convenient to describe valence band as containing imaginary positive charge, positive mass particles called holes.

In a semiconductor we therefore have two charge carriers:

- Electrons +ive mass, -ive charge (conduction band)
- Holes +ive mass, +ive charge (valence band)