04. Electronic Structure

Energy Bands: Insulators, Semiconductors, Metals

Valence band: The highest energy electronic band filled with electrons

Conduction band: The band lying above the valence band. As the name says, it is responsible for conduction.

Insulators: Wide gap between the Valence band and the conduction band

Metals: The valence and conduction bands overlap. Now the electrons can easily go to the conduction band and conduction can occur.

Semiconductors: Similar to insulators, but the gap is much smaller. At room temperature there is enough energy $\sim k_B T$ to promote electrons from the valence band to the conduction band. More precisely, these are known as intrinsic semiconductors.

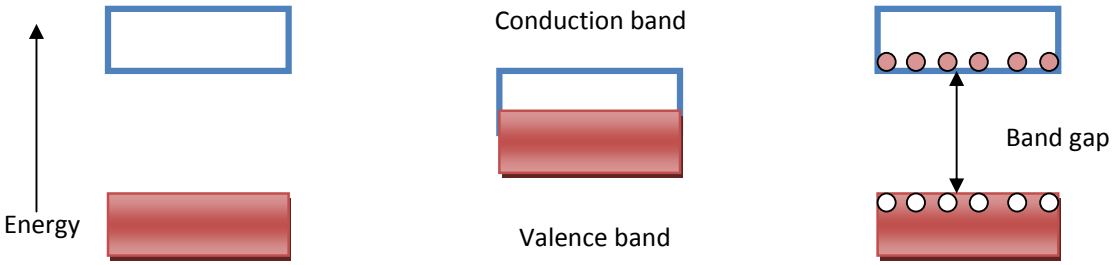


Figure 4.1: The Valence band and the conduction band in an insulator, metal and a semiconductor.

Extrinsic semiconductors: We could introduce suitable atoms in the semiconductors so that they have a different number of valence electrons as compared to the host. For example, doping P in Si gives an extra electron which is unbound and therefore free to conduct. Likewise, doping Al in Si would lead to an absence of electron or presence of a hole which is free to conduct. The former is called an n-type and the latter a p-type doped semiconductor.

Another way to visualize doping is in the case of compound semiconductors such as GaAs where Ga has a formal oxidation state of +3 and As has -3. Now replace one Ga^{3+} by Mn^{2+} ion. In order to maintain charge neutrality, a hole must be doped into the system thereby creating a p-doped GaMnAs.

Reciprocal space

Solids are composed of an Avogadro number of atoms and hence defining the energy levels of each and every atom is an impossible task. However, we do have at our disposal the symmetry of the solid which makes life pretty simple.

Calculate the number of atoms in a 1 cm^3 of Al. The density of Al is 2.7 g cm^{-3}. The electronic structure calculations demand a solution of *n* linear equations, where *n* is the number of orbitals involved. Assuming only outermost *s* and *p* orbitals are involved in bonding and that each equation is solved in one millisecond, how much time is required for performing the calculations of this cube of Al.

We need to worry about the electrons travelling though a solid. Since the solid, assuming infinite, is periodic in each and every direction we need to worry about the different directions that the electron can travel in.

Figure 4.2: Lattice showing different directions

The black dots represent the ions present in the solids. Therefore, the electrons would experience a periodic potential from these ions, the periodicity depending on the direction. This is the same periodicity that diffracts x-rays. Therefore, it can be described by the wavevector k used in diffraction and inversely related to the periodicity by $k = 2\pi/\lambda$ where λ is the wavelength of the incoming x-ray and is related to the spacing between the planes through the Bragg's Law. Thus, all we need to do is to plot the electronic energy as a function of k.

Think of a one-dimensional arrangement of atoms as shown in Figure 4.3. The length of the chain of atoms arranged periodically with a lattice constant a is $L = 10a$. The atoms are present at $x = 0, a, 2a, 3a \dots \dots 10a\ (= L)$. Since we have defined the length to be synonymous with λ, the corresponding wavevectors would be $k = \frac{2\pi}{L}, \frac{4\pi}{L}, \frac{6\pi}{L}, \dots \dots, \frac{20\pi}{L}\ (= \frac{2\pi}{a})$. Here the smallest value of k is $\frac{2\pi}{L}$ and the largest is $\frac{2\pi}{a}$. There is a reciprocal relationship with the direct lattice and hence this k-*space* is also called the *reciprocal-space* or the *dual space*.

a

Figure 4.3: One-dimensional periodic arrangement of atoms

The unit cell in the one-dimensional crystal has length a and in the reciprocal space, which incidentally is also the *Brillouin zone* in this example, has the length $\frac{2\pi}{a}$. Within the Brillouin zone, the electron sites are at the lattice points (now these are in the reciprocal space) $k = 2\pi n/L$.

The Brillouin zone is defined as the reciprocal of the Wigner-Seitz unit cell. The Wigner-Seitz unit cell is not the conventional unit cell that we normally use. Rather it's the smallest possible unit cell that one can sketch. For example, the FCC lattice has four basis units in the conventional unit cell. However, we could as well do with just one of these. Try sketching the Wigner-Seitz unit cells for some basic lattices.

Starting from the 1-D case you should try to go onto two and three dimensions.

Effective Masses

Think of an electron moving through space. The energy of the electron is given by $E = p^2/2m$. Since $p = \hbar k$, the energy can be written as $E = \hbar^2 k^2/2m$. When the electron moves through a solid, this energy gets altered and when we wish to represent it by an equation that looks the same as above we can introduce the concept of an effective mass, m^*. Now,

$$E = \frac{\hbar^2 k^2}{2m^*}$$

which simply states that the energy has a parabolic dependence on the wavevector as shown in Figure 4.4

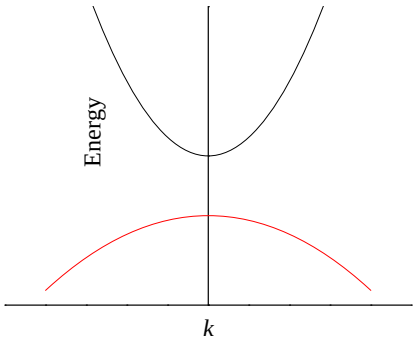


Figure 4.4: Dependence of energy as a function of the wavevector.

The effective mass of the electron (hole), $m_e^*(m_h^*)$, can be evaluated by taking the second derivative of the conduction (valence) band as

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \frac{1}{m^*}$$

As shown in the schematic above, the effective mass of the electron is less than the effective mass of the hole; the slope of the conduction band being steeper than that of the valence band.

Excitons

The Rydberg formula accounts for the energy levels of the hydrogen atom

$$E_H = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{13.6}{n^2}\ \text{eV}$$

where a_0 is the Bohr radius given by $a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 0.0529\ \text{nm}$, μ is the reduced mass of the proton-electron, essentially equal to the free electron mass m_0. The quantum number n can take integral values of 1,2,3…

Likewise, if we replace the proton by a positive variant of the electron (*positron*) that has mass equal to that of an electron but is oppositely charged, the energy would be given by

$$E_{positron} = -\frac{6.8}{n^2}\ \text{eV}$$

This, of course, is the case in free space and the bound electron-positron pair is called a *positronium*. In case of a solid, the analog of a positron is known as an *exciton*, a situation where the electron-hole pair is bound. The reduced mass would now be given by

$$\mu^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*} = \frac{m_e^*}{1 + (m_e^*/m_h^*)}$$

Also, the dielectric constant now is that of the semiconductor and therefore one needs to use $\epsilon = \epsilon_r\epsilon_0$ instead of the value in vacuum.

$$E_{ex} = -\frac{\mu^*/m_0}{(\epsilon_r)^2}\frac{e^2}{4\pi\epsilon_0 a_0 n^2} = -\frac{13.6\mu^*/m_0}{(\epsilon_r)^2\, n^2}\ \text{eV}$$

Although the effective masses are a fraction of the free-electron mass, the permittivity values are in the range of 5 to 15 for the semiconductors. The $(\epsilon_r)^2$ term in the denominator ensures that the energy levels of the exciton are roughly two orders of magnitude smaller than that of the positron.

Also, the *exciton Bohr radius* ,a_B, would now be given by

$$a_B = \frac{\epsilon_r}{\mu^* m_0} a_0 = 0.0529\frac{\epsilon_r}{\mu^* m_0}\ \text{nm}$$

For GaAs: $\mu^* = 0.058\ m_0$, $\epsilon_r = 13.2$. Calculate the ground state exciton energy and the exciton Bohr radius. Compare the results with that of the hydrogen atom. What does the value of a_B imply? ($E_0 = 4.5\ \text{meV},\ \text{a}_\text{B} = 12.0\ \text{nm}$)

The excitons we have discussed, and are almost always found in semiconductors and nanomaterials, are known as *Mott-Wannier* excitons. These are weakly bound and their wavefunction spreads over a large number of atoms. The *Frenkel* excitons are found in molecules and is rather tightly bound on adjacent atoms or molecules, although these can also move around the lattice.