Module 4 : Solid State Chemistry

Lecture 20 : Band Theory of Solids

Objectives

In this lecture you will learn the following

- Formation of energy-level bands in solids.

- Distinction between the band structures of conductors, semiconductors and insulators.

- Elementary theory for obtaining the energy levels in a band.

- Occupation of the levels in a band by electrons.

- Ideas relevant in superconductivity.

20.1 Introduction to Band Structure

In our studies of atoms and molecules we have seen that molecular orbitals are formed by the interaction of atomic orbitals. In molecular orbitals of H_2 for example, the binding orbital σ_s is separated from the antibonding orbital σ_s^* by several electron-Volts (1eV = 23.06 kcal / mol). When three orbitals from three atoms (as in the case of H_3) combine to form MOs, we get three orbitals (σ_s, σ_n and σ_s^*), a bonding, a nonbonding and an antibonding orbital. When N atomic orbitals from N atoms interact, they give N molecular orbitals. When N becomes very large, as in the case of a solid, there will be a large number of orbitals in a given range of energy, say between E_ℓ and E_h. This collection of orbitals or energy levels is referred to as an (energy) band. The study of band structure forms a central theme in the study of electronic structure of solids.

Fig 20.1 illustrate the formation of bands as the number of atoms increases. This is shown for a one dimensional solid. The overlap diagrams have a straight forward extension in three dimensions.

Figure 20.1 Band formation as a function of the number of atoms/s-orbitals in one dimension.

The above figure is for the overlap of s orbitals.

Similar overlap diagrams can be obtained for the overlap of p,d,f... orbitals as well. These are shown in fig 20.2

Figure 20.2 Formation of s, p and d bands. E_h and E_l refer to the highest (most antibonding) and the lowest (most bonding) energy levels in a given band. As we go up in energy in a given band, the number of nodes increases.

20.2 Band structures in insulators, metals and semiconductors

The term band structure refers to the size of various bands, the gap between adjacent bands and the occupation of the levels in the bands by electrons. In the solids formed by systems such as rare gas atoms, all the bands (corresponding to filled shells in atoms) are completely filled with electrons and the unfilled bands (corresponding unoccupied orbitals in the atoms) are fully empty. There is no discernible movement of these electrons when the system is subjected to an external electric field and the substance behaves as an insulator. The same is true for diamond (Fig 20.3) where the filled bonding sp^3 band is widely separated

from the unfilled antibonding sp^3 by a considerable gap and the substance is a well known insulator.

Figure 20.3 Filled and unfilled sp^3 bands in diamond.

In the case of metals such as Li, Na, Mg and Al, the atoms have partially filled shells. The bands in the metals are also partially filled. Consider the case of N electrons occupying a band of N orbitals. Only N / 2 orbitals are occupied and the band is only half full as shown in fig 20.4.

Figure 20.4 : Partly filled band in a metal.

When metals with a band occupancy as in Fig 20.4 are subjected to an external electric field, the electrons are highly mobile and flow "almost freely" in the band leading to high electrical conductivity.

Let us next consider the energy bands in semiconductors, shown in Fig 20.5. Here too, at T = 0K, the valence band is completely filled and the upper or the conduction band is empty and the conductivity is negligible. This is similar to diamond except that the gap between the occupied valence band and the higher unoccupied conduction band is small. As the temperature is increased, some levels of the higher band get occupied due to thermal excitation and the system behaves as a conductor. This is observed in the case of elements like Ge and Si and they are called semiconductors. These materials exhibit increased conductivity with increasing temperature.

Figure 20.5 The band structure of a semiconductor.

Another way of getting semiconducting behaviour is to "dope" pure materials with foreign atoms (dopants) which are either rich in electrons (i.e., atoms that can donate electrons) or are short of electrons (i.e., these atoms can trap electrons). For example, when phosphorus is doped into germanium, the additional electrons in P (the donor band) can occupy the empty conduction band in Ge heading to conducting behaviour. This is called an n-type semiconductor. On the other hand, if germanium or Si is doped with electron "deficient" materials such as Al, the band of the dopant can accept electrons from the valence band of the host. Since the band loses electrons, the charge carriers in the valence band are "positive charges" or "holes". This is referred to as p- type of semiconductivity. In n-type, the charge carriers are negative. The band structures of n- type and p-type semiconductors are shown in Fig 20.6

Figure 20.6 The band structures of n-type and p-type semiconductors

20.3 Energy levels in bands

In this section we outline a simple method to obtain the energy levels in a band . This is similar to the method needed to obtain the π orbital energies of butadiene. Let us consider the bonding (ψ_b) and antibonding orbitals (ψ_a) of a diatomic.

$$\psi_b = c_{1b}\, \phi_1 + c_{2b}\, \phi_2$$

$$\psi_a = c_{1a}\, \phi_1 + c_{2a}\, \phi_2 \qquad\qquad (20.1)$$

We need to determine the coefficients c_{1b}, c_{2b}, c_{1a} and c_{2a} as well as the energies of   and ψ_a. Here

ϕ_1 and ϕ_2 are atomic orbitals. Consider a general MO ψ defined as

$$\psi = c_1 \phi_1 + c_2 \phi_2 \qquad\qquad\qquad (20.2)$$

The normalization of ψ is (since ϕ_1 and ϕ_2 are normalized individually)

$$\int \psi^* \psi \, d\tau = c_1^2 + c_2^2 + 2 c_1 c_2 S \text{ with} \qquad\qquad (20.3)$$

$$S = \int \phi_1 \phi_2 \, d\tau$$

If H is the hamiltonian operator of the molecule, the energy of the molecule is given by

$$E = \int \psi^* H \psi \, d\tau / \int \psi^* \psi \, d\tau \qquad\qquad\qquad (20.5)$$

$$E = [\alpha_1 c_1^2 + \alpha_2 c_2^2 + 2\beta c_1 c_2] / [c_1^2 + c_2^2 + 2 c_1 c_2 S] \qquad (20.6)$$

Here $\alpha_1 = \int \phi_1 H \phi_1 d\tau$, $\alpha_2 = \int \phi_2 H \phi_2 d\tau$ and $\beta = \int \phi_1 H \phi_2 d\tau$ $\qquad (20.7)$

To find the optimum coefficients c_1 and c_2 for bonding and antibonding orbitals, we minimize E with respect to c_1 and c_2 by setting $\partial E / \partial c_1 = 0$ and $\partial E / \partial c_2 = 0$

Taking the derivatives of Eq (20.6) with respect to c_1 and c_2, we get the following two equations.

$$(\alpha_1 - E)c_1 + (\beta - ES) c_2 = 0 \qquad\qquad\qquad (20.8a)$$

$$(\beta - ES)c_1 + (\alpha_2 - E) c_2 = 0 \qquad\qquad\qquad (20.8b)$$

To solve (20.8) the determinant called the secular determinant of equation 20.9 has to be zero.

$$(20.9)$$

$$\begin{vmatrix} \alpha_1 - E & \beta - ES \\ \beta - ES & \alpha_2 - E \end{vmatrix} = 0$$

For identical atoms $\alpha_1 = \alpha_2$ and the two roots of the quadratic equation (20.9) for E (which give E_b and E_a) are

$$E_b = (\alpha + \beta) / (1 + S) \qquad\qquad\qquad (20.10a)$$

and $E_a =$ $\qquad\qquad\qquad (20.10b)$

$$(\alpha - \beta)/(1 - S)$$

Substituting E_b in eq (20.8) we get $c_1 = c_2$ for the bonding orbital and substituting E_a in eq (20.8) we get $c_1 = -c_2$ for the antibonding orbital. Thus the coefficients in 20.1 can be determined.

We can extend the argument to π orbitals of ethylene by taking $S \approx 0$ in eq (20.9) and $\alpha_1 = \alpha_2$ The secular determinant becomes

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} \quad (20.11)$$

and the energies of the bonding and antibonding orbitals are

$$E_b = \alpha + \beta \text{ and } E_a = \alpha - \beta \quad\quad (20.12)$$

Here β is negative and hence the bonding orbital lies lower in energy compared to the antibonding orbital.

For butadiene, assuming $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4, S \approx 0$ and all β s to be the same, the secular determinant becomes

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & 0 & 0 \\ 0 & \beta & \alpha - E & 0 \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} \quad (20.13)$$

and for N atomic orbitals in a linear chain, the secular determinant gets generalized to

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 \,...... & 0\,... \\ \beta & \alpha - E & \beta & 0 & 0 \,...... \\ 0 & \beta & \alpha - E & \beta & 0 \,...... \\ \vdots & & & \beta & \alpha - E & \beta ... \\ \vdots & & & & & \\ 0 & 0 \,....... & & & \beta & \alpha - E \end{vmatrix} \quad (20.14)$$

The solutions for the above secular determinant are the large number of roots of E of eq 20.14. With some algebraic manipulations, they can be shown to be

$$E_k = \alpha + 2\beta \cos(k\pi/(N+1)), \ k = 1,2 \ ...N \quad\quad (20.15)$$

For large N, the energy difference between adjacent levels is very small as illustrated in fig 20.7

Figure 20.7 Energy levels of eq (20.15) in a band

As N becomes very large, the energy difference between E_N and E_1 becomes

$$E_N - E_1 = 4\beta \qquad (20.16)$$

Although this section is sketchy and we have made many approximations (which need to be improved in real solids), we have an expression for the energy levels in a band).

20.4 Population of the band energy levels by electrons.

In our earlier section on bands (with N electrons) in metals, we saw that only N / 2 levels were doubly occupied at T = 0 . The highest occupied MO (HOMO) was called the Fermi level. At temperatures other than T = 0, the occupation of levels does not follow the Boltzmann probability distribution $p(E_i) \alpha\ e^{-E_i\ /\ k_BT}$ but follows the Fermi Dirac distribution which is given by

$$p(E_i) = 1/\ [e^{\ (E_i-\ \mu\ )\ /\ k_BT}\ +1] \qquad (20.17)$$

Here, μ is the value of E_i for which p (E_i) = 1/ 2. μ is called the chemical potential. The Fermi-Dirac distribution includes the effect of the Pauli exclusion principle, according to which no two electrons can have all quantum numbers identical; i.e., for each state (or non-degenerate level), there can be at most one electron of a given spin type. For energies close to and less than μ eq (20.17) differs completely from the Boltzmann distribution. For energies greater than μ and for large T, the second term of the denominator of (20.17) is very small and P (E_i) resembles the Boltzmann distribution

$$p\ (E_i) = e^{\ -\ (E_i\ -\mu\ )\ /\ k_BT} \qquad (20.18)$$

A sketch of $P(E_i)$ vs $(E_i -\mu\ )\ /\ \mu$ is given in fig 20.8

Figure 20.8 Population of electronic energy levels according to Fermi-Dirac distribution.

The curves are labeled by ... .μ / $k_B T$. The distribution at T = 0 is the shaded region where p (E_i) = 1 for $E_i < \mu$ and 0 otherwise.

20.5 Superconductivity

For metals in the usual temperature range around 298 K, resistance decreases with T, or conductivity increases with lowering T. In 1911, Kimberling ones showed that when Hg is cooled to T $\leq$ 4.2K, the resistance to electron flow drops to below 10^{-5} ohms and the metal behaves as a "superconductor". In the superconducting state, electrons flow without any resistance offered by lattice sites or lattice vibrations. Unusual magnetic and entropic behaviour is also exhibited. In the first insightful theory of superconductivity, Bardeen, Cooper and Schrieffer (1957) proposed a theory wherein ordered pairs of electrons are formed at low temperatures. Although the ordering is caused by the interaction of electrons with lattice ions, the "ordered pairs" move freely in the lattice. Considerable efforts have been put in to find high temperature superconductors and nonstoichiometric materials of Pervoskite structures, such as Y $Ba_2 Cu_3 O_{7-x}$ with x $\leq$ 0.1 have shown superconductivity for T $\leq$ T_c = 90 K.

Figure 20.8 (a) A sketch showing unusually low resistance for T<T_c = 4.2K. 20.8 (b) Bands for ordered pairs and normal electrons showing the superconducting band gap of $\triangle$ $\approx$ $5k_B T_c$

20.6   Problems

20.1)   One million Na atoms are placed on a straight line. If the energy of the highest level of the 3s band is 1 ev higher than the lowest energy level of the band and if all the levels in the band are equally spaced, what is the energy difference between adjacent levels? Is the thermal energy ($kT = 207$ cm^{-1} at room temperature) sufficient to excite electrons among these levels ? If the number of atoms is increased to $6 * 10^{23}$, what is the difference in energy between adjacent energy levels? if you treat this as a particle in a box problem, what will be the length of a one-dimensional box whose energy for the n = 1 state corresponds to the above energy difference?

20.2)   The distribution of electrons in the energy levels in the electronic bands follows the Fermi-Dirac distributions. Instead of electrons which are Fermions (particles with half integral spins), if we were to fill these levels with bosons (particles with integral spins, e.g., photons, nuclei of nitrogen atoms) what are the major differences that you would expect?

20.3)   From literature or some common websites, list the name of a few commonly used superconductors in daily life. Also find out the temperature below which they become superconducting, their cost per gram of substance, their structures, name of the inventor and the year of invention and the nature of their specific application.

Recap

In this lecture you have learnt the following

Summary

In this lecture you have been introduced to the band structure of solids . The band structure deals with the closely spaced energy levels of electrons in various groups or bands of levels, the gaps between the bands, the effect of temperature on the occupation of levels, as well as the influence on the band occupancy by dopants. Electron rich dopants lead to n-type semiconductivity wherein the electrons are the charge carriers. In p-type semiconductivity, the charge carriers are +ve charges. The energy levels of a model of a band were obtained and some details of obtaining energy levels and coefficients of AOs in the band MOs were given. The Fermi-Dirac distribution was distinguished from the temperature Boltzmann distribution and some ideas relevant to superconductivity were outlined.