

# 3

## BAND THEORY OF SOLIDS

### 3.1. INTRODUCTION

The free electron theory of metals successfully explained the various properties of metals like heat capacity, thermal conductivity, electrical conductivity, magnetic susceptibility etc. But there remained some properties which were not explained by this theory, for example, the following properties :

- (i) It could not explain the difference between conductors, insulators and semiconductors.
- (ii) It is found that divalent metals (Be, Cd etc.) and trivalent metals (Al, In etc.) are not good conductors even though the theory says that conductivity is proportional to electron concentration. Rather monovalent metals Cu, Ag and Au are good conductors, even though they have less concentration of electrons than divalent and trivalent metals.
- (iii) The shape of Fermi surface is found to be non-spherical in shape which according to the theory should be spherical.
- (iv) Some of the metals exhibit positive hall coefficient (e.g., for Be, Zn etc.), while the free electron theory predicts negative hall coefficient for all the metals.

Similarly, there are many other properties which could not be explained on the basis of free electron theory.

The failure of free electron theory is because of the over simplified assumption that the electrons move in a region of zero or constant potential in the metals, their motion is only restrained by the surface of the metal. However, this is not the case, the potential experienced by electron is very complicated and to a reasonable approximation we can assume that electron move in the periodic potential of the ion cores with periodicity of the lattice. One such periodic potential in one dimensional case is shown in Fig. 3.1.

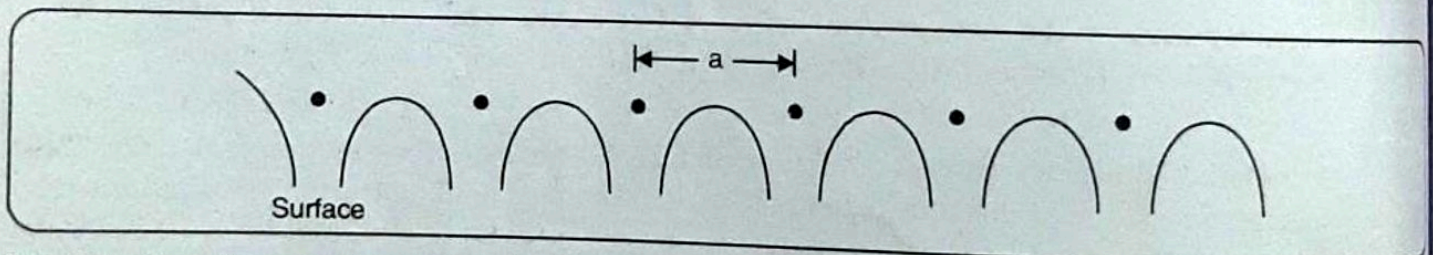


Fig. 3.1 : One dimensional periodic potential experienced by an electron. The positive ion cores are shown by dots separated by lattice constant  $a$

This periodic potential is assumed to be extending up to infinity in all directions but at the surface of the crystal this periodicity is interrupted as shown on left side of the fig. But this could be ignored.

The regular arrangement of atoms in a crystal was not taken into account in the free electron theory. The introduction of this fact forms the basis of the band theory of the metals, which we will provide natural distinction between conductors, insulators and semiconductors. When we consider the motion of electron in a periodic potential we get the given ahead results :



(i) There exist allowed energy bands separated by forbidden energy bands.

(ii) The functions  $E(\vec{k})$  are periodic in  $\vec{k}$ .

However according to free electron theory, the energy of the electron as a function of  $\vec{k}$  is given as,

$$E = \hbar^2 k^2 / 2m \text{ where } k = 2\pi/\lambda$$

where  $\lambda$  is the de-Broglie wavelength associated with electron.

### 3.2. BLOCH THEOREM

One dimensional Schrodinger wave eq. for a free electron which is moving in a constant potential  $V_0$  is given as

$$\frac{d^2\psi}{dx^2} + (2m/\hbar^2)(E - V_0)\psi = 0 \quad \dots(3.1)$$

We can see a solution

$$\psi = \exp(\pm i k x) \quad \dots(3.2)$$

for the above differential equation

where, the kinetic energy of electrons is given as

$$\begin{aligned} E_{kin} &= E - V_0 \\ &= \frac{\hbar k^2}{2m} = \frac{p^2}{2m} \end{aligned}$$

To make the wave function of eq. (3.2) to represent a wave propagating in the  $x$ -direction, we can multiply eq. (3.2) by  $\exp(-i\omega t)$ , where  $\omega = E/\hbar$ .

#### Periodic potential

Let us now consider the one dimensional Schrodinger wave equation for an electron in a periodic potential of period ' $a$ ' (i.e., periodicity of lattice)

$$\text{i.e.,} \quad V(x) = V(x+a) \quad \dots(3.3)$$

The Schrodinger equation is now written as,

$$\frac{d^2\psi}{dx^2} + (2m/\hbar^2)[(E - V(x))]\psi = 0 \quad \dots(3.4)$$

Where  $V(x)$  is given by eq. (3.3). The solution of eq. (3.4) is given by *Bloch theorem*, also known as *Floquet's theorem*, which states that solutions of eq. (3.4) are of the type

$$\psi(x) = \exp(\pm i k x) u_k(x) \quad \dots(3.5)$$

$$u_k(x) = u_k(x+a) \quad \dots(3.5a)$$

where  
i.e., the solutions are of the type of eq. (3.2) but modulated by a function  $u_k(x)$  which is again periodic with the same periodicity of the lattice.

Functions of the type of eq. (3.5) are known as *Bloch functions* and these have the following property.

$$\psi(x+a) = \exp[ik(x+a)] u_k(x+a)$$

i.e.

$$\psi(x+a) = \exp(ikx) \exp(ika) u_k(x)$$



or

$$\begin{aligned}\psi(x+a) &= \exp(ika) \psi(x) \\ &= \gamma \psi(x) \\ \gamma &= \exp(ika)\end{aligned}$$

where

We know that Schrodinger wave equation (3.4) is a second order differential equation and hence there exist only two real independent solutions for this equation say  $f(x)$  and  $g(x)$ , any other solution will be simply a linear combination of the independent solutions.

Hence, if  $f(x+a)$  and  $g(x+a)$  are to be solutions of the eq. (3.4), these should be expressible as

$$f(x+a) = \alpha_1 f(x) + \alpha_2 g(x) \quad \dots(3.6)$$

$$g(x+a) = \beta_1 f(x) + \beta_2 g(x) \quad \dots(3.7)$$

where  $\alpha$ 's and  $\beta$ 's are functions of  $E$ .

Let  $\psi(x)$  be another solution of eq. (3.4), hence it must be represented as

$$\psi(x) = A f(x) + B g(x) \quad \dots(3.8)$$

Therefore,

$$\begin{aligned}\psi(x+a) &= A f(x+a) + B g(x+a) \\ &= (A\alpha_1 + B\beta_1) f(x) + (A\alpha_2 + B\beta_2) g(x)\end{aligned}$$

Now because of eqs. 3.6 and 3.8, we can write

$$\begin{aligned}\text{or} \quad \psi(x+a) &= \gamma [A f(x) + B g(x)] \\ &= \gamma \psi(x)\end{aligned} \quad \dots(3.9)$$

where

$$A\alpha_1 + B\beta_1 = \gamma A$$

$$A\alpha_2 + B\beta_2 = \gamma B$$

or

$$(\alpha_1 - \gamma) A + \beta_1 B = 0 \quad \dots(3.9a)$$

$$\alpha_2 A + (\beta_2 - \gamma) B = 0 \quad \dots(3.9b)$$

Now equation (3.9) have non-vanishing solutions for  $A$  and  $B$  if and only if the determinant of coefficients is zero, i.e.,

$$\begin{vmatrix} \alpha_1 - \gamma & \beta_1 \\ \alpha_2 & \beta_2 - \gamma \end{vmatrix} = 0$$

$$\text{or} \quad \gamma^2 - (\alpha_1 + \beta_2) \gamma + (\alpha_1 \beta_2 - \alpha_2 \beta_1) = 0 \quad \dots(3.10)$$

$$\text{or} \quad \gamma^2 - (\alpha_1 + \beta_2) \gamma + 1 = 0 \quad \dots(3.11)$$

We have written  $\alpha_1 \beta_2 - \alpha_2 \beta_1 = 1$  in eq. (3.10) and this result is proved below.

As  $f(x)$  and  $g(x)$  are solutions of Shrodinger eq. (3.4), we have

$$\frac{d^2 f}{dx^2} + (2m/\hbar^2)[E - V(x)]f = 0$$

and

$$\frac{d^2 g}{dx^2} + (2m/\hbar^2)[E - V(x)]g = 0$$

Multiplying  $f$  eq. by  $g$  and vice versa and then subtracting, we get

$$f \frac{d^2 g}{dx^2} - g \frac{d^2 f}{dx^2} = 0$$

$$fg'' - g''f = 0$$



or

$$\frac{d}{dx}(fg' - gf') = 0$$

$$fg' - gf' = \text{constant}$$

i.e., the wronskian

...(3.12)

$$w(x) = \begin{vmatrix} f(x) & g(x) \\ f'(x) & g'(x) \end{vmatrix} = \text{constant}$$

...(3.12a)

Now from equation (3.7), we may write

$$w(x+a) = \begin{vmatrix} f(x+a) & g(x+a) \\ f'(x+a) & g'(x+a) \end{vmatrix} = \begin{vmatrix} f(x)g(x) & \alpha_1 & \alpha_2 \\ f(x)g'(x) & \beta_1 & \beta_2 \end{vmatrix} \quad \dots(3.13)$$

Hence, combining eqs. (3.12) and (3.13), we get

$$(\alpha_1\beta_2 - \alpha_2\beta_1) w(x) = w(x+a)$$

$$\alpha_1\beta_2 - \alpha_2\beta_1 = 1$$

Therefore, eq. (3.11) gives two roots of  $\gamma$ , so as to satisfy eq. (3.6 a) and hence there are two wave functions  $\psi_1(x)$  and  $\psi_2(x)$ . It must also be noted that  $\gamma_1\gamma_2 = 1$  and  $(\alpha_1 + \beta_2)$  is a real function of energy  $E$ . Let us consider two cases for the energy ranges.

Case (i) For energy ranges  $(\alpha_1 + \beta_2)^2 < 4$

In this case the two roots will be complex conjugate of each other, we can write

$$\gamma_1 = \exp(ika) \text{ and } \gamma_2 = \exp(-ika)$$

where  $k$  is real and the corresponding wave functions  $\psi_1(x)$  and  $\psi_2(x)$  can be written as

$$\psi_1(x+a) = \exp(ika) \psi_1(x) \text{ and } \psi_2(x+a) = \exp(-ika) \psi_2(x) \quad \dots(3.14)$$

i.e., in general

$$\psi(x+a) = \exp[\pm ika] \psi(x)$$

Such functions are the Bloch functions as described by eqs. (3.5) and (3.6)

Case (ii) For energy ranges  $(\alpha_1 + \beta_2)^2 > 4$

In this case the roots are real and will be reciprocals of each other these correspond to wave functions of the type.

$$\psi_1(x) = \exp(\mu x) u(x)$$

$$\psi_2(x) = \exp(-\mu x) u(x),$$

where  $\mu$  is real. These are not acceptable wave functions since these are not bounded and approaches  $\pm \infty$  when  $x$  approaches infinity.

Thus, we find that energy spectrum of an electron in a periodic potential consists of allowed and forbidden energy regions as bands. This will be discussed in further detail in the following section.

### 3.3. THE KRONIG-PENNEY MODEL

Kronig and Penney studied the behaviour of electrons in a periodic potential by considering relatively simple and one dimensional model. It is assumed that the potential energy of an electron has the shape of square wells as shown in Fig. 3.2. The period of the potential is  $(a+b)$ ,

$$\therefore V = \begin{cases} 0 & \text{for } 0 < x < a \\ V_0 & \text{for } -b < x < 0 \end{cases}$$

This type of periodic potential is an approximation of the actual picture.

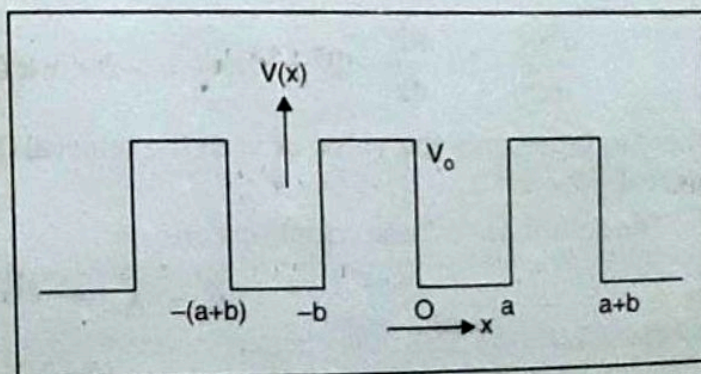


Fig. 3.2 : One dimensional Kronig Penney periodic potential



Now Schrodinger wave equation for the two regions may be written as,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \text{ for } 0 < x < a \quad \dots(3.15)$$

and

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi = 0 \text{ for } -b < x < 0 \quad \dots(3.16)$$

It is assumed that E energy of electron is smaller than  $V_0$

Let

$$\frac{2mE}{\hbar^2} = \alpha^2 \text{ and } \frac{2m(V_0 - E)}{\hbar^2} = \beta^2, \quad \dots(3.17)$$

where  $\alpha$  and  $\beta$  are two real quantities.

So eqs. (3.15) and (3.16) becomes

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0 \text{ for } 0 < x < a \quad \dots(3.18)$$

and

$$\frac{d^2\psi}{dx^2} - \beta^2 \psi = 0 \text{ for } -b < x < 0 \quad \dots(3.19)$$

Since the potential is periodic, so the solution of eqs. (3.18) and (3.19) must be of the form Bloch functions i.e.,

$$\psi(x) = \exp(ikx) u_k(x), \quad \dots(3.20)$$

where  $u_k(x)$  is the periodic function  $x$  with period  $(a+b)$ .

$$\therefore \frac{d\psi}{dx} = ik \exp(ikx) u_k + \exp(ikx) \frac{du_k}{dx}$$

$$\text{and } \frac{d^2\psi}{dx^2} = -k^2 \exp(ikx) u_k + ik \exp(ikx) \frac{du_k}{dx} + ik \exp(ikx) \frac{d^2u_k}{dx^2} + \exp(ikx) \frac{d^2u_k}{dx^2}$$

$$\text{or } \frac{d^2\psi}{dx^2} = -k^2 \exp(ikx) u_k + 2ik \exp(ikx) \frac{du_k}{dx} + \exp(ikx) \frac{d^2u_k}{dx^2} \quad \dots(3.21)$$

Putting equation (3.20) and (3.21) in equations (3.18) and (3.19), we get

$$\frac{d^2u_1}{dx^2} + 2ik \frac{du_1}{dx} - (\alpha^2 - k^2) u_1 = 0 \text{ for } 0 < x < a \quad \dots(3.22)$$

$$\frac{d^2u_2}{dx^2} + 2ik \frac{du_2}{dx} - (\beta^2 + k^2) u_2 = 0 \text{ for } -b < x < 0 \quad \dots(3.23)$$

where  $u_1$  represents the value of  $u_k$  in the interval  $0 < x < a$  and  $u_2$  represents the value of  $u_k$  in the interval  $-b < x < 0$ .

The solutions of these equations are

$$u_1 = A e^{i(\alpha-k)x} + B e^{-i(\alpha+k)x} \text{ for } 0 < x < a \quad \dots(3.24)$$

$$u_2 = C e^{(\beta-ik)x} + D e^{-(\beta+ik)x} \text{ for } -b < x < 0 \quad \dots(3.25)$$

where A, B, C and D are arbitrary constants which can be determined by following boundary conditions.



$$[u_1]_{x=0} = [u_2]_{x=0} \quad \dots(3.26a)$$

$$\left[ \frac{du_1}{dx} \right]_{x=0} = \left[ \frac{du_2}{dx} \right]_{x=0} \quad \dots(3.26b)$$

$$[u_1]_{x=a} = [u_2]_{x=-b} \quad \dots(3.26c)$$

$$\left[ \frac{du_1}{dx} \right]_{x=a} = \left[ \frac{du_2}{dx} \right]_{x=-b} \quad \dots(3.26d)$$

Applying these boundary conditions to equations (3.24) and (3.25), we get

$$A + B = C + D \quad \dots(3.27a)$$

$$A i(\alpha - k) - B i(\alpha + k) = C(\beta - ik) - D(\beta + ik) \quad \dots(3.27b)$$

$$A e^{i(\alpha - k)a} + B e^{-i(\alpha + k)a} = C e^{-(\beta - ik)b} + D e^{(\beta + ik)b} \quad \dots(3.27c)$$

$$A i(\alpha - k) e^{i(\alpha - k)a} - B i(\alpha + k) e^{-i(\alpha + k)a} = C(\beta - ik) e^{-(\beta - ik)b} + D(\beta + ik) e^{(\beta + ik)b} \quad \dots(3.27d)$$

These equations can be solved for non-zero value of A, B, C and D only if the determinant of the coefficients of A, B, C and D becomes zero.

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha - k) & -i(\alpha + k) & \beta - ik & -(\beta + ik) \\ e^{i(\alpha - k)a} & e^{-i(\alpha + k)a} & e^{-(\beta - ik)b} & e^{(\beta + ik)b} \\ i(\alpha - k)e^{i(\alpha - k)a} & -i(\alpha + k)e^{-i(\alpha + k)a} & (\beta - ik)e^{-(\beta - ik)b} & -(\beta + ik)e^{(\beta + ik)b} \end{vmatrix} = 0$$

On solving, we get

$$\frac{\beta^2 + \alpha^2}{2\beta\alpha} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos(a+b) \quad \dots(3.28)$$

In order to make the situation more simple, Kronig and Penney considered the case in which  $V_0$  tends to infinity and  $b$  approaches zero but the product  $b V_0$  remain finite, and is known as *barrier strength* so that the potential barrier becomes delta function. Under these circumstances, eq. (3.27) becomes

$$\frac{m V_0 b}{\hbar^2 \alpha} \sin \alpha a + \cos \alpha a = \cos k a$$

eq. (3.28) can be written more simply as

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a \quad \dots(3.29)$$

where  $P$  is defined as

$$P = m V_0 b \frac{a}{\hbar^2} \quad \dots(3.30)$$

which is a measure of the area  $V_0 b$  of the potential barrier. Large value of  $P$  means that given electron is more strongly bound to a particular potential well.

Now right hand side of eq. (3.29) can assume values between +1 and -1 and hence only those values of  $\alpha a$  are allowed which make left hand side of this equation lie between  $\pm 1$ . Fig. 3.3. shows



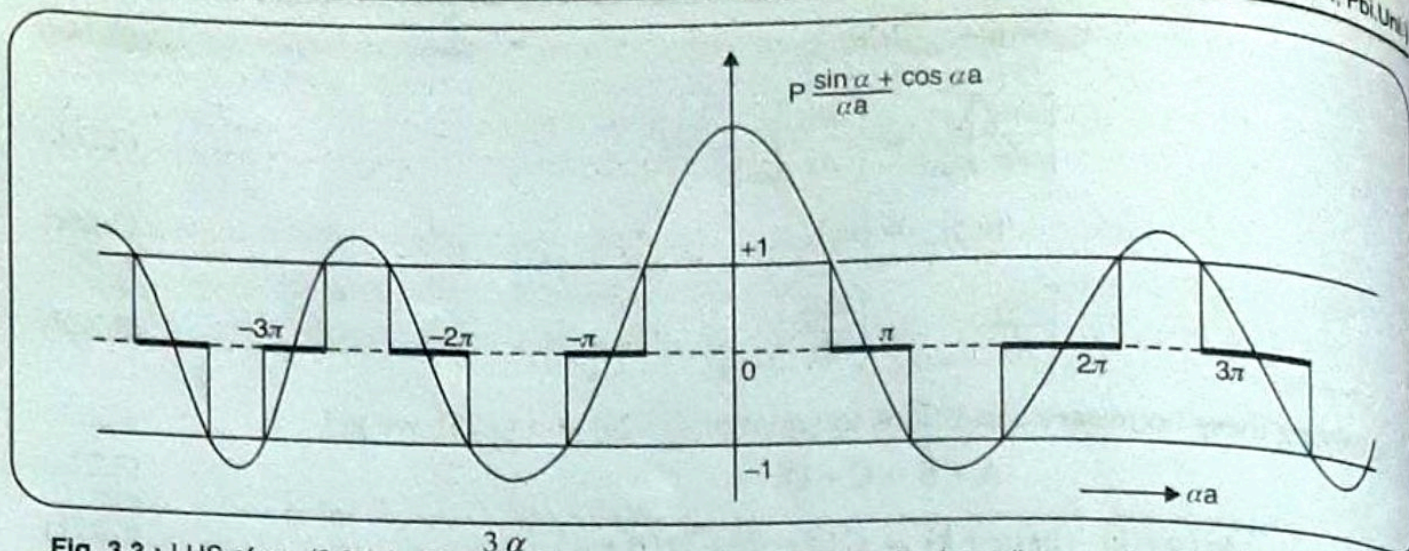


Fig. 3.3 : LHS of eq. (3.29) for  $P = \frac{3\alpha}{2}$  plotted as function of  $\alpha a$ . Heavily drawn lines on abscissa show the allowed regions.

left hand side of this equation as a function of  $\alpha a$  for values  $P = 3\pi/2$ . Since  $\alpha^2$  is proportional to energy  $E$ , hence abscissa gives a measure of energy. We can conclude from Fig. 3.3 the following points.

- The energy spectrum of the electrons consists of energy bands allowed (heavily drawn) and forbidden (lightly drawn).
- The width of allowed energy region or band increases with increasing values of  $\alpha a$  or energy.
- With increasing  $P$  i.e. with increase in binding energy of electron, the width of particular energy allowed energy band decreases. In case  $P \rightarrow \infty$ , the allowed region becomes infinitely narrow and the energy spectrum becomes a line spectrum i.e. insulator.

Since as  $P \rightarrow \infty$

i.e. if

$$\sin \alpha a = 0$$

$$\alpha a = \pm n\pi \text{ with } n = 0, 1, 2, 3, \dots$$

and from eq. (3.17), we obtain

$$E = \frac{\alpha^2 \hbar^2}{2m}$$

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2 \text{ for } P \rightarrow \infty$$

This is the result we obtain for a particle in a box of atomic dimensions with constant potential i.e.  $e^-$  is tightly bound. This result is expected since for large values of  $P$ , tunneling through the barriers becomes improbable.

Let us now consider the case when  $P \rightarrow 0$ , in this case we obtain

$$\cos \alpha a = \cos k a$$

$$\text{i.e., } \alpha = k$$

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

This represents energy of a completely free electron for which any energy value is possible. This result is also expected since by definition when  $P = 0$ , the electrons are free.

These conclusions are represented in Fig. 3.4.

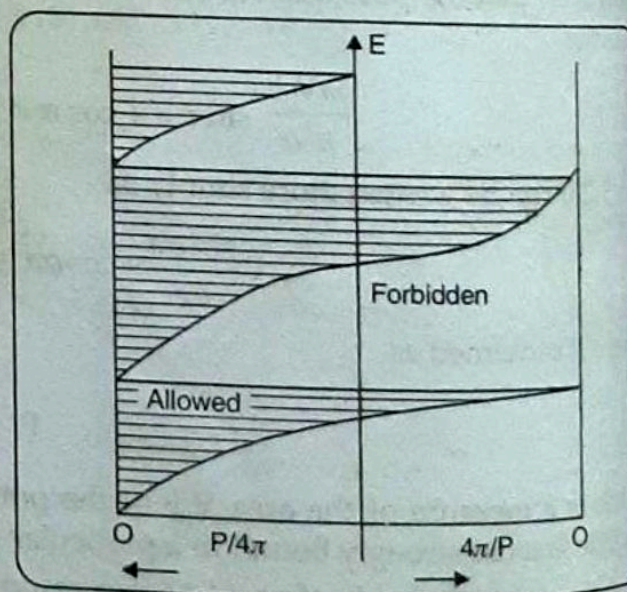


Fig. 3.4 : Allowed and forbidden energy ranges as function of  $P$ .



(iv) Right hand side  $\cos ka$  of eq. (3.29) is an even periodic function and its value does not change whether  $ka$  is positive or negative or it is increased by integer multiple of  $2\pi$ . As a result, total energy  $E$  of the electron is an even periodic function of  $k$  with period  $2\pi/a$ . This periodic repetition of energy is shown in Fig. 3.5(a). This may be considered as obtained by the repetition of the region  $-\frac{\pi}{a} < k < \frac{\pi}{a}$ , this is the first Brillouin zone. This representation is known as repeated zone scheme but the disadvantage in this case is that we obtain a large number of values corresponding to a particular energy  $E$ . However, these are two other schemes viz. *extended zone scheme* and *reduced zone scheme*. These are shown in Fig. 3.5 (b) and 3.5 (c). We find that discontinuities occur at

$$k = \pm n\pi/a \text{ where } n = 1, 2, 3, \dots$$

These  $k$  values define the boundaries of the first, second and third Brillouin zones.

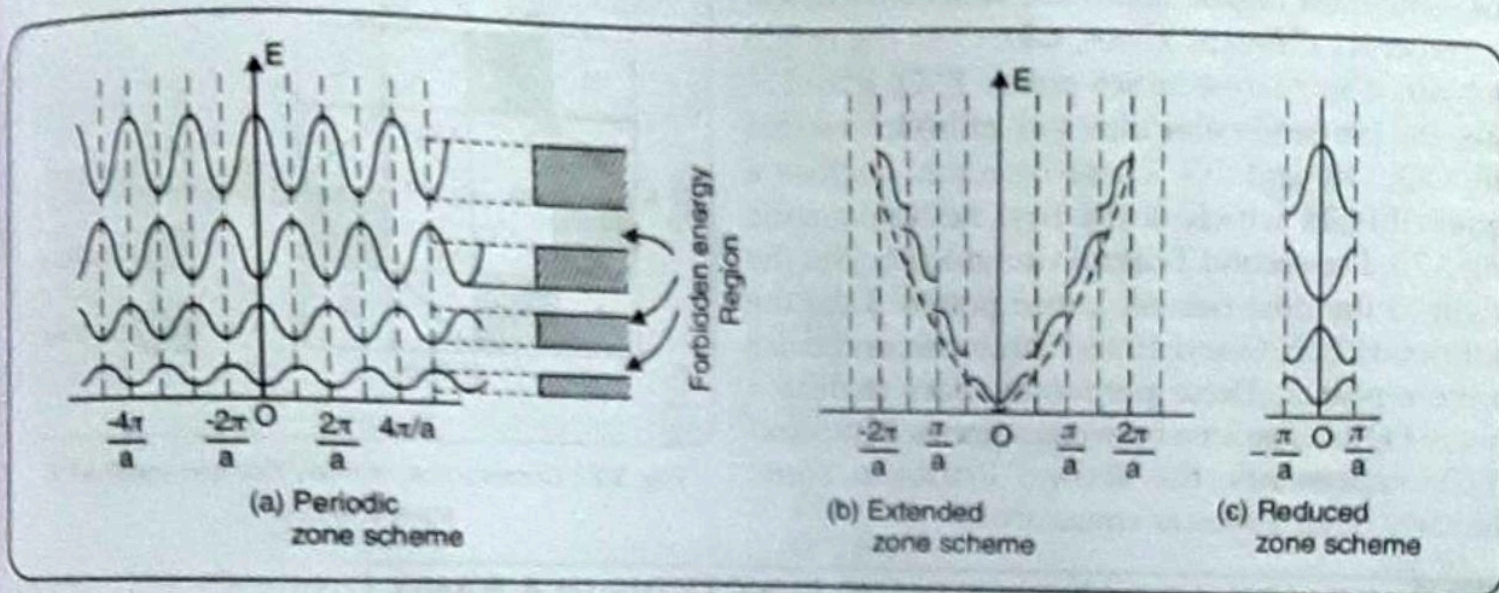


Fig. 3.5 : Constructed three Brillouin zones for a square lattice.

### 3.4. BRILLOUIN ZONES

We know that in Kronig-Penney model that in one dimensional lattice, the energy discontinuities occur when wave  $k$  satisfy the relation

$$k = \pm n\frac{\pi}{a} \text{ where } n = 1, 2, 3, \dots$$

If we consider a line (in one dimensional monoatomic lattice) representing  $k$  values, divided into energy discontinuities into segments of length  $\pm \frac{\pi}{a}$  as shown in Fig 6.6, these line segments are called Brillouin zones. First zone extends from  $-\frac{\pi}{a}$  to  $+\frac{\pi}{a}$  and second zone consists of two parts one extending from  $\frac{\pi}{a}$  to  $\frac{2\pi}{a}$  and other extending from  $-\frac{\pi}{a}$  to  $-\frac{2\pi}{a}$ . Thus, the segment  $-\frac{\pi}{a} < k < \frac{\pi}{a}$  represents first Brillouin zone and the segments  $-\frac{2\pi}{a} < k < -\frac{\pi}{a}$  and  $\frac{\pi}{a} < k < \frac{2\pi}{a}$  represent second Brillouin zone.



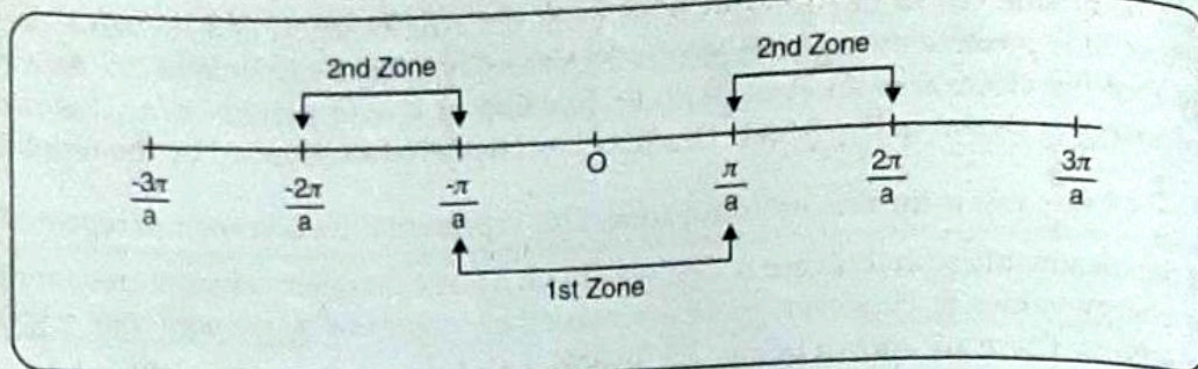


Fig. 3.6

### Construction of zones

Normally only first or reduced zone is sufficient but sometimes higher zones are also constructed. To construct different zones, take O as the origin and join it to nearest lattice points P, Q, R and S. Take the perpendicular bisectors of lattice vectors OP, OQ, OR and OS. These bisectors enclose a square EFGH which is the first Brillouin zone (Fig 3.7.). For second Brillouin zone again join the origin to the next nearest lattice points. Take the mid-points E, F, G and H and draw perpendicular to these points. These perpendiculars enclose a square PQRS. The area between squares PQRS and EFGH represents, the second Brillouin zone. Similarly other zones are constructed.

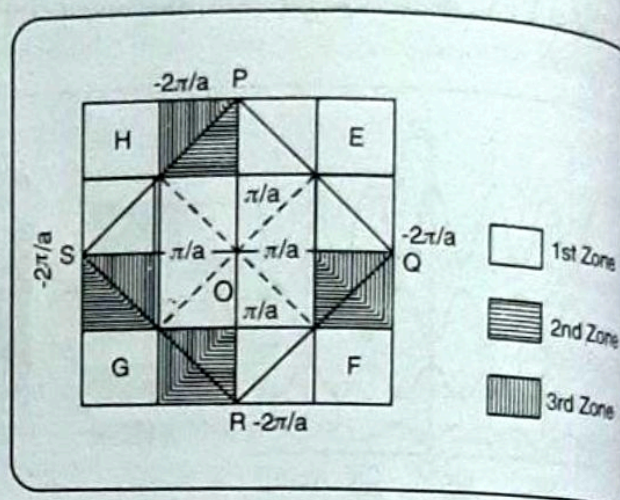


Fig. 3.7 : Construction of three Brillouin zones for a square lattice.

### 3.5. NUMBER OF POSSIBLE WAVE FUNCTIONS IN A BAND

We were considering the crystals to be of infinite dimensions and concluded that there are certain energy ranges within which there is a continuous distribution of energy. Let us now consider a finite crystal of length  $L$ , the following periodic boundary condition must be satisfied.

$$\psi(x+L) = \psi(x) \quad \dots(3.31)$$

Because these are Bloch functions, we have

$$\exp[ik(x+L)] u_k(x+L) = \exp(ikx) u_k(x)$$

Now  $u_k$  is periodic, hence we have

$$k = 2\pi n/L \text{ with } n = \pm 1, \pm 2, \dots \quad \dots(3.32)$$

Hence, the number of possible wave functions in the range  $dk$  are given as

$$dn = \frac{L dk}{2\pi} \quad \dots(3.33)$$

Now  $k$  has value varying from  $-\pi/a$  to  $\pi/a$  in first Brillouin zone, where  $a$  is length of unit cell. Hence, total number of possible states in a band,

$$n = \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk$$

$$n = L/a \text{ i.e. } na = L \quad \dots(3.34)$$

If  $N$  unit cells are there in the length  $L$  of the crystal, we get  $Na = L$ . Comparison of this with eq. (3.34) gives us  $n = N$ .



Thus total number of possible wave function in any energy band is equal to the number of unit cells. Taking into the account Pauli's exclusion principle and electron spin, we can say that each band can be occupied by  $2N$  electrons.

### 3.6 VELOCITY OF ELECTRON

According to de-Broglie theory, velocity of an electron with wave vector  $k$  is same as group velocity of the wave representing the electron, i.e.,

$$v = \frac{d\omega}{dk} \quad \dots(3.35)$$

where  $\omega$  is the angular frequency and is related to the electron energy  $E$  by the relation,

$E = \hbar \omega$  (or  $\omega = \frac{E}{\hbar}$ ). In terms of energy, the velocity is expressed as

$$v = \frac{1}{\hbar} \left( \frac{dE}{dk} \right) \quad \dots(3.36)$$

For a free electron,

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

So

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

We find

$$v = \frac{\hbar k}{m} = \frac{p}{m}$$

In band theory, however  $E$  is, in general not proportional to  $k^2$ , as can be seen in Fig. 3.8 (a), from this variation of  $E$  with  $k$ , we can calculate velocity  $v$  and the  $v$ - $k$  graph is shown in Fig 3.8(b). We observe at the bottom and top of the band, velocity is zero, we also see that velocity increases with  $k$  and is maximum at point  $k = k_0$ , the point of inflection. Beyond this point velocity decreases with increasing energy.

### 3.7 EFFECTIVE MASS OF ELECTRON

The mass of an electron in a crystal, in general, is different from its free mass which is known as effective mass.

Let us consider an electron in external electric field  $e$ . When this field acts on electron for a small time  $dt$ , electron gains some energy

$$dE = e\mathcal{E} dx = e\mathcal{E} v dt$$

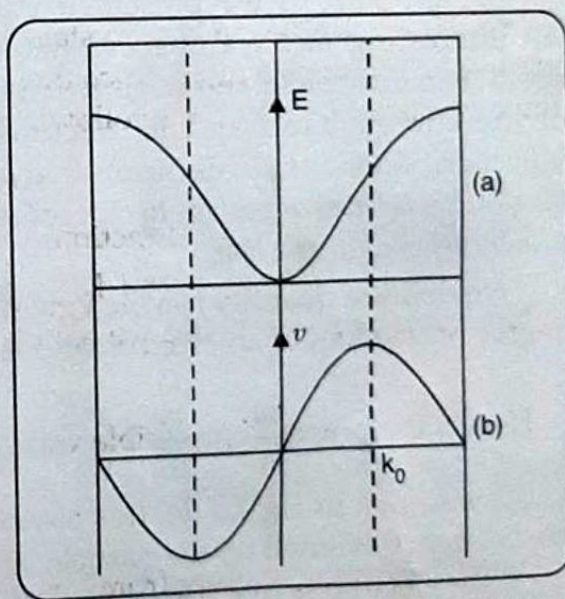


Fig. 3.8 : (a)  $E$  versus  $k$  curve (b)  $v$  versus  $k$  curve



Therefore, from eq. (3.36), we get

$$dE = \frac{e\mathcal{E}}{\hbar} \frac{dE}{dk} dt \quad \dots(3.37)$$

Here it is assumed that there is only one electron in the given Brillouin zone, so that Pauli principle does not come into picture, from eq. (3.37), we have

$$\frac{dk}{dt} = \frac{e\mathcal{E}}{\hbar} \quad \dots(3.38)$$

Now

$$v = \frac{1}{\hbar} \frac{dE}{dk}$$

Hence, to get acceleration, differentiating this equation with respect to time,

$$a = \frac{dv}{dt} = \frac{1}{\hbar} \frac{d^2E}{dk^2} \cdot \frac{dk}{dt} \quad \dots(3.39)$$

From eqs. (3.38) and (3.39), we get

$$a = \frac{e\mathcal{E}}{\hbar^2} \left( \frac{d^2E}{dk^2} \right) \quad \dots(3.40)$$

Comparing this result with classical result

$$a = eF/m$$

It follows that the electron behaves as if it has an effective mass  $m^*$  given as

$$m^* = \hbar^2 \left[ \frac{d^2E}{dk^2} \right]^{-1} \quad \dots(3.41)$$

In Fig. 3.9 (a),  $m^*$  is represented as a function of  $k$ . An interesting fact we observe here is that  $m^*$  is positive in lower half and negative in the upper half of the energy band and  $m^*$  becomes infinite at inflection point  $k = k_0$ . This means that in the upper half the electron behaves as positively charged particle which is usually referred to as a hole.

We define a quantity  $f_k$  which gives a measure of degree of freedom of an electron and is expressed as

$$f_k = \frac{m}{m^*} = \frac{m}{\hbar^2} \left[ \frac{d^2E}{dk^2} \right] \quad \dots(3.42)$$

$f_k$  vs  $k$  is shown in Fig 3.9 (b). It is obvious that when  $m^*$  is large,  $f_k$  is small i.e. the particle is heavy, when  $f_k = 1$ , the electron is free. This effective mass is a new concept which arises due to the interaction of the electron wave packet with the periodic lattice.

In most conductors  $m^* = m$  because the band is only partially filled. But in semiconductors and insulators having almost filled valence bands, the effective mass plays an important role in conduction process. The concept of effective mass is able to account for many experimental observations like high electronic specific heat of transition metals and their high paramagnetic susceptibility.

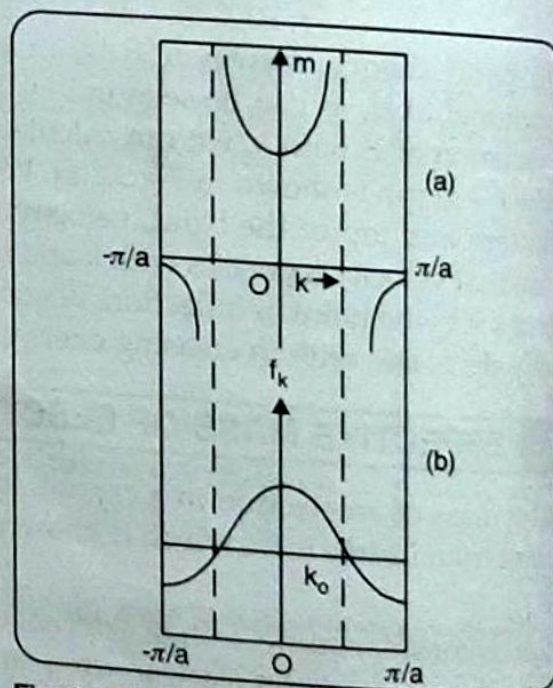


Fig. 3.9 : Plot of effective mass as a function of  $k$ .



### 3.8. DISTINCTION BETWEEN METALS, INSULATORS AND INTRINSIC SEMICONDUCTORS

Let us consider an energy band which is filled with electrons upto  $k_1$  as shown in Fig. (3.10) ( $k_1$  is less than  $\pi/a$ ). As far as the affect of external field is concerned, one is interested in knowing the equivalence to 'free' electrons of the  $N$  electrons in the band. The number of free electrons in a band is given as

$$N_{eff} = \sum f_k \quad \dots (3.43)$$

where the summation extends over all the occupied states in the band for a one-dimensional crystal of length  $L$ , the number of states in the interval  $dk$  is given as,

$$dn = \frac{L}{2\pi} dk \quad \dots (3.44)$$

Because two electrons can occupy each of the states in the shaded region of Fig. 7, the above relation must be multiplied by 2. Hence,

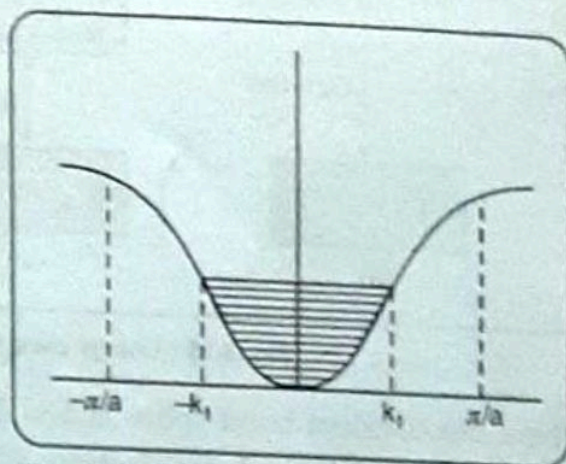


Fig. 3.10 : Energy band filled up to states  $k_1$  at  $T = 0$ .

$$N_{eff} = 2 \int dn f_k = \frac{L}{\pi} \int_{-k_1}^{k_1} f_k dk = \frac{2L}{\pi} \int_0^{k_1} f_k dk$$

Putting the value of  $f_k$  from eq. (3.42), we get

$$N_{eff} = \frac{2L}{\pi} \frac{m}{\hbar^2} \int_0^{k_1} \frac{d^2 E}{dk^2} dk$$

$\therefore$

$$N_{eff} = \frac{2Lm}{\pi\hbar^2} \left( \frac{dE}{dk} \right)_{k=k_1} \quad \dots (3.45)$$

If the band is completely filled,

$$k = \pm \frac{n\pi}{a}; n = 1, 2, 3, \dots$$

$$\frac{dE}{dk} = 0$$

$$N_{eff} = 0$$

and hence

which means that number of free electrons in a completely filled band is zero.

The effective number of electrons reaches a maximum for a band filled upto  $k = k_0$  the inflection point.

In case of insulators there are no effective free electrons. All the bands are completely full in the valence band and conduction band is completely empty and there is a large forbidden energy gap (of the order of 5 – 10 eV) between these two bands and it is impossible to excite any electron across this region Fig. 3.11 (a).

All the bands are then either completely filled or empty at any temperature so the external electric field can not produce any current. So, the conductivity of such materials under ordinary conditions is zero and are called insulators. A representative example of an insulator is diamond



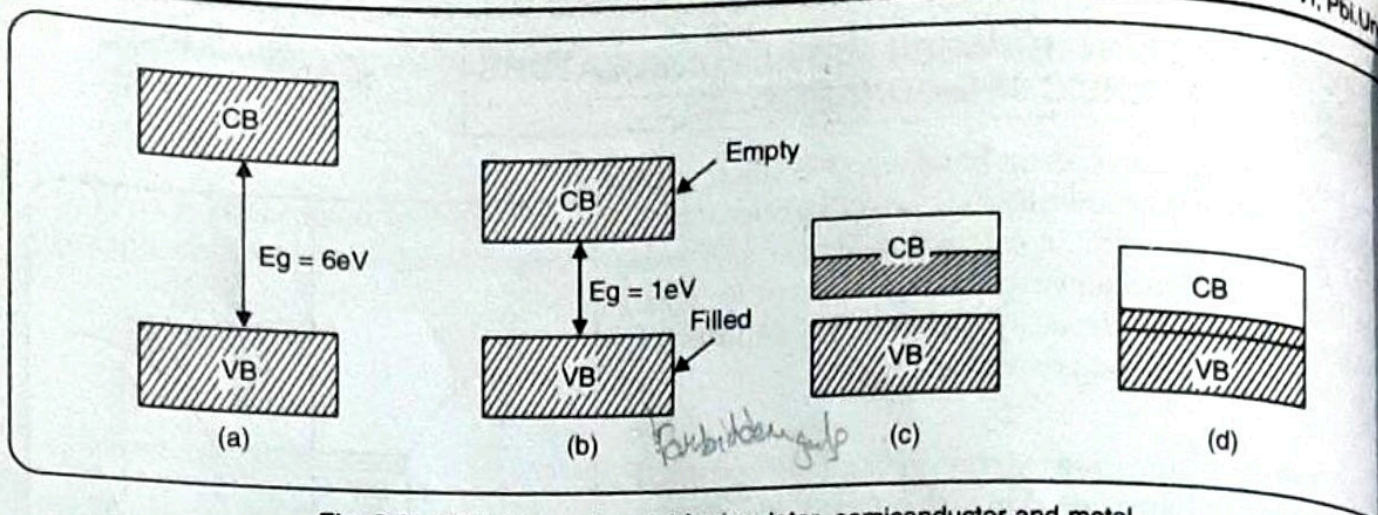


Fig. 3.11 : Energy band model for insulator, semiconductor and metal.

where the covalent bond splits  $2s$  and  $2p$  levels into two bands separated by an energy gap of  $\Delta E_g = 7 \text{ eV}$ ; with the valence electrons filling the lower band.

When the forbidden gap is small, say of the order of  $1 \text{ eV}$  or less Fig 3.11 (b), so that electrons could be excited thermally from states near the top of the filled band to states near the bottom of the next empty band across the band gap. Hence a limited number of electrons are available for conduction in the conduction band which is almost empty, on applying an electric field. The states near top of filled band also contributes to the flow of electric current through the mechanism of hole conduction. A material of this type is called semiconductor. At low temperature ( $0\text{K}$ ) the valence band is completely filled and the conduction band is completely empty. So, a semiconductor virtually behaves as an insulator at low temperature. Even at room temperature some electrons (about one electron for  $10^{14}$  atoms) cross the conduction and impart little conductivity to the semiconductor. As the temperature is increased, more and more electrons cross over to the conduction band and the conductivity increases. Examples of semiconductors are Germanium (band gap  $0.78 \text{ eV}$ ) and silicon (band gap  $1.21 \text{ eV}$ ).

The energy band structure in solids have two possibilities. (i) A solid is a conductor if either its conduction band is not completely filled and the valence band may be completely filled and there is extremely small energy gap between them as shown in Fig. 3.11 (c) e.g. Li, Na, K etc. (ii) The valence band is completely filled and the empty conduction band overlap with valence band Fig. 3.11 (d) (eg; Ba, Cd, Zn etc.) so the energy gap is zero. The electron in the valence band are free to move inside the crystal lattice. The electrons under the influence of small applied field acquire additional energy and move to higher energy state. These mobile electrons constitute current.

### SOLVED EXAMPLES

**Example 3.1.** Prove that for the Kronig-Penney potential with  $P \ll 1$ , the energy of the lowest energy band at  $k = 0$  is

$$E = \frac{\hbar^2 P}{m a^2}$$

**Solution.** We know

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

for  $k = 0$ , we have

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = 1$$