

CHAPTER

8

Band Theory of Solids

8.1. Introduction

Many properties of metals can be explained by using the free electron theory. However there are many properties which can not be explained by this theory at all. For example, free electron theory does not tell us why some chemical elements crystallize to form good conductors of electricity whereas the others are insulators or semiconductors.

In the free electron theory, it was assumed that the electron is free to move inside a box of constant or zero potential. Therefore, no force acts on the electron in moving throughout the body of the metal. However, this is not actually true. When an electron passes near an ion, a force acts on it. There is a regular arrangement of ions in the metallic crystal. Therefore in moving from one place to another, the electron passes over the changing potential of one ion to the other. We may say that electron is under the impact of a periodic potential instead of being in a constant potential as assumed in free electron theory. The most appropriate potential for the physical system would be the muffin tin potential. It takes into account the fact that the electrons which actually take part in the bonding are the valence electrons and they are acted upon by the potential of the nucleus that decays inversely with the distance of the electron from the centre of the nucleus i.e.

$V \propto \frac{1}{r}$. The variation of potential experienced by an electron in perfectly periodic crystal lattice with lattice parameter a may be shown in Figure 8.1. The potential on the surface is shown on the left.

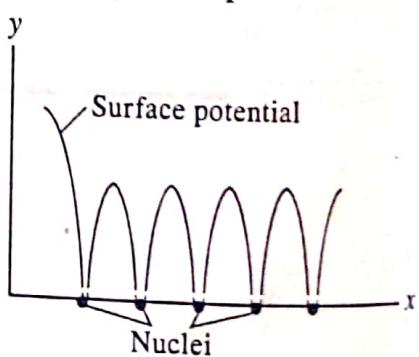


Figure 8.1.

8.2. The Bloch Theorem

In case of free electron theory, it was assumed that the electron moves in a constant potential V_0 . Therefore the one dimensional schrodinger equation for an electron is expressed as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V_0] \psi = 0 \quad \dots(1)$$

The solution to eqn. (1) is the plane waves expressed by

$$\psi(x) = e^{\pm ikx} \quad \dots(2)$$

Substituting eqn. (2) in eqn. (1) and solving, we get

$$E - V_0 = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = E_{\text{kin}}$$

where k is the magnitude of the wave vector and it represents the momentum of electron divided by \hbar .

In case the electron moves in a one dimensional periodic potential, the potential energy of the electron should satisfy the condition.

$$V(x) = V(x + a) \quad \dots(3)$$

where a is the period equal to the lattice constant.

The schrodinger wave equation in this case can be written as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi = 0 \quad \dots(4)$$

The equation (4) can be solved with the help of a theorem called the Bloch theorem. This theorem states that there exist solution of the form

$$\psi(x) = e^{\pm ikx} u_k(x) \quad \dots(5)$$

where

$$u_k(x) = u_k(x + a) \quad \dots(6)$$

The function $\psi(x)$ is called the Bloch function or Bloch wave and represents the free electron wave function (i.e., $e^{\pm ikx}$) modulated near each atom of the lattice by an identical function $u_k(x)$ given by equation (6).

It was proved by Bloch that the periodic field of the crystal lattice only modulates the free electron wave. The Bloch theorem is also termed as Floquet's theorem.

Proof of Bloch Theorem.

Let $\psi_1(x)$ and $\psi_2(x)$ be two real and independent solutions of equation (4). Then the general solution of equation (4) is the linear combination of two functions $\psi_1(x)$, and $\psi_2(x)$, i.e.,

$$\psi(x) = A\psi_1(x) + B\psi_2(x) \quad \dots(7)$$

[∴ second order differential eqn. has only two solutions]

where A and B are arbitrary constants.

Since the potential is a periodic potential, therefore the solutions $\psi_1(x + a)$ and $\psi_2(x + a)$ must also be the solutions of the Schrodinger equation (4) and expressible in terms of $\psi_1(x)$ and $\psi_2(x)$ as

$$\psi_1(x + a) = \alpha_1 \psi_1(x) + \alpha_2 \psi_2(x) \quad \dots(8a)$$

and $\psi_2(x + a) = \beta_1 \psi_1(x) + \beta_2 \psi_2(x) \quad \dots(8b)$

The wave function $\psi(x + a)$ can be represented similar to eqn. (7)

i.e. $\psi(x + a) = A \psi_1(x + a) + B \psi_2(x + a)$

$$= A [\alpha_1 \psi_1(x) + \alpha_2 \psi_2(x)] + B [\beta_1 \psi_1(x) + \beta_2 \psi_2(x)]$$

[using eqns., (8a) and (8b)]

$$\therefore \psi(x+a) = [\Lambda\alpha_1 + B\beta_1] \psi_1(x) + [\Lambda\alpha_2 + B\beta_2] \psi_2(x) \quad \dots(9)$$

Let the constants Λ and B are so chosen that

$$\Lambda\alpha_1 + B\beta_1 = QA \quad \dots(10a)$$

and

$$\Lambda\alpha_2 + B\beta_2 = QB \quad \dots(10b)$$

where Q is another constant.

Using eqns. (10a) and (10b) in eqn. (9),

$$\begin{aligned} \psi(x+a) &= QA \psi_1(x) + QB \psi_2(x) \\ &= Q [A \psi_1(x) + B \psi_2(x)] \end{aligned}$$

$$\Rightarrow \psi(x+a) = Q \psi(x) \quad \dots(11) \text{ [Using eqn. (7)]}$$

Equations (10a) and (10b) can also be written as

$$(\alpha_1 - Q)\Lambda + \beta_1 B = 0 \quad \dots(12a)$$

$$\text{and } \alpha_2 \Lambda + (\beta_2 - Q)B = 0 \quad \dots(12b)$$

Since A and B are non vanishing constants, equations (12a) and (12b) result

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

$$\text{or } (\alpha_1 - Q)(\beta_2 - Q) - \alpha_2 \beta_1 = 0$$

$$\text{or } Q^2 - (\alpha_1 + \beta_2)Q + (\alpha_1 \beta_2 - \alpha_2 \beta_1) = 0 \quad \dots(13)$$

Now we shall show that the quantity $\alpha_1 \beta_2 - \alpha_2 \beta_1 = 1$.

To show this, we find the derivatives of eqn. (8a) and (8b) w.r.t. x .

$$\therefore \psi'_1(x+a) = \alpha_1 \psi'_1(x) + \alpha_2 \psi'_2(x) \quad \dots(14a)$$

$$\text{and } \psi'_2(x+a) = \beta_1 \psi'_1(x) + \beta_2 \psi'_2(x) \quad \dots(14b)$$

where $\psi'_1(x+a) = \frac{d}{dx} \psi_1(x+a)$ and ; similarly, $\psi'_2(x+a)$, $\psi'_1(x)$ and $\psi'_2(x)$ can be found.

The equations (8a), (8b) and (14a), (14b) can collectively be put in matrix form as under.

$$\begin{vmatrix} \psi_1(x+a) & \psi_2(x+a) \\ \psi'_1(x+a) & \psi'_2(x+a) \end{vmatrix} = \begin{vmatrix} \psi_1(x) & \psi_2(x) \\ \psi'_1(x) & \psi'_2(x) \end{vmatrix} \begin{bmatrix} \alpha_1 & \beta_1 \\ \alpha_2 & \beta_2 \end{bmatrix} \quad \dots(15)$$

Now the equation (4) for $\psi_1(x)$ and $\psi_2(x)$ can be written as

$$\frac{d^2 \psi_1(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi_1(x) = 0 \quad \dots(16a)$$

$$\text{and } \frac{d^2 \psi_2(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi_2(x) = 0 \quad \dots(16b)$$

Multiplying eqn. (16a) with $\psi_2(x)$ and eqn. (16b) with $\psi_1(x)$ and then subtracting,

$$\psi_1(x) \frac{d^2\psi_2(x)}{dx^2} - \psi_2(x) \frac{d^2\psi_1(x)}{dx^2} = 0$$

$$\Rightarrow \frac{d}{dx} \left[\psi_1(x) \frac{d}{dx} \psi_2(x) - \psi_2(x) \frac{d}{dx} \psi_1(x) \right] = 0$$

or $\psi_1(x) \psi'_2(x) - \psi_2(x) \psi'_1(x) = \text{Constant}$

or $\begin{vmatrix} \psi_1(x) & \psi_2(x) \\ \psi'_1(x) & \psi'_2(x) \end{vmatrix} = \text{Constant}$

Therefore, from eqn. (15), since

$$\begin{vmatrix} \psi_1(x+a) & \psi_2(x+a) \\ \psi'_1(x+a) & \psi'_2(x+a) \end{vmatrix} = \begin{vmatrix} \psi_1(x) & \psi_2(x) \\ \psi'_1(x) & \psi'_2(x) \end{vmatrix} \begin{bmatrix} \alpha_1 & \beta_1 \\ \alpha_2 & \beta_2 \end{bmatrix}$$

Therefore, using the properties of $\psi_1(x)$ and $\psi_2(x)$,

$$\begin{bmatrix} \alpha_1 & \beta_1 \\ \alpha_2 & \beta_2 \end{bmatrix} = 1 \quad \dots(17)$$

i.e. $\alpha_1 \beta_2 - \alpha_2 \beta_1 = 1$

Using eqn. (17) in eqn. (13), $\dots(18)$

$$Q^2 - (\alpha_1 + \beta_2) Q + 1 = 0$$

Equation (18) is a quadratic in Q and gives two values of Q , which may be real or virtual pending upon the discriminant $(\alpha_1 + \beta_2)^2 - 4$. Following two cases may be considered.

Case I. If energy values are such that $(\alpha_1 + \beta_2)^2 < 4$ i.e., the "disc" is negative. Then the roots of equation (18) shall be complex. But from eqn. (18), the product of roots (let Q_1 and Q_2 be roots) is 1.

i.e., $Q_1 Q_2 = 1$

Therefore, we may say $Q_1 = e^{ika}$

and $Q_2 = e^{-ika}$.

where k is a real number.

Now, if $\psi_I(x)$ and $\psi_{II}(x)$ are the corresponding wave functions, then using eqn. (11),

$$\psi_I(x+a) = e^{ika} \psi_I(x)$$

and

$$\psi_{II}(x+a) = e^{-ika} \psi_{II}(x)$$

Therefore in general, we may write

$$\psi(x+a) = e^{\pm ika} \psi(x) \quad \dots(19)$$

This is the property of Bloch function as given in eqn. (5) and eqn. (6).

Taking x as $(x+a)$ in eqn. (5) we have

$$\psi(x+a) = e^{\pm ik(x+a)} u_k(x+a) = e^{\pm ika} \cdot e^{\pm ikx} \cdot u_k(x) = e^{\pm ika} \psi(x) \quad (\text{Using eqn. (6)})$$

which is the same as equation (19). Thus equation (19) represents the Bloch function and the Bloch theorem is proved.

Case 2. If the energy values are such that the "disc" of equation (18) is positive i.e., $(\alpha_1 + \beta_2)^2 > 4$

Then the roots Q_1 and Q_2 are real

Therefore if

$$Q_1 = e^{+\mu a}$$

then

$$Q_2 = e^{-\mu a}$$

[∴ Product of roots $Q_1 Q_2 = 1$]

Therefore, the solution of schrodinger equation using eqn. (11) can be

$$\psi_I(x) = e^{\mu a} u(x) \text{ and } \psi_{II}(x) = e^{-\mu a} u(x)$$

Such functions are invalid because the ratio $\frac{\psi(x+na)}{\psi(x)}$ approaches infinity as n approaches $\pm\infty$ for such functions. Thus there are no electronic states in the energy region corresponding to the real roots Q_1 and Q_2 .

The above discussion implies that the energy spectrum of the electron in a periodic potential consists of allowed and forbidden regions of energy called energy bands.

8.3. Kronig Penney Model

Kronig and Penney, in 1930, gave a simple model of one dimensional potential as shown in the figure 8.2.

It was assumed that the potential energy of the electron has the form of periodic array of square wells of period $a+b$ such that the potential energy of the electron is zero in the region $0 < x < a$ and V_0 in the region $-b < x < 0$.

The schrodinger wave equation may be written as

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} E \psi(x) = 0 \quad \text{for } 0 < x < a \quad \dots(1)$$

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

Assuming that $E < V_0$, the quantity $V_0 - E$ shall be positive. Let α and β be new quantities such that

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad \dots(3)$$

$$\text{and } \beta^2 = \frac{2m}{\hbar^2} [V_0 - E] \quad \dots(4)$$

Therefore the equations (1) and (2) become

$$\frac{d^2\psi(x)}{dx^2} + \alpha^2 \psi(x) = 0 \quad \text{for } 0 < x < a \quad \dots(5)$$

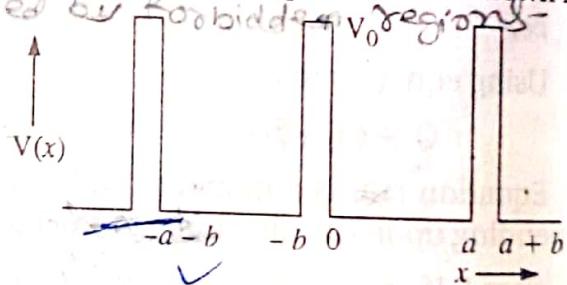


Figure 8.2

PV2010 Discuss Kronig-Penney model for e[–] energy in solids & show how it explain the forbidden bands (9 marks)

$$\frac{d^2}{dx^2} \psi(x) - \beta^2 \psi(x) = 0 \quad \text{for } -b < x < 0 \quad \dots(6)$$

As the potential is periodic, the solution to equations (5) and (6) may be expressed in terms of the Bloch functions.

i.e.

$$\psi(x) = u_k(x) e^{ikx} \quad \dots(7)$$

Such that

$$u_k(x) = u_k(x + a + b) \quad \dots(8)$$

[∴ period = $a + b$]

Now differentiating eqn. (7) w.r.t. x .

$$\frac{d\psi(x)}{dx} = ik u_k(x) e^{ikx} + e^{ikx} \frac{d}{dx} u_k(x)$$

Again differentiating w.r.t. x .

$$\frac{d^2\psi(x)}{dx^2} = i^2 k^2 u_k(x) e^{ikx} + ik \frac{d}{dx} u_k(x) \cdot e^{ikx} + ik e^{ikx} \frac{d}{dx} u_k(x) + e^{ikx} \frac{d^2}{dx^2} u_k(x)$$

$$\text{or} \quad \frac{d^2\psi(x)}{dx^2} = e^{ikx} \left[\frac{d^2}{dx^2} u_k(x) + 2ik \frac{d}{dx} u_k(x) - k^2 u_k(x) \right] \quad \dots(9)$$

Using eqns. (9) and (7) in eqns. (5) and (6), and solving

$$\frac{d^2}{dx^2} u_k(x) + 2ik \frac{d}{dx} u_k(x) - (\alpha^2 - k^2) u_k(x) = 0 \quad \text{for } 0 < x < a \quad \dots(10)$$

$$\text{and} \quad \frac{d^2}{dx^2} u_k(x) + 2ik \frac{d}{dx} u_k(x) - (\beta^2 + k^2) u_k(x) = 0 \quad \text{for } -b < x < 0 \quad \dots(11)$$

The solutions to eqns. (10) and (11) are

$$u_1 = A e^{i(\alpha - k)x} + B e^{-i(\alpha + k)x} \quad \text{for } 0 < x < a \quad \dots(12)$$

$$u_2 = C e^{(\beta - ik)x} + D e^{-(\beta + ik)x} \quad \text{for } -b < x < 0 \quad \dots(13)$$

Since the wave function and its differential must be continuous at the boundary separating the two regions,

$$\therefore u_1 = u_2 \text{ at } x = 0$$

$$\text{and} \quad u_1(a) = u_2(-b)$$

$$\text{Also} \quad \left(\frac{du_1}{dx} \right)_{x=0} = \left(\frac{du_2}{dx} \right)_{x=0} \quad \text{and} \quad \left(\frac{du_1}{dx} \right)_a = \left(\frac{du_2}{dx} \right)_{-b}$$

Therefore, using the condition $u_1(0) = u_2(0)$ in eqns. (12) and (13),

$$A + B = C + D \quad \dots(14)$$

PUR 2009 Describe Kronig-Penney model for the motion of an electron in a periodic Potential. Show from (E-k) graph that materials are classified into conductors, insulators & semiconductors

Using the condition $u_1(a) = u_2(-b)$,

$$A e^{i(\alpha-k)a} + B e^{-i(\alpha+k)a} = C e^{-(\beta-ik)b} + D e^{(\beta+ik)b} \quad \dots(15)$$

Using the condition $\left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0}$,

$$A i(\alpha - k) - B i(\alpha + k) = C (\beta - ik) - D (\beta + ik) \quad \dots(16)$$

and using the condition $\left(\frac{du_1}{dx}\right)_a = \left(\frac{du_2}{dx}\right)_{-b}$

$$A i(\alpha - k) e^{i(\alpha-k)a} - B i(\alpha + k) e^{-i(\alpha+k)a} = C (\beta - ik) e^{-(\beta-ik)b} - D (\beta + ik) e^{(\beta+ik)b} \quad \dots(17)$$

The equations (14), (15), (16) and (17) can be solved for non zero values of A, B, C and D only if the determinant of the coefficients of A, B, C and D vanishes to zero.

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

On expanding the determinant, one obtains

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a+b) \quad \dots(18)$$

To obtain a more convenient result, it was assumed by Kronig and Penney that V_0 tends to infinity and b tends to zero, but the product $V_0 b$ remains finite. (This is the property of Dirac delta functions. Thus potential barriers become Dirac Delta functions).

As $b \rightarrow 0$, $\sinh \beta b \rightarrow \beta b$ and $\cosh \beta b \rightarrow 1$.

Also, using

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} = \frac{\beta^2}{2\alpha\beta} = \frac{\beta}{2\alpha}$$

The equation (18) reduces to

$$\frac{\beta^2 b}{2\alpha} \sin \alpha a + \cos \alpha a = \cos k a \quad \dots(19)$$

Now we define a quantity

$$P = \frac{\beta^2 ab}{2}$$

$$\frac{2P}{ab}$$

...(20a)

i.e.

$$P = \frac{2m}{\hbar^2} [V_0] \frac{ab}{2}$$

[Using eqn. (4) for $V_0 \gg E$]

i.e.

$$P = \frac{mV_0}{\hbar^2} ab$$

...(20b)

The equation (20) is the measure of the area of the potential barrier. Physically speaking, it means that if P increases, the electron is bound more strongly to a particular potential well in the periodic potential system.

Using eqn. (20a) in eqn. (19), one gets

$$\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad \dots(21)$$

It is difficult to solve equation (21), analytically, however graphical variation of $\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a$ against αa is very helpful to draw some important conclusions. The variation of $\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a$ against αa is as shown in Figure 8.3 and the conclusions drawn are explained as under.

PU2019 Discuss the essential features of energy band structure on the basis of Kronig-Penney model.

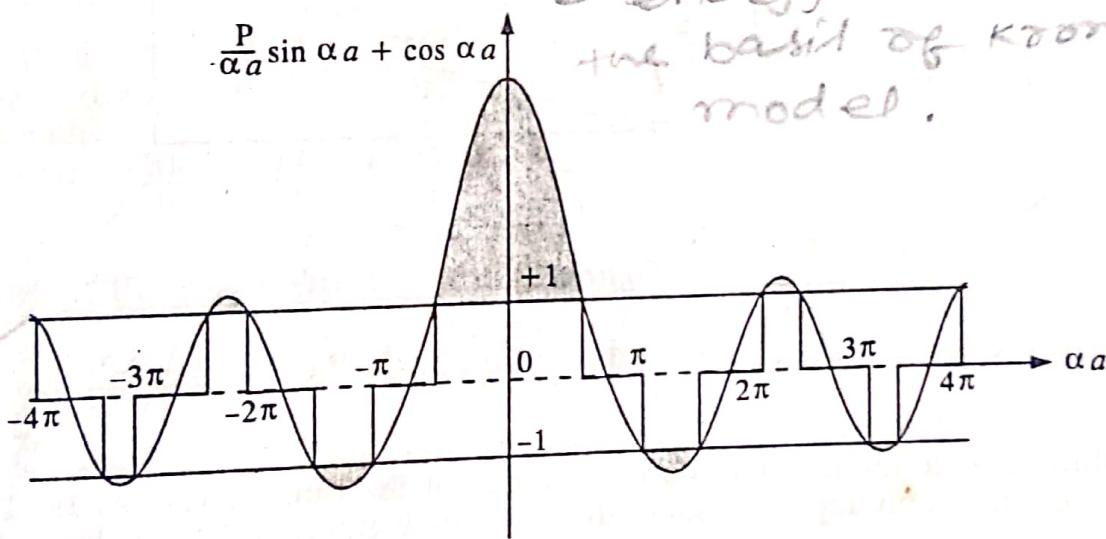


Figure 8.3

1. The value of $\cos ka$, the right-hand side of eqn. (21), must lie between +1 and -1; consequently, the only allowed values of αa are those for which the left hand side of eqn. (21) lies between +1 and -1. The two horizontal lines in the figure (7.3) represent the two extreme values of $\cos ka$ i.e., corresponding to $\cos ka = \pm 1$. Therefore the allowed energy levels have their boundaries corresponding to $\cos ka = \pm 1$

where $n = \text{an integer}$.

i.e.

$$ka = n\pi$$

or

$$k = \frac{n\pi}{a}.$$

This means that the energy spectrum consists of an infinite array of allowed bands (shown by thick lines in the figure) separated by intervals having no energy levels (shown by dotted lines in the figure 8.3). The intervals are called forbidden regions.

2. The width of allowed energy bands increases with the increase in αa i.e., with the increase in energy. [It is due to the fact that $\frac{P \sin \alpha a}{\alpha a}$ decreases on the average with the increase in αa .]

~~3. As P increases, the width of a particular allowed energy band decreases. It means that the width of allowed energy band decreases with increase of binding energy of electrons. In a special case, when $P \rightarrow \infty$, the allowed energy bands are infinitely narrow and are independent of k . In such a case the energy spectrum becomes a line spectrum. As the energy is related to α by the relation.~~

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

[from eqn. (3)]

Therefore the variation of E versus ka can be plotted as shown in Figure 8.4(a).

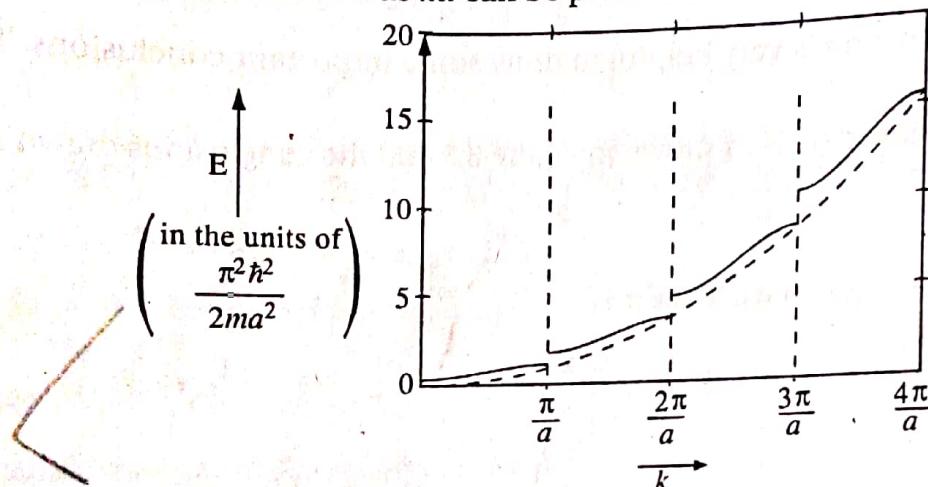


Figure 8.4(a).

From the graph it is clear that there are discontinuities in E versus k graph for $k = \frac{n\pi}{a}$

where $n = 1, 2, 3, \dots$

These values of k define the boundaries of different Brillouin zones i.e., 1st, 2nd, 3rd etc. Since the above figure only represents half the E versus k graph and -ve values of k have not

been taken into consideration, therefore, the first Brillouin zone extends from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$, the

second Brillouin zone from $\frac{\pi}{a}$ to $\frac{2\pi}{a}$ and also from $-\frac{\pi}{a}$ to $-\frac{2\pi}{a}$, and so on.

Special Cases.

Case (a). For $P = 0$, from eqn. (21), we have $\cos \alpha a = \cos ka$

$$\alpha = k \quad \text{or} \quad E = \frac{\hbar^2 k^2}{2m}$$

[Using Eqn. (3)]

\Rightarrow This is the well known equation for a free electron. In this case, there will be no band gap as shown in figure 7.4(a)

Case (b). For $P = \infty$, from eqn. (21), we get

$$\frac{\sin \alpha a}{\alpha a} = 0 \Rightarrow \alpha a = n\pi$$

$$E = \frac{\pi^2 \hbar^2}{2ma^2} n^2$$

[Using eqn. (3)]

or

This represents the energy of an isolated atom. We can distinguish four case based upon the bond strength P that keeps the electron close to the atom and these cases have been diagrammatically shown in Figure 8.4(b).

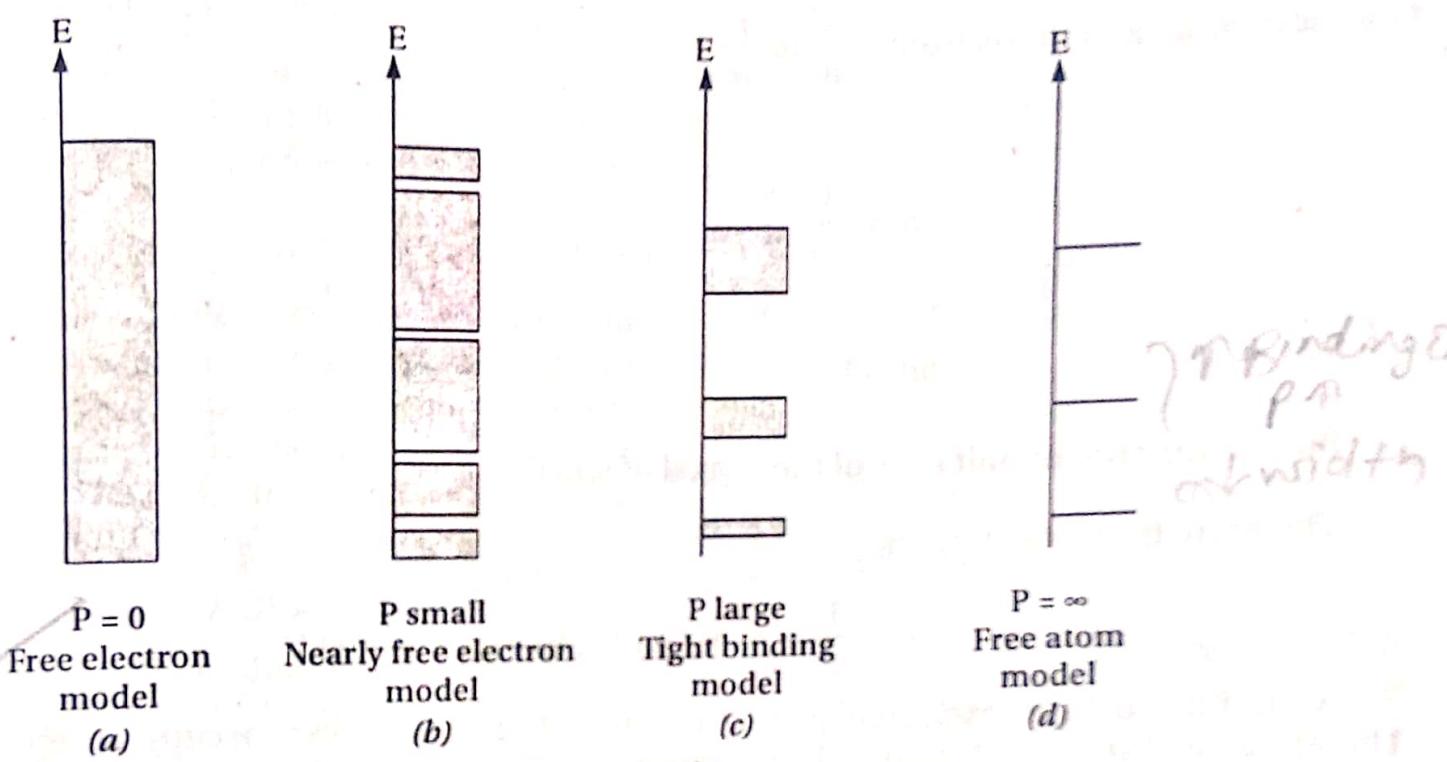


Figure 8.4(b).

Equation (2) represents the variation of v with k . Here we have assumed the electron to be free. However, on the band theory, E is not generally proportional to k^2 . The variation of E with k is as shown in Figure 8.5.

The variation of E and k is used to find dE/dk (slope of graph) to find the velocity of electron. The velocity of electron is zero at

$k = -\frac{\pi}{a}$ and $k = +\frac{\pi}{a}$. At some intermediate region, the velocity of electron is equal to the velocity of the free electron. The velocity becomes maximum for a certain velocity at $k = k_0$ where k_0 is the inflection point of the curve E versus k . The velocity beyond this point decreases and the energy increases.

Define & Prove that (A.I. 2008) P.U 2011, 2009 I.I.T. 2005

8.6. Effective Mass of Electron

In the Bloch approximation an electron in the energy band behaves in such a manner that it has a mass m^* which is different from its actual mass m and is termed as effective mass of the electron.

Consider an electron which is initially in a k state. When an electric field ξ is applied, a change in its energy occurs, which is given by

$$dE = e\xi dx = e\xi v dt \quad \dots(1)$$

where dx is the distance moved by the electron during the time dt and v is its velocity when the electric field is applied.

But from the last section,

$$v = \frac{1}{\hbar} \frac{dE}{dk} \quad [F.Q. - 230]$$

∴ equation (1) becomes

$$dE = e\xi \cdot \frac{1}{\hbar} \frac{dE}{dk} \cdot dt$$

$$\Rightarrow \frac{dk}{dt} = \frac{e\xi}{\hbar}$$

$$\Rightarrow \frac{d}{dt} \left(\frac{p}{\hbar} \right) = \frac{e\xi}{\hbar} \quad [\because p = \hbar k]$$

$$\Rightarrow \frac{d}{dt} p = e\xi$$

i.e.

$$F = e\xi$$

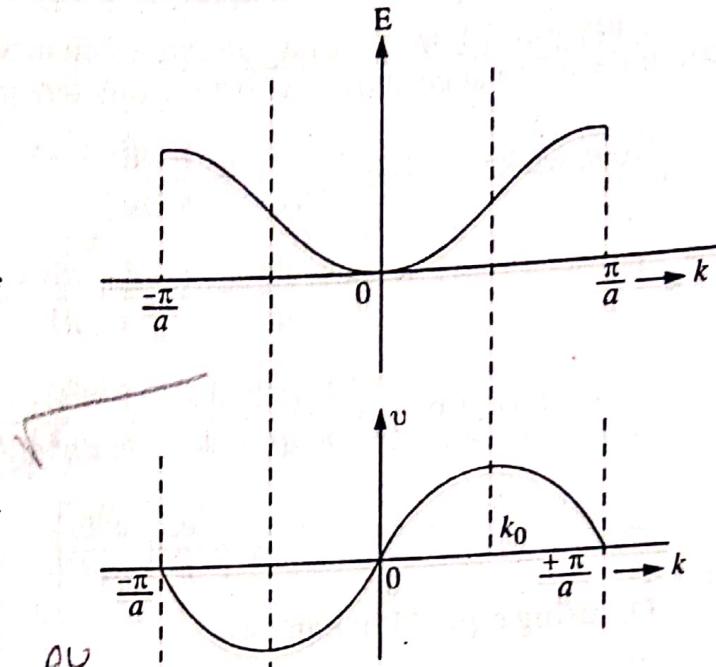


Figure 8.5.

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

... (2)

$$\dots(3) \quad [\because F = \frac{dp}{dt}]$$

Equation (3) shows that the rate of change of momentum p of the crystal is equal to the force $F = e\xi$ in accordance with Newton's second law.

Now, we know that $v = \frac{1}{\hbar} \frac{dE}{dk}$

$$\therefore \frac{dv}{dt} = \frac{1}{\hbar} \cdot \frac{d}{dt} \left(\frac{dE}{dk} \right) = \frac{1}{\hbar} \frac{d^2E}{dk^2} \frac{dk}{dt}$$

$$\therefore \text{acceleration, } a = \frac{1}{\hbar} \frac{d^2E}{dk^2} \frac{dk}{dt} = \frac{1}{\hbar} \frac{d^2E}{dk^2} \left[\frac{e\xi}{\hbar} \right] \quad (\text{Using eqn. (2)})$$

$$\Rightarrow a = \frac{e\xi}{\hbar^2} \left[\frac{d^2E}{dk^2} \right] \quad \dots(4)$$

On using eqn. (3) in eqn. (4)

$$a = \frac{F}{\hbar^2} \frac{d^2E}{dk^2} = \frac{F}{\hbar^2 \left[\frac{d^2E}{dk^2} \right]^{-1}}$$

$$F = m a \quad \dots(5)$$

$$a = \frac{F}{m}$$

Thus, it follows from eqn. (5) that the electron behaves as if it has a mass m^* given

by $m^* = \hbar^2 \left[\frac{d^2E}{dk^2} \right]^{-1} = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2} \right)}$... (6)

This is called the effective mass of the electron. It is clear from eqn. (6) that the effective mass varies with k . The variation of m^* with k in the first Brillouin zone is as shown in Figure 8.6.

The Figure 8.6, shows that m^* may be positive or negative. It is positive at the bottom of energy band and negative at the top. Also m^* becomes infinite at inflection point $k = k_0$. It means that the electron behave as a positively charged particle called "hole" in the upper half of the band.

The degree of freedom of an electron is generally expressed as the ratio of actual mass of electron and the effective mass and is denoted by f_k . Therefore

$$f_k = \frac{m}{m^*} = \frac{m}{\hbar^2} \left[\frac{d^2E}{dk^2} \right]$$

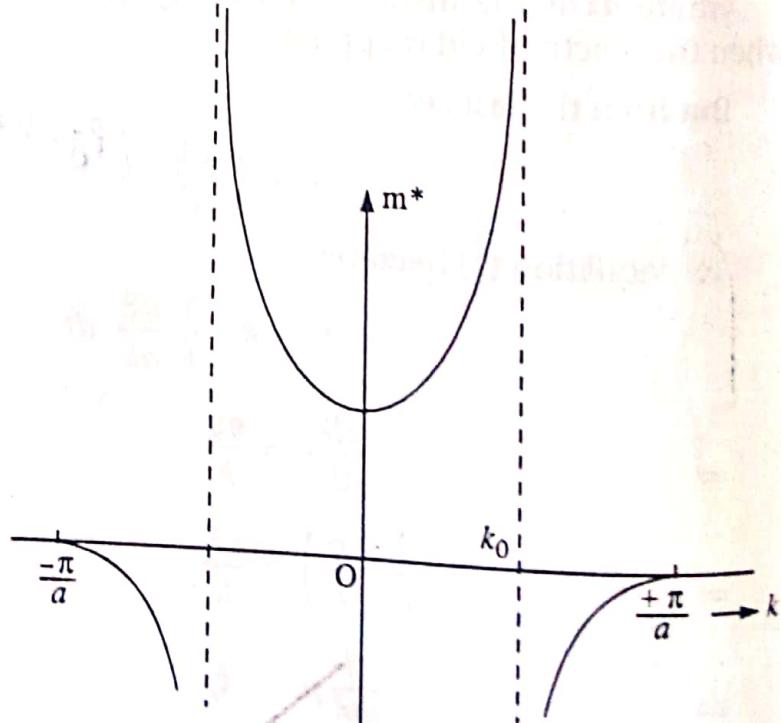


Figure 8.6

If f_k is large, then f_k is a small quantity. Therefore the particle behaves as a heavy particle. If $f_k = 1$, then $m^* = m$, then the electron behaves as a free electron.

In most of the conductors, the band is partially filled, therefore $m^* = m$. The conduction in such conductors is, therefore, due to free electrons. In semiconductors and insulators, however, the effective mass m^* plays a vital role in the phenomenon of conduction and the conduction might be due to both types of charge carriers i.e., electrons as well as positive charge carriers called holes.

8.7. Distinction between Metals, Insulators and Semiconductors

To distinguish between different materials on the basis of band theory, consider an energy band which is filled with electrons upto a certain value k_1 ($k_1 < \frac{\pi}{a}$) as shown in the figure 8.7.

To make conclusions about the conductivity of the band, it is necessary to find the effective number of electrons present in the band. Since the term f_k defined in the preceding section represents the extent upto which an electron in the state k behaves as a free electron, therefore, the sum of all k_f values corresponding to various occupied energy levels gives the effective number of free electrons.

i.e.

$$N_{\text{eff}} = \sum k_f$$

Now the number of states in the interval dk for one dimensional crystal of length L is given by

(1) $dn = \frac{L}{2\pi} dk$

(See last section)

Since two electrons can occupy each of these states in the shaded region of the Figure 8.7, therefore the effective number of electrons can be found by

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

But

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

Therefore

$$N_{\text{eff}} = \frac{mL}{\pi \hbar^2} \int_{-k_1}^{k_1} \frac{d^2 E}{dk^2} dk = \frac{2mL}{\pi \hbar^2} \int_0^{k_1} \frac{d^2 E}{dk^2} dk = \frac{2mL}{\pi \hbar^2} \left[\frac{dE}{dk} \right]_{k=k_1}$$

From the above result, two conclusions can be drawn.

(1) When the band is completely filled i.e., $k = \pm \frac{n\pi}{a}$, where $n = 1, 2, 3 \dots$

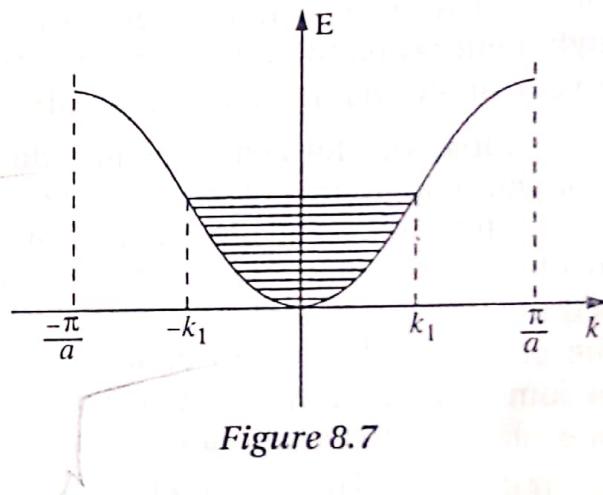


Figure 8.7

Then

$$\left| \frac{dE}{dk} \right|_{k=k_1} = 0$$

Therefore

$$N_{\text{eff}} = \frac{2mL}{\pi \hbar^2} \left[\frac{dE}{dk} \right]_{k=k_1} = 0$$

i.e., the effective number of electrons in a completely filled band is zero.

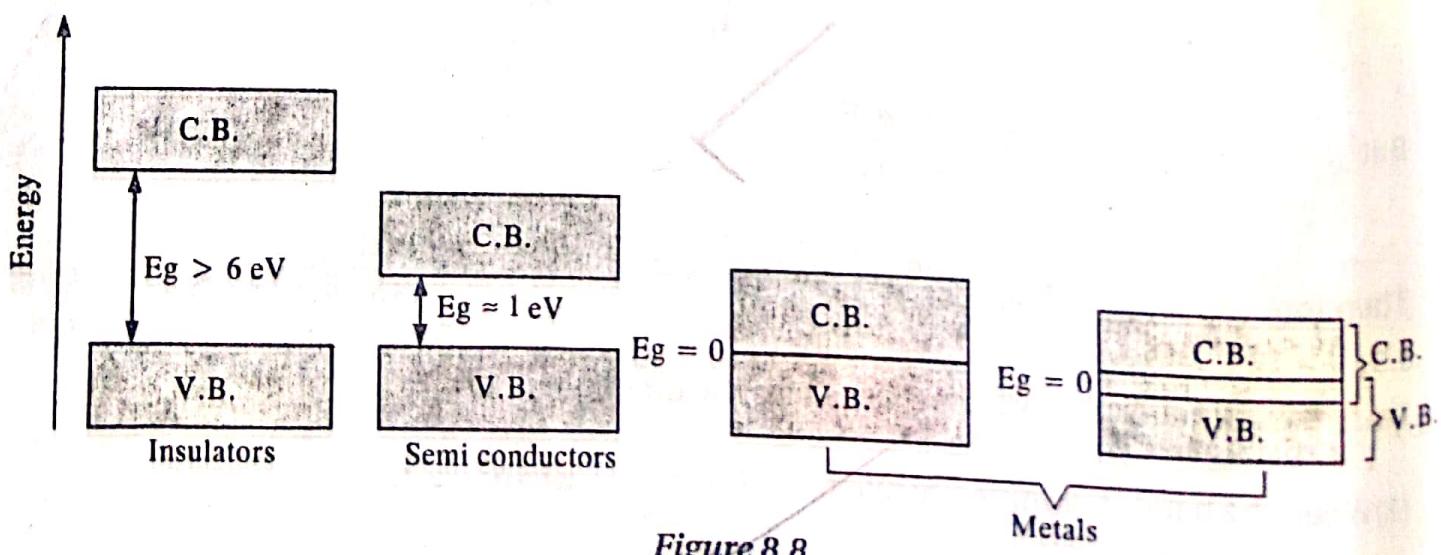
(2) At the inflection point of E versus k curve, $\frac{dE}{dk}$ = maximum. Therefore, effective number of electrons is maximum.

From this discussion, we find that if certain energy bands in a solid are completely filled and the others are completely empty and there is a large gap between the two energy bands, the solid is an insulator. When an electric field is applied, electrons do not get activated to higher energy band even if the temperature is increased. Therefore the conductivity of insulator is very small. Diamond is an example of the insulator with an energy gap of 7 eV.

A substance for which the forbidden energy region (energy gap) is relatively small (≈ 1 eV) is a semiconductor. At absolute zero temperature, the lower band (valence band) remains completely filled and the higher band (conduction band) is empty. Thus the material is an insulator at absolute zero. As the temperature is increased, some electrons in the valence band acquire thermal energies to cross over the energy gap and move to conduction band. Therefore, the electrons are free to conduct electricity for small values of electric field. The material becomes conducting and is called semiconductor. Germanium with an energy gap of 0.785 eV and silicon with energy gap of 1.21 eV are two naturally occurring semiconductors.

If the energy band of a solid is incompletely filled, it behaves as a conductor. The incomplete filling only occurs at absolute zero. At non zero temperature, some electrons from upper filled band (valence band) excite into the next empty band (conduction band) to conduct electricity when an electric field is applied. Na, K, Li etc. are such conductors. There is another possibility of the material to behave as a conductor. If completely filled valence band and the empty conduction band overlap with each other, the energy gap is zero. Ba, Cd etc. are such conductors.

The band diagrams for insulators, semiconductors and conductors (metals) is as shown in Figure 8.8.



Example 2. Using the Kronig Penney model, show that the energy of electron becomes $E = \frac{\hbar^2 k^2}{2m}$ if the electron is a free electron.

Solution. For a free electron, $V_0 = 0$.

Therefore $P = \frac{mV_0 ab}{\hbar^2} = 0$

\therefore from equation

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

We have

$$\cos \alpha a = \cos ka \text{ i.e., } \alpha a = ka$$

or

$$\alpha = k$$
...(1)

But

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

Therefore, form eqn. (1).

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

Conceptual Problems

Q. 1. What are Bloch functions ?

Ans. If an electron moves in a one dimensional periodic potential, the potential energy of electron should satisfy the condition

$$V(x) = V(x + a)$$

where a is the period equal to lattice constant.

Then the schrodinger equation for this case can be written as

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

The solution to this equation can be put in the form

$$\psi(x) = e^{\pm ikx} u_k(x)$$
...(1)

where $u_k(x) = u_k(x + a)$.

The function $\psi(x)$ represented by eqn. (1) is termed as the Bloch function or Bloch wave.

Q. 2. On what assumption is the Kronig Penney model based ?

OR

What is the basic assumption in Kronig-Penny model ?

Ans. Kronig Penney model is based upon the assumption that atoms form an equally spaced

(RU. 2002)

array with an average distance a between them and the electron moves in the periodic potential which is zero for $0 < x < a$ and V_0 for $-b < x < 0$ such that the repetition period is $a + b$.

What conclusions can be drawn from Kronig Penney model ?

- Following conclusions are drawn from the Kronig Penney model.
1. The energy spectrum consists of an infinite array of allowed energy bands separated by intervals having no energy levels called the forbidden regions.
 2. The width of allowed energy bands increases with the increase in αa i.e., with the increase in energy.
 3. The width of allowed energy band decreases with increase in binding energy of electrons.
 4. If P is zero, the energy spectrum becomes continuous. This is the case of free electron model.

Q.4. What is meant by energy gap ?

OR

Q.5. What are energy gaps or band gaps ?

(PbI. U. 2004)

OR

Q.6. What do you understand by energy gap ?

(G.N.D.U. 2005)

Ans. According to Kronig Penney model, the energy spectrum of a solid consists of an infinite array of allowed energy bands separated by intervals having no energy levels. These intervals are called forbidden energy regions or energy gap or forbidden band.

Q.7. Ans. What is a valence and a conduction band ?

The highest band which is occupied by the valence electrons is called valence band whereas the band which is completely empty at 0K is called the conduction band.

Q.8. Ans. What is the value of approximate energy gap in

(a) insulators (b) semiconductors (c) metals.

(a) For insulators, energy gap is very large and is generally greater than 6 eV.

(b) For semiconductors, energy gap is approximately 1 eV.

(c) For metal, there is no energy gap between the valence band and conduction band.

Q.9. Ans. What is Brillouin zone ?

According to Kronig Penney model, the discontinuity of energy occurs at the points in the E versus k curve, where the condition $k = \frac{n\pi}{a}$ is satisfied. Here n is a non zero integer. The region separating the segment of k values between $\frac{+\pi}{a}$ and $\frac{-\pi}{a}$ is called first Brillouin zone. Similarly the segment between $\frac{-\pi}{a}$ to $\frac{-2\pi}{a}$ and $\frac{\pi}{a}$ to $\frac{2\pi}{a}$ forms the second Brillouin zone and so on.

Short Answer Type Questions

1. What is meant by Bloch Theorem and Bloch functions ?