UNIT 10 BAND THEORY OF SOLIDS

Structure

10.1 INTRODUCTION

In Unit 9, you have studied the free electron theory of metals. One of the basic assumptions of this theory is that positively charged ions in a metal crystal do not influence the motion of free electrons. Obviously such an assumption over-simplifies the actual situation in crystalline solids including metals. Still, the theory gives good insight into wide range of metallic properties such as electrical conduction, heat capacity and thermal conductivity. Some important questions, however, remained unanswered. For example, free electron theory predicts that electrical conductivity is directly proportional to the number density of free electrons implying thereby that bivalent and trivalent metals should have larger electrical conductivities than those of monovalent metals. But this inference is not supported by experimental observations. Further, it also does not explain why some solids are conductors and some others are not.

Most of such limitations of free electron theory were overcome by considering a more realistic model of solid. It was proposed that in a solid, electrons move under the influence of a periodic potential due to ions arranged along a periodic lattice. The energy spectrum of such electrons consists of allowed and forbidden energy bands and the theory developed on the basis of this model is called *Band Theory of Solids*. For ease in mathematical analysis, Kronig and Penney proposed that one-dimensional periodic potential of a crystal can be considered equivalent to a series of potential wells. In Sec.10.2 you will learn the Kronig-Penney model and the consequences of energy bands on the motion of electrons in a solid. You will also learn how band theory leads to the concept of hole – a concept of utmost importance for understanding electrical properties of a group of solids called semiconductors. The existence of energy bands provides a basis to categorise solids as metal, insulator and semiconductor. In Unit 2, you have learnt about Brillouin zone. In Sec. 10.3, you will learn how is this geometrical concept useful in the study of band theory of solids. Determination of electron transport parameters such as charge carrier concentration is necessary for making devices. These parameters of metals as well as semiconductors can be determined on the basis of the Hall effect about which you will learn in Sec. 10.4.

One of the important successes of the band theory of solids was theoretical understanding of semiconductors and their physical properties which you will learn in the next unit.

Objectives

After studying this unit, you should be able to:

*   list the limitations of the free electron theory;
*   state Bloch theorem;
*   discuss the results of Kronig-Penney model and formation of energy bands;
*   explain how Kronig-Penney model describes the motion of electrons in metals and provides the basis for categorisation of solids;
*   relate Brillouin zone to energy bands; and
*   explain the significance of Hall effect experiment with respect to band theory and obtain an expression for Hall coefficient.

10.2 AN ELECTRON IN A PERIODIC POTENTIAL

You may recall from Unit 9 that, according to the free electron theory, a metal crystal can be considered analogous to an empty box containing free electrons. The lattice ions do not influence the motion of electrons in any way. That is, electrons move completely randomly all around the volume of the crystal. However, this description is not enough to understand various properties of solids. From Unit 9, you will recall that the separation between neighbouring atoms in a metal is less than the sum of their radii and it is reasonable to assume that orbitals of electrons belonging to these atoms overlap. As a results, electrons find themselves in potential field of lattice ions. That is, electrons experience a potential field.

To appreciate the nature of potential field experienced by electrons in a solid, let us first understand the nature of potential field of an isolated positively charged ion for an electron. Refer to Fig.10.1a which depicts the variation of potential energy of a conduction electron with respect to its separation from a positively charged ion. The negative value of the potential energy indicates that the force between the ion and electron is attractive. Fig. 10.1b shows the potential energy curve for an electron under the influence of two ions. Note that the resultant curve in between the ions gets modified. Now, recall that ions in a crystalline solid are arranged along a periodic lattice. Therefore, in a one-dimensional (1-D) periodic crystal lattice, the potential energy of electron will be due to a series of equidistant ions as shown in Fig.10.1c. The potential experienced by an electron in such an arrangement of ions is periodic in nature.
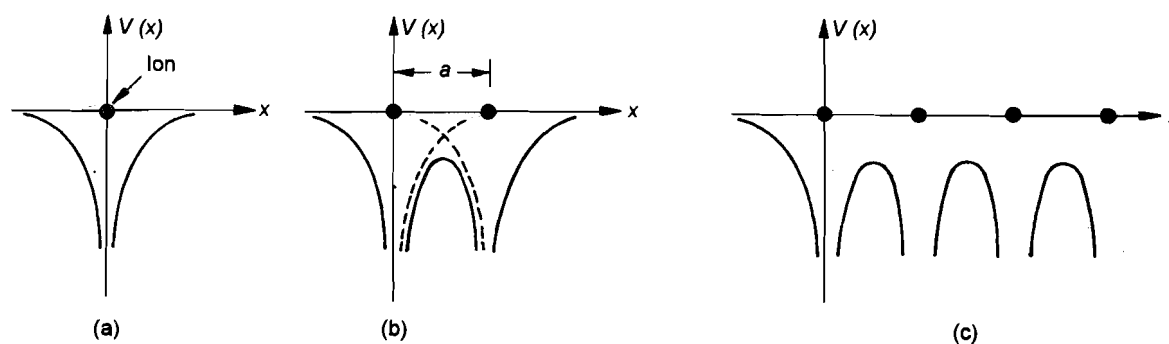

Fig.10.1: Potential energy of an electron due to a) an ion; b) two ions separated by a distance *a*; and c) series of equidistant ions representing 1-D periodic crystal

In the previous unit we solved the Schrödinger equation to investigate the behaviour of free electrons in a metal where it was assumed that ions do not influence the motion of electrons, i.e., electrons move in a constant (zero) potential. To understand the behaviour of electrons in a periodic potential, we should solve the same equation

incorporating periodic nature of potential. The 1-D Schrödinger equation for an electron in a periodic potential is given by

$$\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right)[E - V(x)]\,\psi(x) = 0 \tag{10.1}$$

where $V(x)$ is the periodic potential experienced by an electron in the crystal and $\psi(x)$ and E are respectively the wavefunction and the energy of an electron.

For simplicity we have assumed a 1-D periodic lattice with lattice constant a. Thus, the periodicity of potential $V(x)$ can be expressed as

$$V(x + a) = V(x). \tag{10.2}$$

To proceed further, we must know how to solve Eq. (10.1) with this kind of potential. This problem was first tackled by F. Bloch who showed that the general solution of Schrödinger equation with a periodic potential is

$$\psi(x) = u_k(x)\,e^{\pm ikx} \tag{10.3}$$

where $u_k(x)$ is a periodic function with periodicity of the lattice:

$$u_k(x) = u_k(x + a). \tag{10.3a}$$

In Eq. (10.3), $k\left(=\dfrac{2\pi}{\lambda}\right)$ is the wave number associated with deBroglie wavelength λ of electron. The wavefunction given by Eq. (10.3) is called **Bloch function** and the result that $\psi(x)$ *can be expressed as a plane wave modulated by a periodic function is called* the **Bloch theorem**. Further, the Bloch function is modulated by the periodicity of the lattice because

$$\psi(x + a) = u_k(x + a)\,e^{\pm ik(x+a)}$$

$$= \psi(x)\,e^{\pm ika} \tag{10.4}$$

using Eqs. (10.3) and (10.3a).

Without proving the Bloch theorem, we shall use its results to investigate the effect of periodic potential on the energy of electrons in a solid. However, for potential field shown in Fig.10.1c, it is difficult to solve the Schrödinger equation even with the help of Bloch theorem. A way out of this problem was suggested by Kronig and Penney. They proposed a simplified version of the actual potential experienced by an electron and solved the Schrödinger equation. You will learn the details of Kronig-Penney model now.

10.2.1 Kronig-Penney Model

Kronig and Penney proposed that the potential experienced by an electron in a 1-D crystalline solid can be represented by a periodic array of potential wells as shown in Fig.10.2.
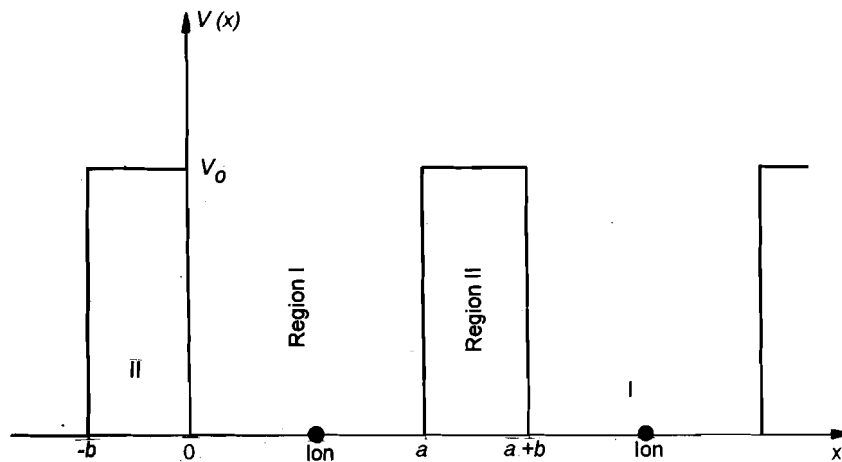
Fig.10.2: Potential well representation of the periodic potential experienced by an electron due to ions in a 1-D crystal of solid

The nature of potential well representation can be understood by comparing Fig.(10.2) with Fig.(10.1c) which represents potential of an electron in a 1-D crystal. The characteristic features of Fig.(10.1c) are:

a) when electron is in the vicinity of an ion, its potential energy has a finite negative value (say, $-V_0$); and

b) when electron is away from an ion (that is, when it is between two ions, its potential energy is zero.

You know that taking zero of potential energy is a matter of convenience; important thing is the relative value of potential energy between two point. *In this context, Fig.(10.1c) shows that when an electron is in the vicinity of an ion, potential energy is lower than its value when electron is in-between the ions.* This feature must be incorporated in any representation of the potential of an electron in a periodic crystal.

Now, refer to Fig.10.2. First of all, note that the origin of coordinate system has been shifted to $-V_0$ along the potential axis. Each potential well (regions I) represents the potential of an electron in the vicinity of an ion. Each of these regions is of width a and the value of potential is zero. Two consecutive potential wells are separated by a distance b (regions II) and the value of the potential in each of these regions is V_0. Region II in Fig. 10.2 corresponds to the situation when electron is in-between the ions. Thus, in Kronig-Penney model, we find that when electron is in the vicinity of an ion, its potential is lower than when it is in-between ions. There is complete correspondence between electron potential in a periodic crystal (Fig.10.1c) and its potential wells representation (Fig.10.2) except for the fact that, in the latter, the lattice constant is $(a + b)$ instead of a. The potential of electron for the two regions can, therefore, be expressed as

$$V(x) = \begin{cases} 0 \text{ for region I } (0 < x < a) \\ V_0 \text{ for region II } (-b < x < 0) \end{cases} \qquad (10.5)$$

Thus, for the Kronig-Penney model, we write Schrödinger equation for two distinct regions separately:

$$\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right) E\,\psi(x) = 0 \quad \text{for region I;} \quad 0 < x < a \qquad (10.6)$$

and

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$$\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right)\left(E - V_0\right)\psi(x) = 0 \quad \text{for region II}; \quad -b < x < 0. \quad (10.7)$$

Now, let us assume that the energy E of electron is less than the height of the potential barrier, V_0. Note that this assumption is quite justified because at room temperature, electrons do not acquire sufficient thermal energy to escape from the crystal. Next, we introduce two real quantities α and β by defining

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad (10.8)$$

and

$$\beta^2 = \frac{2m(V_0 - E)}{\hbar^2}. \quad (10.9)$$

Since $V_0 > E$, β will be a positive quantity. In terms of α and β, Eqs. (10.6) and (10.7) respectively take the form

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi(x) = 0; \quad 0 < x < a \quad (10.10)$$

and

$$\frac{d^2\psi}{dx^2} - \beta^2\psi(x) = 0; \quad -b < x < 0. \quad (10.11)$$

According to Bloch theorem, the solution of these differential equations is given by

$$\psi(x) = u_k(x)e^{ikx} \quad (10.12)$$

To solve Eqs. (10.10) and (10.11), we should use the expression for $\psi(x)$ as given by Eq. (10.12) and apply appropriate boundary conditions. However, this involves complex mathematics. For details, see *Appendix* at the end of the unit. Here it is sufficient to quote the result since we are interested in the physical significance of the result obtained by solving these equations. It is found that solutions of these equations can exist only if the following condition is satisfied:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta}\sinh\beta b\sin\alpha a + \cosh\beta b\cos\alpha a = \cos k(a + b). \quad (10.13)$$

To simplify above expression, Kronig-Penney made an assumption regarding the nature of potential encountered by electrons: as $V_0 \to \infty$, $b \to 0$ in such a way that V_0 times b, which represents the *area* of the potential barrier, is finite. Physically, it means that the electrons are not completely free. Further, this assumption implies that

$$\sinh\beta b \to \beta b$$

and

$$\cosh\beta b \to 1.$$

Then Eq. (10.13) reduces to

$$\frac{\beta^2 - \alpha^2}{2\alpha}b\sin\alpha a + \cos\alpha a = \cos ka. \quad (10.14)$$

Further, by combining Eqs. (10.8) and (10.9), we can write (see margin remark)

$$\frac{\beta^2 - \alpha^2}{2\alpha} b = \frac{P}{\alpha a} \tag{10.15}$$

where

$$P = \frac{ma}{\hbar^2} V_0 b. \tag{10.16}$$

Since $V_0 b$ represents the strength of potential barrier for electron (Fig.10.2), Eq. (10.16) implies that P is a measure of the strength of attraction between electron and an ion. In other words, the value of P is a measure of how strongly an electron is bound in a crystal.

Using the result contained in Eq. (10.15) in Eq. (10.14), we get

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a \tag{10.17}$$

You may like to know: What does Eq. (10.17) signify? You should realise that the condition expressed by Eq. (10.17) must be satisfied if the wavefunction ψ (given by Eq. (10.12)) is to represent an electron in a periodic potential. Further, it can also be used for obtaining useful information about the energy spectrum of electrons. Now, before proceeding further, you should answer an SAQ to fix these ideas.

Margin:

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

$$= \frac{b}{2\alpha} \left[\frac{2m(V_0 - E)}{\hbar^2} - \frac{2mE}{\hbar^2} \right]$$

$$= \frac{bm}{\alpha} \left(\frac{V_0 - 2E}{\hbar^2} \right)$$

Since $V_0 \gg E$, we can neglect the second term within the brackets to obtain

$$\frac{\beta^2 - \alpha^2}{2\alpha} b = \frac{m}{\alpha \hbar^2} V_0 b$$

$$= \frac{P}{\alpha a}$$

SAQ 1

a) What is the origin of the periodic potential field experienced by electrons in a crystalline solid?

b) If the wavefunction $\psi(x)$ is to represent an electron in a crystalline solid, what should be its nature?

Spend
3 min.

To further appreciate the significance of Eq. (10.17) for energy of an electron, it is instructive to plot $\left(P \dfrac{\sin \alpha a}{\alpha a} + \cos \alpha a \right)$ vs. αa. Such a plot for $P = \dfrac{3\pi}{2}$ is shown in Fig.(10.3). Note from Eq. (10.17) that irrespective of the value of ka, the right hand side can take values between $+1$ and -1 only. This imposes limits on values the LHS: only those values of $\left(P \dfrac{\sin \alpha a}{\alpha a} + \cos \alpha a \right)$ are allowed which are in the range $+1$ to -1.

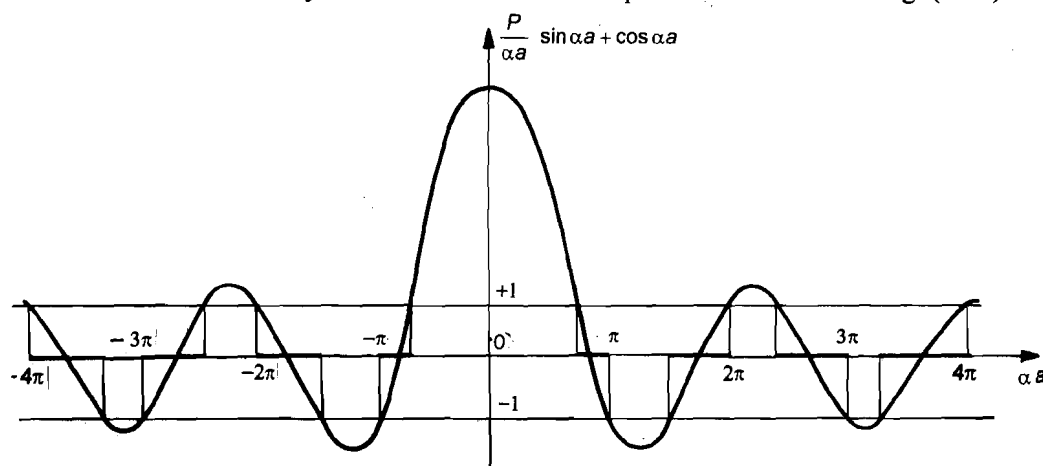These limits are shown by the horizontal solid lines parallel to αa-axis in Fig. (10.3).

For plot shown in Fig.10.3, value of αa has been taken as multiples of π because it simplifies the tabulation of data as well as gives better insight about the energy spectrum of electron.

Fig. 10.3: Plot of $\left(P \dfrac{\sin \alpha a}{\alpha a} + \cos \alpha a \right)$ against αa for $P = 3\pi/2$

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Now, before we discuss inferences flowing from the plot in Fig.(10.3), you should convince yourself about its nature by solving the following SAQ.

SAQ 2

Tabulate values of $\left(\dfrac{P}{\alpha a}\sin\alpha a + \cos\alpha a\right)$ for different values of αa between 0 and 3π

to show allowed and forbidden values of LHS of Eq. (10.17). Take $P = \dfrac{3\pi}{2}$.

Solving SAQ 2, you must have noted that for some value of αa, such as O and $\dfrac{5\pi}{4}$,

value of $\left(\dfrac{P}{\alpha a}\sin\alpha a + \cos\alpha a\right)$ is greater than $|1|$ and cannot be equal to $\cos ka$, RHS of Eq. (10.17).

From Fig.10.3, you will also note that:

- For certain values of αa, the curve crosses ± 1 along $\left(\dfrac{P}{\alpha a}\sin\alpha a + \cos\alpha a\right)$ axis. It implies that the corresponding energy values are not permissible to electrons. **Therefore, we can conclude that the energy spectrum of electron consists of groups or bands of energy levels comprising allowed energy bands and forbidden energy bands.**

- As the value of αa and hence **the energy of an electron increases, the width of the allowed energy bands increases**. This is because the value of the first term in LHS of Eq. (10.17) decreases as αa increases. You should convince yourself about this conclusion by solving the following SAQ.

SAQ 3

Using Eq. (10.17), show that the width of allowed energy bands increases as energy of electron is increased.

- Fig.10.3 has been drawn for a fixed value of P (= $3\pi/2$). You may ask: Does the value of P affect band width? And if so, how? From Eq. (10.17), it can be seen that as P increases, the width of a particular allowed band decreases. You should convince yourself about this statement by calculating the value of

$\left(\dfrac{P}{\alpha a}\sin\alpha a + \cos\alpha a\right)$ for the first allowed band $\left(\dfrac{\pi}{2} \le \alpha a \le \pi\right)$ for three increasing

values of P such as $\dfrac{3\pi}{2}$, $\dfrac{5\pi}{2}$ and $\dfrac{7\pi}{2}$. Since P is a measure of the strength of

potential barrier, larger values of P implies that an electron is strongly bound to its parent atom. That is, condition that P is large represents the physical situation that an electron is in the constant potential; P small implies that electron is a completely free particle. It is instructive to obtain expressions for energy of an electron for these two cases. You will learn to do so now.

i) $P \to \infty$: In this case, Eq. (10.17) can be rewritten as

$$\sin\alpha a = \frac{\alpha a\,(\cos ka - \cos\alpha a)}{P}$$

For $P \to \infty$, $\sin\alpha a \to 0$. This implies that

$$\alpha\, a = \pm n\,\pi; \qquad\qquad n = 1, 2, 3, \cdots$$

$$\alpha^2 = \frac{n^2\pi^2}{a^2}.$$

Comparing this expression for α^2 with that given by Eq. (10.8), we obtain

$$E = \frac{h^2}{8ma^2}n^2; \qquad n = 1, 2, 3,... \qquad\qquad (10.18)$$

Do you recognise this expression? It is same as Eq. (9.13) of Unit 9 which gives energy of an electron moving in a constant potential. This means that the condition $P \to \infty$ leads us to the results of Sommerfeld free electron model. It is understandable because very large value of P implies that the strength of the potential barrier ($P \approx V_0 b$) is so strong that electron cannot escape from an isolated potential well. The energy spectrum for $P \to \infty$ is shown in the right portion of Fig.10.4. Note that it consists of discrete energy levels which is consistent with the energy spectrum of electron as per the Sommerfeld model. *Thus, we may conclude that the Sommerfeld model is a special case of the Kronig-Penney model, that is, the band theory of solids.*

ii) $P \to 0$: In this case the first term on the left hand side of Eq. (10.17) will vanish and the expression reduces to

$$\cos \alpha a = \cos ka.$$

From this equality, it readily follows that

$$\alpha a = ka$$

or

$$\alpha^2 = k^2.$$

Again, comparing this value of α^2 with that given in Eq. (10.8), we get

$$E = \frac{p^2}{2m} \qquad\qquad (10.19)$$

$P \to 0$ $P \to \infty$

Fig.10.4: Energy spectrum of electrons for different strengths of the potential field in a crystalline solid

where $p = \hbar k$ is the momentum of electron.

This expression gives the energy of a free electron and all energies are allowed as shown in the left portion of Fig.10.4. This situation corresponds to the Drude-Lorentz model. Thus, Drude-Lorentz and Sommerfeld models are particular cases of **Kronig-Penney model**. You would indeed agree that this feature of band theory is a significant improvement over the free electron theory.
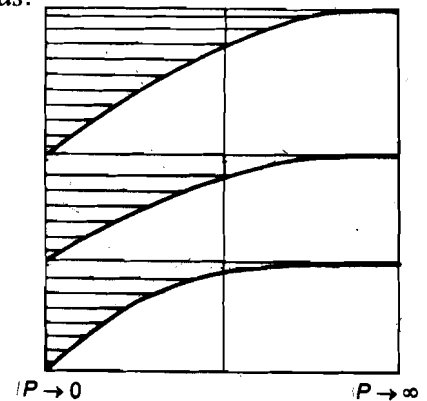
● Yet another important conclusion relates to dispersion relation (E vs. k curve) for electrons in a periodic potential. It is obvious from Eq. (10.17) that for a given value of αa (and hence energy E), the RHS can take only one value. But, cosine function is an even periodic function. Therefore, $\cos ka$ will have the same value for $\pm ka$ as well as for $\pm ka \pm 2n\pi$; $n = 1, 2, 3,....$ It suggests that the energy of an electron is an even periodic function of k with period 2π. Further, to obtain dispersion curve, you should note that discontinuities in the energy spectrum will appear for

$$\cos k a = \pm 1 = \cos (\pm n \pi)$$

or

$$k a = \pm n \pi.$$

That is, energy spectrum will be discontinuous at

$$k = \frac{n\pi}{a}; \qquad n = \pm 1, \pm 2, \pm 3,... \qquad (10.20)$$

Let us pause for a while and ask: What does this result tell us? It suggests that the first forbidden band in the energy spectrum will appear at $k = \pm \pi/a$, the second forbidden band will appear at $k = \pm 2\pi/a$ and so on. The dispersion curve for the electron in a periodic potential is shown in Fig.10.5a. The corresponding allowed and forbidden energy bands are shown in Fig.10.5b. Note that the higher the energy of the band the larger its width in energy. We will further discuss the dispersion relation later in this unit in connection with Brillouin zones.
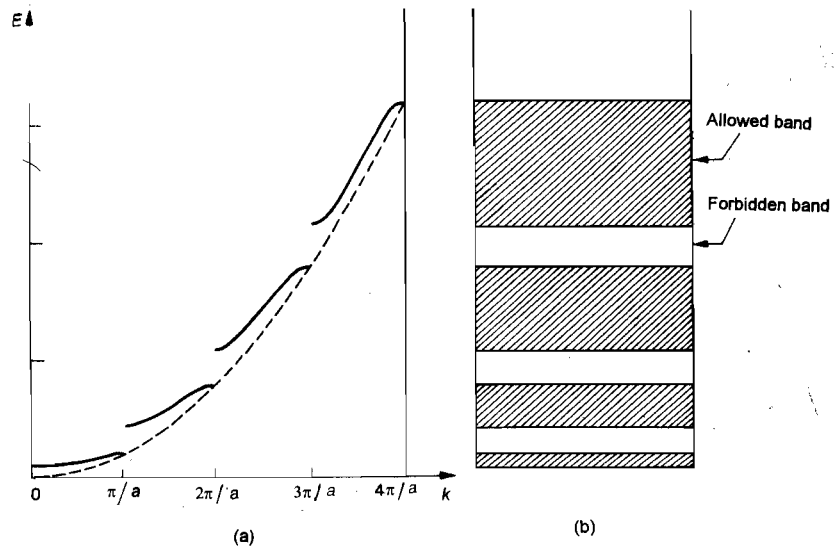

(a)   (b)

**Fig.10.5: a) Plot of energy against wave number of an electron in a 1-D crystal; and
b) corresponding energy bands**

Energy States in a Band

At this point, you may ask: Are the energy states in an allowed energy band continuous? If not, why? It is observed that though very closely separated, the energy levels in a band are discrete. To know the number of energy states in a band, let us consider a 1-D crystal of length L having N unit cells. L and N are connected through the relation

$$L = N (a + b)$$

where $(a + b)$ is the distance between two neighbouring ions. The cyclic boundary condition on the wavefunction $\psi(x)$ is

$$\psi (x + L) = \psi (x). \qquad (10.21)$$

But $\psi(x)$ is Bloch function given by Eq. (10.3) as

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

On applying the boundary condition (Eq. (10.21)) on $\psi(x)$, you will obtain (see margin remark)

margin:

$$\psi (x + L) = u_k (x + L) e^{ik(x+L)} = \psi(x)$$

$$\therefore \quad u_k(x) e^{ikx} = u_k (x + L) e^{ik(x+L)}$$

or

$$e^{ikx} = e^{ikx} e^{ikL}$$

$$(\because \ u_k(x) = u_k(x + L))$$

This implies that

$$e^{ikL} = 1$$

and it holds for

$$k L = 2\pi n; \quad n = 0, \pm 1, \pm 2, \cdots$$

or

$$k = \frac{2\pi n}{L}.$$

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$$k = \frac{2\pi n}{L} \; ; \qquad n = 0, \pm 1, \pm 2, \pm 3, \ldots \qquad (10.22)$$

What does this result signify? It indicates that k can take discrete set of values $0, \pm 2\pi/L, \pm 4\pi/L, \pm 6\pi/L, \ldots$, etc, and, therefore, energy E is quantized. If length L of the 1-D crystal is large, separation between energy levels in a band becomes small, and they form a quasi-continuous band. For macroscopic specimens, this is indeed the case. Now suppose we take an arbitratry interval dk in k-space and wish to know the number of energy states whose k-values lie in this interval. Under the assumption that L is large and energy levels in a band is quasi-continuous, we can write the number of possible energy states in the interval dk as

$$d\,n = \frac{L}{2\pi} d\,k. \qquad (10.23)$$

Hence, total number of energy states in the first allowed energy band (for k values in range $-\pi/a$ to $+\pi/a$) can be obtained by integrating Eq. (10.23);

$$n = \int dn = \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \left(\frac{L}{2\pi}\right) d\,k = \frac{L}{2\pi}[k]_{-\frac{\pi}{a}}^{\frac{\pi}{a}} = \frac{L}{2\pi}\frac{2\pi}{a} = \frac{L}{a}$$

Thus,

$$n\,a = L \qquad (10.24)$$

If the separation between the potential wells (Fig.10.2) is very-very small, that is, $b \approx 0$, we can write $(a + b) \approx a$. Thus, we get

$$N(a + b) = N\,a = L \qquad (10.25)$$

You should note that width of each band is equal to $2\pi/a$. Therefore, the result obtained for first allowed band has been generalised for all allowed bands in a crystal.

Comparing Eqs. (10.24) and (10.25), we obtain

$$N\,a = n\,a$$

or

$$n = N$$

That is, the total number of energy states (n) for an electron in an allowed band of a crystalline solid is equal to the number of unit cells. Further, since each energy state can accommodate two electrons – one with spin up and another with spin down – maximum number of electrons which can occupy an allowed energy band is $2N$. So, *when the number of electrons in an energy band is equal to twice the number of unit cells in the crystal, the band is completely filled.* This conclusion has far reaching consequences. You will learn later in this unit that it enables us to distinguish metal from insulator and semiconductor.

So far, you have studied about the allowed and forbidden energy bands for an electron in the periodic potential of a crystalline solid. You can also explain how many electrons can occupy an allowed energy band and at what values of the wave number discontinuity would occur in the energy spectrum. In addition, the band theory also provides a completely new perspective on some of the physical parameters such as velocity and mass of an electron in a crystalline solid. You will learn it now.

10.2.2 Energy Bands and Motion of Electrons

You may recall from Unit 9 that energy of free electrons is proportional to the square of the wave number. But the dispersion curve (E vs. k curve) predicted by the band

theory do not show parabolic relationship between E and k, particularly near the boundaries of bands. You may note in Fig.10.5 that at the boundaries, the E vs. k curve deviates from the parabolic nature as predicted by free electron theory. This deviation has important implications for the microscopic parameters of electrons. In particular, the velocity and mass of an electron changes significantly. Let us see how.

Velocity

You know that the group velocity of a wave is defined as

$$v = \frac{d\omega}{dk}$$

where ω and k respectively denote the angular frequency and wave number of the wave. In this case we shall consider de Broglie wave associated with an electron.

Since energy of electron $E = \hbar\omega$, the expression for group velocity in terms of E takes the form

$$v = \frac{d\omega}{dk} = \frac{d\omega}{dE} \cdot \frac{dE}{dk} = \frac{1}{\hbar}\frac{dE}{dk} \qquad (10.26)$$

since $\dfrac{d\omega}{dE} = \dfrac{1}{\hbar}$.

For a completely free electron, $E = \hbar^2 k^2 / 2m$. Using this relation in Eq. (10.26) we find that

$$v = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{\hbar^2 k^2}{2m}\right) = \frac{\hbar k}{m} = \frac{p}{m}. \qquad (10.27)$$

This result shows that the velocity of a completely free electron is a linear function of k. To see how this relation is influenced by the band theory, let us consider the region bound by $-\pi/a < k < \pi/a$ of the E vs. k curve (Fig.10.5). For this region, the E vs. k and v vs. k curves for an electron are shown in Figs.10.6a and b respectively.

On comparing these figures, you will notice that

- *the velocity of an electron becomes zero for $k = \pm \pi/a$ of the band.* This is understandable because at these points, the energy is independent of the wave number, that is, $(dE/dk) = 0$.

- *as the energy increases from $k = 0$, the velocity increases at first linearly, attains a maximum value for $k = k_0$ and then decreases to zero at top of the band.* The point at which $k = k_0$ is called **point of inflection** of the E vs. k curve.

These features of the velocity of electrons in a crystalline solid are unique predictions of the band theory. As per the free electron theory, velocity of an electron increases as second power of energy.

Effective Mass

You know that in an electric field, electrons experience a force and get accelerated; stronger the applied field, higher is the acceleration. You may now ask the question: Does an electron in a crystalline solid also behave similarly? It is not so because, as you have seen above, the v vs. k curve of an electron in a solid is different from that of a completely free electron. *This is because the (effective) mass of an electron in a crystalline solid placed in an electric field is different from its free mass.* To appreciate the concept of effective mass, let us consider an electron of mass m moving

(a)

(b)

(c)

$-\pi/a \qquad 0 \qquad \pi/a$
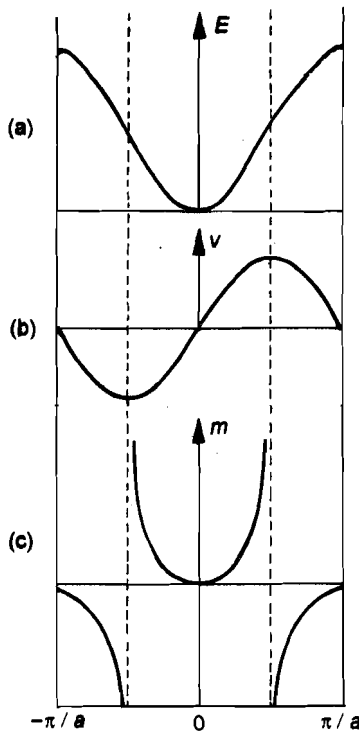
Fig.10.6: Variation of a) energy; b) velocity; and c) mass of an electron with respect to its wave number in the first allowed energy band

under the influence of a periodic potential. The velocity of such an electron is given by Eq. (10.26). Thus, the acceleration can be written as

$$a = \frac{dv}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right)$$

$$= \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dk}\right)\frac{dk}{dt}$$

$$= \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}. \qquad (10.28)$$

Using the E vs. k curve, we can obtain (d^2E/dk^2). To find variation of the wave number with time, let us assume that the electric field $\mathcal{E}$ acts on an electron for time dt and during this time interval, it acquires a velocity v. Thus, the work done on the electron increases its kinetic energy:

$$dE = (e\mathcal{E})\times(v\,dt)$$

$$= (e\mathcal{E})\left(\frac{1}{\hbar}\frac{dE}{dk}\right)dt.$$

By re-arranging terms, we obtain

$$\frac{dk}{dt} = \frac{e\mathcal{E}}{\hbar}.$$

Using this result in Eq. (10.28), we get

$$a = \left(\frac{1}{\hbar}\right)\left(\frac{d^2E}{dk^2}\right)\left(\frac{e\mathcal{E}}{\hbar}\right).$$

On inverting the expression, we find that

$$e\mathcal{E} = \frac{\hbar^2}{d^2E/dk^2}\,a. \qquad (10.29)$$

If we compare this result with the equation of motion, force = mass × acceleration, we find that the **effective** mass, m^* of an electron in a crystalline solid placed in an electric field is

$$m^* = \frac{\hbar^2}{\left(d^2E/dk^2\right)}. \qquad (10.30)$$

Note that effective mass of an electron in a crystalline solid depends on the variation of energy with the wave number. For example, if you use Eq. (10.19) which expresses relation between energy and wave number of a completely free electron, you will find that m^* is equal to m, the rest mass of the electron. The effective mass comes into play because we assume that electron is acted upon by the external field $\mathcal{E}$ only.

The variation of effective mass with wave number is shown Fig.10.6c. You may note that in the lower half of the energy band, m^* is positive. However, in the upper half of the band, i.e., beyond the point of inflection, m^* is negative: **the electron has a negative effective mass!** You may ask: What is the physical significance of the

According to free electron theory, the energy of a completely free electron is given by Eq. (10.19):

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

Thus,

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

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

Substituting this expression for (d^2E/dk^2) in Eq. (10.30), we get,

$$m^* = \frac{\hbar^2}{\left(d^2E/dk^2\right)} = \frac{\hbar^2}{\hbar^2/m} = m.$$

negative effective mass? You should note that, beyond the point of inflection, velocity of electron decreases as k increases. That is, the electric field which accelerates the electron for $k < k_0$, decelerates it for $k > k_0$. It is as if the deceleration is caused by the negative effective mass of the electron. *In other words, beyond the point of inflection, the electron behaves as if it is a positively charged particle (called hole)!* The concept of hole – electron with negative effective mass – has made significant contribution in our understanding about semiconductors. You will study about these in Unit 11. Before proceeding further, you should solve the following SAQ.

SAQ 4

The energy of an electron in a crystalline solid is related to the wave number k by the relation

Spend 3 min.

$$E = \frac{10\,\hbar^2 k^2}{m}$$

Calculate its velocity and effective mass.

10.2.3 Classification of Solids in Metal, Insulator and Semiconductor

You must have observed that electric appliances have ebonite handles but aluminium or steel base or body. In a physics laboratory, copper wires are used for electrical connections and tungsten wires are used in resistance boxes and rheostats. In a transistor, germanium, silicon or their alloys are used. This is because of the varied responses of these materials to electric field. The ability of a solid to conduct electric current may be explained in terms of availability of free electrons in it. It means that free electrons are not readily available in insulators and pure semiconductors. To address this question, let us once again consider the energy spectrum of electrons in a crystalline solid consisting of allowed and forbidden energy bands.

Refer to Fig.10.7 which shows the lowest allowed band filled only upto a given value, say k_1 ($< \pi/a$) of k. Let us define a parameter f_k, which gives the extent to which an electron with a given k is free to move under the influence of an applied field, as:
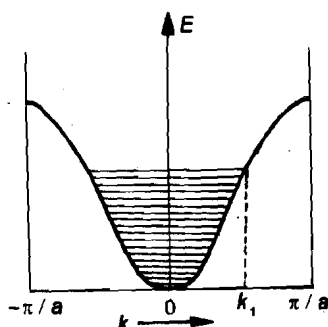

Fig.10.7: Partially filled lowest allowed band of a solid

$$f_k = \frac{m}{m^*} = \frac{m}{\hbar^2}\left[\frac{d^2 E}{dk^2}\right] \tag{10.31}$$

You would definitely like to know: What does f_k signify? Note from Eq. (10.31) that if the effective mass of an electron in a band is large, f_k will be small. In this situation, electron is relatively heavy and hence may not participate in electrical conduction at low field values. *That is, when an electric field is applied, the electrical conduction will depend upon the number of effectively free electrons rather than on the total number of free electrons in a band.* Further, we can express the number of effectively free electrons as

$$N_{\text{eff}} = \sum f_k \tag{10.32}$$

where the summation extends over all the occupied energy states of the band. If separation between the energy levels is small, we can replace summation over discrete levels by a continuous distribution and write

$$N_{\text{eff}} = \int dn\, f_k$$

Using Eqs. (10.23) and (10.31) we get

$$N_{eff} = \frac{2mL}{\pi \hbar^2} \int_0^{k_1} \left(\frac{d^2 E}{dk^2} \right) dk$$

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

(10.33)

The factor of 2 has been included because each energy state can accommodate two electrons. For a completely filled band, we have

$$k = \pm n\pi/a; \qquad n = 1, 2, 3...$$

and

$$\frac{dE}{dk} = 0 \qquad \text{at } k = \pm \frac{n\pi}{a}.$$

So, Eq. (10.33) reduces to

$$N_{eff} = 0$$

(10.34)

That is, in a completely filled band, the effective number of free electrons is zero. Physically, you can appreciate this result by referring to v vs. k diagram in Fig.10.6b. Corresponding to any velocity v of an electron, there is another electron with velocity $- v$ so that the net velocity in the energy band is zero. Further, Eq. (10.33) shows that N_{eff} will be maximum for k value where dE/dk has the maximum. From Fig. (10.6), it is evident that (dE/dk) is maximum at the point of inflection. The point of inflection refers to nearly half-filled band. Therefore, the effective number of free electrons in a band will be maximum if it is filled upto this point.

Now, refer to Fig.10.8a. It shows allowed and forbidden energy bands. You will note that some of the lower energy bands are completely filled and N_{eff} is zero. The highest partially or completely filled band is known as *valence band* and the next allowed unfilled band is known as *conduction band*. Note that only these two bands are of interest to us. It is because all other bands remain unaffected at ordinary temperatures and electrical fields; you should, however, keep in mind that other bands also exist. On the basis of these energy band diagrams we differentiate between metal, insulator and semiconductor.
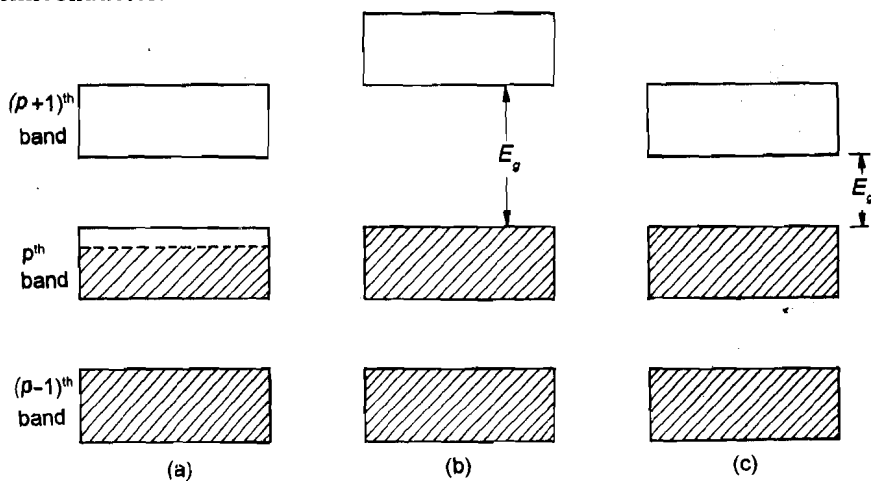

Fig.10.8: Different configurations of energy spectrum

Suppose that the pth allowed band is partially filled and the $(p-1)^{th}$ and $(p+1)^{th}$ bands are respectively completely filled and completely empty.

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According to the band theory, the pth allowed band consists of a large number of energy levels. Since this band is partially filled, there are empty energy levels in which electrons can be accommodated. The energy difference between the levels within a band is very small. Electrons in filled levels can move to empty levels within the band even if a very small amount of energy is supplied to them. Thus, when an electric field is applied to a solid specimen having this type of energy spectrum, the electrons in the partially filled band will gain energy, move to empty higher energy levels in the same band and are, therefore, available for electrical conduction. Such solids are called **metals**. The partially filled band is known as the **conduction band**.

Now let us consider another type of energy spectrum depicted in Fig.10.8b. In this case, the pth band is completely filled but the $(p+1)^{th}$ band is completely empty. The energy gap (the forbidden band) between these two bands is, say E_g. Electrons in the pth band can move to the empty $(p+1)^{th}$ band only when they receive energy more than or equal to E_g. Therefore, if the applied electric field is not strong enough to supply this much energy, electrical conduction will not take place. The energy gained by electrons at ordinarily applied electric fields is much less than E_g. Thus, solids with energy spectrum as shown in Fig.10.8b correspond to **insulators**.

Lastly, let us consider the third type of energy spectrum, which is shown in Fig.10.8c. Comparing this spectrum with the one shown in Fig.10.8b, you will observe that the only difference between the two lies in the value of the energy gap E_g. You may now like to know: How does the value of E_g influence the behaviour of solids? At absolute zero, solids with energy spectrum as in Fig.10.8c also behave as insulators. But, at temperature T, electrons in the valence band gain energy equal to k_BT and if $k_BT > E_g$, it is quite possible that some electrons in the valence band may get excited to the conduction band. Therefore, at temperatures above absolute zero, the energy spectrum shown in Fig.10.8c will contain empty energy levels at the top of the valence band as well as filled energy levels at the bottom of the conduction band. The availability of empty levels in the allowed bands facilitates electrical conduction in such solid. Solids with small energy gap between their valence and conduction bands tend to conduct electricity as temperature is raised from zero. Such solids are called **semiconductors. Note that at T = 0 K, there is no difference between an insulator and a semiconductor in so far as the electrical conduction is concerned.**

On the basis of above discussions, we can understand a few experimental observations on electrical conduction in metals. Recall from Unit 9 that conductivity of a metal is proportional to the concentration of electrons. It implies that divalent and trivalent metals should have larger values of conductivity than that of monovalent metals. This prediction does not conform to experimental observation. The explanation of this variance is provided by band theory which predicts that feasibility of electrical conduction is guided by a parameter called number of effectively free electrons (N_{eff}) available for electrical conduction and not on the total number of valence (free) electrons. From Eq. (10.33), it is obvious that N_{eff} depends on the nature of energy bands and which is more or less same for all metals irrespective of their valencies and hence conductivities of metals are of the same order of magnitude.

You now know that Kronig-Penney model introduced the concept of allowed and forbidden energy bands which affect the dynamical behaviour of electrons significantly. One of the salient features of band theory is that it provides a basis for constructing Brillouin zone pattern of the crystals and thereby helps in the determination of crystal structure. In the following, you will learn how band theory predicts the Brillouin zones.

10.3 ENERGY BANDS AND BRILLOUIN ZONES

Refer to Fig.10.5 again. You will note that discontinuities in the energy spectrum of electrons in a crystalline solid occurs at the k values given by

$$k = \frac{n\pi}{a} = \frac{2\pi}{\lambda}$$

so that

$$2a = n\lambda. \tag{10.35}$$

If a denotes the separation between the planes normal to the direction of propagation of electron wave, then Eq. (10.35) represents Bragg's law ($2d\sin\theta = n\lambda$) for electrons for $\theta = \pi/2$. The similarity between discontinuity in energy spectrum and Bragg's diffraction condition is a consequence of the wave nature of electron. Therefore, Eq. (10.35) implies that for this relation between a and λ, electrons are reflected back and cannot propagate in the crystal giving rise to the discontinuity in the E vs. k curve.

In view of this, we can say that the region bound between $k = -\frac{\pi}{a}$ and $k = +\frac{\pi}{a}$ on the

E vs. k curve (Fig. 10.4) represents the first Brillouin zone. The regions between $-\frac{\pi}{a}$

and $-\frac{2\pi}{a}$ and $\frac{\pi}{a}$ and $\frac{2\pi}{a}$ represents other Brillouin zone and so on. These values of k represent the Brillouin zone boundaries because the corresponding energy values are not permissible to electrons in a periodic potential. Fig.10.9 shows a few Brillouin zones in one dimension.

You may recall from Unit 4 that Brillouin zone boundaries are the reflecting planes for X-rays. Thus, we can obtain the X-ray diffraction pattern and crystal structure of a solid if we know its Brillouin zone pattern.
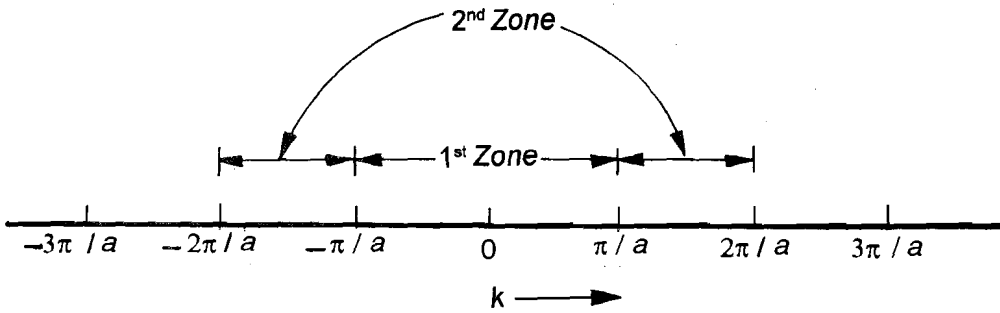

Fig.10.9: First few Brillouin zones for a 1-D crystal

In order to construct Brillouin zone patterns using the results of band theory, let us consider the motion of an electron in a 2-D square crystal. It is convenient to use the wave numbers k_x and k_y as coordinate axes for the construction of Brillouin zones. The space defined by these axes is called **k-space**, which is equivalent to reciprocal space because distances in k-space are reciprocal to the distances in crystal. The condition for energy discontinuity is given by Eq. (10.20):

$$k = \frac{n\pi}{a}; \qquad n = \pm1, \pm2, \pm3,...$$

Thus, the boundaries of the first Brillouin zone for 2-D square lattice crystal will be given by

$$k_x n_1 + k_y n_2 = \frac{\pi}{a}\left(n_1^2 + n_2^2\right), \tag{10.36}$$

where n_1 and n_2 are integers corresponding to k_x and k_y axes.

Thus, to draw the first zone, we must choose n_1 and n_2 such that it leads to

$k_x + k_y = \pm \dfrac{\pi}{a}$. This is possible for two different sets of values of n_1 and n_2:

i) $\quad\quad n_1 = \pm 1, \quad$ and $\quad n_2 = 0$.

With these values of n_1 and n_2, Eq. (10.36) gives

$$k_x = \pm \frac{\pi}{a}$$

ii) $n_1 = 0$ and $n_2 = \pm 1$, we get,

$$k_y = \pm \frac{\pi}{a}$$

The first Brillouin zone with these values of the coordinates k_x and k_y will be a square $PQRS$ as shown in Fig.10.10.
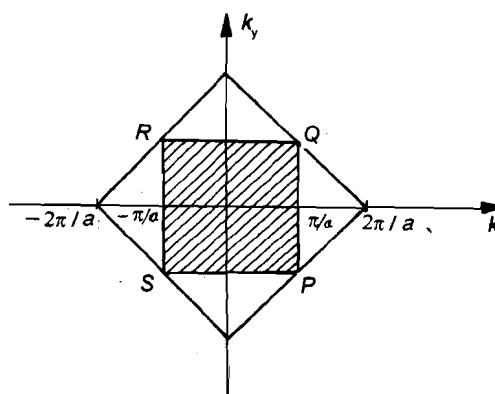

Fig.10.10: First Brillouin zone for a 2-D square lattice crystal

In order to fix your ideas about Brillouin zones, you should answer an SAQ.

Spend
4 min.

SAQ 5

Sketch the second Brillouin zone for a 2-D square crystal.

Solving SAQ 5, you have seen that the second Brillouin zone of a 2-D crystal lattice consists of four separate parts. However, note that the total area of the second zone is equal to that of the first Brillouin zone. Further, it is also possible to construct Brillouin zones for real 3-D crystal lattices. We do not include it in this unit to avoid mathematical complexities. *You may recall from Unit 3 that first Brillouin zone can be taken as a unit cell of a crystal lattice in reciprocal space. Therefore, band theory calculations leading to construction of Brillouin zones provide an analytical tool to determine crystal structure of a solid.*

In Sec. 10.2, you learnt that the effective mass of an electron in a band acquires negative value if it is near the top of the band, that is, if its wave number is greater than k_0 – wave number at the point of inflection. An electron with negative effective mass behaves like a positively charged particle having same amount of charge. You may like to know: Is there any experiment to check this prediction of band theory? The Hall effect measurement enables us to determine the sign of charge carriers and check this prediction. Further, the study of Hall effect is also used for determining carrier concentration in solids which is of crucial importance for designing solid state devices. In addition, this experiment can be used for determining whether an extrinsic

semiconductor is n-type or p-type. However, in the following, we confine our discussion of Hall effect for metals only.

10.4 HALL EFFECT

In Hall effect experiment, an electric field ε_x is applied to a rectangular parallelepiped shaped metallic specimen. We take this as the positive x-axis. Let the current density due to this field be j_x (Fig.10.11a). A magnetic field B_z is applied normal to the specimen. We take this as the positive z-direction.
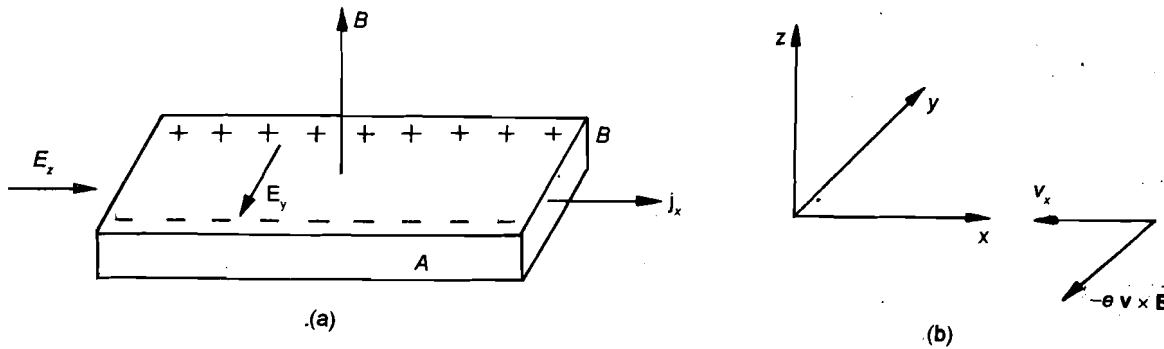

Fig.10.11: Schematic diagram of Hall effect experiment

You know from the course on Electric and Magnetic Phenomena (PHE-07) that a moving charge experiences a force due to the applied magnetic field. This force acts in a direction perpendicular to both the applied magnetic field and the direction of motion of the charge and deflects it. For the directions of magnetic field and moving charges (since j_x is along positive x direction, motion of electrons will be along negative x direction), this deflection will be along the negative y-direction as shown in Fig.10.11b. Electrons, however, cannot move very far and accumulate on one surface, A of the specimen (Fig. 10.11b). On the opposite surface, B, positive charges (deficiency of electrons) begins to accumulate simultaneously. Due to accumulation of opposite charges on the opposite surfaces of the specimen, an electric field ε_y develops along negative y-direction which opposes further accumulation of electrons on the lower surface. This field is called **Hall field** and, in equilibrium, it counter-balances the force on moving electrons due to magnetic field.

To obtain an expression for the Hall field, you should recall that the force experienced by a charge q moving with a velocity $\mathbf{v}$ in a magnetic field $\mathbf{B}$ is given by

$$\mathbf{F} = q\,(\mathbf{v} \times \mathbf{B}) \tag{10.37}$$

To appreciate the direction of this force, note that if the charge carrier is electron, q becomes $-e$ in Eq. (10.37) and direction of $\mathbf{F}$ is opposite to $(\mathbf{v} \times \mathbf{B})$. However, for the current flowing along positive x-direction, the direction of v for electron is along negative x-direction. So, $(\mathbf{v} \times \mathbf{B})$ is along positive y-direction and, therefore, $\mathbf{F}$ is along negative y-direction. So, for electrons as charge carriers, we can write

$$F_y = -e\,v_x\,B_z$$

In steady state, F_y is balanced by the force $(-e\,\varepsilon_y)$ due to Hall field. Thus, we obtain

$$-e\,\varepsilon_y = -e\,v_x\,B_z$$

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or

$$\varepsilon_y = v_x B_z \tag{10.38}$$

This relation gives the Hall field and can be written in terms of measurable quantities if we use the expression for current density along the x-axis:

$$j_x = - ne \, v_x$$

or

$$v_x = - \frac{j_x}{ne} \tag{10.39}$$

where n is concentration of electrons.

Substituting this expression for v_x in Eq. (10.38), we get

$$\varepsilon_y = - \frac{j_x B_z}{ne}$$

Table 10.1: Hall co-efficient of some metals at room temperature

or

$$\frac{\varepsilon_y}{j_x B_z} = - \frac{1}{ne} = R_H \tag{10.40}$$

Metals	$R_H \times 10^{-10}$ (Vm^3 A^{-1} Tesla^{-1})
Lithium (Li)	– 1.70
Copper (Cu)	– 0.55
Zinc (Zn)	+ 0.33
Aluminium (Al)	– 0.30
Berelium (Be)	+ 2.70
Sodium (Na)	– 2.62

where R_H is called **Hall co-efficient** or **Hall constant**. You may note that the Hall field developed in metallic conductor is proportional to both: current flowing in conductor and the magnetic field in which it is placed.

This is a very useful result because it shows that Hall coefficient depends only on concentration of electrons. Measurement of R_H is, in fact, a standard technique for experimental determination of electron concentration in metals. In addition, it also provides a test of the free electron theory of metals which assumes that valence electrons become free electrons participating in transport phenomenon in metals. Experimental values of the Hall co-efficients of some metals is given in Table 10.1. Note that the values of R_H for Zn and Be are positive. From Eq. (10.40), it is obvious that positive R_H means electrical conduction by positively charged carriers. This is an interesting observation because free electron theory assumes that electrons are the only charge carriers in metals!

The positive Hall co-efficient can be explained on the basis of band theory. The band structure of these metals is such that the conduction bands are more than half-filled. Thus, electrons at the top half of the band participate in electrical conduction. These electrons have negative effective mass and they behave as positively charged carriers. This feature of the Hall coefficient – its sign depends on the sign of the charge carriers – becomes very useful in the study of semiconductors where both types of charge carriers – electrons and holes – play important role simultaneously.

Now let us summarise what you have learnt in this unit.

10.5 SUMMARY

- An electron in a crystalline solid move under the influence of a periodic potential due to ions. According to **Kronig-Penney model**, the periodic potential due to ions in a 1-D crystal can be represented by a series of equidistant potential wells.

- According to **Bloch theorem**, the wavefunction representing an electron in a periodic potential can be expressed as a plane wave modulated by a periodic function; that is,

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

where $u_k(x) = u_k(x + a)$; a being the lattice constant.

- Solutions of the Schrödinger equation for **an electron in a periodic potential** can exist only if the following relation holds:

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

where $P = \frac{ma}{\hbar^2} V_0 b$ is a measure of the strength of attraction between electron and ion. This relation shows that a) energy spectrum of an electron consists of allowed and forbidden energy bands; b) as energy of electron increases, width of allowed bands increases; and c) as P increases, width of the allowed bands decreases.

- Free electron theory of metals proposed by Drude-Lorentz and Sommerfeld are particular cases of band theory of solids. These two particular cases respectively correspond to electron as a completely free particle and in a constant potential field.

- The **dispersion relation** of an electron in a periodic potential shows that the discontinuities in energy spectrum occurs at the Brillouin zone boundaries i.e. at $k = \pm n\pi/a$; $n = 1,2,3, \ldots$

- Number of energy states in an allowed band in a crystalline specimen is equal to the number of unit cells in it. This means that total number of electrons that can be accommodated in a band is twice the number of unit cells in a specimen.

- According to band theory, the velocity and mass of an electron in a crystalline solid is significantly different from those of a free electron. Velocity of an electron near the top of the band decreases with increasing energy. Similarly, mass of electron is different from its rest mass. The **(effective) mass** of an electron in a crystalline solid is given by

$$m^* = \frac{\hbar^2}{\left(d^2 E / dk^2\right)}$$

- Electron near the top of the band has **negative effective mass** which means that electron behaves like a positively charged particle (called hole).

- For a completely filled band, the effective number of free electrons is zero and when the band is half-filled, maximum number of effectively free electrons are available for electric conduction. This conclusion of the band theory enables us to differentiate metals from insulators and semiconductors.

- According to band theory, **metals have partially filled band whereas insulators and semiconductors have completely filled conduction and completely empty valence bands separated from each other by an energy gap, E_g.** However, energy gap in semiconductors is much less than that of an insulator; therefore, as temperature is raised from absolute zero, electrical conduction may take place in semiconductors.

• The value of wave number for which discontinuities appear in the E vs. k curve of an electron represent the **Brillouin zone boundaries** because the corresponding energy values are not allowed to electrons. Therefore, it is possible to construct Brillouin zone patterns of solids on the basis of their E vs. k curves. Since first Brillouin zone is a unit cell of the crystal in reciprocal space, we can determine the crystal structure of the solid on the basis of its Brillouin zone pattern.

• **Hall effect** experiment is used for determining the concentration and sign of carriers in metals as well as in semiconductors. Positive value of Hall coefficient observed for some metals cannot be explained on the basis of free-electron theory. Band theory, however, do account for **positive Hall co-efficient of metals** in terms of negative effective mass of electrons at the top of the band. This experiment also enables us to test the predictions of free electron theory regarding concentration of charge carriers in metals. The Hall co-efficient is given by

$$R_H = \frac{\varepsilon_y}{j_x B_z} = -\frac{1}{ne}$$

10.6 TERMINAL QUESTIONS   *Spend 35 min.*

1. A 2-D square lattice has side 2.5 $\overset{\circ}{A}$. What will be the momentum of an electron whose wave terminates at the boundary of first Brillouin zone? Also calculate energy of the electron.

2. When 90 mA current is passed through a sodium specimen under the magnetic field 2.0 Weber m^{-2}, the Hall voltage is 0.09 mV. The width of the specimen is 0.04 mm. Calculate the carrier concentration.

3. For a 2-D square lattice of side 0.02 $\overset{\circ}{A}$, calculate the momentum of electron corresponding to the boundary of the first Brillouin zone.

10.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions (SAQs)

1. a) In a crystalline solid, atoms are arranged along a periodic lattice. In those solids in which the valence electrons are loosely bound to the constituent atoms, such as metals, the valence electrons become *free* leaving positively charged ions at lattice sites. The free (conduction) electrons experience potential field due to the positively charged ions. Since ions are arranged along a periodic lattice, the potential field due to them is also periodic.

   b) Since an electron experience a periodic potential in a crystalline solid, the wave function describing such an electron must have the form of Bloch function given by

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

   where $u_k(x) = u_k(x + a)$, a being the lattice constant.

2. Values of $\left(\dfrac{P}{\alpha a}\sin\alpha a + \cos\alpha a\right)$ for different values of αa and $P = 3\pi/2$ is tabulated below:

αa	$\left(\dfrac{P}{\alpha a}\sin\alpha a + \cos\alpha a\right)$	
0	5.71	
$\pi/4$	4.97	
$\pi/2$	1.0	1st allowed band (width = 0.5π)
$3\pi/4$	0.7	
π	-1.0	
$5\pi/4$	-1.55	
$3\pi/2$	-1.0	2nd allowed band (width = 0.5π)
$7\pi/4$	0.1	
2π	1.0	
$9\pi/4$	1.18	
$\dfrac{28\pi}{12}$	1.05	
$\dfrac{19\pi}{8}$	0.96	3rd allowed band (width = 0.66π)
$10\pi/4$	0.60	
$11\pi/4$	-0.32	
3π	-1.00	

3. Refer to the answer of SAQ 2 which gives $\left(\dfrac{P}{\alpha a}\sin\alpha a + \cos\alpha a\right)$ for different values of αa for fixed value of P ($= 3\pi/2$). Note that these values have been tabulated at the intervals of $\pi/4$ in αa. The second allowed band covers the range $\dfrac{3\pi}{2} \leq \alpha a \leq 2\pi$ and the width of the band is $0.5\,\pi$. However, the third allowed band covers the range $\dfrac{19\pi}{8} \leq \alpha a \leq 3\pi$ giving width of the band equal to $0.66\,\pi$.

You can show that the allowed band width will further increase for increasing values of αa. Thus, as energy of electron increases, allowed energy band width increases.

4. We have

$$E = \frac{10\hbar^2 k^2}{m}$$

From Eq. (10.26)

$$v = \frac{1}{\hbar}\frac{dE}{dk} = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{10\hbar^2 k^2}{m}\right) = \frac{20\hbar k}{m}.$$

From Eq. (10.30), effective mass of an electron is

$$m^* = \frac{\hbar^2}{\left(d^2 E / dk^2\right)}$$

We have

$$\frac{dE}{dk} = \frac{d}{dk}\left(\frac{10\hbar^2 k^2}{m}\right) = \frac{20\hbar^2 k}{m}$$

$$\therefore \quad \frac{d^2 E}{dk} = \frac{d}{dk}\left(\frac{dE}{dk}\right) = \frac{d}{dk}\left(\frac{20\hbar^2 k}{m}\right) = \frac{20\hbar^2}{m}$$

$$\therefore \quad m^* = \frac{\hbar^2 \times m}{20\hbar^2} = \frac{m}{20}.$$

5. We know that discontinuities in dispersion curve appear at (Eq. (10.20))

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

For second Brillouin zone, we must take $n = \pm 2$. So, $k = \pm \dfrac{2\pi}{a}$. For a 2-D squa

lattice, this condition transforms to

$$k_x n_1 + k_y n_2 = \frac{\pi}{a}\left(n_1^2 + n_2^2\right)$$

with $n_1^2 + n_2^2 = 2$.

Following combinations of values of n_1 and n_2 will satisfy above condition:

$n_1 = +1, \quad n_2 = +1 \qquad$ which gives $k_x + k_y = \dfrac{2\pi}{a}$

$n_1 = +1, \quad n_2 = -1 \qquad$ which gives $k_x - k_y = \dfrac{2\pi}{a}$

$n_1 = -1, \quad n_2 = +1 \qquad$ which gives $-k_x + k_y = \dfrac{2\pi}{a}$

$n_1 = -1, \quad n_2 = -1 \qquad$ which gives $-k_x - k_y = \dfrac{2\pi}{a}$

These are equations of straight lines and taking k_x and k_y as axes, we get the following figure for the second Brillouin zone:
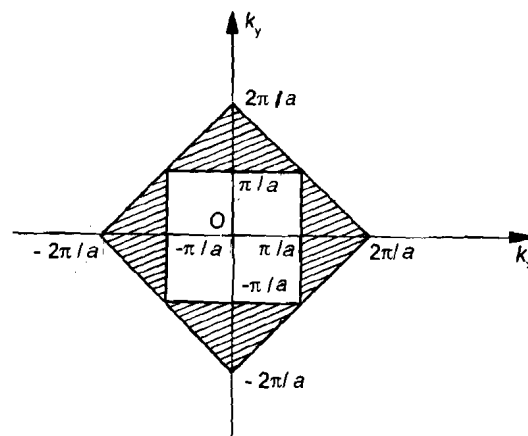

Fig.10.12: Second Brillouin zone (shown by shaded regions) of a 2-D square lattice

Terminal Questions (TQs)

1. You know that the boundaries of first Brillouin zone of a square lattice is given by (Eq. (10.20))

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

    where 'a' is the lattice constant. We have,

    $$a = 2.5\,\overset{\circ}{A} = 2.5 \times 10^{-10}\text{m}.$$

    Momentum of an electron at the boundary of first Brillouin zone can be written as (taking $n = 1$ in above expression for the wave number),

    $$p = \hbar k = \hbar.\frac{\pi}{a} = \left(1.05 \times 10^{-34}\,\text{Js}\right) \times \frac{3.14}{2.5 \times 10^{-10}\,\text{m}}$$

    $$= 1.38 \times 10^{-24}\,\text{kg.ms}^{-1}$$

    Corresponding value of the energy of electron is

    $$E = \frac{p^2}{2m} = \frac{(1.38 \times 10^{-24}\,\text{kg.ms}^{-1})^2}{2 \times (9.1 \times 10^{-31}\,\text{kg})} = 1.04 \times 10^{-18}\,\text{J} = 10.4\,\text{eV}.$$

2. Hall co-efficient, R_H is defined as the Hall electric field per unit current density per unit magnetic field. So, if V_H is the Hall voltage and b and d are the lengths of the edges of a parallelepiped parallel to y- and z-axes respectively (refer to Fig.10.11), we can write

    $$\varepsilon_H = \frac{V_H}{b}$$

    and

    $$j_x = \frac{I_x}{bd}$$

    where I_x is current.

    So, we can write Hall co-efficient as

    $$R_H = \frac{\dfrac{V_H}{b}}{\dfrac{I_x}{bd}B_z} = \frac{V_H d}{I_x B_z}$$

    We have,

    $$V_H = 0.09\,\text{mV} = 0.09 \times 10^{-3}\,\text{V}; \quad I_x = 90\,\text{mA} = 90 \times 10^{-3}\text{A};$$

    $$d = 0.04\,\text{mm} = 0.04 \times 10^{-3}\,\text{m}; \text{ and } B_z = 2\,\text{Wb m}^{-2}$$

Thus,

$$R_{\mathrm{H}} = \frac{\left(0.09 \times 10^{-3}\,\mathrm{V}\right) \times \left(0.04 \times 10^{-3}\,\mathrm{m}\right)}{\left(90 \times 10^{-3}\,\mathrm{A}\right) \times \left(2\,\mathrm{Wb\,m}^{-2}\right)}$$

But, from Eq. (10.40), the magnitude of Hall co-efficient is given by

$$R_{\mathrm{H}} = \frac{1}{ne}$$

$$\therefore \quad n = \frac{\left(90 \times 10^{-3}\,\mathrm{A}\right) \times \left(2\,\mathrm{Wb\,m}^{-2}\right)}{(0.09 \times 10^{-3}\,\mathrm{V}) \times (0.04 \times 10^{-3}\,\mathrm{m}) \times (1.6 \times 10^{-19}\,\mathrm{C})}$$

$$= 3.1 \times 10^{26}\,\mathrm{m}^{-3}$$

3. We know that the first Brillouin zone lies in the range $-\dfrac{\pi}{a} < k < \dfrac{\pi}{a}$. So, we have to calculate the momentum of an electron whose wave number, $k = \pm\,\dfrac{\pi}{a}$. And momentum of an electron is given by

$$p = \hbar\, k$$

$$= \hbar \left(\frac{\pi}{a}\right)$$

$$= \frac{\left(1.05 \times 10^{-34}\,\mathrm{Js}\right) \times \left(3.14\right)}{\left(0.02 \times 10^{-10}\,\mathrm{m}\right)}$$

$$= 164 \times 10^{-24}\,\mathrm{kg\,ms}^{-1}.$$

APPENDIX: SOLUTION OF SCHRÖDINGER EQUATION FOR KRONIG-PENNEY MODEL

As per the Kronig-Penney model, Schrödinger equation for two distinct potential regions can be written as (Eqs. (10.10) and (10.11)):

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi(x) = 0 \qquad 0 < x < a \qquad (A.1)$$

and

$$\frac{d^2\psi}{dx^2} - \beta^2 \psi(x) = 0 \qquad -b < x < 0 \qquad (A.2)$$

The solution of these differential equations was suggested by Bloch as under,

$$\psi(x) = u_k(x) e^{ikx} \qquad (A.3)$$

So,

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left[e^{ikx} \frac{du_k}{dx} + u_k ik\, e^{ikx} \right]$$

$$= -k^2 e^{ikx} u_k + 2ike^{ikx} \frac{du_k}{dx} + e^{ikx} \frac{d^2 u_k}{dx^2} \qquad (A.4)$$

Let us assume that $u_k(x) = u_1$ for $0 < x < a$ and $u_k(x) = u_2$ for $-b < x < 0$. Under these assumptions, using Eqs. (A.3) and (A.4) in Eqs. (A.1) and (A.2), we get

$$\frac{d^2 u_1}{dx^2} + 2ik \frac{du_1}{dx} + \left(\alpha^2 - k^2\right) u_1 = 0 \qquad (A.5)$$

and

$$\frac{d^2 u_2}{dx^2} + 2ik \frac{du_2}{dx} - \left(\beta^2 + k^2\right) u_2 = 0 \qquad (A.6)$$

Solution of differential equation (Eq. (A.5)) can be written as,

$$u_1 = e^{px}$$

Substituting this in Eq. (A.5), we get,

$$p^2 e^{px} + 2ikp e^{px} + \left(\alpha^2 - k^2\right) e^{px} = 0$$

$$p^2 + 2ikp + \left(\alpha^2 - k^2\right) = 0$$

$$p = \frac{-2ik \pm \sqrt{-4k^2 - 4\left(\alpha^2 - k^2\right)}}{2}$$

$$p = -ik \pm i\alpha$$

Thus, we have

$$p_1 = -ik + i\alpha = i(\alpha - k)$$

and

$$p_2 = -ik - i\alpha = -i(\alpha + k)$$

Thus, we can write the general solution as

$$u_1 = A e^{p_1 x} + B e^{p_2 x}$$

$$= A e^{i(\alpha - k)x} + B e^{-i(\alpha + k)x} \tag{A.7}$$

where A and B are constants.

Similarly, substituting the solution $u_2 = e^{px}$ in Eq. (A.6) and solving as above, we can write the general solution as

$$u_2 = C e^{(\beta - ik)x} + D e^{-(\beta + ik)x} \tag{A.8}$$

where C and D are constants.

To obtain the values of constants A, B, C and D, we apply the following boundary conditions on Eqs. (A.7) and (A.8):

i) $\left[u_1(x) \right]_{x=0} = \left[u_2(x) \right]_{x=0}$

ii) $\left[\dfrac{du_1(x)}{dx} \right]_{x=0} = \left[\dfrac{du_2(x)}{dx} \right]_{x=0}$

iii) $\left[u_1(x) \right]_{x=a} = \left[u_2(x) \right]_{x=-b}$

iv) $\left[\dfrac{du_1(x)}{dx} \right]_{x=a} = \left[\dfrac{du_2(x)}{dx} \right]_{x=-b}$

Applying (i) on Eqs. (A.7) and (A.8), we get

$$(A+B) = (C+D) \tag{A.9}$$

Applying (ii) on Eqs. (A.7) and (A.8), we get

$$i(\alpha - k)A - i(\alpha + k)B = (\beta - ik)C - (\beta + ik)D \tag{A.10}$$

Applying (iii) on Eqs. (A.7) and (A.8), we get

$$A e^{i(\alpha - k)a} + B e^{-i(\alpha + k)a} = C e^{-(\beta - ik)b} + D e^{(\beta + ik)b} \tag{A.11}$$

Applying (iv) on Eqs. (A.7) and (A.8), we get

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

Eqs. (A.9) to (A.12) will have non-vanishing solutions if and only if the determinant of the coefficients of A, B, C and D vanishes. That is,

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

(A.13)

To solve this determinant, let us write it as

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ a & b & c & d \\ e & f & g & h \\ ae & bf & cg & dh \end{vmatrix} = 0$$

Expanding and rearranging terms we get

$$(e - g)(f - h)(bd + ac) + (g - f)(e - h)(bc + ad)$$

$$= (h - g)(f - e)(ab + cd)$$

(A.14)

Substituting the values of a, b, c, d, e, f, g and h from Eq. (A.13), in Eq. (A.14) and simplifying we get,

$$\frac{\beta^2 - \alpha^2}{2i\alpha\beta}\left[\left(e^{i\alpha a} - e^{-i\alpha a}\right)\left(e^{\beta b} - e^{-\beta b}\right)\right]$$

$$= \left[2e^{-ik(a+b)} + 2e^{ik(a+b)}\right] - \left[\left(e^{i\alpha a} + e^{-i\alpha a}\right)\left(e^{\beta b} + e^{-\beta b}\right)\right]$$

Dividing throughout by 2, we get

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta}\left[\frac{e^{i\alpha a} - e^{-i\alpha a}}{2i}\left(e^{\beta b} - e^{-\beta b}\right)\right]$$

$$= \left[e^{ik(a+b)} + e^{-ik(a+b)}\right] - \left[\left(e^{i\alpha a} + e^{-i\alpha a}\right)\frac{e^{\beta b} + e^{-\beta b}}{2}\right]$$

Now, using the following relations

$$\sin x = \frac{e^{ix} - e^{-ix}}{2i} \; ; \qquad \cos x = \frac{e^{ix} + e^{-ix}}{2} \; ;$$

$$\sinh x = \frac{e^{x} - e^{-x}}{2} \; ; \text{ and } \quad \cosh x = \frac{e^{x} + e^{-x}}{2}$$

we can write

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

or

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta}\sinh\beta b \sin\alpha a + \cosh\beta b \cos\alpha a = \cos k(a+b) \qquad (A.15)$$

This is the desired relation expressed as Eq. (10.13).