

insulate. When we considered the solid as a collection of free electrons in a box, we imposed the condition that the wave function vanishes at the walls of the box—that is, on the surface of the sample, allowing the conduction electrons to move in a region of constant potential. Obviously this approximation of the potential inside the crystal is too drastic.

It is now suggested to disregard the surface and to treat the crystal as an infinite array of lattice points. To do this, slightly different forms of boundary conditions, called cyclic or periodic boundary conditions, have been developed. Inside a real crystal, there is a periodic arrangement of positively charged ions through which the electrons move. The motion of a representative electron is shown in Fig. 6.42 (a). The potential of the electron at the positive ion site is zero and is maximum in between. So along any line passing through the centres of the positive ions, the potential variation must be as shown in Fig. 6.42 (b). We find that the potential varies periodically, with the same period as the lattice. We have now to study the motion of the electron in such a lattice and energy states it can occupy. The appropriate Schrödinger equation for the motion of the electron is given by

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

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} [E - V(x)]\psi = 0 \quad (6.170)$$

where, the potential function $V(x)$ has the periodicity of the lattice given by

$$V(x) = V(x + a) \quad (6.171)$$

with a as the periodicity of the lattice.

Bloch has shown that an equation of the type (6.170) has a solution of the form

$$\psi(x) = u_K(x)e^{iKx} \quad (6.172)$$

where, $u_K(x)$ has the periodicity of the lattice given by

$$u_K(x) = u_K(x + a) \quad (6.173)$$

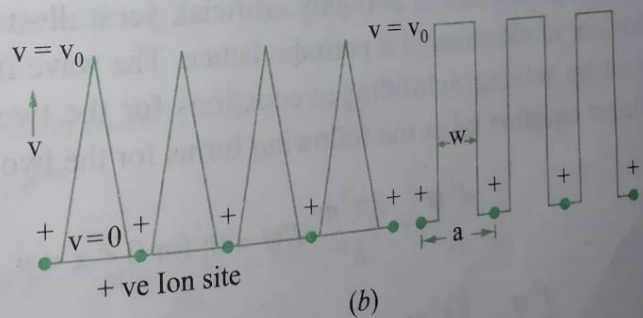
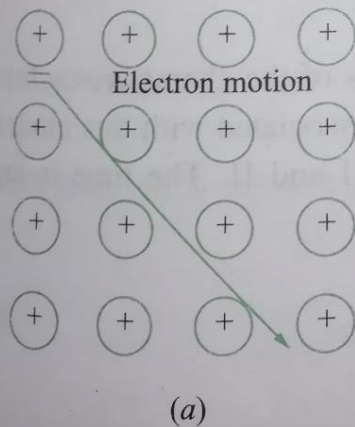


Fig. 6.42 One-dimensional periodic potential distribution for a crystal

In three dimensions $\varphi(r) = e^{ikr} u_k(r)$

XXXVII. ELECTRON IN A PERIODIC FIELD OF A CRYSTAL (THE KRONIG-PENNEY MODEL)

For the treatment of our problem, a periodic repetition of the potential well of Fig. 6.10, i.e., a periodic arrangement of potential wells and potential barriers, is most probably very close to reality and is best suited for the calculation. Such a periodic potential is shown in Fig. 6.43 for the one-dimensional case.

Although this model is highly artificial, yet it illustrates many of the characteristic features of the behaviour of electrons in a periodic lattice. The wave functions associated with this model are calculated by solving Schrödinger equations for the two regions I and II. The time-independent Schrödinger equation takes the following forms for the two regions

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} E\psi = 0; \text{ for } 0 < x < a$$

and

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V_0) \psi = 0; \text{ for } -b < x < 0$$

Making use of Bloch's theorem, the solution can be written in the form

$$\psi(x) = u_K(x)e^{iKx}$$

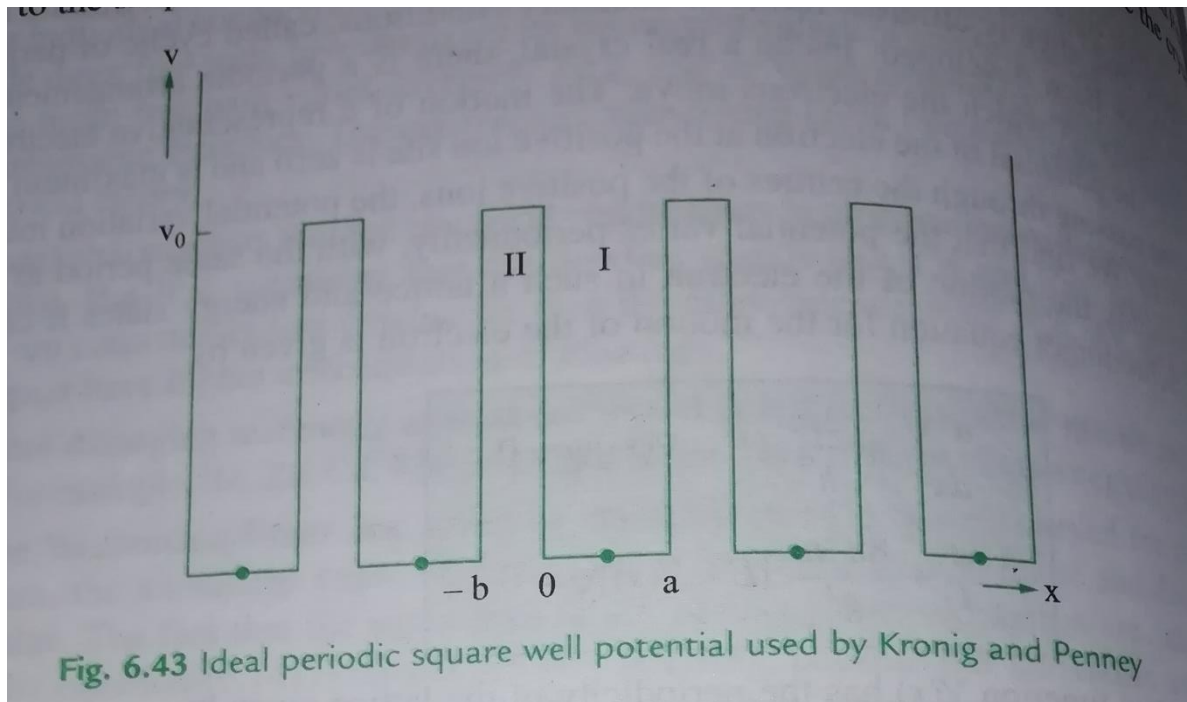


Fig. 6.43 Ideal periodic square well potential used by Kronig and Penney

Assuming that the total energy E of the electron is less than the potential energy V_0 , we define two real quantities α and β such that

$$\alpha^2 = \frac{8\pi^2 m E}{h^2} \quad (6.176)$$

$$\beta^2 = \frac{8\pi^2 m}{h^2} (V_0 - E) \quad (6.177)$$

Thus,

$$\frac{d^2 \psi}{dx^2} + \alpha^2 \psi = 0; \text{ for } 0 < x < a \quad (6.178)$$

and

$$\frac{d^2 \psi}{dx^2} - \beta^2 \psi = 0; \text{ for } -b < x < 0 \quad (6.179)$$

The solution that will be appropriate for both the regions suggested by Bloch is of the form

$$\psi(x) = u_K(x) e^{iKx}$$

On differentiating this equation, one gets

$$\frac{d\psi}{dx} = e^{iKx} \frac{du_K}{dx} + u_K iK e^{iKx}$$

and

$$\frac{d^2 \psi}{dx^2} = e^{iKx} \frac{d^2 u_K}{dx^2} + iK e^{iKx} \frac{du_K}{dx} + iK e^{iKx} \frac{du_K}{dx} - K^2 e^{iKx} u_K$$

i.e.,

$$\frac{d^2 \psi}{dx^2} = -K^2 e^{iKx} u_K + 2iK e^{iKx} \frac{du_K}{dx} + e^{iKx} \frac{d^2 u_K}{dx^2}$$

Substituting these values in equations (6.178) and (6.179), we get

$$\frac{d^2 u_1}{dx^2} + 2iK \frac{du_1}{dx} + (\alpha^2 - K^2) u_1 = 0; \text{ for } 0 < x < a \quad (6.180)$$

and

$$\frac{d^2 u_2}{dx^2} + 2iK \frac{du_2}{dx} - (\beta^2 + K^2) u_2 = 0; \text{ for } -b < x < 0 \quad (6.181)$$

where, u_1 represents the value of $u_K(x)$ in the interval $0 < x < a$ and u_2 the value of $u_K(x)$ in the interval $-b < x < 0$.

The solution of the differential equation (6.180) is of the form

$$u_1 = e^{mx}$$

$$\frac{du_1}{dx} = m e^{mx} \text{ and } \frac{d^2 u_1}{dx^2} = m^2 e^{mx}$$

Substituting these values in equation (6.180), we get

$$m^2 e^{mx} + 2iK m e^{mx} + (\alpha^2 - K^2) e^{mx} = 0$$

$$m^2 + 2iK m + (\alpha^2 - K^2) = 0$$

$$m = \frac{-2iK \pm \sqrt{-4K^2 - 4(\alpha^2 - K^2)}}{2}$$

$$m = -iK \pm i\alpha$$

$$m_1 = -iK + i\alpha = i(\alpha - K)$$

$$m_2 = -iK - i\alpha = -i(\alpha + K)$$

i.e.,

and

Thus, the general solution is

$$u_1 = A e^{m_1 x} + B e^{m_2 x}$$

$$u_1 = A e^{i(\alpha - K)x} + B e^{-i(\alpha + K)x}$$

where, A and B are constants.

Similarly equation (6.181) can be written as

$$m^2 + 2iKm - (\beta^2 + K^2) = 0$$

$$m = \frac{-2iK \pm \sqrt{-4K^2 + 4(\beta^2 + K^2)}}{2}$$

$$m = -iK \pm \beta$$

$$m_1 = -iK + \beta = (\beta - iK)$$

$$m_2 = -iK - \beta = -(\beta + iK)$$

i.e.,

Thus,

$$u_2 = C e^{m_1 x} + D e^{m_2 x}$$

$$u_2 = C e^{(\beta - iK)x} + D e^{-(\beta + iK)x}$$

where, C and D are constants. The values of the constants A , B , C and D can be obtained by applying boundary conditions.

$$[u_1(x)]_{x=0} = [u_2(x)]_{x=0}; \quad \left[\frac{du_1(x)}{dx} \right]_{x=0} = \left[\frac{du_2(x)}{dx} \right]_{x=0}$$

and

$$[u_1(x)]_{x=a} = [u_2(x)]_{x=-b}; \quad \left[\frac{du_1(x)}{dx} \right]_{x=a} = \left[\frac{du_2(x)}{dx} \right]_{x=-b}$$

Applying these conditions, we get

(i)

$$(A + B) = (C + D)$$

(ii)

$$[A i(\alpha - K) e^{i(\alpha - K)x} - B i(\alpha + K) e^{-i(\alpha + K)x}]_{x=0} = [C(\beta - iK) e^{(\beta - iK)x} - D(\beta + iK) e^{-(\beta + iK)x}]_{x=0}$$

i.e.,

(iii)

$$i(\alpha - K)A - i(\alpha + K)B = (\beta - iK)C - (\beta + iK)D$$

(iv)

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

i.e.,

$$[A i(\alpha - K) e^{i(\alpha - K)a} - B i(\alpha + K) e^{-i(\alpha + K)a}] = [C(\beta - iK) e^{(\beta - iK)x} - D(\beta + iK) e^{-(\beta + iK)x}]_{x=-b}$$

$$= C(\beta - iK) e^{-(\beta - iK)b} - D(\beta + iK) e^{(\beta + iK)b}$$

Equations (6.184), (6.185), (6.186) and (6.187) will have non-vanishing solutions if and only if the determinant of the coefficients A , B , C and D vanishes. This requires that

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

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

Now,

$$(\beta^2 - \alpha^2) = \frac{8\pi^2 m}{h^2} (V_0 - E) - \frac{8\pi^2 m}{h^2} E = \left(\frac{8\pi^2 m}{h^2} \right) [V_0 - 2E]$$

Since $V_0 \gg E$,

$$\beta^2 - \alpha^2 = \frac{8\pi^2 m}{h^2} (V_0)$$

Substituting this in the above equation, we get

$$\left(\frac{8\pi^2 m V_0}{2\alpha \beta \hbar^2} \right) \beta b \sin \alpha a + \cos \alpha a = \cos Ka$$

where, $p = \frac{m V_0 ab}{\hbar^2}$

i.e.,

$$\left(\frac{m V_0 ab}{\hbar^2} \right) \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos Ka$$

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

The term $V_0 b$ is called the *barrier strength*. The term $P = \frac{m V_0 ab}{\hbar^2}$ in equation (6.190) is sometimes referred as the *scattering power* of the potential barrier. It is a measure of the strength with which electrons in a crystal are attracted to the ions on the crystal lattice sites. Also

$$\alpha^2 = \frac{8\pi^2 m E}{\hbar^2}, \text{ or } E = \frac{\alpha^2 \hbar^2}{8\pi^2 m}$$

and

$$K = \frac{2\pi}{\lambda}$$

Equation (6.190) is a condition of the existence of a solution for the electron wave function.

There are only two variables in equation (6.190), namely α and K . The right hand side of equation (6.190) is bounded since it can only assume values between +1 and -1. If we plot the left-hand side of this equation against αa , it will be possible to determine those value of α (and hence energy) which are

permissible; that is, permit $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ to take values between +1 and -1.

When each of these values is set equal to $\cos Ka$, K is determined. Then α can be found from equation (6.180).

Figure 6.44 shows this plot for a value of P assumed arbitrarily as $3\pi/2$. Indicated in the figure are the permitted values of this function, shown as a solid line between white portions. This, then, give rise to the concept of ranges of permitted values of α for a given ion lattice spacing a , and since

$E = \frac{\alpha^2 \hbar^2}{8\pi^2 m}$, permitted bands of energy are predicted. The following interesting conclusions may be drawn:

1. The allowed ranges of αa which permit a wave-mechanical solution to exist are shown in the figure as the white portions. Thus the motion of electrons in a periodic lattice is characterised by bands of allowed energy separated by forbidden regions.

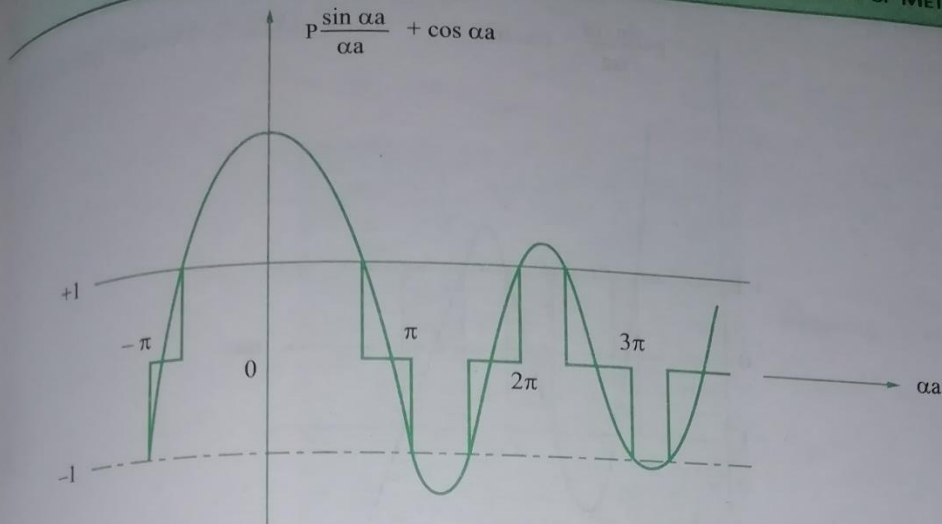


Fig. 6.44 Graph of $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos Ka$ with $P = 3\pi/2$

2. As the value of αa increases, the width of allowed energy bands also increases and the width of the forbidden bands decreases; this is a consequence of the fact that the first term of equation (6.190) decreases on the average with increasing αa .
3. Let us now consider the effect of varying P . It is known that P is a measure of the potential barrier strength. If $V_0 b$ is a large, i.e., if P is large, the function described by the left hand side of the equation (6.190) crosses $+1$ and -1 region at a steeper angle as shown in Fig. 6.45 (a). Thus the allowed bands are narrower and the forbidden bands are wider.

Also in equation (6.190), when $\alpha a = \pm n\pi$, $\cos \alpha a = \cos Ka$ with $Ka = \pm n\pi$; or $K = \pm \frac{n\pi}{a}$. These values of K are points of discontinuity in the $(E - K)$ curve for electrons in the crystal.

In the limit $P \rightarrow \infty$ the allowed band reduces to one single energy level; that is, we are back to the case of discrete energy spectrum existing in isolated atoms.

$P \rightarrow \infty$ it follows from equation (6.190) that $\sin \alpha a = 0$; or $\alpha a = \pm n\pi$

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

Referring equation (6.176),

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

$$E = \left[\frac{n^2 \pi^2 \hbar^2}{a^2 2m} \right] = \left[\frac{n^3}{2m} \right] \left[\frac{\pi^2 \hbar^2}{4\pi^2} \right]$$

$$E = \frac{n^2 \hbar^2}{8ma^2}$$

(6.191)

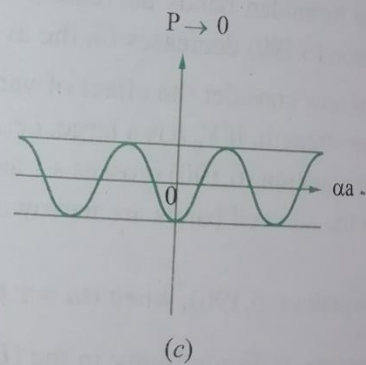
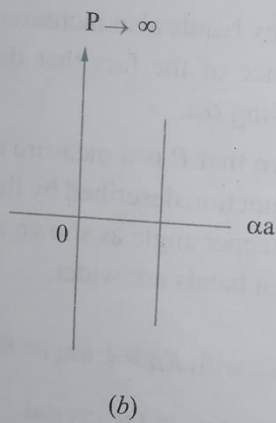
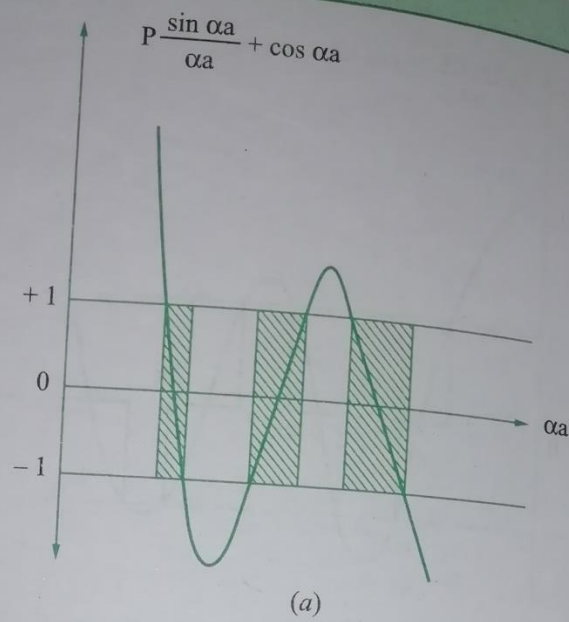


Fig. 6.45 (a) The left-hand side of equation (6.190) for $P = 3\pi/2$ as a function of αa ; (b) $P \rightarrow \infty$; (c) $P \rightarrow 0$

Here E is independent of K . The energy level in this case are discrete and the result is similar to the energy levels of a particle in a constant potential box of atomic dimensions. This is expected because for large P tunnelling through the barrier becomes almost improbable.

4. The other extreme case, when $P \rightarrow 0$, leads to

Thus,

$$\cos \alpha a = \cos Ka$$

$$\alpha = K$$

$$\alpha^2 = K^2$$

i.e.,

(6.176),

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

$$E = \left(\frac{\hbar^2}{2m} \right) K^2$$

$$E = \left(\frac{h^2}{8\pi^2 m} \right) \left(\frac{2\pi}{\lambda} \right)^2$$

$$E = \left(\frac{h^2}{2m} \right) \frac{1}{\lambda^2}$$

$$E = \left(\frac{h^2}{2m} \right) \frac{p^2}{h^2} = \frac{p^2}{2m} = \frac{1}{2}mv^2$$

Referring equation (

20.6 ORIGIN OF ENERGY BANDS

In Kronig-Penney model, an equation was obtained for energy eigen values of an electron moving in a periodic potential. It was observed that the electrons have energy values only between allowed energy bands. The allowed energy bands are separated by forbidden energy bands. The discontinuities in the energy values arise at points $\alpha a = \pm n \pi$ ($n \neq 0$).

The allowed values are given by

$$E = \frac{\hbar^2 k^2}{2m} \quad \dots(1)$$

where k is wave number, $k = \pm (n \pi / a)$

n takes the values, $n = \pm 1, \pm 2, \pm 3, \dots$

a = Atomic periodicity.

20.12

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Equation (1) gives the E - k curve. It is clear that E - k curve is a parabola. Due to discontinuities in the energy values (energy gaps), the parabola is discontinuous while in case of free electron, this is a continuous parabola. Figure (10) shows the E - k curve.

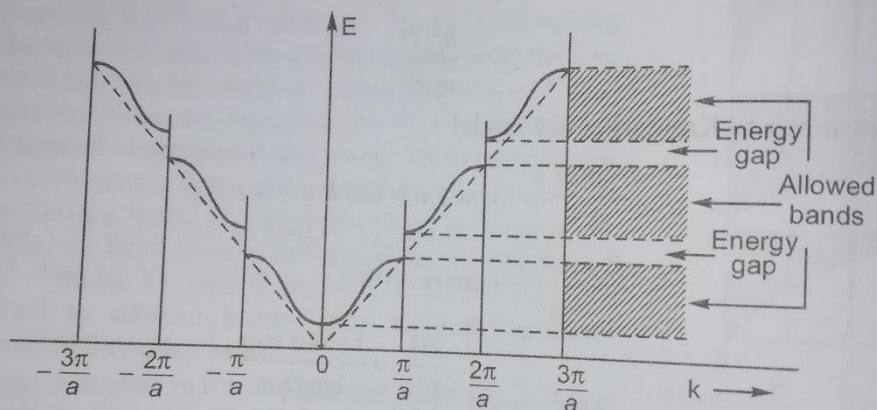


Fig. (10) E - k curve for an electron in periodic potential

At $k = \pm \frac{\pi}{a}$, E has two values. The lower belonging to region $-\frac{\pi}{a}$ to $\frac{\pi}{a}$ and higher between $\frac{\pi}{a}$ to $\frac{2\pi}{a}$ (or $-\frac{\pi}{a}$ to $-\frac{2\pi}{a}$). There is a definite gap in energy at the boundary of these two regions.

The dotted curve shows the free electron parabola $= \frac{h^2 k^2}{8\pi^2 m}$. From the graph we see that the electron has allowed energy values in the region or zone extending from $K = -\frac{\pi}{a}$ to $K = +\frac{\pi}{a}$. The zone is called the first Brillouin zone. After a break in the energy values called the forbidden region or band or zone, we get another allowed zone of energy values in the region extending from $K = -\frac{2\pi}{a}$ to $K = +\frac{2\pi}{a}$. This zone is called the second Brillouin zone. Similarly the other higher order Brillouin zones can be defined.

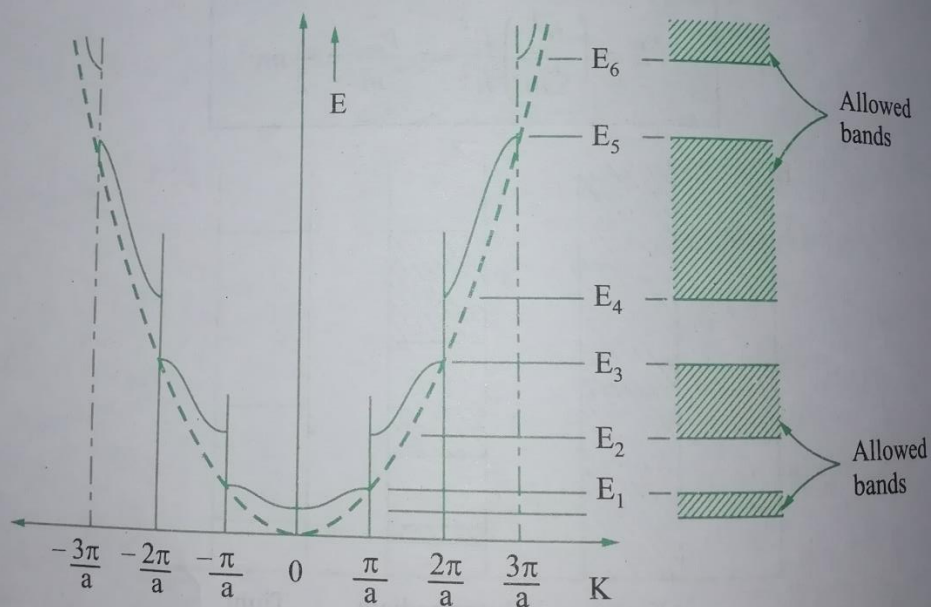


Fig. 6.47 The relation between energy and wave number of a one-dimensional lattice

Thus we see that the various Brillouin zones are demarcated by the values of the propagation vector ' K '. Since ' K ' is a vector, and has different values along different directions, it is pertinent to the question as to how the limiting values of K in different directions can be determined and factors the value of K depends. In as much as the zone picture of the crystal is found to be fruitful in understanding of the electron propagation in periodic structures, it is necessary to study the demarcation of the Brillouin zone boundaries and the part played by the propagation vector.

The main point we have to note is that in a constant potential lattice, the electron energy levels are quasicontinuous, whereas in a free electron lattice, the energy levels are separated.

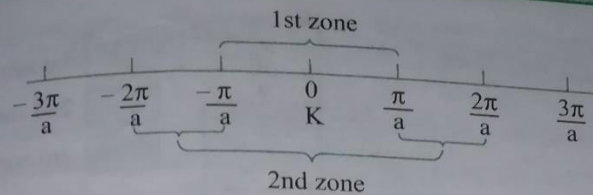


Fig. 6.48 The first two Brillouin zones for one-dimensional case

Brillouin Zones in Two Dimensions

Now consider the motion of an electron in the field of two-dimensional square lattice. The motion of the electron in two dimensions can now be discussed using a wave number ' K ', which, as before, is measured in the direction of propagation of the wave. The wave number K can be analysed into components along the x and y axes, which are respectively, K_x and K_y .

To sketch the first Brillouin zone, we note that along the K_x axis in Fig. 6.49, the values of $\pm \frac{\pi}{a}$ represent the limits of the zone. Similarly, along the K_y axis the values of $\pm \frac{\pi}{a}$ also represent the limits of the zone. In general, the condition for any energy discontinuity is

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

So in two dimensions the condition reads

$$K_x n_1 + K_y n_2 = \frac{\pi}{a} (n_1^2 + n_2^2)$$

where, n_1 and n_2 are integers corresponding to the single integer n and referring to each of the axes. To sketch the first zone, n_1 and n_2 are made equal in turn to ± 1 , or 0. The equations of the lines bordering the first zone are therefore

$$\begin{aligned} n_1 = \pm 1, n_2 = 0, \text{ giving } K_x &= \pm \frac{\pi}{a} \\ n_1 = 0, n_2 = \pm 1, \text{ giving } K_y &= \pm \frac{\pi}{a} \end{aligned}$$

Thus a square passing through the points A, B, C and D gives the first Brillouin zone.

The second Brillouin zone should obviously pass through the points E, F, G and H. The complete picture of the second zone is obtained by taking n_1 and n_2 as the next integers in the series above those used for the first zone. These are $n_1 = \pm 1$ and $n_2 = \pm 1$. The equations giving the boundaries of the second zone are

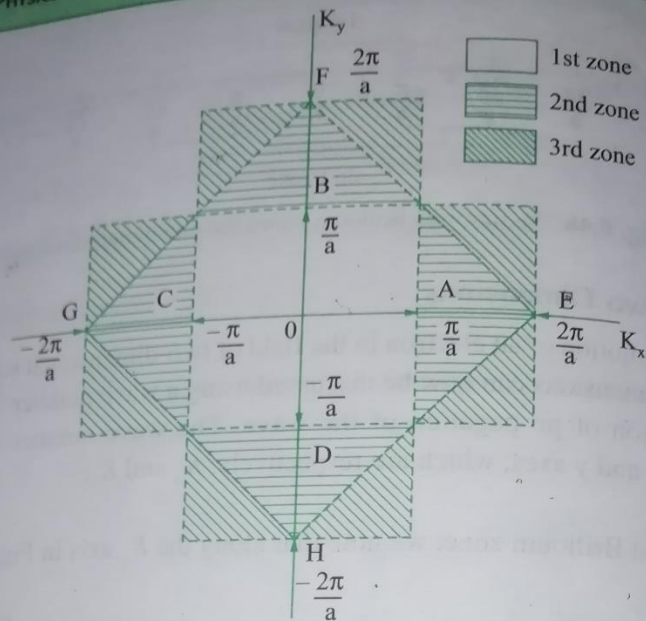


Fig. 6.49 The first three Brillouin zones for a two-dimensional square lattice

$$n_1 = +1, n_2 = +1, \text{ giving } K_x + K_y = \frac{2\pi}{a}$$

$$n_1 = -1, n_2 = +1, \text{ giving } -K_x + K_y = \frac{2\pi}{a}$$

$$n_1 = +1, n_2 = -1, \text{ giving } K_x - K_y = \frac{2\pi}{a}$$

$$n_1 = -1, n_2 = -1, \text{ giving } -K_x - K_y = \frac{2\pi}{a}$$

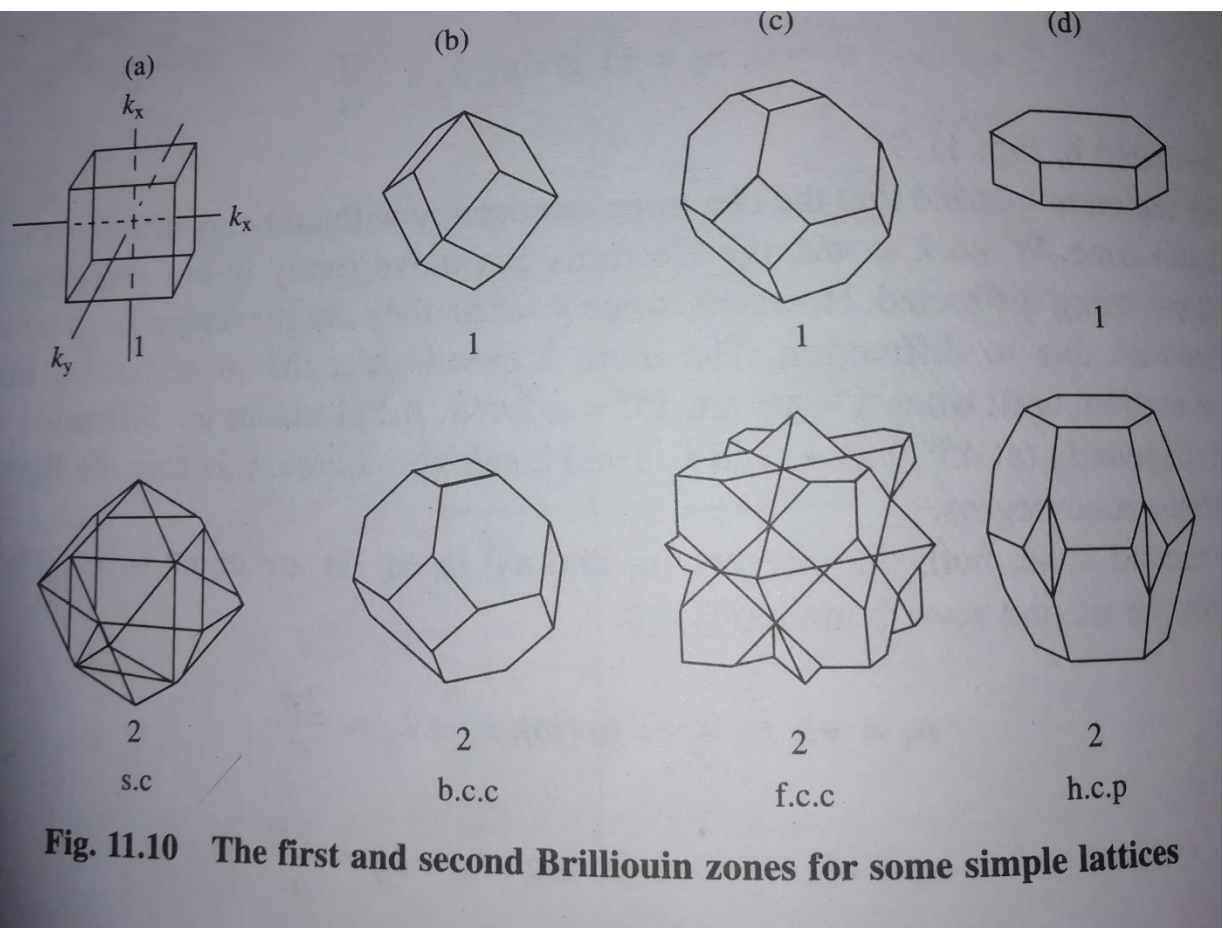
The above four equations describe a set of four lines at 45° to the K_x and K_y axes passing through E, F, G and H. The second Brillouin zone is thus the region between the squares ABCD and EFGH. The third Brillouin zone is obtained giving n_1 and n_2 values of $0, \pm 1$ and ± 2 .

Brillouin Zones in Three Dimensions

The equation used to describe the zones in three dimensions is given by

$$K_x n_1 + K_y n_2 + K_z n_3 = \left(\frac{\pi}{a}\right)(n_1^2 + n_2^2 + n_3^2)$$

The first zone for a simple cubic lattice is clearly a cube intersecting the K_x , K_y and K_z axes at the points π/a . Just as in the triangular form of the second zone in two dimensions, the second zone in three dimensions is obtained by adding a pyramid to each face to the first zone cube.



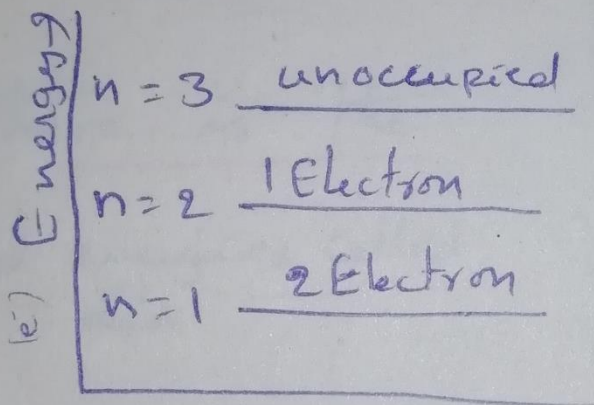


Fig. (1)

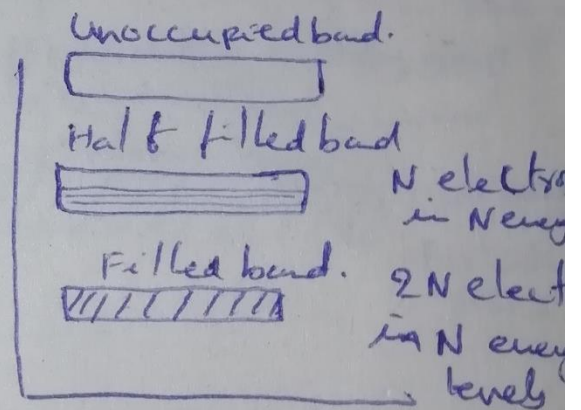


Fig. (2)

36.8 ENERGY BAND DIAGRAMS FOR SOME TYPICAL SOLIDS

(a) **Lithium:** Let us consider the element lithium belonging to Group 1 in the periodic table. The electron configuration of lithium atom is $1s^2 2s^1$. The $1s$ shell is closed and there is only one electron at the $2s$ level. In solid lithium, $1s$ and $2s$ bands form corresponding to the $1s$ and $2s$ levels, as illustrated in Fig. 36.12.

Both $1s$ and $2s$ bands have N levels each. The $1s$ band is completely filled as $2N$ electrons occupy N energy levels whereas the $2s$ band is half-filled because the N available electrons fill

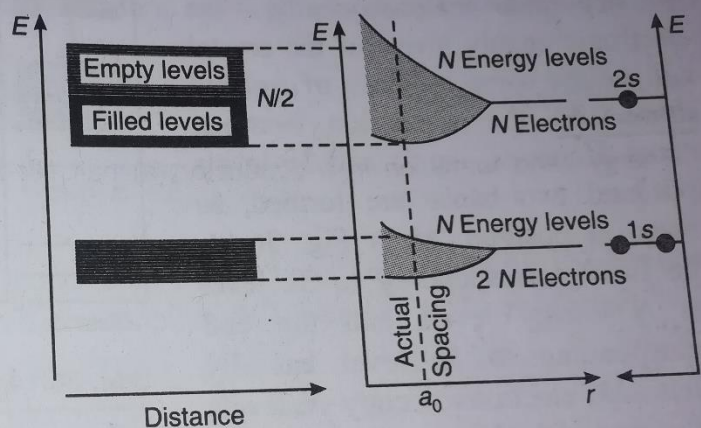
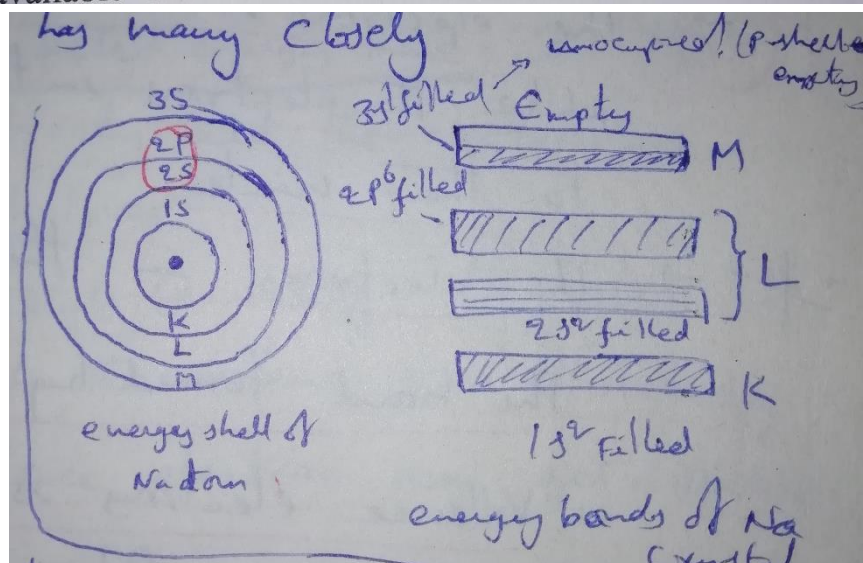


Fig. 36.12:

Energy level splitting and energy band configuration in lithium solid showing half-filled $2s$ band.



36.6 ENERGY BAND DIAGRAM

An energy band diagram is a graphic representation of the energy levels associated with the top energy band and the next lower energy band in a solid. The energy band diagram shows two bands with a gap in between (see Fig. 36.8). The upper band is called the **conduction band** and the lower energy band is called the **valence band**. These two bands are separated by a forbidden band. This energy gap is more popularly called **band gap** and is denoted by the symbol E_g . The conduction band corresponds to the energy values of *free electrons* that have broken their valence bonds, and hence have become free to move in the crystal. The bottom of the

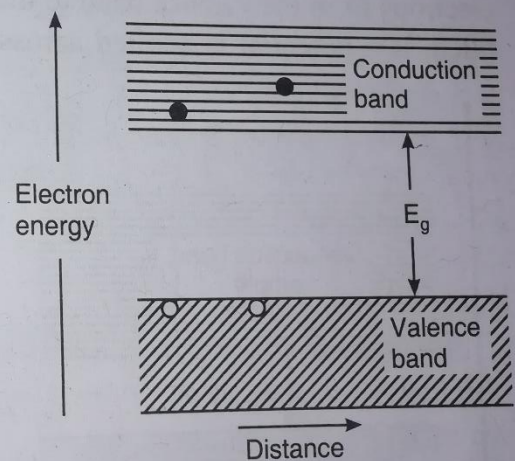


Fig. 36.8:

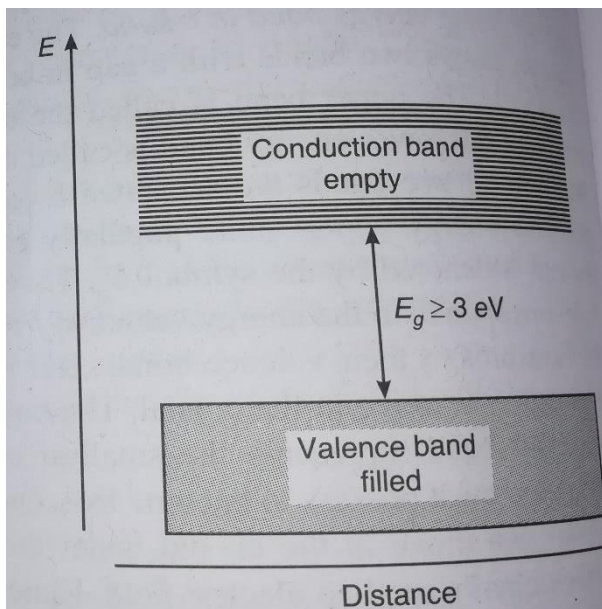


Fig. 36.11:

Energy band structure of an insulator

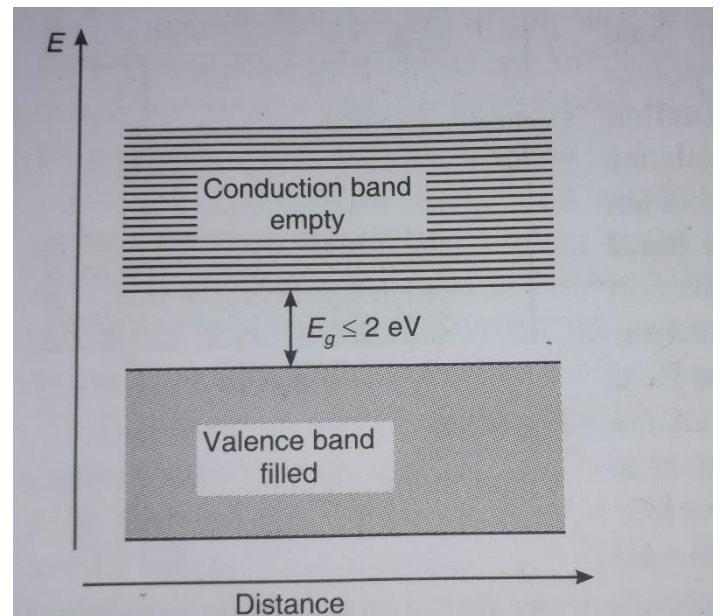
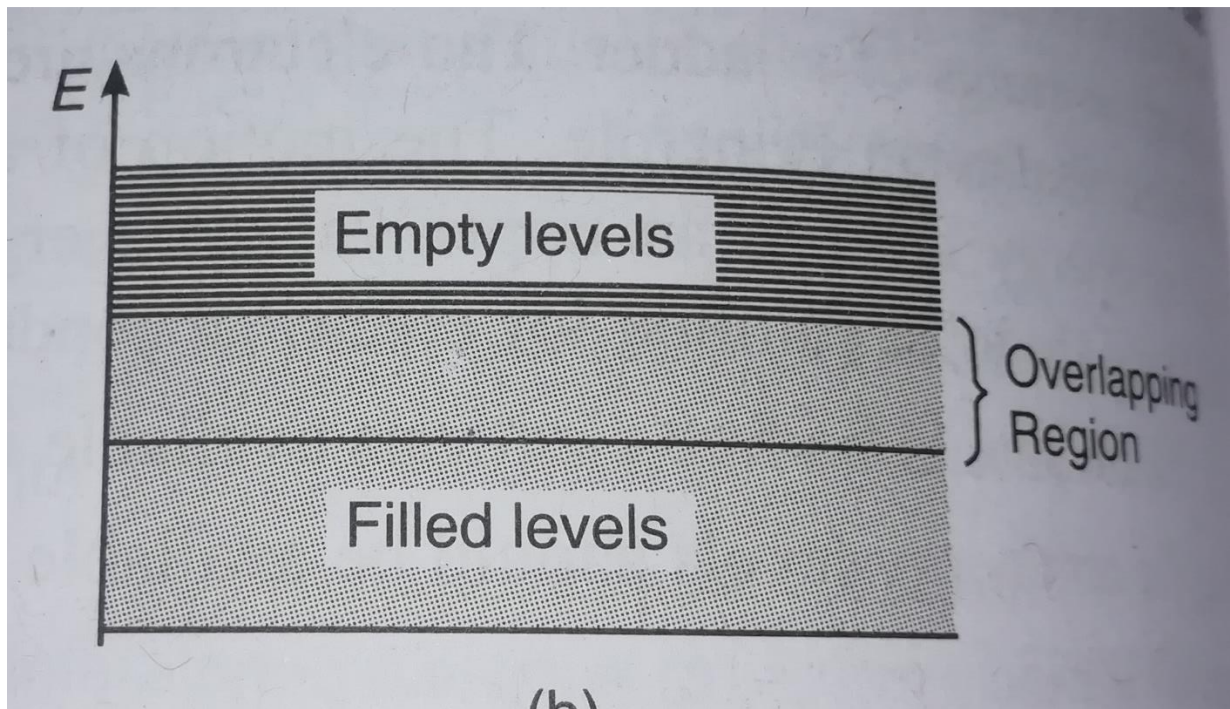


Fig. 36.10:

Energy band structure of a semiconductor



Conductor