

## QUANTUM PHYSICS & BAND THEORY OF SOLIDS

**(Module-III - Chapter -3 - Syllabus: Applications of Quantum Physics:** Particle in a 1-D box (Eigen Value and Eigen Function)- 3-D Analysis (Qualitative)- Tunnelling Effect (Qualitative) Electron in a periodic potential (qualitative treatment) - Kronig-Penney model (qualitative treatment) – the origin of energy bands formation in solids.

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### **\*\* Particle in a one-dimensional potential box:**

**(or) Particle in potential well:**

**(or) Show that the energies of a particle in a potential box are quantized**

**(or) Derive the equation for Eigen energies and Eigen function of a particle.**

Let us consider a potential box of width ‘L’, infinite depth, and infinitely hard walls. Let ‘m’ be the mass of a particle moving with velocity ‘v’ along the x-direction between two rigid walls A & B. The particle will not lose any energy in collision with the walls, hence its total energy remains constant, let it be ‘E’. When the particle is in motion, the potential energy is minimum (inside V=0), and at the surface of the box is V =  $\infty$ .

We know that Schrödinger’s time-independent 1D wave equation  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E-V)}{\hbar^2} \psi = 0$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \because \text{potential energy}(V) = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \quad \text{----- (1)} \quad \text{where } k^2 = \frac{2mE}{\hbar^2} \quad \text{----- (1a)}$$

This is the wave equation for a free particle inside a potential well.

Let the general solution of above equation is  $\psi(x) = A \sin kx + B \cos kx$  ----- (2)

where A and B are constants

For calculation of A, B; let us apply the boundary conditions  $\psi(x) = 0$  at  $x = 0$  ----- (3)

$$\psi(x) = 0 \text{ at } x = L \quad \text{----- (4)}$$

Applying 1<sup>st</sup> boundary condition, [Substituting Eq.(3) in (2)]  $0 = A \sin 0 + B \cos 0$

$$B = 0 \quad \text{----- (5)}$$

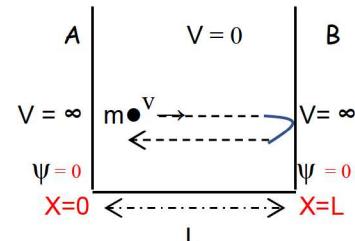
Applying 2<sup>nd</sup> boundary condition, [Substituting Eq.(4) & (5) in Eq. (2)]

$$0 = A \sin kL + 0 \cos kL$$

$$A \sin kL = 0$$

It means A = 0 (or)  $\sin kL = 0$

but A and B cannot be zero



$$\therefore \sin kL = 0 \quad \rightarrow \quad kL = n\pi, \quad n = 1, 2, 3, \dots$$

$$k = \frac{n\pi}{L} \quad \text{----- (6)}$$

$$\text{Comparing Eq.(1a) \& (6)} \quad k^2 = \frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2}$$

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad \text{or} \quad E = \frac{n^2\hbar^2}{8mL^2}$$

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

From above Eq. it is clear that energy is inversely proportional to mass and square of the length. From the above equation, it is clear that a particle has certain values of energy. It means the total energy is quantized, and  $n$  is the quantum number.

The lowest energy level of the particle is obtained when  $n = 1$  and  $E_1$  is called a zero-point energy system.

$$\text{When } n = 1 \rightarrow \quad E_1 = \frac{\hbar^2}{8mL^2}$$

$$\text{When } n = 2 \rightarrow \quad E_2 = \frac{4\hbar^2}{8mL^2} = 4E_1$$

$$\text{When } n = 3 \rightarrow \quad E_3 = \frac{9\hbar^2}{8mL^2} = 9E_1$$

$$\therefore \text{In general, the energy level is } E_n = n^2 E_1 \quad \text{----- (7)}$$

From the above equations, it is clear that particles in the box are having discrete energy values, these energy values are called eigenvalues of energy [ $E_1, E_2, E_3, \dots$ ].

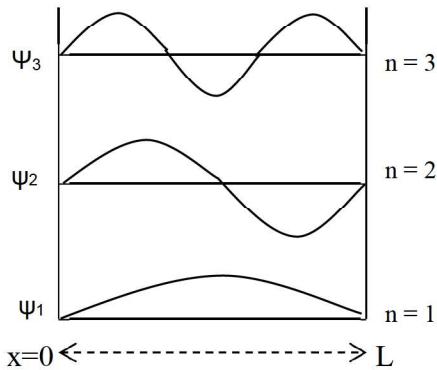


Fig.(a) the electron waves functions

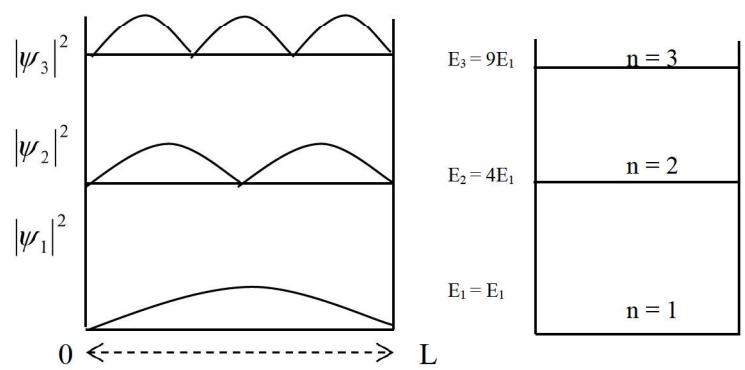


Fig.(b) Corresponding probability density functions

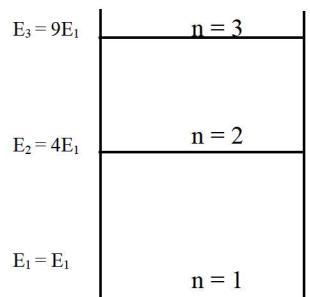


Fig.(c) Representation of energy levels of particles in 1D box

Fig.2(a) & (b): Ground state and first 2 excited states of an electron in a potential well

In fig. 2(a) The wave function  $\psi_1$  has 2 nodes at  $x = 0, x = L$ , the wave function  $\psi_2$  has 3 nodes at  $x = 0, \frac{L}{2}, L$ , the wave function  $\psi_3$  has 4 nodes at  $x = 0, \frac{L}{3}, \frac{2L}{3} & L$ , thus  $\psi_n$  has  $(n + 1)$  nodes.

$$\therefore \text{Eq.(2)} \quad \rightarrow \quad \psi(x) = A \sin kx \quad (\because B = 0)$$

$$\text{Sub. 'k' in the above eq.} \quad \psi(x) = A \sin \frac{n\pi}{L} x \quad \text{----- (8)}$$

The calculation of 'A' in equation (8) can be obtained by applying the condition of normalization condition. (*Equating the total probability of finding the particle inside the potential well is equal to unity, this process is called normalized*)

$$\text{Net density is } \int_0^L |\psi|^2 dx = 1$$

$$\int_0^L A^2 \sin^2 \left( \frac{n\pi x}{L} \right) dx = 1$$

$$A^2 \int_0^L \frac{1}{2} \left( 1 - \cos \frac{2n\pi x}{L} \right) dx = 1 \quad (\because \cos 2\theta = 1 - 2\sin^2 \theta)$$

$$\frac{A^2}{2} \left[ x - \left( \frac{L}{2n\pi} \right) \sin \frac{2n\pi x}{L} \right]_0^L = 1$$

$$\frac{A^2 L}{2} - 0 = 1 \quad \rightarrow \quad \frac{A^2 L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

$\therefore$  The normalized wave function (Eq.8)

$$\boxed{\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x}$$

The wave function ( $\psi_n$ ) and corresponding energy ( $E_n$ ) are often called eigen functions and eigen energies.

### \*\* Particle in a 3-D box (or) 3-D Analysis of a particle (Qualitative analysis):

Let us consider a 3-dimensional potential box with sides  $a, b$ , and  $c$ . Let 'm' be the mass of a particle moving with velocity 'v' along the three directions (x, y, z-axis) inside the box. The wave function can be calculated by using Schrödinger's time-independent wave equation.

The eigen function along the x, y and z direction is  $\psi(x, y, z) = \psi_{nx}(x) \cdot \psi_{ny}(y) \cdot \psi_{nz}(z)$

The normalized wave function along 3 directions is

$$\psi(x, y, z) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \cdot \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \cdot \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}$$

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

The total energy of the particle is  $E_n = E_{nx} + E_{ny} + E_{nz}$

$$E_n = \frac{\hbar^2}{8m} \left[ \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

where  $n_x, n_y, n_z$  are three quantum numbers

For a cubical box i.e.  $a = b = c$

$$\psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a} \sin \frac{n_z \pi z}{a}$$

$$E_n = \frac{\hbar^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2]$$

$$E_n = \frac{n^2 \hbar^2}{8ma^2} \quad \text{where } n^2 = n_x^2 + n_y^2 + n_z^2$$

$$\text{For a ground state in 3D analysis } E_1 = \frac{3 \hbar^2}{8ma^2}$$

**Note:**

**Degeneracy:**

For different combinations of quantum numbers, the wavefunction is found to be

$$\psi_{112} = \sqrt{\frac{8}{a^3}} \sin \frac{\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{2\pi z}{a}$$

$$\psi_{121} = \sqrt{\frac{8}{a^3}} \sin \frac{\pi x}{a} \sin \frac{2\pi y}{a} \sin \frac{\pi z}{a}$$

$$\psi_{112} = \sqrt{\frac{8}{a^3}} \sin \frac{2\pi x}{a} \sin \frac{\pi y}{a} \sin \frac{\pi z}{a}$$

The corresponding energies are

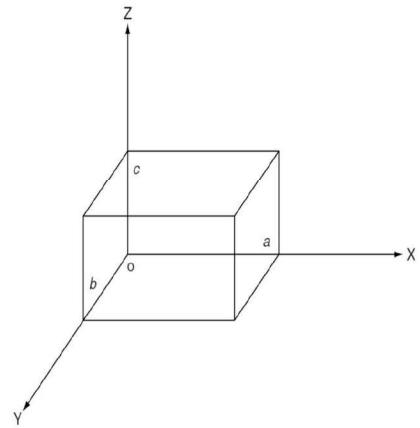
$$E_{112} = \frac{\hbar^2}{8ma^2} [1^2 + 1^2 + 2^2] \rightarrow E_{112} = \frac{6 \hbar^2}{8ma^2}$$

$$E_{121} = \frac{\hbar^2}{8ma^2} [1^2 + 2^2 + 1^2] \rightarrow E_{121} = \frac{6 \hbar^2}{8ma^2}$$

$$E_{211} = \frac{\hbar^2}{8ma^2} [2^2 + 1^2 + 1^2] \rightarrow E_{211} = \frac{6 \hbar^2}{8ma^2}$$

Here we obtain obtained energy values same but different wave functions for the three sets of (112), (121), and (211). This phenomenon is known as the degree of degeneracy.

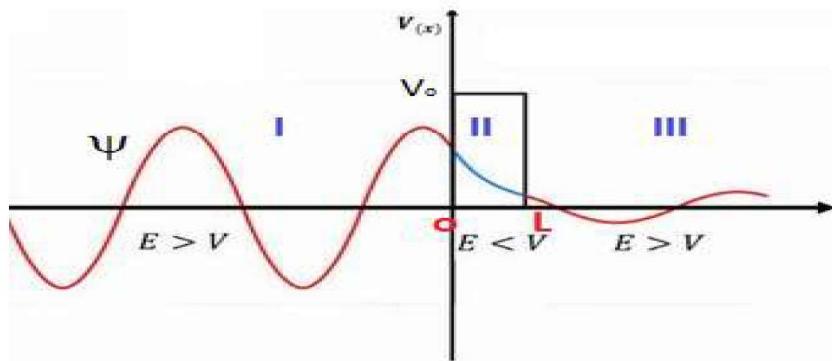
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## \*\* Tunnelling Effect: (Qualitative analysis)

According to the classical idea, when a particle strikes the hard wall and has no chance of leakage of the particle through it. But the behavior of the quantum particle is different due to its owing wave nature. We know that when an electromagnetic wave (light) strikes the transparent material, part undergoes reflection and as well as refraction. Similarly, when a de Broglie's particle strikes the walls of the potential well, part undergoes reflection and part penetrates through the barrier, this phenomenon is called the tunneling effect.

Let  $V_0$  be the potential barrier and  $L$  be the thickness of the barrier. the region is divided into three regions i.e. I, II, III. The potential energy is zero in I, III regions ( $x < 0$ ,  $x > L$ ) and it has a constant potential in regions II ( $0 < x < L$ ). In regions, I and III the total energy equal is to kinetic energy, and in regions II the total energy is partly kinetic and party potential energy.



Applying Schrödinger's time-independent wave equation in I, III regions

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E-V)}{\hbar^2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \because \text{potential energy}(V) = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \quad \text{----- (1)} \quad \text{where } k^2 = \frac{2mE}{\hbar^2}$$

Similarly, applying Schrödinger's time-independent wave equation in the II region

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E-V_0)}{\hbar^2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + K_o^2 \psi = 0 \quad \text{----- (2)} \quad \text{where } K_o^2 = \frac{2m(E-V_0)}{\hbar^2}$$

the solution for the above equation in the I, II, and III regions are

$$\psi_1 = Ae^{ikx} + Be^{-ikx}, \quad \psi_2 = Ce^{kx} + De^{-kx}, \quad \psi_3 = Ee^{ikx} + Fe^{-ikx},$$

In region III no particle comes from the right, hence  $F = 0 \rightarrow \psi_3 = Ee^{ikx}$

In region I,  $Ae^{ikx}$  represents the de Broglie's wave traveling along the X-direction with amplitude A and  $Be^{-ikx}$  represents the wave reflected along -Ve X-direction with amplitude B. In region II,  $\psi_2$  is not zero in the barrier, but it exponentially decreases (part penetrates through the barrier), this phenomenon is called the tunneling effect. The coefficient of reflection (R) and coefficient of penetration (T) is represented by the equations

$$R = \frac{|B|^2}{|A|^2} \quad T = \frac{|D|^2}{|A|^2}$$

### **\*\* Electron in a periodic potential:** (qualitative treatment)

According to the free electron theory of metals, a conduction electron inside the metal experience a constant potential or zero potential but these electrons will not come out of the metal since infinite potential exists at the surface. The free electron theory explains electrical conductivity, specific heat, para magnetism, etc. This theory fails to explain the difference between conductors, semiconductors, and insulators.

To overcome this problem, Bloch proposed the periodic potential. Let an electron moving in the ionic crystal, it experiences varying potentials (shown in Fig.a). The potential of an electron at the +Ve ion side is zero and is maximum in between the two +Ve ions. The potential experienced by an electron, when it passes through the +ve is shown in Fig.(b). (The potential is negative because of an attractive force between electrons and positive ions.)

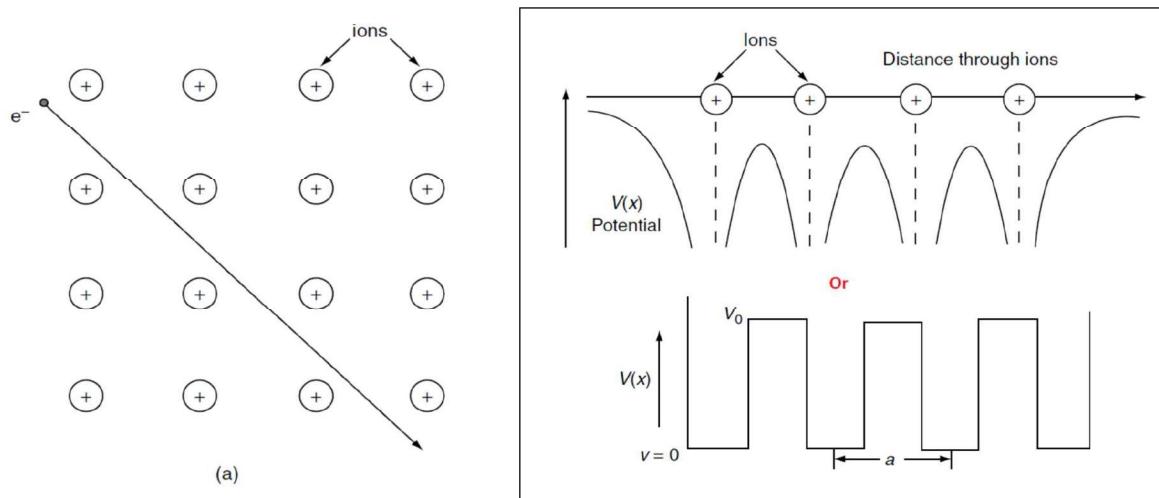


Fig. (a) Electron motion in ionic solid.

Fig. (b) Potential experienced by an electron in a row of ions  
(or) Rectangular potentials

The energy of an electron can be known by solving Schrödinger one dimensional time-independent wave equation (along X-axis) given by  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E - V)}{\hbar^2} \psi = 0$

Bloch showed a solution of Schrödinger equation is  $\psi(x) = U_k(x) e^{ikx}$

Where  $U_k(x)$  is a periodic function,  $e^{ikx}$  is the plane wave,  $k = \frac{2\pi}{\lambda}$  is the propagation vector,

and  $\lambda$  is the wavelength of de Broglie's wave associated with the moving electron.

**\*\* Kronig-Penney model:** (qualitative treatment)

(or) **Motion of electron in a periodic potential:**

In 1931, Kronig-Penney assumed a potential experienced by an electron in a row of ions in rectangular potential wells and barriers. According to them, an electron has variable potential energy due to the presence of immobile lattice ions (atoms) in a crystal, hence potential is not uniform. The rectangular potential wells and barriers in a one-dimensional lattice, it is shown in Fig.1. Let 'a, b' be the width of the potential well (I) and potential barrier (II). Inside the well potential energy of the electron is zero and in the barrier region, it possesses a constant potential of  $V_0$ .

The energies and wave function of electrons associated with this model can be calculated by using Schrödinger time independent equation for two regions (I & II).

Applying Schrödinger equation to the region I & II then

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad (\text{for } 0 < x < a) \quad \text{----- (1)}$$

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

$$\text{Let } a^2 = \frac{2mE}{\hbar^2} \quad \text{----- (3a)} \quad \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad \text{----- (3b)}$$

$$\text{Eq.(1)} \Rightarrow \frac{\partial^2 \psi}{\partial x^2} + a^2 \psi = 0 \quad \text{----- (4)}$$

$$\text{Eq.(2)} \Rightarrow \frac{\partial^2 \psi}{\partial x^2} - \beta^2 \psi = 0 \quad \text{----- (5)}$$

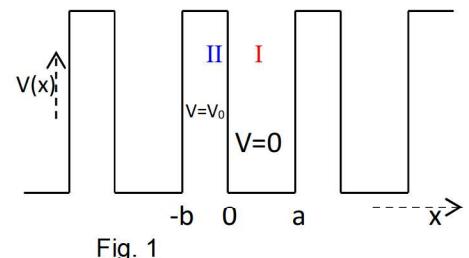


Fig. 1

Bloch showed that the solution of this type of varying potentials as  $\psi(x) = U_k(x) e^{ikx}$  ----- (6)

where  $\psi(x)$  is Bloch function,  $U_k(x)$  is periodic function, 'k' is propagation vector =  $\frac{2\pi}{\lambda}$

Differentiating Eq.(6) twice & substituting in Eq. (4) & (5), on solving we get

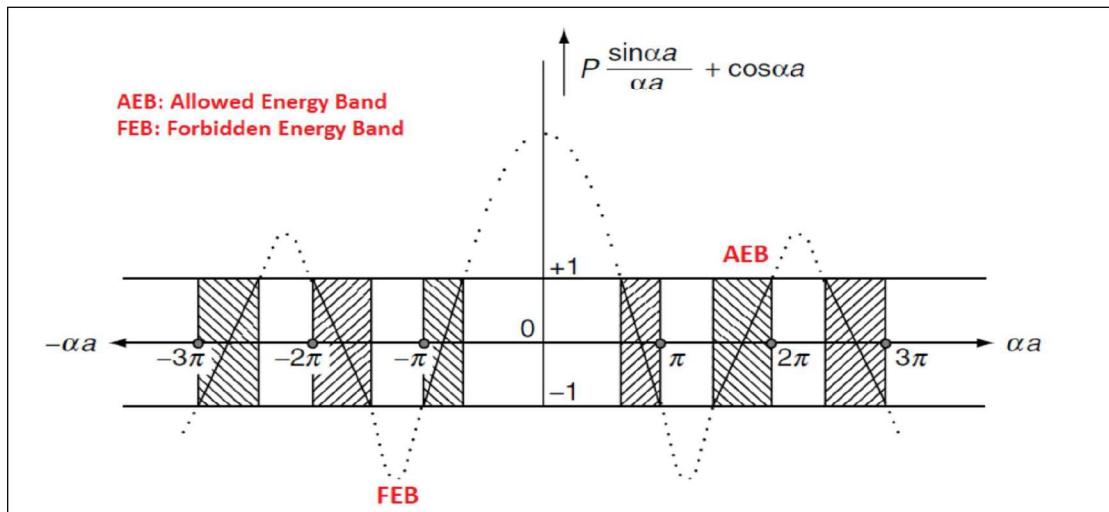
$$\frac{p}{aa} \sin \alpha a + \cos \alpha a = \cos ka \quad \text{----- (7)}$$

$$\text{where } P = \frac{mV_0 ba}{\hbar^2} \quad \alpha^2 = \frac{2mE}{\hbar^2} \quad k = \frac{2\pi}{\lambda}$$

'P' is known as the **scattering power** of the potential barrier &  $V_0 b$  is called **barrier strength**.

In Eq.(7) the RHS maximum value is '+1' and the minimum value is '-1'.

A graph is drawn between ( $\alpha a$ ) versus LHS of Eq.(7) [shown in the bottom Fig.]



This Figure illustrates the following interesting physics facts

- i) The energy spectrum consists of the number of allowed and forbidden energy bands.
- ii) As the value of ( $\alpha a$ ) increases, the width of allowed energy bands (AEB) increases and the width of the forbidden energy band (FEB) decreases.
- iii) As 'P' (scattering power) increases, the width of the allowed band decreases.
- iv) **As  $P \rightarrow \infty$** , the allowed energy region becomes infinitely narrow and the energy spectrum is a line spectrum.

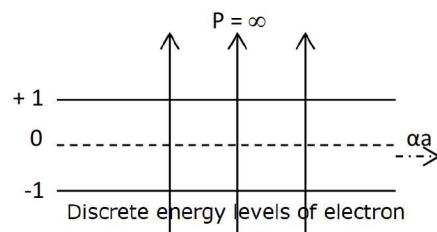
Let  $P \rightarrow \infty$ , then from Eq. (7)  $\sin \alpha a = 0$

Where  $\alpha a = \pm n\pi$

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

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

$$\alpha^2 = \frac{n^2 \pi^2}{a^2} = \frac{2mE}{\hbar^2} \quad (\because \text{from Eq. 3a})$$



$$E = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \rightarrow E = \frac{n^2 h^2}{8ma^2} \quad \because \hbar = \frac{h}{2\pi}$$

This expression shows that the energy spectrum of the electron contains discrete energy levels separated by forbidden regions.

#### v) When $P \rightarrow 0$

$$\text{Eq.(7)} \rightarrow \cos \alpha a = \cos ka$$

$$\alpha a = ka \rightarrow \alpha = k \rightarrow \alpha^2 = k^2$$

$$\alpha^2 = \frac{2mE}{\hbar^2} = k^2 \quad (\because \text{from Eq. 3a})$$

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

$$E = \frac{\frac{h^2}{(2\pi)^2} \frac{(2\pi)^2}{\lambda^2}}{2m} \quad (\because \hbar = \frac{h}{2\pi}, k = \frac{2\pi}{\lambda})$$

$$E = \frac{h^2}{2m\lambda^2}$$

$$E = \frac{h^2 m^2 v^2}{2m h^2} \quad (\because \text{from de-Broglie's Eq., } \lambda = \frac{h}{mv})$$

$$E = \frac{1}{2} mv^2$$

This equation shows that all the electrons are completely free to move in the crystal. Hence no energy level exists. i.e. all the energies are allowed to the electrons. It supports the classical free electron theory (Electron moving with constant potential).

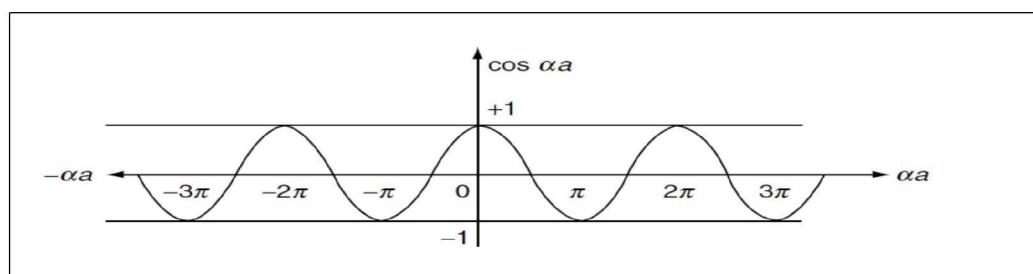


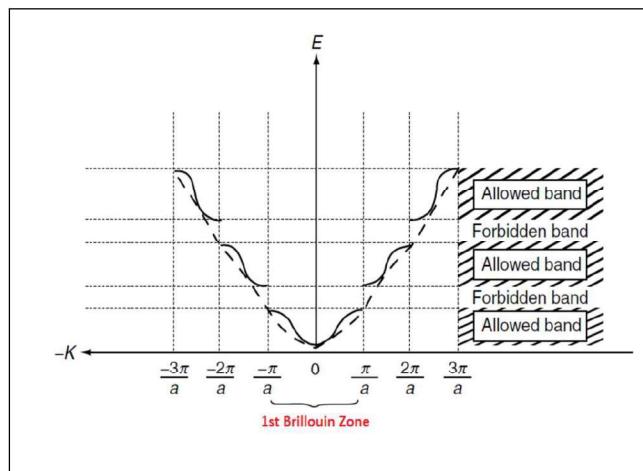
Fig: Energy curve for free electrons as  $P \rightarrow 0$

**Note: E-K diagram (or) Brillouin zones:**

It is possible to plot the total energy of the electron versus wave number is known as the E-K diagram. From the graph, it is clear that electrons have allowed energy values between the region  $K = -\frac{\pi}{a}$  to  $+\frac{\pi}{a}$ . This is called the  $1^{\text{st}}$  Brillouin zone.

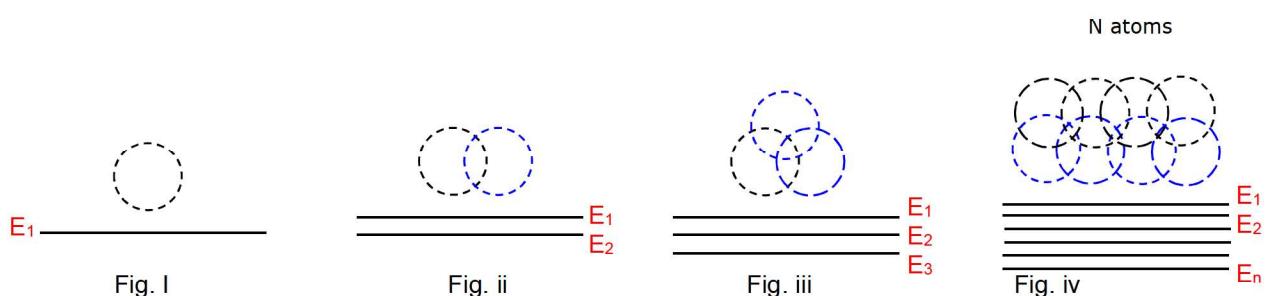
After a break in the energy values, is called the forbidden region. The electrons have another allowed zone of energy values in the regions extended from  $K = \frac{\pi}{a}$  to  $\frac{2\pi}{a}$  and  $K = -\frac{\pi}{a}$  to  $-\frac{2\pi}{a}$ , this zone is called as  $2^{\text{nd}}$  Brillouin zone.

As 'P' decreases, the discontinuous E-K graph will reduce to a continuous parabolic graph as shown by the dotted lines and the forbidden bands disappear. Then, the energy values are practically continuous.



**\*\* Origin of Energy band formation in solids:**

In an isolated atom, the electrons are tightly bound and have discrete energy levels. When two identical atoms are brought closer, the outermost orbits of these atoms will overlap with each other. When the wave functions of the electrons of different atoms begin to overlap the energy levels split into two (Fig. ii). If there are 'N' atoms, the energy levels split into 'N' levels of energy (Fig. iv). The levels are so close together and this forms a continuous band. The width of this band depends on the degree of overlap of electrons of adjacent atoms.



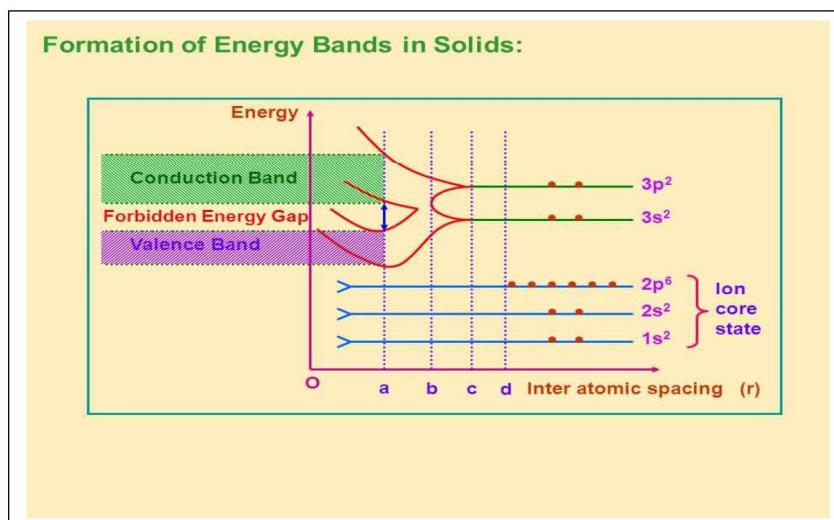
With the decrease of interatomic distance, the valence band and conduction band overlap each other. In solid many atoms are brought together so that the split energy levels form a set of bands very closely spaced with a forbidden energy gap.

In general, the band corresponding to the outermost orbits is called the conduction band and the next inner band is the valence band. The gap between these two allowed bands is called the

forbidden energy gap (or) band gap. In general valence electrons occupied in the valence band, they are responsible for the electrical, thermal, and optical properties of solids. The electrons in the conduction band are called free electrons.

The electron in the valence band can reach the conduction band only if it is supplied with a minimum energy of  $E_g$ . If the energy (light / heat / electric) is less than  $E_g$ , the electron remains in the valence band.

The conductance of non-metals depends on the ability of the electrons to jump over the valence band to the conduction band. In the valence band, if it is half filled / partially filled, the electrons move to the conduction band. If the valence band is completely filled with electrons, then these electrons may not move to the conduction band.



- The electron density of conductors is very large (above  $10^{28}$  electrons/m<sup>3</sup>).  
*Ex. All metals*
- The electron density of semiconductors is moderate (in the order of  $10^{14}$  electrons/m<sup>3</sup>).  
*Ex. Germanium ( $E_g = 0.72\text{ eV}$ ), Silicon ( $E_g = 1.1\text{ eV}$ )*
- The electron density of insulators is very low (in the order of  $10^7$  electrons/m<sup>3</sup>).  
*Ex. Diamond (5 eV), Rubber, Glass (4 eV)*

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