KRONIG PENNEY MODEL

In the free electron theory it is assumed that the potential to which the valence electrons are subjected is constant and, therefore, it can be taken to be equal to zero, while solving Schrödinger's equation. But this is not true for the valence electron in ionic and co-valent crystalline solids because in such solids the electrons are localised near the parent nuclei. This gives rise to a periodically varying potential. Thus, in an actual case the constant potential should be replaced by a periodically varying potential.

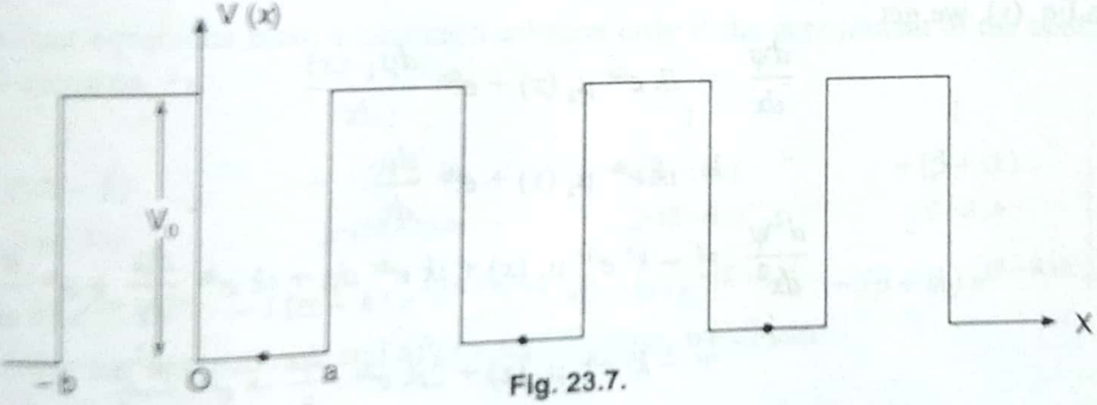

Fig. 23.7.

Kronig and Penney model illustrates the behaviour of electrons in a periodic potential by assuming a relatively simple one dimensional model of periodic potential as shown in Fig. 23.7, which shows the periodic potential energy of a valence electron in the X-direction.

Basic Assumptions

In Kronig Penney model it is assumed that the potential energy of an electron in a linear array of positive nuclei has the form of a periodic array of square wells with period $(a + b)$.

At the bottom of the well, *i.e.*, for $0 < x < a$ the electron is assumed to be in the vicinity of a nucleus and the potential energy is taken as zero, whereas outside a well, *i.e.*, for $-b < x < 0$ the potential energy is assumed to be V_0.

Analytical Treatment

Although this model employs a very crude approximation to the type of periodic potential existing inside a lattice, yet it is very useful to illustrate various important features of the quantum behaviour of the electron in the periodic lattice.

The Schrodinger's equations for the two regions are

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

and

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

We shall assume that the energy E of the electron under consideration is smaller than V_0 and define two real quantities α and β given by

$$\alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \qquad \text{...}(iii)$$

Eqs. (*i*) and (*ii*) can now be written as

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

and

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

The potential is periodic, and is given by

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

where $(a + b)$ is the period.

Using Bloch theorem, the solution of wave equation for a periodic potential will be of the form of a plane wave modulated with the periodicity of the lattice and will be given by

$$\psi(x) = e^{ikx}\mu_k(x) \qquad \text{...}(v)$$

where $\mu_k(x)$ is the periodic function in x with period $(a + b)$, *i.e.*,

$$\mu_k(x) = \mu_k(x + a + b)$$

From Eq. (*v*), we get

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

$$= ik\,e^{ikx}\mu_k(x) + e^{ikx}\frac{d\mu}{dx} \qquad \text{...}(vi)$$

and

$$\frac{d^2\psi}{dx^2} = -k^2 e^{ikx}\mu_k(x) + ik\,e^{ikx}\,d\mu + ik\,e^{ikx}\frac{d\mu}{dx} + e^{ikx}\frac{d^2\mu}{dx^2}$$

$$= -k^2 e^{ikx}\mu_k(x) + 2ik\,e^{ikx}\frac{d\mu}{dx} + e^{ikx}\frac{d^2\mu}{dx^2} \qquad \text{...}(vii)$$

Substituting the values of $\psi(x)$ from Eq. (*v*) and $\frac{d^2\psi}{dx^2}$ from Eq. (*vii*) in Eqs. (*iv*) (*a*) and (*b*), we get

$$-k^2 e^{ikx}\mu + 2ik\, e^{ikx}\frac{d\mu}{dx} + e^{ikx}\frac{d^2\mu}{dx^2} + \alpha^2 e^{ikx}\mu = 0$$

(In the above Equation instead of $\mu_k(x)$, we have used μ only)

$$\frac{d^2\mu}{dx^2} + 2ik\frac{d\mu}{dx} + (\alpha^2 - k^2)\mu = 0 \qquad \text{... (viii)}$$

$$0 < x < a$$

$$\frac{d^2\mu}{dx^2} + 2ik\frac{d\mu}{dx} - (\beta^2 + k^2)\mu = 0 \qquad \text{... (ix)}$$

$$-b < x < 0$$

The solutions of these equations are

$$\mu_1 = A\, e^{i(\alpha-k)x} + B\, e^{-i(\alpha+k)x} = 0 \qquad \text{... (x)}$$

$$0 < x < a$$

$$\mu_2 = C\, e^{(\beta-ik)x} + D\, e^{-(\beta+ik)x} = 0 \qquad \text{... (xi)}$$

$$-b < x < 0$$

Where *A*, *B*, *C* and *D* are constants.

These constants must be chosen in such a manner that the following boundary conditions are satisfied, *i.e.*, the wave function ψ and its derivative $\frac{d\psi}{dx}$ are single valued and continuous

$$(\mu_1)_{x=0} = (\mu_2)_{x=0};\ \left(\frac{d\mu_1}{dx}\right)_{x=0} = \left(\frac{d\mu_2}{dx}\right)_{x=0} \qquad \text{... (xii)}$$

$$(\mu_1)_{x=a} = (\mu_2)_{x=a};\ \left(\frac{d\mu_1}{dx}\right)_{x=a} = \left(\frac{d\mu_2}{dx}\right)_{x=b} \qquad \text{... (xiii)}$$

The first two conditions are imposed because of the requirement of continuity and the other two conditions are required because of periodicity of $\mu_k(x)$.

The application of these boundary condition to Eqs. (*x*) and (*xi*), gives

$$A + B = C + D$$

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

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

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

These four equations have a non-zero solution only if the determinant of the coefficients *A*, *B*, *C* and *D* vanishes, *i.e.*,

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

On solving the determinant and after simplification, we obtain

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

To simplify this equation Kronig and Penney considered the case when $V_0 \to \infty$ and $b \to 0$ but the product $V_0 b$ has a finite value, *i.e.*, the potential barriers become *delta functions*. Under these conditions the model is modified in such a way that it represents a series of wells separated by infinitely thin potential barriers of infinitely large potential. The limiting value of $V_0 b$ as $V_0 \to \infty$ and $b \to 0$ is known as *barrier strength*.

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

Also from Eq. (*iii*),

$$\beta^2 + \alpha^2 = \frac{2mV_0}{\hbar^2}$$

or

$$\frac{\beta^2 + \alpha^2}{2\alpha\beta} = \frac{mV_0}{\alpha\beta\hbar^2}$$

∴ Eq. (*xv*) becomes

$$\frac{mV_0}{\alpha\beta\hbar^2} \beta b \sin \alpha a + \cos \alpha a = \cos ka$$

$$\left[\frac{mV_0 b}{\alpha\hbar^2}\right] \sin \alpha a + \cos \alpha a = \cos ka \quad \text{... (xvi)}$$

Let us now define a quantity $P = \frac{mV_0 ba}{\hbar^2}$, which is a measure of the area $V_0 b$ of the potential barrier.

$$\therefore \quad P\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad \text{... (xvii)}$$

The physical significance of the quantity P is that if P is increased the area of the potential barrier is increased and the given electron is bound more strongly to a particular potential well. When $P \to 0$, the potential barrier becomes very weak which mean that electrons are *free electrons*. In this case we obtain from Eq. (*xvii*)

$$\alpha a = ka \quad \text{or} \quad \alpha = k$$

Now,

$$\alpha^2 = \frac{2mE}{\hbar^2} = k^2 \quad \text{... (xviii)}$$

Hence,

$$E = \frac{k^2\hbar^2}{2m} = \frac{h^2k^2}{8\pi^2 m} \quad \text{... (xviii)(a)}$$

This result is the same as obtained by the free electron model. Equation (*xvii*) also gives the condition which must be satisfied so that solutions of the wave equation may exist. Since cos *ka* lies between + 1 and – 1, the left hand side [of Eq. (*xvii*)] should take up only those values of αa for which its values lie between + 1 and – 1. Such values of αa, therefore, represent wave like solutions of the form

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

and are *allowed values*. The other values of αa are *not allowed*.

If we plot a graph between $\left(\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a\right)$ and αa for the value of $P = \frac{3\pi}{2}$, we get the curve shown in Fig. 23.8.

From Eq. (xviii) $\alpha = \sqrt{\frac{2mE}{\hbar^2}}$. Therefore, the abscissa is a measure of energy and by finding value of αa at any point the energy represented by the function at that point is calculated. The values of αa satisfying the equation

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

obtained by drawing lines parallel to αa –axis at a distance cos ka from it and if ka is continuously varied from 0 to π, *i.e.*, cos ka from + 1 to – 1, we obtain all possible values of αa and hence values of energy can be calculated. These possible values of αa are shown by thick lines.

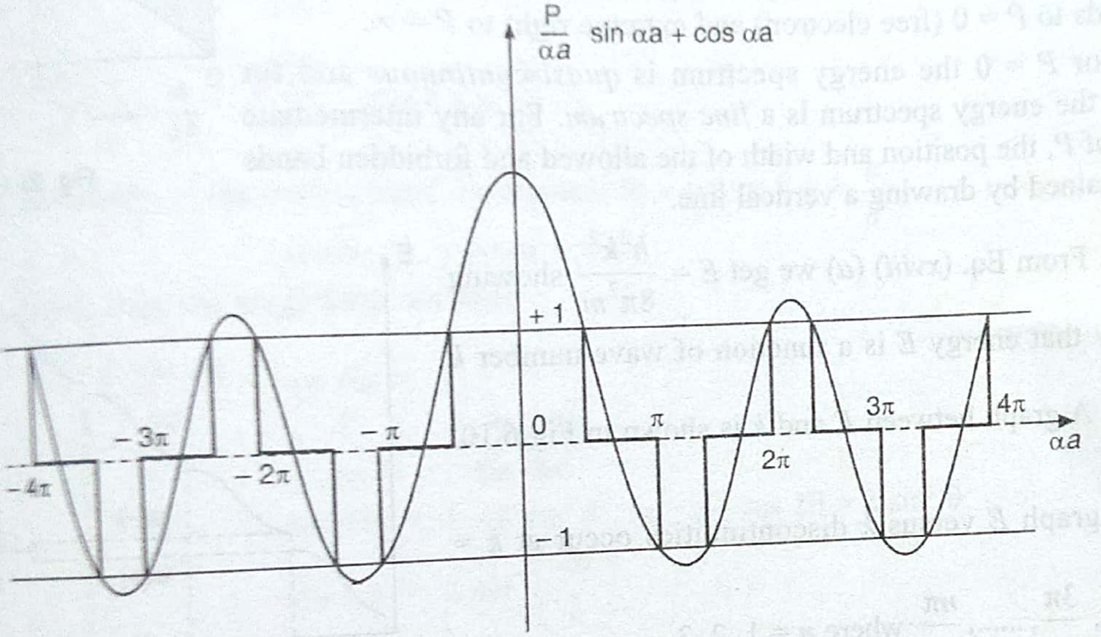

Fig. 23.8

From Fig. 23.8, the following conclusions are drawn:

Conclusions. 1. *Allowed and forbidden energy bands*. The energy spectrum consists of an infinite number of *allowed energy bands* (shown thick) separated by intervals in which there are no energy levels (shown dotted). These are known as *forbidden regions* or *bands*.

The boundaries of the allowed energy levels correspond to the values of cos $ka = \pm 1$

$$ka = n\pi \quad \text{or} \quad k = \frac{n\pi}{a}$$

2. As αa increases the term $P\frac{\sin \alpha a}{\alpha a}$ on the left hand side of Eq. (*xvii*) decreases so that width of allowed energy bands increases and hence forbidden energy regions become narrower.

3. The width of allowed energy bands decreases with the increasing value of P (*i.e.*, with the increasing binding energy of the electron). When $P \to \infty$, the allowed energy bands become infinitely narrow and are independent of k, *i.e.*, energy spectrum becomes a line spectrum.

When $P \to \infty$ the allowed energy ranges of αa reduces to points given by

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

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

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2} \quad \dots (xix)$$

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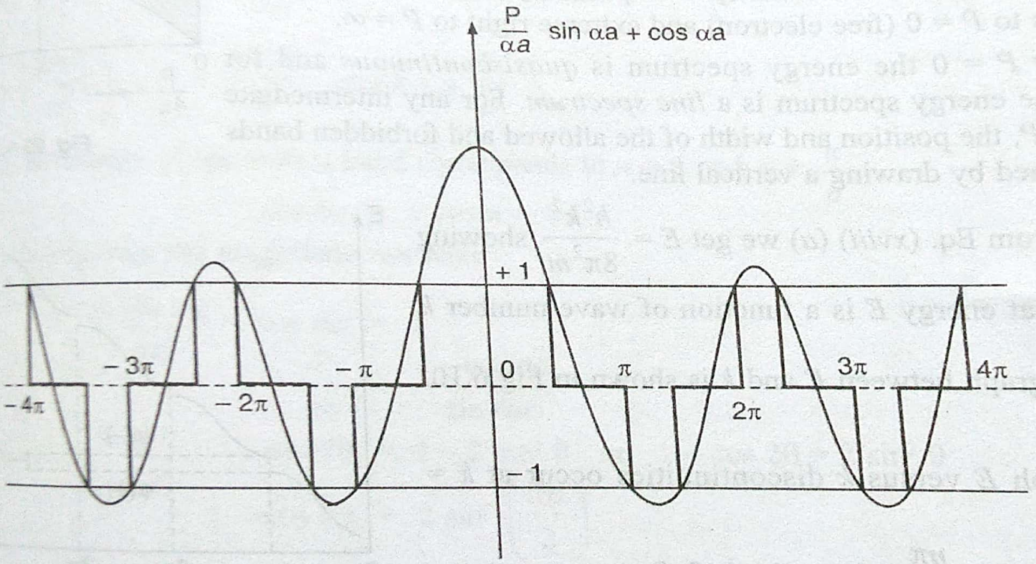

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