

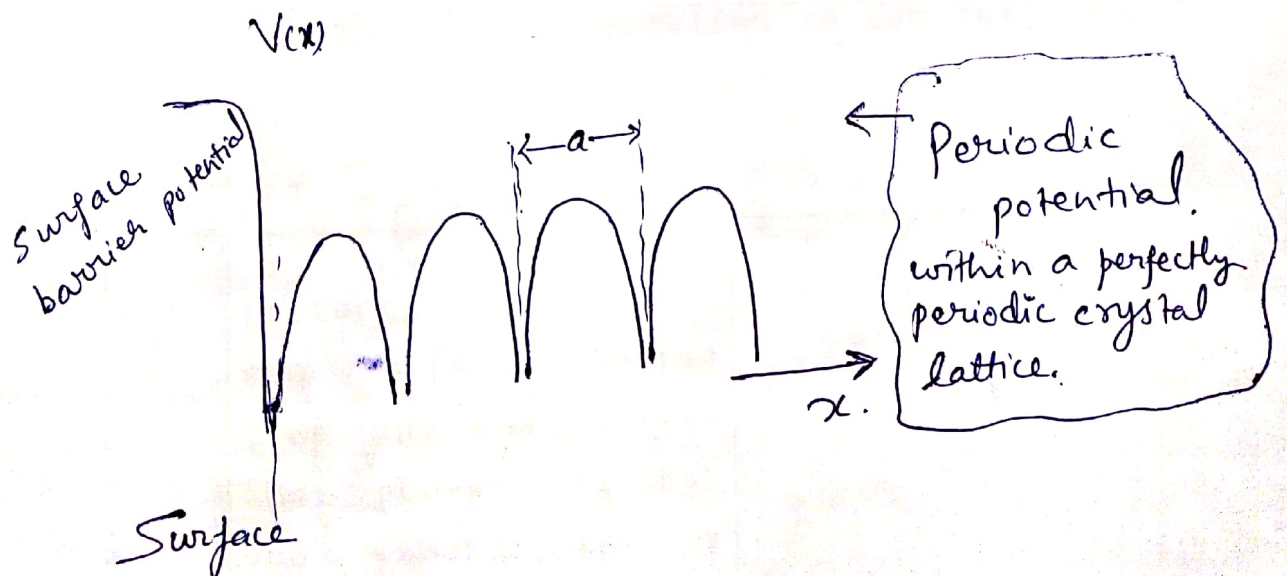
Electron Energy Bands "Elementary Band Theory"

Free electron model describes that the conduction electrons ~~move~~ within the metal move in a region of constant potential which act like a classical free particle. This model could help in describing some properties of metal but it was helpless to describe other properties of solids like why some solids are insulator and some are good conductor of electricity. This model could not explain some other properties as -

- positive Hall effect by Be, Zn, Cd.
- wrong indication of number of conduction electrons per atom in some metals

These and more other problems were sorted out by

"band theory of solids". The periodic potential is used in ^{band theory} instead of constant potential energy. Then by solving one electron time-independent Schrodinger wave eqⁿ, we can get the allowed electron energy states. These states appear in the form of bunches i.e. very close energy levels. The region between two successive energy bands is called as forbidden energy gap or band gap.



Consequences of periodicity: [Bloch Theorem] ①

As discussed earlier, we assume a periodic potential energy function

$$V(\vec{r}) = V(\vec{r} + \vec{T}_n) \quad \text{--- ①}$$

where T_n is arbitrary translation vector in the direct lattice

$$\vec{T}_n = u\vec{a} + v\vec{b} + w\vec{c}$$

Since $V(\vec{r})$ is periodic in periodic crystal, it can be written as

$$V(\vec{r}) = \sum_{\vec{g}} V_{\vec{g}} e^{i\vec{g} \cdot \vec{r}} \quad \text{--- ②}$$

where \vec{g} is reciprocal lattice vector

Now the Schrodinger Eqⁿ for one electron can be written in time-independent form as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}) \quad \text{--- ③}$$

Consider the general plane wave solⁿ of Eqⁿ ③

$$\psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \quad \text{--- ④}$$

Substituting $\psi(\vec{r})$ from Eq ④ into Eqⁿ ③ & ②

$$\sum_{\vec{k}} \left(-\frac{\hbar^2}{2m} \nabla^2 C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \right) + \sum_{\vec{g}} V_{\vec{g}} e^{i\vec{g} \cdot \vec{r}} \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} = \sum_{\vec{k}} E C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \quad \text{--- ⑤}$$

$$\sum_{\vec{k}} \left[\frac{\hbar^2 k^2}{2m} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} - \sum_{\vec{k}} E C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \right] + \sum_{\vec{k}} \sum_{\vec{g}} C_{\vec{k}} V_{\vec{g}} e^{i(\vec{k} + \vec{g}) \cdot \vec{r}} = 0$$

Equating the coefficients of $e^{i\vec{k} \cdot \vec{r}}$,

$$\left(\frac{\hbar^2 k^2}{2m} C_{\vec{k}} - E C_{\vec{k}} \right) + \sum_{\vec{g}} V_{\vec{g}} C_{\vec{k} - \vec{g}} = 0$$

$$\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{g}} V_{\vec{g}} C_{\vec{k} - \vec{g}} = 0 \quad \text{--- ⑥}$$

Total number of allowed k -values for electrons wave will be equal to the number of unit cells, say N . For each value of k corresponding to $C_{\vec{k}}$ where k -values differ from others by \vec{g} , i.e. $C_{\vec{k}}$ is coupled to $C_{\vec{k} - \vec{g}}$, $C_{\vec{k} - \vec{g}'}$, $C_{\vec{k} - \vec{g}''}$. The solⁿ of N eqⁿs. can be interpreted as a superposition of plane waves of wave vector $k, k - \vec{g}, k - \vec{g}', k - \vec{g}''$, etc.

Then wavefunⁿ with corresponding eigen value E_k

$$\Psi_k = \sum_g C_{k-g} e^{i[(k-g) \cdot r]} \quad \text{--- 7}$$

$$= \sum_g C_{k-g} e^{-ig \cdot r} e^{ik \cdot r}$$

$$= U_k(r) e^{ik \cdot r} \quad \text{--- 8}$$

Where $U_k(r) = \sum_g C_{k-g} e^{-ig \cdot r}$ --- 9

Thus $U_k(r)$ modulates the wave $e^{ik \cdot r}$ ~~into~~ to a form that serves as a solution to the wave eqⁿ (3) for a single electron state k . This provides the ~~statement~~ statement of Bloch theorem with $\Psi_k(r) = U_k(r) e^{ik \cdot r}$. This is the exact wavefunⁿ in which $U_k(r)$ is periodic

$$U_k(r + T_n) = U_k(r) \quad \text{--- (10)}$$

Proof of Bloch theorem :- The periodic boundary condition allow the k -values of $\Psi_k(r)$ and forms a set of these values. This set of k -values need to be reproduced by applying boundary condition. on Ψ_k , consider a ~~one~~ one dimensional crystal having length L and N atoms. The distance betⁿ. two atoms is 'a'. ~~Crystal length~~ Crystal length is positioned along x -axis.

Then $\Psi_k(x) = U_k(x) e^{ik \cdot x}$ --- (11)

On moving distance 'a' along x -axis.

$$\Psi_k(x+a) = U_k(x+a) e^{i[k \cdot (x+a)]}$$

$$= U_k(x+a) e^{ik \cdot x} e^{ik \cdot a}$$

$$= C U_k(x) e^{ik \cdot x} \quad \text{[using eqⁿ. 10]}$$

$$= C \Psi_k(x) \quad \text{--- (12)}$$

where $C = e^{ik \cdot a}$ --- (13)

If we assume the crystal in the form of ring and apply the translation that after N steps the electron will be at the same atom from where it was started. at x position.

$$\Psi_k(x + Na) = \Psi_k(x + L) = \Psi_k(x) \quad \text{--- (14)}$$

Then, using Eqⁿ (12)

$$\Psi_K(x+L) = C^N \Psi_K(x) \quad \text{--- (15)}$$

where $C^N = 1 = e^{i2\pi n}$

$$C = e^{i\left(\frac{2\pi n}{N}\right)} \quad \text{--- (16)}$$

Comparing (16) with (13)

$$e^{ik \cdot a} = e^{i\frac{2\pi n}{N}}$$

$$k \cdot a = \frac{2\pi n}{N}$$

$$k = \frac{2\pi n}{Na} = \frac{2\pi}{L} \cdot n$$

with $n = 0, \pm 1, \pm 2, + \dots$

For $n = \pm N$, $k = \pm \frac{2\pi}{Na} \cdot N = \pm \frac{2\pi}{a}$

This means that $+k$ & $-k$

are differing by $\frac{2\pi}{a}$ value. $\frac{2\pi}{a}$ is a one-dimensional reciprocal lattice. $\frac{2\pi}{a}$ is the shortest for a one-dim. lattice. $\Psi_{k+g} = \Psi_k$. Thus two values of k correspond to the same wavefunⁿ. The set of k -values in 3-dim crystal

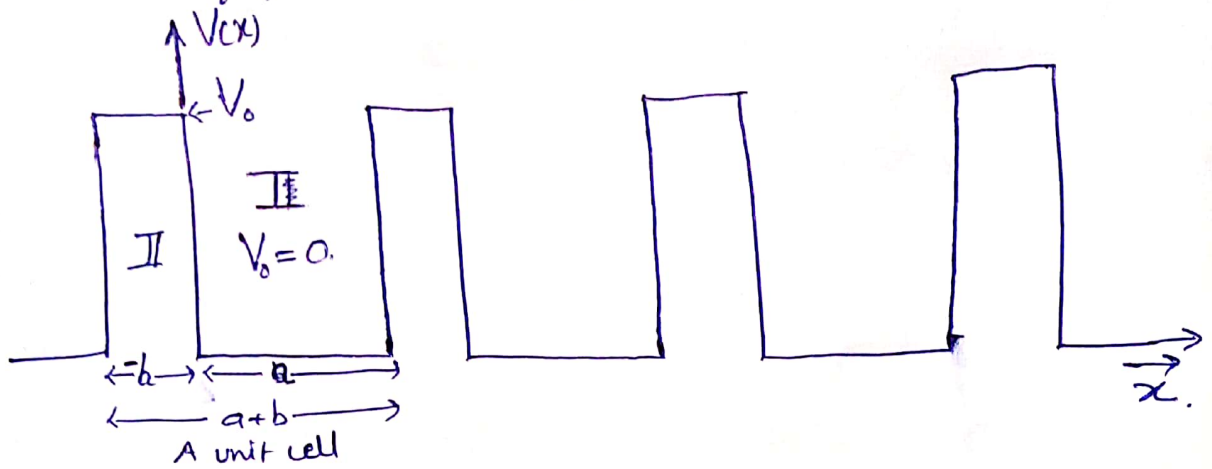
$$k_x = \frac{2\pi}{L} \cdot n_x, \quad k_y = \frac{2\pi}{L} \cdot n_y, \quad k_z = \frac{2\pi}{L} \cdot n_z.$$

This form of k_x, k_y & k_z corresponds to the boundaries of Brillouin zone for phonons. This confirms that the Bloch funⁿ in Eqⁿ (8) is appropriate to describe electrons moving in the periodic crystal potential.

KRONIG-PENNEY MODEL :-

(5)

The behaviour of electron in one-dimensional periodic potential has been understood by using Kronig-Penney model. Consider a chain of potential energy as shown in Fig. below.



For this array of potential, exact solution of Schrodinger eqⁿ is possible

The Schrodinger eqⁿ.

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

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad \text{--- (1)}$$

Since the potential is periodic so. wave funⁿ. must have the Bloch form.

$$\psi(x) = u(x) e^{ikx} \quad \text{--- (11)}$$

Substituting Eqⁿ (11) in (1), but before that

$$\frac{\partial \psi(x)}{\partial x} = \frac{du(x)}{dx} e^{ikx} + u(x) (ik) e^{ikx}$$

$$\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{d^2 u(x)}{dx^2} e^{ikx} + \frac{du(x)}{dx} (ik) e^{ikx} + ik \frac{du(x)}{dx} e^{ikx}$$

$$+ ik \cdot u(x) (ik) e^{ikx}$$

$$= \frac{d^2 u(x)}{dx^2} e^{ikx} + ik \frac{du(x)}{dx} e^{ikx} + ik \frac{du(x)}{dx} e^{ikx} - k^2 u(x) e^{ikx}$$

Now substituting $\frac{\partial^2 \psi(x)}{\partial x^2}$ in Eqⁿ (1)

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

$$\frac{d^2 u(x)}{dx^2} + 2ik \frac{du(x)}{dx} + \left[\frac{2mE}{\hbar^2} - \frac{2mV(x)}{\hbar^2} - k^2 \right] u(x) = 0$$

$$\frac{d^2 u(x)}{dx^2} + 2ik \frac{du(x)}{dx} - \left[k^2 - \frac{2mE}{\hbar^2} + \frac{2mV(x)}{\hbar^2} \right] u(x) = 0$$

$$\frac{d^2 u(x)}{dx^2} + 2ik \frac{du(x)}{dx} - \left[k^2 - \alpha^2 + \frac{2m}{\hbar^2} V(x) \right] u(x) = 0 \quad \text{--- (III)}$$

where $\alpha^2 = \frac{2mE}{\hbar^2}$

Now, consider the two regions, I & II in which the wave funⁿ can be written as $u_I(x)$ & $u_{II}(x)$, Then, Eqⁿ (III) can be written separately for two regions as the value of potential is different in both the regions.

Region I: $\frac{d^2 u_I(x)}{dx^2} + 2ik \frac{du_I(x)}{dx} - [k^2 - \alpha^2] u_I(x) = 0$. IV $\left[\begin{matrix} V(x) = 0 \\ \text{in Region I} \end{matrix} \right]$

Region II: $\frac{d^2 u_{II}(x)}{dx^2} + 2ik \frac{du_{II}(x)}{dx} - \left[k^2 - \alpha^2 + \frac{2mV_0}{\hbar^2} \right] u_{II}(x) = 0$

$$\frac{d^2 u_{II}(x)}{dx^2} + 2ik \frac{du_{II}(x)}{dx} - [k^2 - \beta^2] u_{II}(x) = 0 \quad \text{--- (V)}$$

where $\beta^2 = \frac{2m(E - V_0)}{\hbar^2}$ imaginary quantity

The general solⁿ of Eqⁿ IV & V are.

$$u_I(x) = A e^{i(\alpha - k)x} + B e^{-i(\alpha + k)x} \quad \text{--- (VI)}$$

$$\& u_{II}(x) = C e^{i(\beta - k)x} + D e^{-i(\beta + k)x} \quad \text{--- (VII)}$$

where A, B, C & D are constants

Now applying boundary conditions.

$$\left. \begin{aligned} u_1(0) &= u_2 \\ \left(\frac{du_1}{dx} \right)_{x=0} &= \left(\frac{du_2}{dx} \right)_{x=0} \end{aligned} \right\} \left. \begin{aligned} u_1(a) &= u_2(-b) \\ \left(\frac{du_1}{dx} \right)_{x=a} &= \left(\frac{du_2}{dx} \right)_{x=-b} \end{aligned} \right\} \text{--- (VIII)}$$

Using the boundary on u_1 & u_2 in Eqⁿ - VI & VII

$$A + B = C + D$$

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

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

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

Now the coefficients A, B, C & D can be obtained by vanishing the determinant of their coefficient

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

Expanding the determinant, which leads to the following result

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

For region $V_0 < E < \infty$
Real quantity

In the range $0 < E < V_0$, β is imaginary then. $\beta = i\gamma$

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

When $V_0 \rightarrow \infty$ & $b \rightarrow 0$. There is a possibility of tunnelling from one region to another. Then $bV_0 \rightarrow \text{finite}$

$$\sinh \gamma b \rightarrow \gamma b \quad \& \quad \cosh \gamma b \rightarrow 1, \quad \gamma^2 - \alpha^2 \rightarrow \gamma^2$$

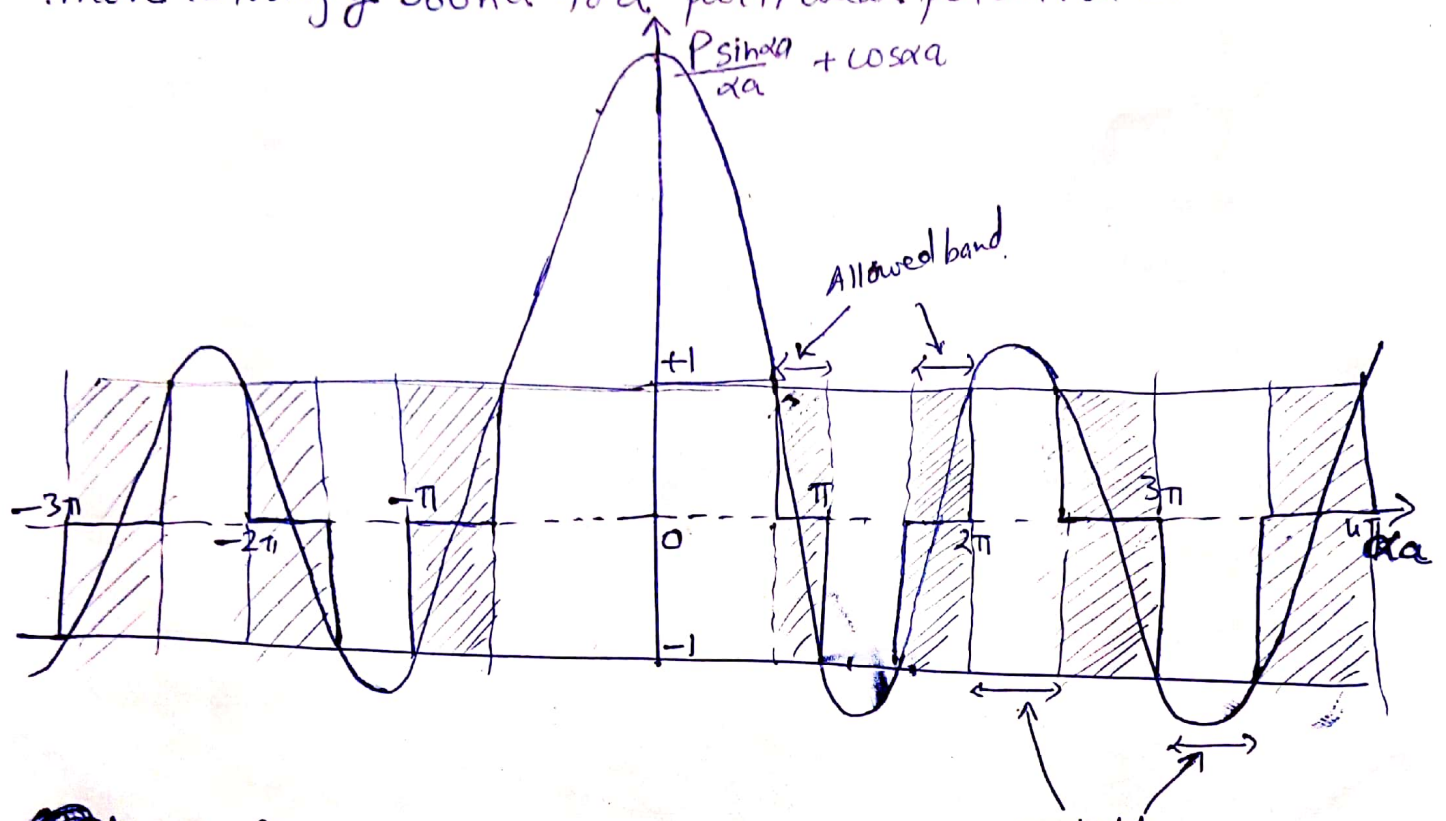
Then Eqⁿ reduces to

$$\frac{\gamma^2}{2\alpha\gamma} \gamma b \sin \alpha a + \cos \alpha a = \cos k a$$

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

$$P \cdot \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos Ka \quad \text{--- XI}$$

where $P = \gamma^2 \frac{ab}{2} = \frac{mV_0 ab}{\hbar^2}$ P is a measure of the area of the potential well. If P is increased, the electron is more strongly bound to a particular potential well.



Plot of LHS of Eqⁿ XI as a funⁿ of αa is shown by solid continuous line. Talking about RHS, it must exist between +1 to -1. That is why the solⁿ of Eqⁿ XI exists only within the limit of +1 to -1.

Allowed energy band is shown by the curve within +1 to -1 while the forbidden energy gap is the region outside the limit of ± 1 .

Some points:-

- ① If $V_0 b$ is large, then P will be large, that is why LHS is crossing +1 to -1 region. Allowed band will be ~~not~~ narrow and forbidden gap will be wide.

⑧ ② If $P \rightarrow \infty$, $\sin \alpha a \rightarrow 0$, i.e. $\alpha a = \pm n\pi$
 with $n = 1, 2, 3, 4, \dots$

$$\frac{\sqrt{2mE_n} \times a}{\hbar} = \pm n\pi$$

$$\Rightarrow \frac{2mE_n}{\hbar^2} a^2 = \pm n^2 \pi^2$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad \text{Energy of } n\text{th level.}$$

This is the expression of potential well of width 'a'.
 Allowed becomes very narrow i.e. line spectrum.

③ If $P = 0$, $\cos \alpha a = \cos ka$.

$$\alpha = k.$$

$$\frac{2mE}{\hbar^2} = k^2$$

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

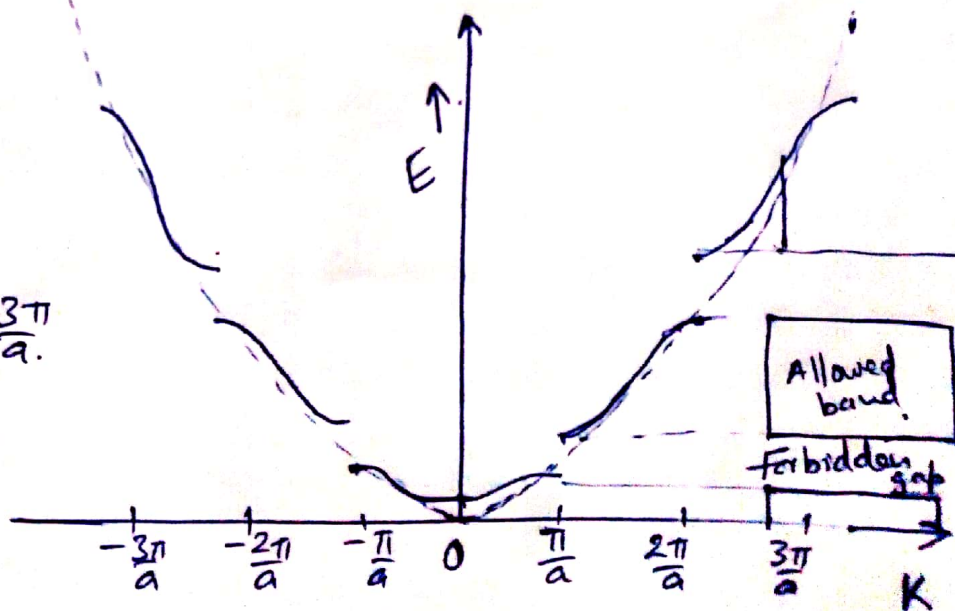
This is the energy of free electron.

④ At boundary of allowed band, $\cos ka = \pm 1 = \cos n\pi$
 with $n = 1, 2, 3, \dots$

$$ka = n\pi$$

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

$$k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}$$



1st Brillouin Zone

2nd B.Z.

2nd Brillouin Zone

Zone Schemes for Energy Bands :-

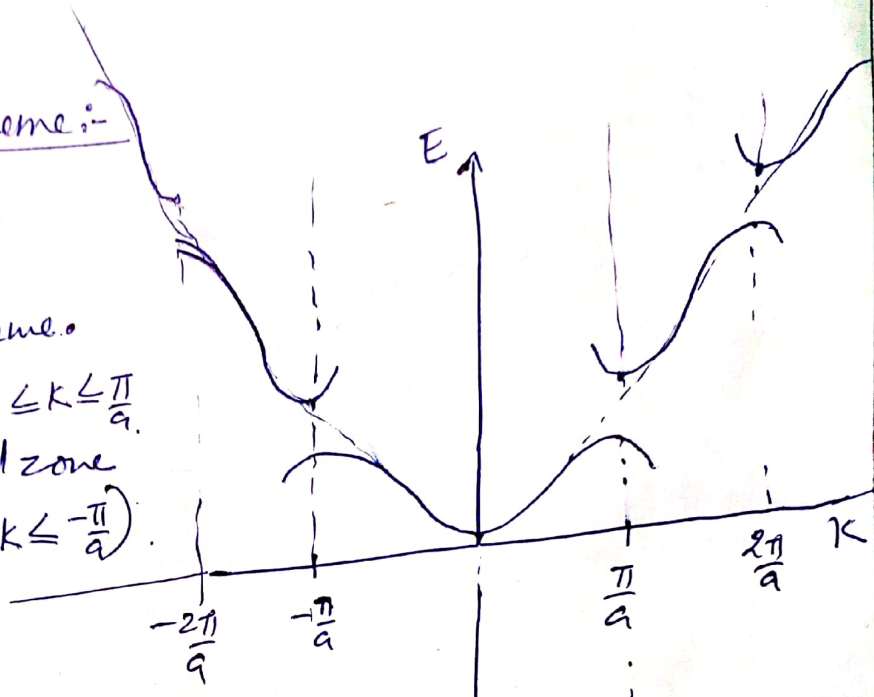
Three zone schemes are there to draw energy bands :-

- a) The extended zone scheme
- b) The reduced zone scheme
- c) The periodic zone scheme.

a) Extended Zone Scheme :-

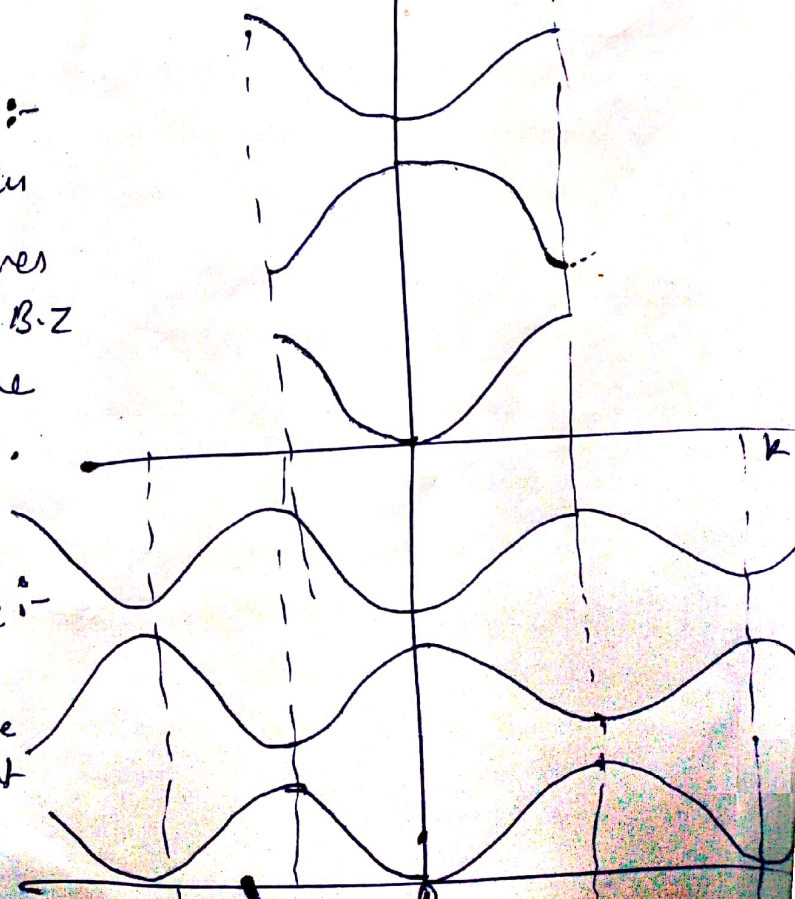
Figure to the right side shows the plot of $E-k$ in extended zone scheme.

First band is in zone $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$ & next higher i.e. second zone $(\frac{\pi}{a} \leq k \leq \frac{2\pi}{a})$ & $(-\frac{2\pi}{a} \leq k \leq -\frac{\pi}{a})$ and so on.



b) The reduced zone scheme :-

All energy bands are shown in first Brillouin zone. The curves in two segments of second B.Z are translated to first zone by reciprocal vector $\frac{2\pi}{a}$ & $-\frac{2\pi}{a}$ and so on for other zones.

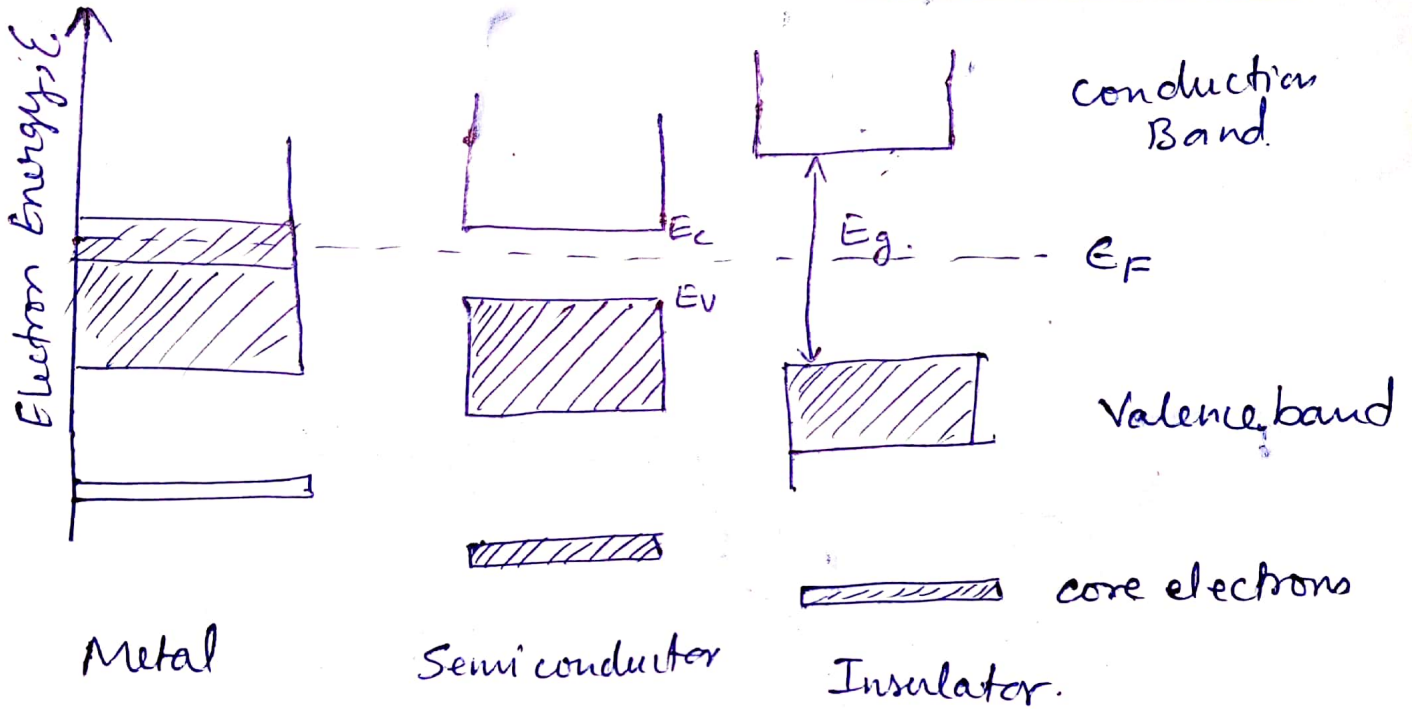


c) The ~~extended~~ periodic zone scheme :-

Energy bands are drawn in each zone in this scheme or shown in the figure to right hand side.

Comparison of conductor, insulator & semiconductor

II



For more details refer to "Elements of Solid State Physics" Third Edition. by J. P. Srivastava. PHI Learning.
 → "Introduction to Solid State Physics" by Charles Kittel, Eighth Edition. John Wiley & Sons.

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