Expression for the Electrical Conductivity:

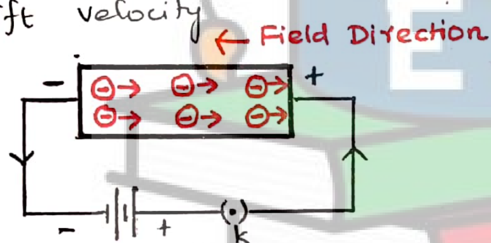
Definition:-

It is the quantity of Electrical charges flowing per unit time (t) per unit area (A) maintained at a unit potential gradient (E).

$$\boxed{\sigma = \frac{Q}{tAE} = \frac{ne^2\tau}{m^*}} \ \Omega^{-1}m^{-1}$$

Derivation:

When an electrical field applied to an electron of charge 'e', It moves in a opposite direction with the applied field with a constant velocity (v_d) known as "drift velocity"



Here the force experienced by the electron by external field

$$F = eE \quad \text{—} (1)$$

and the acceleration gained by the electron 'a' is given by

$$\text{acceleration } a = \frac{\text{velocity}}{\text{Time}} = \frac{v_d}{\tau}$$

$$\therefore a = \frac{v_d}{\tau}$$

$$v_d = a\tau \quad \text{—} (2)$$

We know that from Newton's II law,

$$F = ma \quad \text{—} (3)$$

By comparing eqns (1) & (3)

$$eE = ma$$

$$a = \frac{eE}{m} \quad \text{—} (4)$$

Substituting eqn (4) in eqn (2)

$$v_d = \frac{eE\tau}{m} \quad \text{—} (5)$$

If $n \to$ no. of free electron

$e \to$ charge of an electron

Then current density interms of 'v_d' is given by

$$J = nev_d \quad \text{—} (6)$$

Substitute eqn (5) in eqn (6)

$$J = ne\frac{eE\tau}{m}$$

$$J = \frac{ne^2E\tau}{m} \quad \text{—} (7)$$

From the definition of Charge density is directly proportional to applied electric field.

$$J \propto E$$

$$J = \sigma E \quad \text{—} (8)$$

Comparing eqns (7) & (8) we get

$$\sigma E = \frac{ne^2\tau E}{m}$$

$$\boxed{\sigma = \frac{ne^2\tau}{m}} \quad \text{—} (9)$$

Eqn (9) is the expression for the electrical conductivity.

Thermal Conductivity:

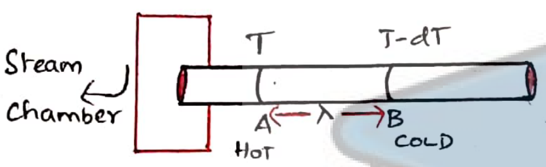
Definition:

It is the amount of heat Conducted per unit area (A), per unit time (t) maintained at unit temperature gradient.

$$K = \frac{Q}{dT/dx} = \frac{n v^2 k_B \tau}{2}$$

Derivation:-

Consider a unifor metallic rod contain free electron.



Here A & B → Cross-sectional area near hot & cold end

T, T-dT → Temp at A & B.

λ → Mean free path

The average K·E of electrons Crossing A

$$E_1 = \frac{1}{2} m v^2 = \frac{3}{2} k_B T \quad — (1)$$

|||ly K·E of free electron at 'B'

$$E_2 = \frac{3}{2} k_B (T - dT) \quad — (2)$$

Excess energy carried out by electrons from A to B

$$K \cdot E = \frac{3}{2} k_B T - \frac{3}{2} k_B (T - dT)$$

$$= \frac{3}{2} k_B T - \frac{3}{2} k_B T + \frac{3}{2} k_B dT$$

$$K \cdot E = \frac{3}{2} k_B dT \quad — (3)$$

Assume, the electron can move in all possible direction, then the no. of electron crossing per unit area, per unit time from 'A' to 'B'.

$$n = \frac{1}{6} n v \quad — (4)$$

∴ The excess average energy carried from A to B is given by

$$E = \frac{1}{6} n v \times \frac{3}{2} k_B dT$$

$$E = \frac{1}{4} n v k_B dT \quad — (5)$$

Hence the net amount of heat transformed from 'A' to 'B'.

$$Q = \frac{1}{4} n v k_B dT - \left[-\frac{1}{4} n v k_B dT \right]$$

$$Q = \frac{1}{2} n v k_B dT \quad — (6)$$

from the definition, we know that

$$Q = K \cdot \frac{dT}{dx}$$

$$Q = K \cdot \frac{dT}{\lambda} \quad — (7)$$

By comparing eqn (7) & (6)

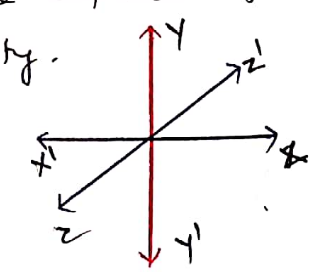
$$K \frac{dT}{\lambda} = \frac{1}{2} n v k_B dT$$

$$K = \frac{1}{2} n v k_B \lambda \quad — (8)$$

wkt $\lambda = \tau v$

$$\therefore \boxed{K = \frac{1}{2} n v^2 k_B \tau} \quad — (9)$$

Eqn (9) is the expression for thermal conductivity.



Wiedemann - Franz Law:-

Definition:-

The ratio between thermal conductivity to the electrical conductivity is directly proportional to the absolute temperature

$$\frac{K}{\sigma} \propto T$$

$$\frac{K}{\sigma} = LT \quad \text{where } L \rightarrow \text{Lorentz no.}$$

$$L = 1.12 \times 10^{-8} \, W\Omega K^{-2}$$

Derivation:-

It is derived from the expression of electrical & thermal conductivity

we know that

$$\sigma = \frac{ne^2\tau}{m} \qquad K = \frac{1}{2} n v^2 k_B \tau.$$

$$\therefore \frac{K}{\sigma} = \frac{\frac{1}{2} n v^2 k_B \tau}{\frac{ne^2\tau}{m}} = \frac{mv^2 k_B}{2e^2} = \frac{k_B}{e^2}\frac{mv^2}{2}$$

We know that $\frac{1}{2}mv^2 = \frac{3}{2}k_B T$

$$\therefore \frac{K}{\sigma} = \frac{3}{2}\frac{k_B^2 T}{e^2} = \frac{3}{2}\left[\frac{k_B}{e}\right]^2 T$$

$$\frac{K}{\sigma} = LT$$

where $L = \frac{3}{2}\left[\frac{k_B}{e}\right]^2$

This law holds good for low temp.

Postulates of free electron theory:-

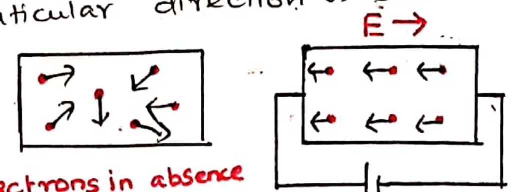
① A metal consits of large no. of free electrons. These electrons move freely throughout the volume of the metal.

②. They move randomly in all possible directions just like the gas molecules move in a container.

③ In the absence of an electric field the free electrons move in all directions in a random manner.

They collide with other free electrons and positive ion core during the motion.

As the motion is random, the resultant velocity in any particular direction is zero.



Electrons in absence of Elec. field

e's in applied elec. field.

④. When the electric field is appli ~~with~~ the electron get some amount of energy. These electron moves towards +ve potential.

As a result of collision, the free electrons acquire a constant avg. velocity known as drift velocity.

⑤. The velocity ~~of~~ & the energy distribution of free electrons are governed by classical Maxwell distribution function.

Success of classical free elec. theory:-

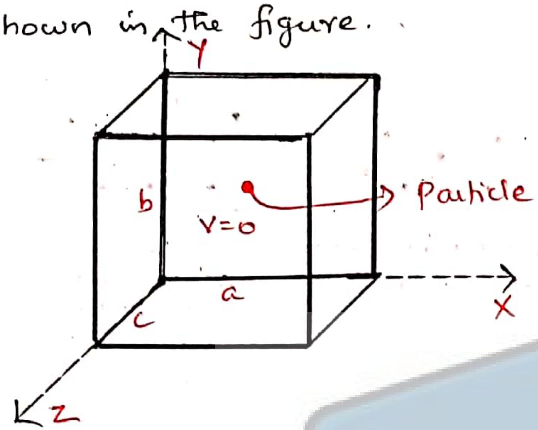
* It is used to
  * Verify Ohm's law
  * Explain electrical & thermal conductivities of metal.
  * Derive Wiedemann - Franz law.
  * Explain optical properties of metals.

Failures of Classical free elec. theory:-

* Elec & thermal conductivities of semi cond. & insulators cannot be explained by this theory.
* All the free electrons absorb the supplied energy. But practically only few e's absorb energy
* Photo elec. effect, Compton effect cannot be explained by this theory.

Particle in 3D Box:

Consider a particle of mass 'm' moving three dimensionally in a box of lengths a, b & c as shown in the figure.



The potential function is given by

$V(x,y,z) = 0$ for $0 < x < a$, $0 < y < b$, $0 < z < c$

$V(x,y,z) = \infty$ for $0 \geq x \geq a$, $0 \geq y \geq b$, $0 \geq z \geq c$

The solution of one dimensional potential box can be extended for a three dimensional box.

In 3 dimensional box, instead of one quantum number 'n', we have to use three quantum numbers n_x, n_y and n_z corresponding to the three coordinate axes namely x, y and z respectively.

The Eigen function and eigen value of a particle moving in a one dimensional potential well can be derived as follows.

One dimensional Schroedinger's time independent wave equation of a free particle is given by

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad -(1)$$

Substituting $\frac{2mE}{\hbar^2} = k^2$ in eqn (1)

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad -(2)$$

The general solution of eqn (2) is given by

$$\psi(x) = A\sin kx + B\cos kx \quad -(3)$$

Where A and B are two constants.

A & B can be determined by boundary conditions.

Condition - 1

$\psi = 0$ at $x = 0$.

(3) $\Rightarrow$ $0 = A\sin 0 + B\cos 0$

$0 = 0 + B \times 1$

$B = 0$

Condition - 2

$\psi = 0$ at $x = a$

(3) $\Rightarrow$ $0 = A\sin ka + 0$

$A\sin ka = 0$

It is found that either $A = 0$ or $\sin ka = 0$

Since $B = 0$, 'A' cannot be zero

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$\therefore \sin ka = 0$

(ie) $ka = n\pi$

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

$$k^2 = \frac{n^2\pi^2}{a^2} \quad \text{--- (4)}$$

we know that

$$k^2 = \frac{2mE}{\hbar^2} = 2mE \cdot \frac{4\pi^2}{h^2}$$

$$k^2 = \frac{8\pi^2 mE}{h^2} \quad \text{--- (5)}$$

Comparing eqns (4) & (5)

$$\frac{n^2\pi^2}{a^2} = \frac{8\pi^2 mE}{h^2}$$

$$E_n = \frac{n^2h^2}{8ma^2} \quad \text{--- (6)}$$

Substituting $k = \frac{n\pi}{a}$ in eqn (3)

$$\psi_n(x) = A \sin \frac{n\pi x}{a} \quad \text{--- (7)}$$

The constant 'A' can be determined by normalisation of wave function

The value of 'A' is given by

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

$\therefore$ Eqn (7) $\Rightarrow$ $\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ --- (8)

The eqn (6) and eqn (8) give eigen value and eigen function of a particle moving in an one dimensional box.

These two equations can be extended to three dimensional potential box as follows.

Energy of the particle

$$E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z}$$

$$E_{n_x n_y n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

$$\boxed{E_{n_x n_y n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right]} \quad \text{--- (9)}$$

The corresponding normalised wave function of the particle in the three dimensional box is given by

$$\psi_{n_x n_y n_z} = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x\pi x}{a}\right) \sqrt{\frac{2}{b}} \sin\left(\frac{n_y\pi y}{b}\right) \sqrt{\frac{2}{c}} \sin\frac{n_z\pi z}{c}$$

$$\psi_{n_x n_y n_z} = \sqrt{\frac{2}{a}}\sqrt{\frac{2}{b}}\sqrt{\frac{2}{c}} \sin\left(\frac{n_x\pi x}{a}\right) \sin\left(\frac{n_y\pi y}{b}\right) \sin\left(\frac{n_z\pi z}{c}\right)$$

$$\boxed{\psi_{n_x n_y n_z} = \sqrt{\frac{8}{abc}} \sin\left[\frac{n_x\pi x}{a}\right] \sin\left[\frac{n_y\pi y}{b}\right] \sin\left[\frac{n_z\pi z}{c}\right]} \quad \text{--- (10)}$$

The eqns (9) & (10) give the eigen value and eigen function of a particle in 3D Box.

For cubical box $a = b = c$

$\therefore$ The eigen value and eigen function are given by

$$\boxed{E_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]}$$

$$\boxed{\psi_{n_x n_y n_z} = \sqrt{\frac{8}{a^3}} \sin\left[\frac{n_x\pi x}{a}\right] \sin\left[\frac{n_y\pi y}{a}\right] \sin\left[\frac{n_z\pi z}{a}\right]}$$

Fermi Distribution function:-

Definition:

It is the probability of occupation of electrons among different energy levels at absolute temperature.

It is given by

$$\boxed{F(E) = \frac{1}{1+e^{(E-E_F)/K_BT}}}$$

Where $E \rightarrow$ Energy level to be considered.

$E_F \rightarrow$ Fermi energy level.

$K_B \rightarrow$ Boltzmann Constant

$T \rightarrow$ Absolute Temperature.

If $F(E)=1$, the energy level is occupied by an electron.

If $F(E)=0$, the energy level is vaccant

If $F(E) = 0.5$, then there is 50% chance for the electron to occupy.

Case (i)

If $E < E_f$ at $T = 0K$

Then $F(E) = \frac{1}{1+e^{(E-E_F)/K_BT}}$

$$= \frac{1}{1+e^{(E-E_F)/0}}$$

$$= \frac{1}{1+e^{-\alpha}} = \frac{1}{1+0} = 1$$

$$\boxed{F(E) = 1}$$

Thus at $T=0K$, 100% chance for the electrons to occupy the energy levels.

Case (ii)

If $T = 0K$ at $E > E_F$

Then $F(E) = \frac{1}{1+e^{(E-E_F)/K_BT}}$

$$= \frac{1}{1+e^{\alpha}} = \frac{1}{1+\alpha}$$

$$\boxed{F(E) = 0}$$

Thus 0% chance for the electron to occupy the energy levels

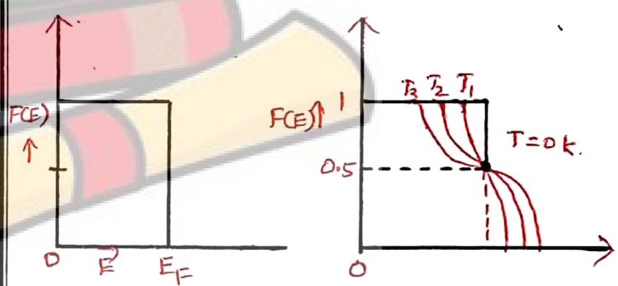
Case (iii)

If $T > 0K$ at $E = E_F$

$$F(E) = \frac{1}{1+e^0} = \frac{1}{1+1}$$

$$F(E) = \frac{1}{2} \quad \text{or} \quad \boxed{F(E) = 0.5}$$

There is 50% chance for the electrons to occupy the fermi energy level



Variation of E_F with respect to temperature.

When $T=0K$, occupation is upto E_F

When $T>0K$ valence electrons got breakdown in its bond and exited to conduction band.

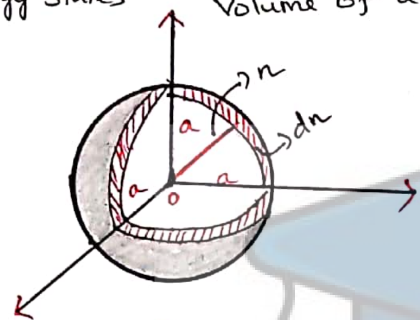
Density of Energy States:-

Definition:

It is defined as the no. of available energy states presented per unit volume of a metal piece.

$$Z(E)\,dE = \frac{N(E)\,dE}{V}$$

$$\text{Density of Energy States} = \frac{\text{No. of avaliable energy state between } E \,\&\, E+dE}{\text{Volume of a metal.}}$$



Let us consider a sphere inside a cubical metal piece of side 'a'.

* Here n_x, n_y, n_z are the coordinate axes.
* $n \rightarrow$ inner radius of the sphere.
* E and E+dE are the energy of the inner and outer shell of the sphere.
* The sphere consists of no. of shells, between inner and outer shell each represents a energy level.

The no of available energy states within the thickness of the sphere of radius 'n'

$$n = \frac{1}{8}\left[\frac{4\pi n^3}{3}\right] \quad \text{—(1)}$$

Iii'ly the energy states within the sphere of radius (n+dn)

$$n+dn = \frac{1}{8}\left[\frac{4}{3}\pi(n+dn)^3\right] \quad \text{—(2)}$$

Hence, the no. of avaliable energy states between (n & n+dn) the energy interval E and E+dE.

$$N(E)\,dE = \frac{1}{8}\left[\frac{4}{3}\pi(n+dn)^3 - \frac{4}{3}\pi n^3\right]$$

$$= \frac{1}{8}\left[\frac{4}{3}\pi\left(\cancel{n^3} + 3n^2dn + 3ndn^2 + dn^3 - \cancel{n^3}\right)\right]$$

$$N(E)dE = \frac{1}{8}\left[\frac{4}{3}\pi\left(3n^2dn + 3ndn^2 + dn^3\right)\right]$$

$\because$ dn very small, neglecting the higher orders,

$$N(E)dE = \frac{1}{8}\left[\frac{4}{3}\pi\left(3n^2dn\right)\right]$$

$$N(E)\,dE = \frac{\pi}{2}n^2dn \quad \text{—(3)}$$

We know that

the energy of an electron in a cubical metal piece. of side 'a' is

$$E = \frac{n^2h^2}{8ma^2} \quad \text{—(4)}$$

Differentiating eqn (4) we have

$$dE = \frac{2n\,dn \cdot h^2}{8ma^2}$$

(ie) $$n\,dn = \frac{8ma^2}{2h^2} \cdot dE \quad \text{—(5)}$$

From eqn (4)

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

$$n = \left[\frac{8ma^2E}{h^2}\right]^{1/2} \quad \text{—(6)}$$

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Hence eqn (3) can be written as

$$N(E)dE = \frac{\pi}{2} n \cdot ndn \quad \text{—(7)}$$

By substituting eqn (5) & (6) in (7)

$$N(E)dE = \frac{\pi}{2}\left[\frac{(8m)^{1/2} a E^{1/2}}{h}\right]\left[\frac{8ma^2 dE}{2h^2}\right]$$

$$\therefore N(E)dE = \frac{\pi}{2} \frac{(8m)^{3/2} a^3 E^{1/2} dE}{2h^3} \quad \text{—(8)}$$

Here $a^3 = V \rightarrow$ volume

$\therefore$ Density of energy states

$$Z(E)dE = \frac{N(E)dE}{V}$$

$$Z(E)dE = \frac{\pi (8m)^{3/2} \cancel{V} E^{1/2} dE}{4h^3 \cdot \cancel{V}}$$

$$Z(E)dE = \frac{\pi}{4h^3}(8m)^{3/2} E^{1/2} dE \quad \text{—(9)}$$

According to Pauli's exclusion principle in each state 2 electrons can be accomodated.

$$\therefore Z(E)dE = 2 \times N(E)dE$$

$$\therefore Z(E)dE = 2 \times \frac{\pi}{4h^3}(8m)^{3/2} E^{1/2} dE$$

$$\boxed{Z(E)dE = \frac{\pi}{2h^3}(8m)^{3/2} E^{1/2} dE} \quad \text{—(10)}$$

Carrier Concentration in Metals:

The no. of electrons per unit volume in a given energy interval is calculated by

$$n_c = \int Z(E) F(E) dE \quad \text{—(11)}$$

we know that

$$Z(E)dE = \frac{\pi}{2h^3}(8m)^{3/2} E^{1/2} dE$$

$$= \frac{\pi}{2h^3}(8)^{3/2}(m)^{3/2} E^{1/2} dE$$

$$= \frac{\pi}{2h^3}(4)^{3/2} \cdot (2)^{3/2} \cdot (m)^{3/2} E^{1/2} dE$$

$$= \frac{\pi}{2h^3} 2^3 \cdot (2m)^{3/2} \cdot E^{1/2} dE$$

$$Z(E)dE = \frac{4\pi}{h^3}(2m)^{3/2} \cdot E^{1/2} dE \quad \text{—(12)}$$

~~If~~ $F(E) = 1$ for energy levels $E = 0$ to $E = E_{F_0}$

Then eqn (11) becomes

$$n_c = \frac{4\pi}{h^3}(2m)^{3/2} \int_0^{E_{F_0}} E^{1/2} dE$$

$$n_c = \frac{4\pi}{h^3}(2m)^{3/2}\left[\frac{E^{3/2}}{3/2}\right]_0^{E_{F_0}}$$

$$= \frac{4\pi}{h^3}(2m)^{3/2} \cdot \frac{2}{3}\left[E_{F_0}\right]^{3/2}$$

$$\boxed{n_c = \frac{8\pi}{3h^3}(2mE_{F_0})^{3/2}} \quad \text{—(13)}$$

Fermi Energy:-

From eqn (13), we know that the carrier concentration n_c can be written as

$$n_c = \frac{8\pi}{3h^3}(2m)^{3/2}(E_{F_0})^{3/2}$$

$$\frac{3n_c}{8\pi} \frac{h^3}{(2m)^{3/2}} = \left[E_{F_0}\right]^{3/2}$$

By raising power on bothsides by 2/3

$$E_{F_0} = \left[\frac{3n_c}{8\pi} \frac{h^3}{(2m)^{3/2}}\right]^{2/3}$$

$$\boxed{E_{F_0} = \left[\frac{3n_c}{8\pi}\right]^{2/3}\left[\frac{h^2}{2m}\right]} \quad \text{—(14)}$$

Effective Mass of Electron:-

Definition:-

The mass acquired by an electron, when it is accelerated in a periodic potential is called effective mass (m^*)

Derivation:-

Consider a crystal subjected to electric field (E). Then the velocity gained by the electrons (v) It is described by the wave vector (k) & it is equivalent to the wave packet moving with a group velocity (v_g).

$$v_g = \frac{d\omega}{dk} \quad — ①$$

where $\omega \rightarrow$ angular velocity ($2\pi\nu$)
$k \rightarrow$ wave vector.

we know that

$$E = h\nu \qquad (or)\ \omega = 2\pi\nu$$

$$\nu = \frac{\omega}{2\pi}$$

$$E = \frac{h\omega}{2\pi} \qquad \hbar = \frac{h}{2\pi}$$

$$E = \hbar\omega$$

$$\omega = \frac{E}{\hbar} \quad — ②$$

∴ Eqn ① can be written as

$$v_g = \frac{d}{dk}\left[\frac{E}{\hbar}\right]$$

$$v_g = \frac{1}{\hbar}\left[\frac{dE}{dk}\right] \quad — ③$$

Under this condition the acceleration 'a' of an electron

$$a = \frac{dv_g}{dt}$$

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

$$a = \frac{1}{\hbar}\,\frac{d^2E}{dk^2}\cdot\frac{dk}{dt} \quad — ④$$

The momentum of an electron from de-Broglie wave length

$$p = \frac{h}{\lambda}$$

$$p = \frac{h}{2\pi}\cdot\frac{2\pi}{\lambda}$$

$$p = \hbar\,\frac{2\pi}{\lambda}$$

$$p = \hbar k \quad — ⑤$$

Differentiate eqn ⑤ w.r.t. 't'

$$\frac{dp}{dt} = \hbar\frac{dk}{dt} \quad (or) \quad \frac{dk}{dt} = \frac{F}{\hbar} \quad — ⑥$$

[Force acting on the electron $F = \frac{dp}{dt}$]

Hence eqn ④ can be written as

$$a = \frac{1}{\hbar}\cdot\frac{d^2E}{dk^2}\cdot\frac{F}{\hbar}$$

$$a = \frac{F}{\hbar^2}\,\frac{d^2E}{dk^2}$$

$$F = \left[\frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)}\right] a \quad — ⑦$$

When an electric field is applied, acceleration of the electron due to field.

$$a = \frac{eE}{m^*} = \frac{F}{m^*}$$

$$F = m^* a \quad — ⑧$$

Comparing eqns ⑦ & ⑧

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

$$\boxed{m^* = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)}} \quad \text{--- (9)}$$

Eqn (9) → Effective mass of an electron is not constant, but depends on the value $\frac{d^2E}{dk^2}$

Case(i): $\frac{d^2E}{dk^2} = +ve$, $m^* = +ve$

Case (ii) $\frac{d^2E}{dk^2} = -ve$, $m^* = -ve$

Case (iii) $\frac{d^2E}{dk^2}$ → more, m^* is ~~higher~~ lesser

Case (iii) $\frac{d^2E}{dk^2}$ → less m^* is ~~less~~ large.

Tight Binding Approximation:-

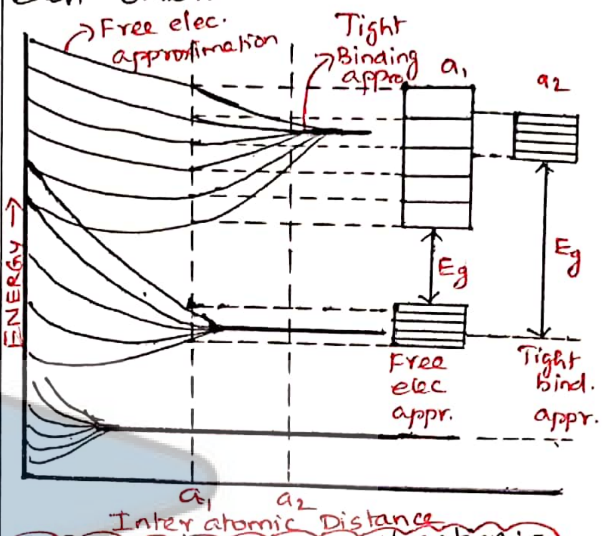
Before discussing about the tight binding approximation, let us know about free electron approximation.

Free electron approximation:-

In solids, ionic core which are tightly bounded to lattice location exists. The electrons are free to move throughout the solid. This is called the free electron approximation.

In free electron approximation,

* The P.E of the e^- is assumed to be lesser than its total energy.
* The width of the band gap (E_g) are smaller than the allowed band. (fig)
* The interaction between the neighbouring atoms will be very strong.
* As the atoms are closer to each other, the inter atomic distance decreases and hence the wave functions overlap with each other.



Tight binding approximation:-

Instead of beginning with the solid core, we begin with the electrons, (ie) all the electrons are bounded to the atoms. In otherwords, atoms are free while the electrons are tightly bounded. This is called tight bound approximation.

In tight binding approximation:

* The P.E of the electrons is nearly equal to the total energy
* The width of the forbidden bands (E_g) are larger than the allowed bands.
* Therefore the interactions between the neighbouring atom will be weak.
* As the atoms are not closer, the inter atomic distance increases and hence the wave functions will not overlap.