-) The probability that a particle will be found at a given place in a space at a given instant of time is characterized by a function $\psi(r, t)$; such function ψ is known as

x, y, z

wave function. The wave function (ψ) has no meaning itself. when it is operated by Schrondinger wave eqn ; It describes the motion of the particle associated with it.
The only quantity having the physical meaning is square of its magnitude and is represented by a quantity P. The quantity P is called probability density of the particle. Hence

$$P = |\psi|^2$$

since ψ may be real or imaginary Hence,

$$P = |\psi|^2 = \psi^* \psi$$

wheres

ψ^* is imaginary
ψ is real

The probability of finding a particle in the volume element $dV(dx, dy, dz)$ is given by

$$P\,dv = |\psi|^2\,dv$$

or

$$= \psi^* \psi\,dv$$

The total probability density of a ~~pa~~ finding a particle in the entire space can be given by

$$= \int_x \int_y \int_z \psi^* \psi\,dv$$

According to Maxwell the total probability of finding a particle in the entire space is equal to unity.
Hence,

$$\int_x \int_y \int_z |\psi|^2\,dv = 1$$

This is called Normalizing condition of wave function.

* Expectation value of dynamical quantity.

→ One of the consequence of uncertainity principle is that momentum, energy, position and other quantity of the particle cannot be determined exactly. We can take the average values of these dynamical quantity. The average values in the quantum mechanics are called expectation values. Hence, it is defined as the average of result of a large no of measurements on independent system.

The expectation value of any function $f(r)$ can be written as :-

$$\langle f(r) \rangle = \int_{-\infty}^{\infty} \psi^* f(r) \psi \, dr$$

* Application of SWE :-

(1) Energy well model of metal

(2) H- atom

(1) Show that energy that confined in an infinite potential well is quantized. and ~~has~~ hence determine its normalized wave function of an electron confined in an infinite potential.

→ Consider a particle ~~that is~~ i.e electron restricted to move along X-axis betn $x=0$ and $x=L$. The potential energy of the particle is zero inside the well (box) but rises to infinity on outside the well i.e

$$\left.\begin{aligned} V(x) &= 0 \quad 0 < x < L \\ V(x) &= \infty \quad x \leq 0 \text{ and } x \geq L \end{aligned}\right\} \text{—— i)}$$

we have schrondinger wave eqn, as

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

or, $$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{— ii)}$$

where,

$$k^2 = \frac{2mE}{\hbar^2} = \text{wave number} \quad \text{— iii)}$$

The periodic soln of eqn ii) can be given by

$$\psi(x) = A\sin kx + B\cos kx \quad \text{— iv)}$$

where, A and B are constants which are to be determined,

Since particle cannot have infinite energy so, it cannot exist outside the box. Therefore ψ must be zero outside the box. So, ψ must be zero at the wall $x=0$ and $x=L$.

Using the boundary condition,

$$\psi(x) = 0 \quad \text{at} \quad x=0 \;\; \& \;\; x=L$$

Hence eqn iv) becomes

$$0 = 0 + 1B \Rightarrow B = 0$$

Eqn iv) becomes,

$$\psi(x) = A\sin kx \quad \text{— v)}$$

Using boundary condition,

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

Now eqⁿ 5) becomes,

$$0 = A\sin kL$$

or, $\sin kL = 0 = \sin n\pi$; $n = 1, 2, 3,$

$$kL = n\pi$$

$$\text{or } k = \frac{n\pi}{L} \quad \text{—— (vi)}$$

From eqⁿ iii) and (vi)

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

$$\boxed{\text{or } E_\infty = \frac{n^2\pi^2\hbar^2}{2mL^2}} \quad \text{—— (vii)}$$

This shows that energy of particle confined in a infinite potential well is quantized.

for Normalized wave function :-
Using Boundary condition $B = 0$ and $k = \frac{n\pi}{L}$

in eqⁿ iv) we have,

$$\psi(x) = A\sin\frac{n\pi x}{L} \quad \text{—— (viii)}$$

Calculation of normalizing value of A :-

or $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

or $\int_0^L |\psi|^2 dx = 1$

or $\int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = 1$

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

or $A^2 \left[\int_0^L \frac{1}{2} dx - \int_0^L \cos\frac{2n\pi x}{L} dx\right] = 1.$

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

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

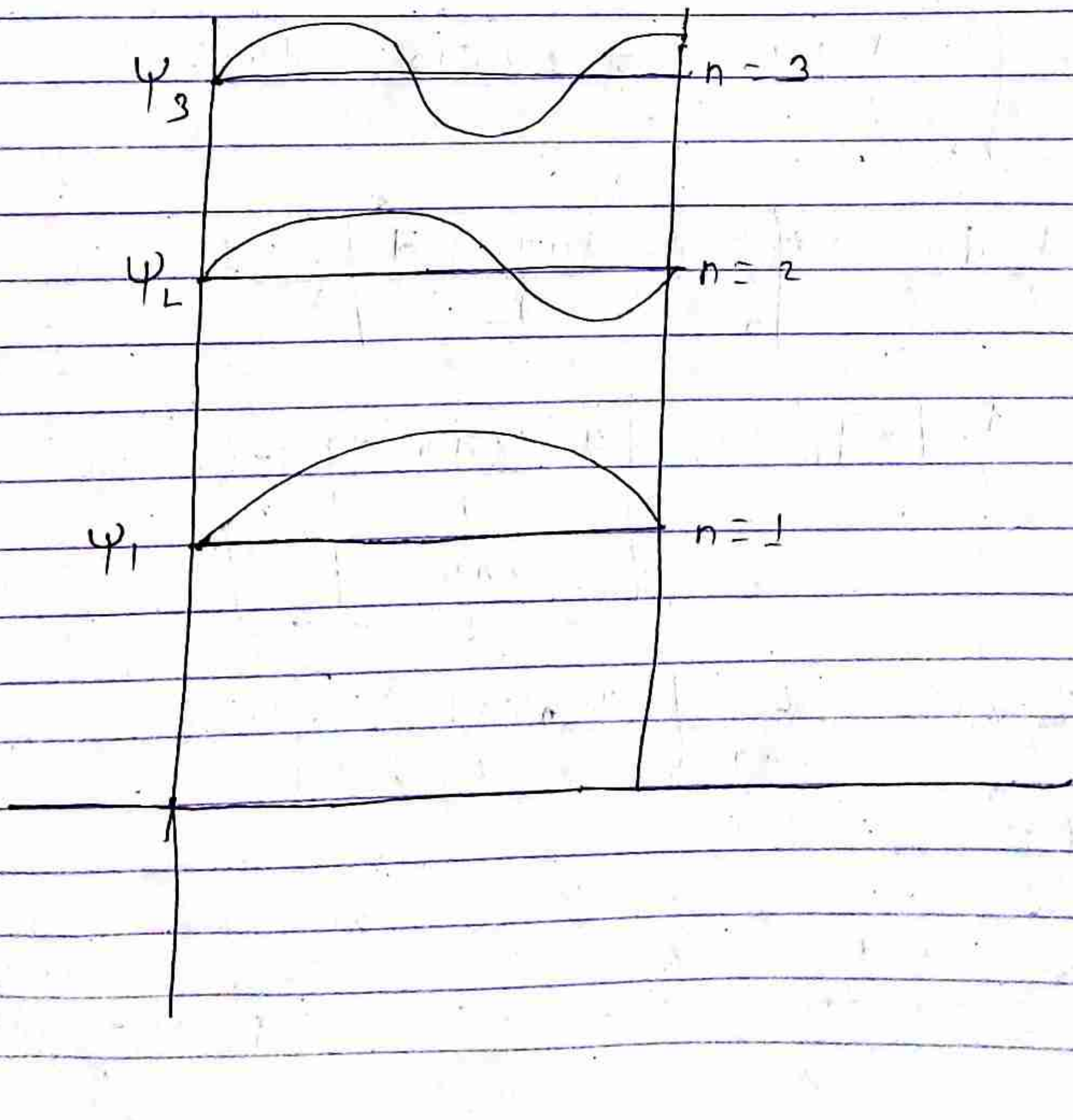
or $A^2 \times \frac{L}{2} - 0 = 1$

or $A^2 \times \frac{L}{2} = 1 \qquad A^2 = \frac{2}{L} \quad \therefore A = \sqrt{\frac{2}{L}}$

Hence, normalized wave function can be reduced to $\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$ —— (ix)

This is required normalized wave function of Schrondinger wave eqn.

The graphical representation of energy eigen values and probability density are shown in the fig.



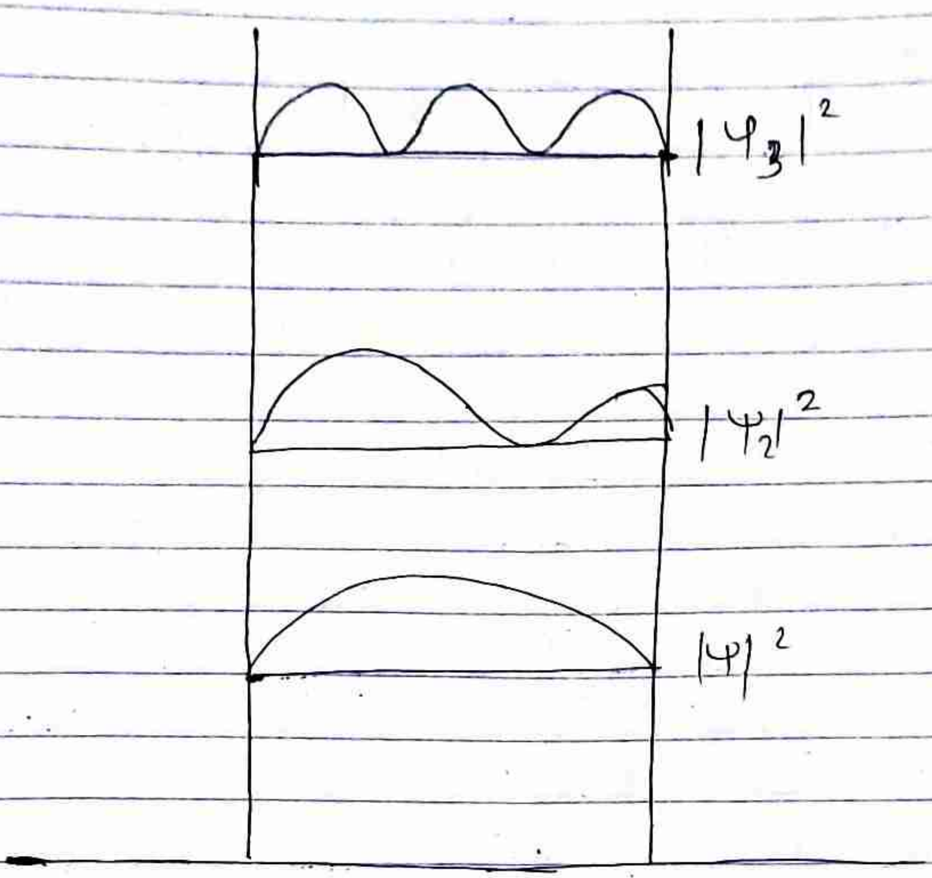


fig probability density

(1) Find the expectation value of position and momentum for the normalized wave function $\psi_{(x)} = \left(\frac{2}{L}\right)^{1/2} \sin \frac{2n\pi}{L} x$

we have,

Expectation value of position can be written as

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x)\, \psi_{(x)}\, dx.$$

$$= \int_{0}^{L} |\psi|^2\, x\, dx,$$

$$= \int_0^L \frac{2}{LL} \sin^2 \frac{2n\pi}{L} x \, dx.$$

$$= \cancel{\frac{2}{L^2}} \cancel{\int_0^L} \cancel{1 - \cos}$$

$$= \frac{1}{L^2} \int_0^L 1 - \frac{\cos \cdot \frac{2 \times 2n\pi}{L}}{2n\pi}$$

(2) H-atom :-

* outline of H- atom :-

The H-atom is the system of two particles, proton and electron, bonded by electrostatic force of attraction. The reduced mass of ~~a~~ proton and electron is given by

$$\mu = \frac{m_p m_e}{m_p + m_e}$$

where

m_p = mass of proton

m_e = mass of electron

since electron is represented by wave system which is bounded by Coloumb's field. Hence, potential energy of electron in nucleus of H-atom is given by

$$V(r) = \frac{e}{4\pi\epsilon_0 r} \times (-e) = \frac{-e^2}{4\pi\epsilon_0 r}$$

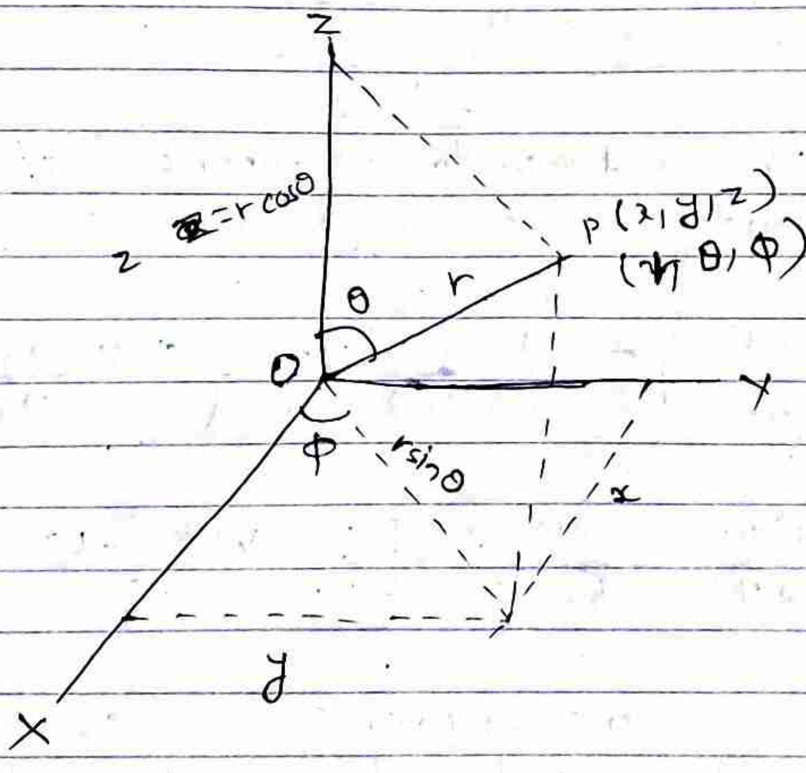
The Schrondinger wave equation is given by

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}\left[E - V\right]\psi = 0$$

where,

$$\bar{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ is a Laplacian operator.

or $$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]\psi = 0 \quad \text{--- i)}$$



The geometry suggests that it is convenient to use the spherical polar coordinates rather than the rectangular co-ordinate to solve the SWE for H-atom

The relation betn cartesian (Rectangular) coordinates and polar coordinates are given as:-

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\} \text{---} (2)$$

$$\left.\begin{aligned} r^2 &= x^2+y^2+z^2 \\ \tan\phi &= \frac{y}{x} \\ \cos\theta &= \frac{z}{r} \end{aligned}\right\} \text{---} (3)$$

Now eqn I) can be reduced to in spherical polar co-ordinates using eqn (2) and (3) as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) +$$

$$\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]\psi = 0 \text{ --- } (4)$$

This is SWE in spherical polar co-ordinates for H-atom. This eqn consist of radial and angular parts of the eqn. for the wave function (ψ). Hence,

$$\psi = (r, \theta, \phi)$$

separation of Radial and angular parts of SWE of H-atom.

In order to separate the radial and angular parts we have,

$$\psi(r, \theta, \phi) = R(r), Y(\theta, \phi) \quad (5)$$

using eq^n 5) in eq^n (4) we have,
we using, $R(r) = R$ and $Y(\theta, \phi) = Y$

$$\frac{Y}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right] + \frac{R}{r^2}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial Y}{\partial \theta}\right) +$$

$$\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial \phi^2} + \frac{2\mu}{\hbar^2}[E-V]RY = 0 \quad (6)$$

multiplying by r^2 and dividing by RY on both sides of eq^n (6),

$$\frac{1}{R}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right] + \frac{1}{Y}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial Y}{\partial \theta}\right) +$$

$$\frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial \phi^2} + \frac{2\mu}{\hbar^2}r^2[E-V] = 0$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right] + \frac{2\mu}{\hbar^2}r^2[E-V] =$$

$$-\frac{1}{Y}\left[\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial Y}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial \phi^2}\right] = \lambda \text{ (say)}$$

$$-(7)$$

In eq^n 7) the radial path and angular path must be equal to each other and is equal to λ called separation constant.

The LHS of eqns (7) can be written as

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=\lambda \quad \text{—— 8)}$$

Dividing by r^2 and multiplying by R on both sides of eq^n (8) we have,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu R}{\hbar^2}(E-V)=\frac{\lambda R}{r^2}$$

or $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2\mu}{\hbar^2}(E-V)-\frac{\lambda}{r^2}\right]R=0$$

—— eq^n 9)

This eq^n 9) is known as ~~radiati~~ radial eq^n of H-atom.

Again, the angular part of eq^n 7) can be written as

$$-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=\lambda$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\Big] = -\lambda Y$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}+\lambda Y = 0 \quad \text{—(10)}$$

The eq^n (10), also can be separated into two parts by putting

$$Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$

$$= (\Theta,\Phi)$$

Now eq^n (10) is reduced to

or, $$\frac{1}{\sin\theta}\times\Phi\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1\,\Theta}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}+\lambda\Theta\Phi = 0$$

—(11)

Multiplying by $\sin^2\theta$ and dividing by Θ and Φ in eq^n (11)

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}+\lambda\sin^2\theta = 0$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\lambda\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi^2}{\partial\phi^2} = m_l^2 \text{ (say)}$$

—(12)

In the eqn 12) LHS containing the term of Θ must be equal to ~~RHS~~ RHS containing term Φ which is equal m_l^2.

The LHS of eqn 12 can be written as

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\lambda\sin^2\theta = m_l^2$$

— eqn 13

Dividing ~~as~~ by $\sin^2\theta$ and multiplying by Θ of eqn 13 on both sides,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{\lambda\Theta}{\cancel{\Theta}} = \frac{m_l^2\Theta}{\sin^2\theta}$$

— 14)

This eqn 14) gives is known as Θ eqn for H-atom.

Again,

The right side of eqn 12) can be written as.

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = m_l^2$$

or $$\frac{\partial^2\Phi}{\partial\phi^2} = -\Phi m_l^2$$

or, $$\frac{\partial^2 \Phi}{\partial \phi^2} + \Phi m_l^2 = 0 \quad \text{—} (15)$$

The eqn (15) is Azimuthal eqn ~~eq~~ and Φ eqn of H-atom.

The eqn (9), (14) and (15) are three separate eqns of SWE for H-atom.

* without solving the SWE for H-atom. Discuss the quantum number.

The solution of SWE for H-atom are well known in mathematics. Hence their solution associated with quantum number are discussed as:-

(1) when we solve the radial eqn 9) the soln for R remains finite everywhere are those for which

$$E = \frac{-me^4}{8\epsilon_0^2 h^2} \times \frac{1}{n^2} = -\frac{13.6\,eV}{n^2}$$

where,

$n = 1, 2, 3 \ldots\ldots$

This eqn is in complete agreement with prediction of ~~Bo~~ Bohr theory. Hence three quantum number for the simple model of H-atom are given as

Principle quantum number $(n) = 1, 2, 3 \ldots$
orbital quantum number $(l) = 0, 1, 2, 3 \ldots (n-1)$

magnetic quantum number $(m_l) = 0, \pm 1, \pm 2, \pm 3 \ldots \pm l$

2) when we solve the azimuthal eqn or Φ eqn
The solⁿ for Φ is

$$\Phi(\phi) = Ae^{im_l\phi}$$

$$= \frac{1}{\sqrt{2\lambda}} e^{i m_l(\phi)}$$

for this function to be singled value the permitted values of m_l are
$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l$

3) when we solve the polar eqn for Θ, the solⁿ for Θ are finite everywhere are those for which $l = 0, 1, 2, \ldots l$
where l are known as orbital quantum number

* Quantum Mechanical Free electron model

→ Many of difficulties encountered by classical free electron model were removed by advent of quantum mechanics. The following two assumptions are modified in free electron model by Sommerfeild as :-

a) The electron must be treated quantum mechanically. This will quantized the energy spectrum of electron gas.

b) The electron must obey Pauli's exclusion principle i.e no two electron can have the same set of quantum number.

Derive the fermi energy of electron and density of state SWE. and quantum mechanical free electron model.

> The energy which corresponds to topmost field of quantum state or energy level at 0K is known as fermi energy.

In order to study the behaviour of electron in the cubic crystal we consider a time independent SWE for free particle as

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \quad \text{--- i)}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ is a Laplacian operator

where,

$k^2 = \frac{2m}{\hbar^2} E$ is a square of wave vector.

Hence eqⁿ i) becomes,

$$\nabla^2 \psi + k^2 \psi = 0 \quad \text{— (ii)}$$

The general solⁿ for eqⁿ (ii) for travelling wave is given by

~~Consider~~

$$\psi(r) = Ae^{i(\vec{k} \cdot \vec{r})} \quad \text{— (iii)}$$

where A is normalizing constant.

suppose electron is confined in cubical crystal of length of edge L. The eqⁿ iii) also can be written as

$$\psi(r) = Ae^{i(k_x x + k_y \cdot y + k_z \cdot z)} \quad \text{— (iv)}$$

where

k_x, k_y, k_z are wave vectors along X-axis, Y-axis and Z-axis respectively.

Since ~~ψ~~ wave vector ψ is periodic with length L wrt x, y, z. Hence boundary condition for the wave vector ψ is given by

$$\left.\begin{aligned}\psi(x+L, y, z) &= \psi(x, y, z)\\ \psi(x, y+L, z) &= \psi(x, y, z)\\ \psi(x, y, z+L) &= \psi(x, y, z)\end{aligned}\right\} \text{— (v)}$$

Applying the first boundary ~~periodic~~ condition to the eq^n 4)

$$Ae^{i(k_x(x+L) + k_y y + k_z z)} = Ae^{i(k_x x + k_y y + k_z z)}$$

$$Ae^{i(k_x x + k_y y + k_z z)} \cdot e^{ik_x L} = Ae^{i(k_x x + k_y y + k_z z)}$$

$$e^{ik_x L} = 1 = e^{i2\pi n} \quad \text{(for real part)}$$

$$k_x L = 2n\pi$$

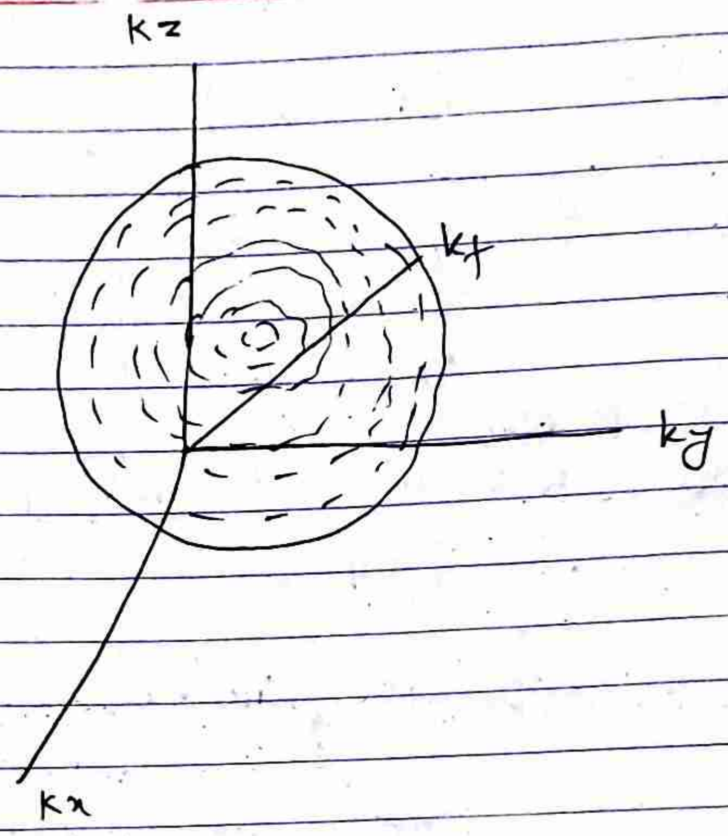
$$k_x = \frac{2n\pi}{L}$$

The similar result can be obtained for $k_y, k_z = \frac{2n\pi}{L}$

In the system of n free electrons occupied by orbitals in the ground state may be represented by points in the sphere in the k-space as shown in the fig.

(The space associated with momentum which described in terms of ~~by~~ wave vectors to discuss the complete knowledge of behaviour of electrons in the crystal)

k-space



The energy of the surface of sphere represents fermi energy and such sphere is known as fermi sphere of radius k_f

Here k is represented by k_f.

Then

$$k_f^2 = \frac{2m}{\hbar^2} E_f$$

or)

$$E_f = \frac{\hbar^2}{2m} k_f^2 \quad \text{——— (vi)}$$

It is found that total no of orbitals in ~~fermi sphere~~ k-space sphere equal to ratio of volume of fermi sphere to the volume of volume element i.e

$$N = 2 \frac{\text{volume of femi sphere}}{\text{volume of volume element}}$$

The factor 2 appears for no of orbitals present in a energy level for ~~mechanical~~ magnetic quantum number m_L.

Hence,

$$N = \frac{2 \times \frac{4}{3}\pi k_f^3}{\left(\frac{2\pi}{L}\right)^3}$$

$$k_f^3 = \frac{\left(\frac{2\pi}{L}\right)^3 \times N}{2 \times \frac{4}{3}\pi}$$

$$= \frac{\frac{8\pi^3}{L^3} \times N}{\frac{8\pi}{3}} = \frac{3\pi^2}{L^3} \times N = \frac{3\pi^2 N}{V}$$

where $L^3 = V$ is the volume of cubic crystal.

$$k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Expression for fermi energy,

$$E_f = \frac{\hbar^2}{2m} \times \left(\frac{3\pi^2 N}{V}\right)^{2/3} \quad [\text{frome } q^n \text{ vi}]$$

This is the expression for fermi energy at 0K.

Density of state :-

It is defined as no of orbitals ~~the~~ ~~per~~ lines present in per unit energy range
It is denoted by
$D(E)$
if dN be the no of orbitals lying in energy range dE ~~then~~

$$\therefore D(E) = \frac{dN}{dE} \quad \text{——— (vii)}$$

From eqn of femi energy

$$E_f = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$\text{or} \quad \left(\frac{3\pi^2 N}{V}\right)^{2/3} = \frac{2m}{\hbar^2} \times E_f$$

or $$\frac{3\pi^2 N}{V} = \left(\frac{2m}{\hbar^2} E_f\right)^{3/2}$$

or $$N = \left(\frac{2m}{\hbar^2} \times E_f\right)^{3/2} \times \frac{V}{3\pi^2 N}$$

$$= \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot E_f^{3/2} \quad \text{— (viii)}$$

~~From~~ using eq^n (8) in eq^n (7)

$$D(E) = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \times \frac{3}{2} E_f^{1/2}$$

$$= \frac{V}{\cancel{3}2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_f^{1/2} \quad \text{— (ix)}$$

This gives the density of ~~energy~~ state.

* Black Theorem :-

→ As earlier discussed in free electron theory, the 1-D SWE for an electron moving in a constant potential V_0 is given by

$$\frac{\partial^2 \psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \quad \text{— (i)}$$

The solution for plane wave type is given by

$$\psi(x) = Ae^{ikx}. \quad \text{— (ii)}$$

For electron moving in periodic potential the S.W.E is given by

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

where
V_x = periodic potential periodic with Lattice constant a

Hence,
$$V(x) = V(x+a) \quad \text{— (iv)}$$

The eqn (iv) is known as bloch theorem.

According to this theorem, solutions of eqn (iv) are which can be modulated plane wave type of eqn (2) by ~~$u_k(x)$~~ $U_k(x)$ as

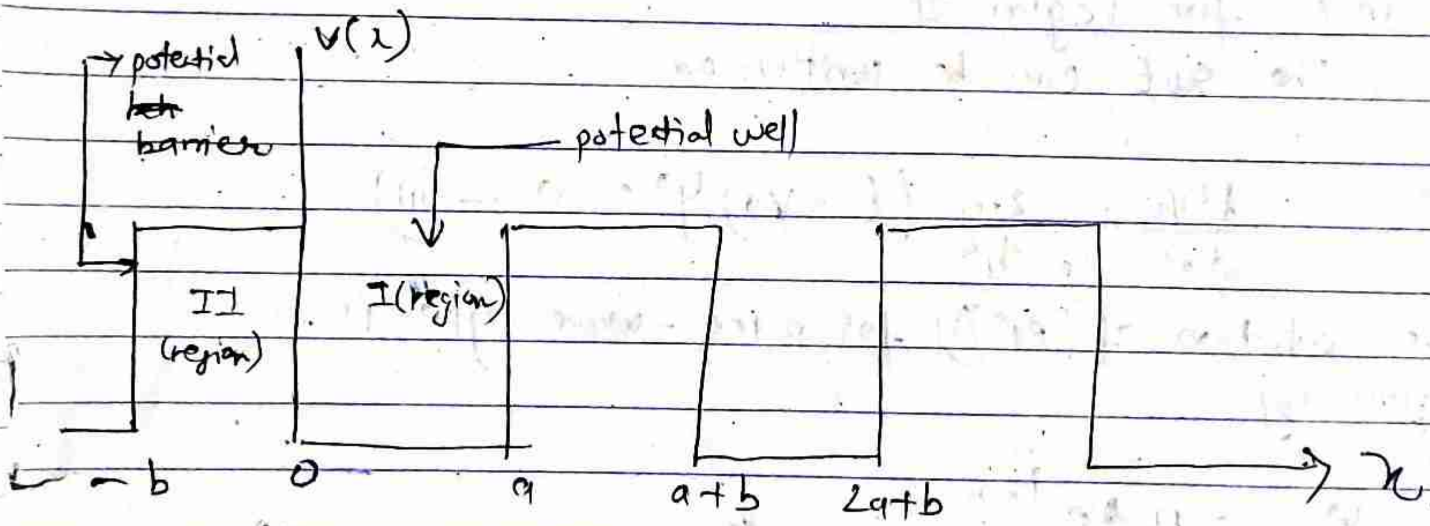
$$\psi(x) = U_k(x)\,e^{ikx} \quad \text{— (V)}$$

The eqn (V) is known as bloch function with periodicity of U_k as

$U(x) = U(x+a)$

* Kroney Penny model (KP model)
(Motion of electron in periodic potential)

This model is very useful to illustrate the quantum behaviour of electrons in a periodic potential. It assumes that potential energy of an electron in a linear array of positive nuclei is the form of periodic array of square well with period of $(a+b)$ as shown in the fig.



The SWE of one electron moving in the periodic potential is given by $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - V(x)\right]\psi = 0$

— i)

The potential function ~~for~~ $v(x)$ is given by

$v(x) = 0$ for region I $(0 < x < a)$

& $v(x) = V_0$ for region II $(-b < x < 0)$

The SWE for region I can be written as

$$\frac{d^2\psi_1}{dx^2} + \frac{2m}{\hbar^2}[E]\psi = 0 \quad \text{— ii)}$$

and for region II

The SWE can be written as

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \quad \text{— iii)}$$

The solution of eq^n ii) for plane-wave type is given by

$\psi(x) = u_0 e^{ikx}$

(where $\alpha^2 = \frac{2m}{\hbar^2}E$ $\left[\frac{d^2\psi_1}{dx^2} + \alpha^2\psi_1 = 0 \quad \text{— iv)}\right]$)

If $E < V_0$ then

The eq iii) can be written as

$$\frac{d^2\psi_2}{dx^2} - \beta^2\psi_2 = 0 \quad \text{— (v)}$$

The potential is periodic. Hence from Bloch theorem the solution of SWE in general can be written as.

$$\psi(x) = U_k\, e^{ikx} \quad \text{— (vi)}$$

For region I equation (vi) can be written as

$$\psi_1 = u_1 e^{ikx}$$

$$\frac{d\psi_1}{dx} = u_1\, ik \times e^{ikx} + e^{ikx}\frac{du_1}{dx}.$$

$$\cancel{\frac{d^2\psi_1}{dx^2} = (ik)^2\psi_1 \; \frac{d(u_1 ik e^{ikx})}{dx}}$$

$$\frac{d^2\psi_1}{dx^2} = \frac{d\, u_1(ik)e^{ikx}}{dx} + \frac{d\left(e^{ikx}\frac{du_1}{dx}\right)}{dx}.$$

$$= u_1(ik)(ik)e^{ikx} + ike^{ikx}\frac{du_1}{dx}$$

$$+ \frac{du_1}{dx}\cdot 2k\, e^{ikx} + e^{ikx}\times\frac{d^2u_1}{dx^2}$$

$$= (-k^2)u_1 e^{ikx} + 2ike^{ikx}\frac{du_1}{dx} + e^{ikx}\frac{d^2u_1}{dx^2}$$

— (viii)

using eqn (viii) in (iv)

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi_1 = 0$$

$$(-k^2)\, u_1 e^{ikx} + 2ik\, e^{ikx} \frac{du_1}{dx} + e^{ikx} \cdot \frac{d^2u_1}{dx^2}$$

$$+ \alpha^2 u_1 \cdot e^{ikx} = 0$$

or $$(-k^2)u_1 + 2ik\frac{du_1}{dx} + \frac{d^2u_1}{dx^2} + \alpha^2 u_1 = 0$$

or $$\frac{d^2u_1}{dx^2} + 2ik\frac{du_1}{dx} + (\alpha^2 - k^2)\, u_1 = 0 \quad \text{— (viii)}$$

(for region I)

Similarly ~~for~~ the result obtained for eqn (v) can be written as (for region II)

$$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (\beta^2 + k^2)\, u_2 = 0$$

— (ix)

Periodic solns for eqn (viii) is given as

$$u_1 = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x} \quad \text{--- (x)}$$

and,

for Region II

$$u_2 = Ce^{(\beta - ik)x} + De^{-(\beta+ik)x} \quad \text{--- (xi)}$$

where,

A, B, C and D are constants which can be determined using point boundaries condition following

$$u_1(0) = u_2(0),\ \& \left(\frac{du_1}{dx}\right)_{x=0} \left(\frac{du_2}{dx}\right)_x = 0 \quad \text{--- (xii)}$$

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

we get, --- (xiii)

$$A+B = C+D$$

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

$$Ae^{i(\alpha-k)a} + Be^{+i(\alpha+k)b} = Ce^{(\beta-ik)a} + De^{+(\beta+ik)b}$$

or, $$Ai(\alpha-k)e^{i(\alpha-k)a} - Bi(\alpha+k)e^{i(\alpha+\beta)b} =$$

$$C(\beta-ik)e^{i(\beta-ik)a} - D(\beta+ik)e^{(\beta+ik)b}$$

— (14)

The eq^n (14)

$$A+B-C-D=0$$

$$Ai(\alpha-k) - Bi(\alpha+k) - C\left|(\beta-ik)+D(\beta+ik)\right| = 0$$

$$Ae^{i}(\alpha-k)e^{i(\alpha-k)a} - Bi(\alpha+k)e^{i(\alpha+\beta)b} -$$

$$C(\beta-ik)e^{i(\beta-ik)a} + D(\beta+ik)e^{(\beta+ik)b} = 0$$

— (15)

The non zero solution of these eq^n can be found only when if the determinant of coefficient ~~a, b, c~~ A, B, C, and ~~d~~ D. vanishes.

$$\begin{array}{c|cccc|}
A & 1 & 1 & -1 & 1 \\
B & i(\alpha-k) & -(i\alpha+k) & -(\beta-ik) & -(\beta+ik) \\
C & e^{i(\alpha-k)a} & e^{i(\alpha+k)b} & -e^{(\beta-ik)a} & -e^{(\beta+ik)b} \\
D & i(\alpha-k)e^{i(\alpha-k)a} & -i(\alpha+k)e^{i(\alpha+\beta)b} & -(\beta-ik)e^{i(\beta-ik)a} & -(\beta+ik)e^{(\beta+ik)b}
\end{array} = 0$$

Solving these determinants, we get for $\beta >> \alpha$ and $b \to 0$

$$\frac{\beta^2}{2\alpha} b \sin\alpha a + \cos\alpha a = \cos ka \quad \text{--- (14)}$$

let $P = \dfrac{\beta^2 ab}{2}$ — (15)

$$\frac{P}{a\alpha} \sin\alpha a + \cos\alpha a = \cos ka \quad \text{--- (16)}$$

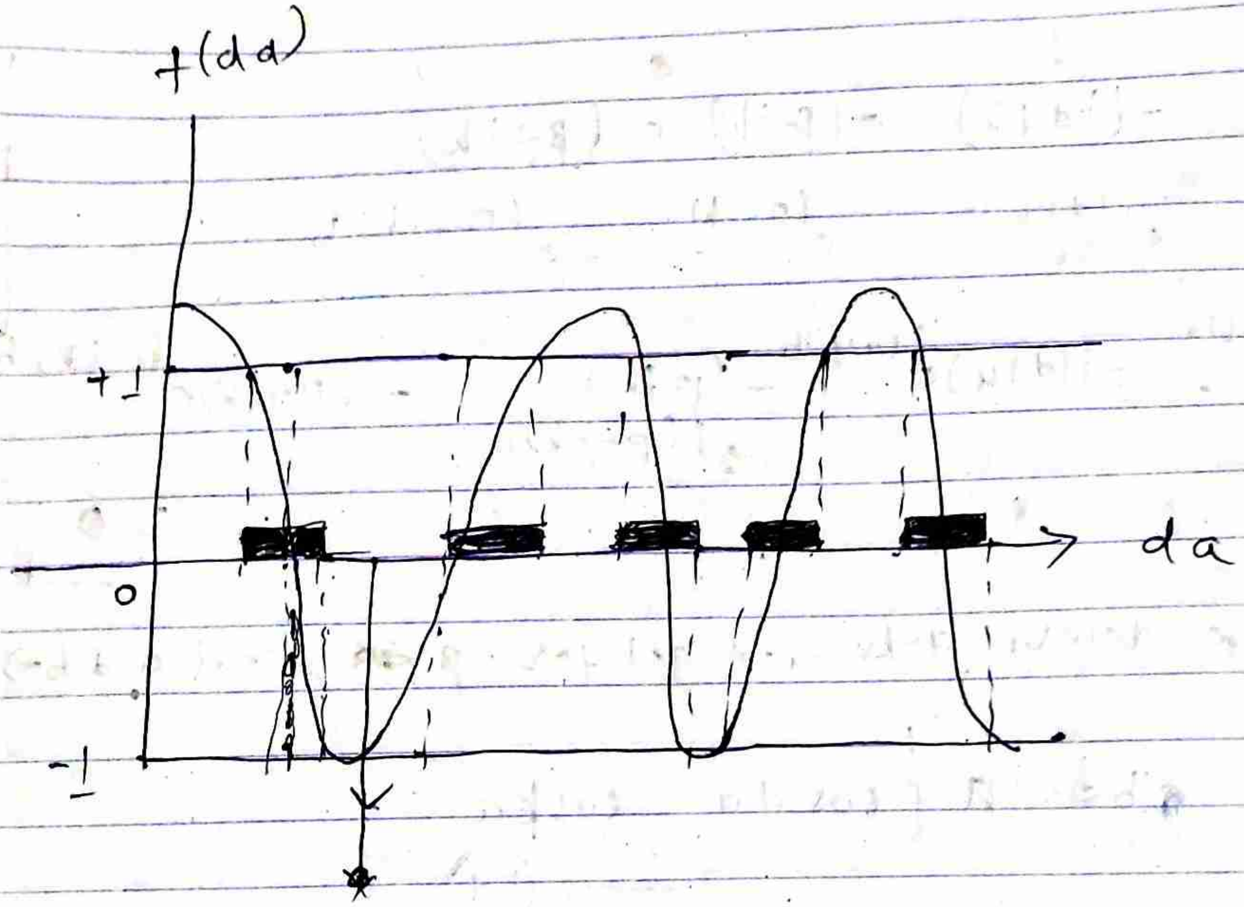
The eqn (16) is a relation betn α and k so it also relates the total energy E of electron to its momentum P.

The graph plotted betn $\dfrac{P}{a\alpha} \times \sin\alpha a + \cos\alpha a$

v/s αa. in the fig a&b is shown

Discuss the k P model using the block theorem.
Derive the dispersion relation for the quantum behaviour of electron in periodic potential square ~~wave~~ well.

118



* Effective mass :-

The electron in the crystal are not completely free but influenced with the periodic potential of lattice ions as a result ~~thee~~ their motion is different from that of electron in free space. and mass alters, such altered mass of the particle is called effective mass.

This effective mass of particle can be calculated using semi-classical and quantum mechanical approach.

According to quantum mechanical approach, the group velocity

$$v_g = \frac{d\omega}{dk} \Rightarrow \frac{d\hbar\omega}{d\hbar k} = \frac{dE}{\hbar dK} \quad \text{— i)}$$

where,

$E = \hbar\omega$ is energy of particles.

According to classical mechanics, the work done on the particle by the electric force is equal to energy of particle.

$$dW = F\,dx$$

$$dE = F\,dx$$

$$\frac{dE}{dt} = F\frac{dx}{dt} = F \times v_g \quad \text{— ii)}$$

Since group velocity (v_g) must be equal to particle velocity (v_p) in the periodic potential.

Hence,

$$v_g = v_p = v$$

and

if $\mathcal{E}$ is the external electric field, applied to the crystal to gain the accl^n. Hence force experienced by electron in the crystal is given by

$$F = e\mathcal{E}$$

From eqⁿ 2)

$$\frac{dE}{dt} = e\mathcal{E}\,v \quad \text{--- (iii)}$$

Using eqⁿ i) in (iii) we get,

$$\frac{dE}{dt} = e.\mathcal{E}\,\frac{1}{\hbar}\frac{dE}{dk} \quad \text{--- (iv)}$$

Let a be the accⁿ acquired by the electron in the electrical field. Hence,

$$a = \frac{dv}{dt} = \frac{d}{dt}\left(\frac{1}{\hbar}\frac{dE}{dk}\right) \quad \text{--- (v)}$$

Using eqⁿ iv) in v) finally we get,

$$a = \frac{e\mathcal{E}}{\hbar^2}\frac{d^2E}{dk^2} = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dt}\right) = \frac{1}{\hbar}\frac{e\mathcal{E}}{\hbar}\frac{d^2E}{dk^2}$$

or $$\frac{a\hbar^2}{\frac{d^2E}{dk^2}} = e\mathcal{E} = m^* a$$

$$\therefore m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}$$ is known as effective mass.

Semi Conductor

* Derive the expression for the concentration of electrons in conduction band of semiconductor and concn of hole in the valence band.

→ The concentration of electrons in the conduction band is given by

$$N_e = \int_{E_c}^{\infty} D(E) f(E)\, dE \quad \text{— i)}$$

where, $D(E)$ is density of state
$f(E)$ is fermi - dirac distribution function

$$f(E) = \frac{1}{e^{\frac{E-E_f}{k_BT}} + 1} = \frac{1}{\left(e^{\frac{E-E_f}{k_BT}} + 1\right)}$$

and

$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E_f^{1/2}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} (E - E_c)^{1/2}$$

Now eqn i) becomes,

$$N_e = \int_{E_c}^{\infty} \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} \frac{(E-E_c)^{1/2}}{\left(e^{\frac{E-E_f}{k_BT}} + 1\right)}\, dE$$