UNIT - III

# PRINCIPLES OF QUANTUM MECHANICS

## # Introduction :-

Classical mechanics explained successfully the motion of objects which are directly observable & observable with the help of instruments like microscope. When the objects which are not observable even with the help of the instruments, classical concepts can not be applied.

Classical mechanics fails to explain the stability of atom and also it fails to explain the spectrum of hydrogen atom. the phenomena of black body spectrum, photoelectric effect, compton effect, specific heat of solids and atomic spectra.

The phenomena in the realm of atoms, nuclei and elementary particles are commonly refered to as 'Quantum phenomena. The currently accepted basic mathematical theory of quantum physics is known as "Quantum Mechanics".

Quantum Mechanics was developed from the quantum theory and This theory was based on the idea that most physical quantities like energy, angular momentum etc, can take up only certain discrete values and can not vary continuously. This theory was first used successfully by



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Max planck to explain the black body radiation. The theory was later used to explain the photo electric effect, compton effect and the hydrogen spectrum successfully.

# Waves and particles :-

**Particle :-** The concept of a particle is easy to grasp. It has mass, it is located at some definite point, it can move from one place to another, it gives energy when slowed down or stopped.

Thus, a particle is specified by its

(i). mass ($m$),
(ii). velocity ($v$),
(iii). momentum ($p = mv$) and
(iv). energy ($E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$)

**Wave :-** The concept of a wave is a bit more difficult than that of a particle. Actually a wave is a spread out disturbance and is specified by its,

(i) frequency ($\nu$),
(ii). wavelength ($\lambda$),
(iii). phase of wave velocity ($V_p$),
(iv). amplitude ($A$), and
(v) intensity ($I$) ($I \propto A^2$)



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**Wave - particle Duality :-** Wave theory of light could satisfactorily explain the phenomena of interference, diffraction and polarization which the Quantum (particle) theory could not explain.

On the other hand, the quantum theory proposes that light consists of individual energy packets - photons - regarded as particles. This particle theory explains photo electric effect and Compton effect which the wave theory could not explain.

However, even in the particle (Quantum) theory, the energy of a photon is given by

$$\therefore \boxed{E = h\nu} \longrightarrow (1)$$

where $h \rightarrow$ is the planck's constant ($h = 6.625 \times 10^{-34}$ Joule-sec)

& $\nu \rightarrow$ is the frequency

Again, frequency ($\nu$) is the property of a wave.

Thus, two different theories are to be followed to explain the same phenomenon. Ultimately, we have to reconcile that "Light travels in the form of waves and absorbs or gives out energy in the form of particles".

i.e., Light has got a dual character, and some times behaves as a wave and some times as a particle.

This is called the wave particle duality of light.



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According to de-Broglie, matter also behaves some times as a particle and some times as a wave. This is called the wave particle duality of matter.

# de-Broglie Hypothesis - Matter Waves :-

According to de-Broglie's hypothesis, matter also behaves some time as a particle and some time as a wave. This is called the wave particle duality of matter.

A material particle of mass 'm' moving with a velocity "v" behaves like a wave of wavelength 'λ' and the corresponding wavelength is called the de Broglie wavelength and the wave is called a "Matter wave" (or) 'de-Broglie wave'. The wavelength of the matter wave is given by,

$$\boxed{\lambda = \frac{h}{mv} = \frac{h}{p}} \longrightarrow (1)$$

de-Broglie wavelength

where, $m \rightarrow$ is the mass of the material particle

$v \rightarrow$ its velocity

& $p \rightarrow$ is its momentum

proof:- ⟨Derivation of de-Broglie wavelength⟩

According to planck's theory of radiation, the energy



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of a photon is given by

$$E = h\nu = h\left(\frac{c}{\lambda}\right) \longrightarrow (2) \quad \left(\because \nu = \frac{c}{\lambda}\right)$$

where c, is the velocity of light in vaccum

Accdding to Einstein energy-mass relation,

$$E = mc^2 \longrightarrow (3)$$

From equations (2) & (3), we get

$$mc^2 = \frac{hc}{\lambda} \quad \text{(or)}$$

$$\lambda = \frac{hc}{mc^2} \quad \text{(or)}$$

$$\therefore \boxed{\lambda = \frac{h}{mc}} \longrightarrow (4)$$

where, $mc = p$ momentum associated with photon

If we consider the case of a material particle of mass 'm' and moving with a velocity 'v', i.e., momentum $p = mv$, then the wavelength associated with this particle is given by,

$$\therefore \boxed{\lambda = \frac{h}{mv} = \frac{h}{p}} \longrightarrow (5)$$

de-Broglie wavelength

eqn (5) is called de-Broglie's equation.



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case(i):-

If E is the kinetic energy of the material particle,

then, $E = \frac{1}{2} mv^2$ (or)

$= \frac{1}{2} mv^2 \left(\frac{m}{m}\right)$

$= \frac{1}{2} \frac{m^2v^2}{m}$

$E = \frac{p^2}{2m}$ $(\because p = mv)$

$\therefore p^2 = 2mE$ (or)

$$\boxed{p = \sqrt{2mE}} \longrightarrow (6)$$

$\therefore$ de-Broglie wavelength

$$\therefore \boxed{\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}} \longrightarrow (7)$$

Case(ii): de-Broglie wavelength associated with electrons

Let us consider the case of an electron of mass "m" and charge "e" being accelerated by a potential V volts, then its K.E., E is given by

$E = eV \longrightarrow (8)$

making this substitution in eqn (7) we get



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$$\therefore \boxed{\lambda = \frac{h}{\sqrt{2meV}}} \rightarrow (9)$$

Substituting,

Planck's constant $h = 6.625 \times 10^{-34}$ JS

Mass of the electron $m = 9.11 \times 10^{-31}$ kg

charge of the electron $e = 1.632 \times 10^{-19}$ C

we get, $$\lambda = \frac{6.625 \times 10^{-34} \text{ JS}}{\sqrt{2 \times 9.11 \times 10^{-31} \text{ kg} \times 1.63 \times 10^{-19} \text{ C} \times V}}$$

$$\lambda = \frac{12.27}{\sqrt{V}} \times 10^{-10} \text{ m} \quad \text{(or)} \rightarrow (10)$$

$$\lambda = \frac{12.27}{\sqrt{V}} \text{ Å} \rightarrow (11) \quad \text{(or)}$$

$$\therefore \boxed{\lambda = \frac{1.227}{\sqrt{V}} \text{ nm}} \rightarrow (12)$$

The above eqn shows the de-Broglie wave length associated with an electron in the presence of a potential V.

# Properties of Matter waves :-

A de-Broglie wave or a matter wave has got the following characteristic properties:



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The de Broglie wavelength

$$\boxed{\lambda = \frac{h}{mv} = \frac{h}{p}} \longrightarrow ①$$

(i). Lighter is the particle, smaller is the mass (m) and larger is the wavelength of the matter wave.

(ii). Smaller is the velocity (v) of the particles, larger is the wavelength.

(iii). For $v = 0$, $\lambda = \infty$. This means that, matter waves are exhibited by any particle that is in motion.

(iv). Matter waves are associated with both charged & chargeless particles (like neutrons). This is because, there is no term including electrical charge in eq$^n$ ①.

(v). The wavelength of matter waves depends on the velocity of matter particles. This means that the velocity of matter waves is not a constant whereas the velocity of EM waves in a medium is a constant.

(vi). The velocity of matter waves can be greater than the velocity of light.

(vii). The wave nature and particle nature cannot be exhibited simultaneously (at the same time).

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## § Experimental Study of Matter Wave :-
(Experimental Evidence for Matter Waves)

According to de Broglie's concept of matter waves, any material particle of mass 'm', moving with a velocity 'v' behaves like a wave of wavelength $\lambda = h/p$.

The most important property of a light (EM) wave is "diffraction". If de Broglie's concept of matter waves were true, then a material particle like electron, proton or neutron should also show diffraction.

In the following two experiments it is showed that particles (electrons) exhibit the diffraction :

(i). Davison & Germer Experiment

(ii). G.P. Thomson Experiment

# DAVISSON AND GERMER'S EXPERIMENT :-

First experimental evidence for the matter waves (de-Broglie's hypothesis) was given by Davisson and Germer in 1927. This was the first experimental support to de-Broglie's hypothesis.

In this experiment they demonstrated that streams of electrons are diffracted when they are scattered from crystals.



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## Experimental Arrangement :-

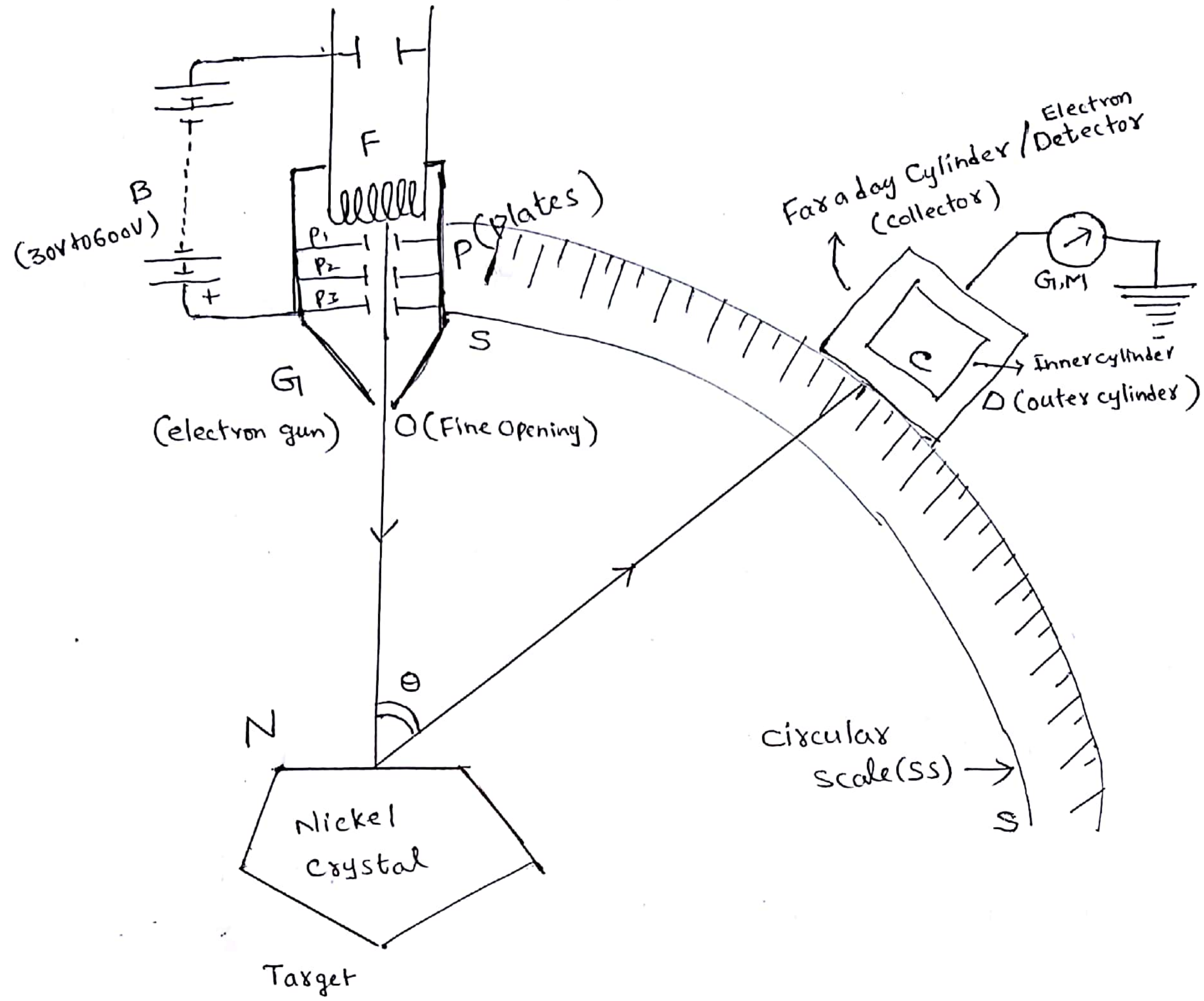


Fig (a): Davisson and Germer's Experiment

In the experimental arrangement, Davisson and Germer accelerated the electrons from a hot tungsten filament F by maintaining a constant potential difference between F and the plate P as shown in fig (a). The electrons emerge through a fine opening "O" in the plate and fall normally on the surface of a nickel crystal (N).



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The electron beam gets scattered in different directions and their respective intensities are measured with the help of a Faraday Cylinder (C) which is connected to a circular scale SS and a galvanometer G.M.

Faraday cylinder "C" called the collector acts as an electron detector. The Faraday cylinder consists of two cylinders "C" (inner cylinder) and "D" (outer cylinder). A retarding potential is maintained b/w "C" & "D" so that only fast moving electrons only can enter into the inner cylinder (C).

Collector "C" can be rotated along a graduated circular scale SS, so that the intensity of the scattered beam can be determined as a function of the scattering angle ($\theta$).

The accelerating potential V provided by the battery B can be (between F & P) changed from 30V to 600V. The retarding potential will be (between C & D) 9/10th of the accelerating potential each time.

## Experimental Procedure :-

The collector is moved to various positions along the circular scale SS. At each position the deflection in galvanometer is noted. This represents the intensity I of scattered electrons. Scattering angle "$\theta$" is measured on circular scale (SS).



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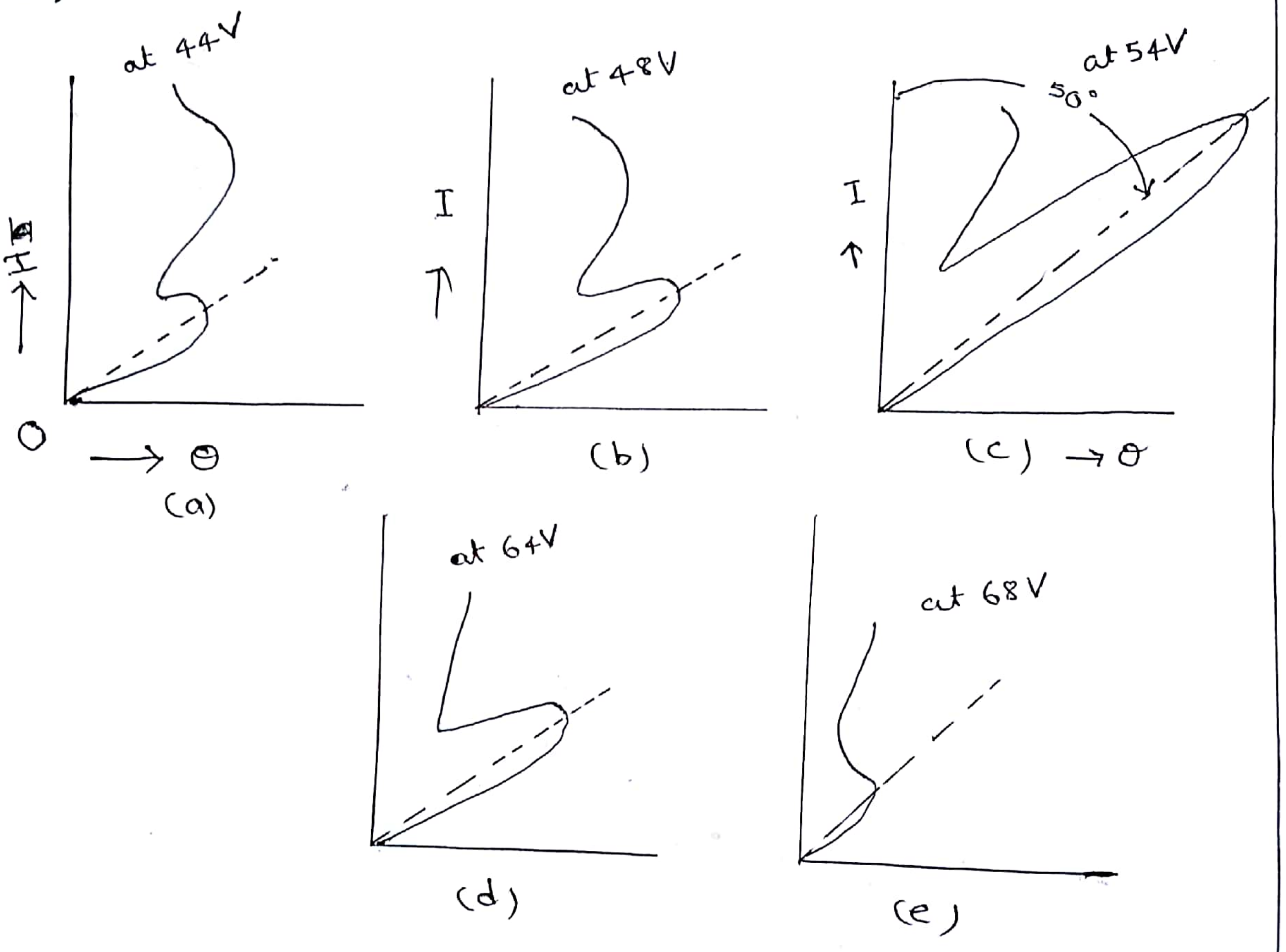
Now the intensity I of scattered electrons is plotted against the scattering angle (θ). The experiment is repeated for several accelerating voltages (V). The curves obtained at several voltages are as shown in fig (2).




Fig(2):- Graphs showing variation in intensity (I) and scattering angle (θ) for different accelerating voltages (V) in Davisson Germer experiment

Observations And Conclusions:-

From fig (2) it is clear that, a strong peak (bump) occurs at V = 54V and θ = 50°.



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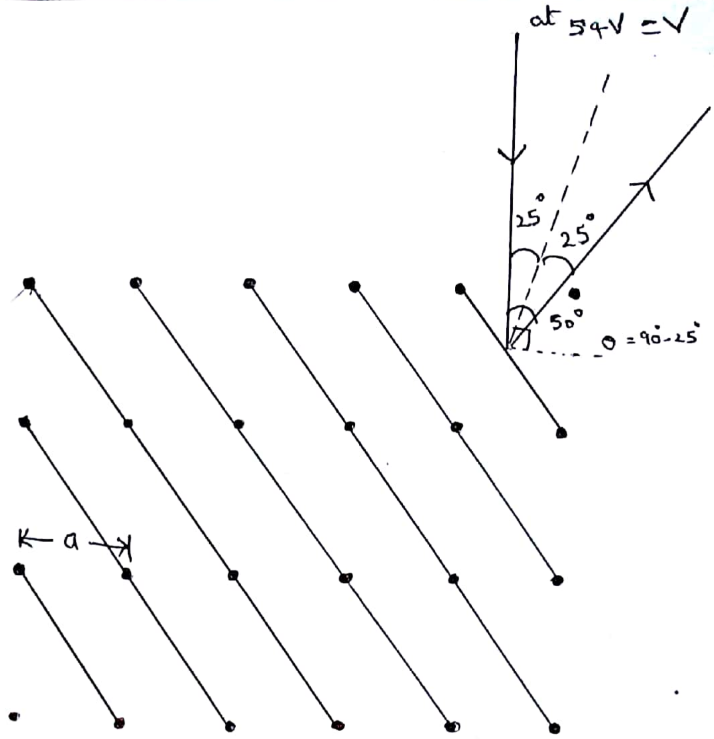
In the Nickel crystal all the atoms are arranged in a regular fashion, hence it could acts as a plane diffraction grating with interatomic distance

$a = 2.15 \times 10^{-10} m$,

$\theta' = 25°$.




Fig(3): Nickel crystal Acting as a grating

Now, applying Bragg's law,

$$2d \sin\theta = n\lambda \rightarrow (1)$$

Here, $d = a \sin\theta'$

$= 2.15 \times 10^{-10} m \times \sin 25°$

$$d \simeq 0.909 \times 10^{-10} m \rightarrow (2)$$

$\therefore$ eqn (1) $\Rightarrow$

$$2 \times 0.909 \times 10^{-10} \times \sin(90° - 25°) = n\lambda \quad (\because n = 1)$$
$$= 1\lambda$$

$$\therefore \lambda = 1.648 \times 10^{-10} m \text{ (or)}$$

$$\boxed{\lambda = 1.648 A°} \rightarrow (3)$$

Result:-

We have de-Broglie wavelength associated with electron is

$$\lambda_D = \frac{12.26}{\sqrt{V}} A°$$

at $V = 54$ Volts, $\lambda_D = \frac{12.26}{\sqrt{54}} A° \simeq 1.668 °A$

$$\therefore \boxed{\lambda = 1.668 A°} \rightarrow (4)$$



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As the two values are in good agreement, this experiment confirms the de-Broglie concept of matter waves.

# Difference between matter wave and Electromagnetic (light) wave :-

| Matter Wave | E.M Wave |
|---|---|
| (1). Matter wave is associated with moving particle. | Oscillating charged particle gives rise to EM wave. |
| (2). Wavelength depends on the mass of the particle & its velocity. $\lambda = \frac{h}{mv}$ | Wavelength depends on the energy of photon. $E = h\nu = \frac{hc}{\lambda}$ ($\because c = \nu\lambda$) $\therefore \lambda = \frac{hc}{E}$ |
| (3). Can travel with a velocity greter than the velocity of light. | Travels with velocity of light. $c = 3\times10^8 m/s$ |
| (4). Matter wave is not EM wave. | Electric field and Magnetic field oscillate perpendicular to each other. |

PROBLEMS :-

(1). Calculate the wavelength associated with an electron Imp raised to a potential 1600V.



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Sol:- We have de-Broglie wavelength associated with an electron is $\lambda_D = \frac{12.26}{\sqrt{V}} A^\circ \rightarrow (1)$

given $V = 1600V$

$$\therefore \lambda_D = \frac{12.26}{\sqrt{1600}} A^\circ$$

$$\therefore \boxed{\lambda_D \simeq 0.3065 A^\circ} \rightarrow (2)$$

(Ans)

(2). If the kinetic energy of the neutron is 0.025eV, Calculate its de Broglie wavelength.
(mass of neutron = $1.674 \times 10^{-27}$ kg)

Sol:- Given kinetic energy of the neutron is

$E = 0.025 eV$ (or)

$= 0.025 \times 1.6 \times 10^{-19}$ joules

we have, de Broglie wavelength associated with energy is $\lambda = \frac{h}{\sqrt{2mE}} \rightarrow (1)$

where $h = 6.626 \times 10^{-34}$ J-sec

mass of neutron $m = 1.674 \times 10^{-27}$ kg

$$\therefore \lambda = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 1.674 \times 10^{-27} \times 0.025 \times 1.6 \times 10^{-19}}}$$

$= 18.104 \times 10^{-11}$ m



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$\therefore$ $\boxed{\lambda = 0.181\,nm}$ (Ans) $\longrightarrow$ (2)

(3). Calculate the de Broglie wavelength associated with a proton moving with a velocity of 1/10th of velocity of light. (mass of proton $= 1.67 \times 10^{-27}$ kg)

Sol:- Velocity of proton $v = \frac{1}{10}$th of velocity of light (c)

$$= \frac{1}{10} \times 3 \times 10^{8} \text{ m/sec}$$

$$v = 3 \times 10^{7} \text{ m/sec}$$

Mass of proton $(m) = 1.67 \times 10^{-27}$ kg

Hence, de Broglie wavelength associated with a proton is

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

$$= \frac{6.626 \times 10^{-34} \text{ Joul-sec}}{1.67 \times 10^{-27} \text{ kg} \times 3 \times 10^{7} \text{ m/sec}}$$

$$\boxed{\lambda = 1.323 \times 10^{-14} \text{ m}} \longrightarrow (3)$$

(Ans)

(4). Calculate the de Broglie wavelength of an electron which has been accelerated from rest on application of potential of 400 volts.

Sol:- We know de Broglie wave length associated with $e^-$

$$\lambda = \frac{12.26}{\sqrt{V}} A^{\circ} = \frac{12.26}{\sqrt{400}} A^{\circ}$$

$\therefore$ $\boxed{\lambda = 0.613\,A^{\circ}}$ (Ans) $\longrightarrow$ (4)



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# Heisenberg's Uncertainty principle :-

Statement :- " The uncertainty principle states that the position and momentum of a particle can not be determined simultaneously (at a time) to any desired degree of accuracy."

If $\Delta y$ be the uncertainty in the position of particle and $\Delta p$ the uncertainty in the momentum of particle, then according to uncertainty principle,

$$\Delta y . \Delta p \geq \frac{h}{4\pi} \quad (\text{or}) \quad \Delta y . \Delta p \sim h \longrightarrow (1)$$

where $h$ is planck's constant

In the above eq$^n$, if $\Delta y$ is small ; $\Delta p$ will be large and vice-versa.

The same relation holds for the energy and time also. If $\Delta E$ is the uncertainty in energy and $\Delta t$ is the uncertainty in time, then

$$\Delta E . \Delta t \geq \frac{h}{4\pi} \longrightarrow (2)$$

Illustration of Heisenberg uncertainty principle :-

Let us consider the wave nature of the electron (material particle) and see how it leads to the uncertainty principle.



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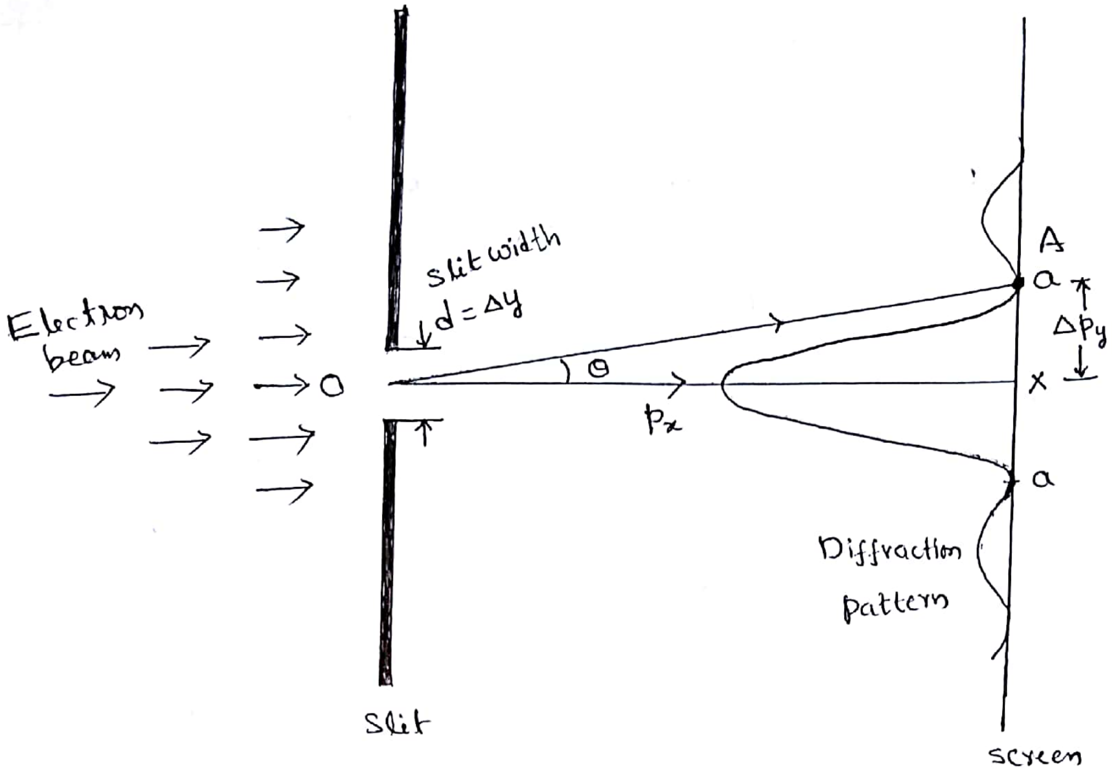


Fig (a). Diffraction of electrons by a Single Slit

Let us consider a monoenergetic beam of electrons incident on the slit of width $d = \Delta y$ as shown in fig (a). The electrons can be diffracted and the diffraction pattern will be as shown in fig (a).

The original initial momentum $p_x$ is only along the OX direction (before diffraction). There is no momentum component along y-direction initially.

After diffraction, let $p_y$ be the momentum of the electron of as it reaches the 1st minimum at "a". The angle of diffraction is "θ". This $p_y$ itself represents the uncertainty in momentum $\Delta p_y$ along y-direction.

from $\Delta OAX$,

$$\tan\theta \approx \frac{\Delta p_y}{p_x}$$

for small $\theta$ values

$$\theta \approx \frac{\Delta p_y}{p_x} \longrightarrow (3)$$

from the diffraction formula, we have

$$n\lambda = d\sin\theta \longrightarrow (4)$$

For the first order diffraction $n=1$ and $d = \Delta y$,

hence, we have $1(\lambda) = \Delta y \sin\theta$

for small $\theta$ values,

$$\lambda = \Delta y.\theta \quad (\text{or})$$

$$\theta \approx \frac{\lambda}{\Delta y} \longrightarrow (5)$$

From equations (3) & (5), we have

$$\frac{\Delta p_y}{p_x} = \frac{\lambda}{\Delta y} \quad (\text{or})$$

$$\Delta p_y.\Delta y \approx \lambda p_x \longrightarrow (6)$$

From, de Broglie hypothesis if an electron moves along $x$-direction, $\lambda = \dfrac{h}{mv_x} = \dfrac{h}{p_x} \longrightarrow (7)$

and consequently, $\Delta p_y.\Delta y \approx \dfrac{h}{\cancel{p_x}}.\cancel{p_x}$



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$$\therefore \boxed{\Delta p_y \cdot \Delta y \approx h} \longrightarrow (8)$$

This is nothing but the Heisenberg's uncertainty principle.

Thus, "we cannot measure simultaneously, the momentum and the position of a particle to as much accuracy as we desire."

Problem:

(1) What voltage must be applied to an electron microscope to produce electrons of wavelength 0.40A°?

Solution:- deBroglie wavelength $\lambda = \frac{h}{p}$

$$= \frac{h}{\sqrt{2mE}} \quad (\because p = \sqrt{2mE})$$

$$\therefore \lambda = \frac{h}{\sqrt{2meV}} \quad (\because E = eV) \longrightarrow (1)$$

Here, $h = 6.6 \times 10^{-34}$ joul-sec

$m = 9.1 \times 10^{-31}$ kg (electron mass)

$e = 1.6 \times 10^{-19}$ C (electron charge)

$\lambda = 0.40A^0 = 0.40 \times 10^{-10}$ m

$V = ?$

$$\therefore 0.4 \times 10^{-10} = \frac{6.6 \times 10^{-34}}{\sqrt{2 \times (9.1 \times 10^{-31}) \times (1.6 \times 10^{-19}) \times V}}$$



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$$\therefore \boxed{V = 960 \text{ Volts}} \longrightarrow (2) \quad (\text{Ans})$$

# Schrodinger's Time Independent Equation :-

Let us consider a system of stationary waves associated with a material particle of mass 'm'. Let x, y, z be the coordinates of the particle and $\psi$ be the wave function.

The differential equation of a wave motion is given by

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \nabla^2 \psi \longrightarrow (1)$$

$$\therefore \frac{\partial^2 \psi}{\partial t^2} = v^2 \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) \longrightarrow (2)$$

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

& $v$ = is the wave velocity

The solution of equation (1) is given by,

$$\psi = \psi_0 \sin \omega t \quad (\text{or})$$

$$\therefore \boxed{\psi = \psi_0 \sin 2\pi \upsilon t} \longrightarrow (3)$$

where $\upsilon \rightarrow$ is the frequency of the stationary wave

Differentiating eqn (3) twice w.r.to 't' we get

$$\frac{\partial \psi}{\partial t} = \psi_0 (2\pi\upsilon) \cos 2\pi \upsilon t \quad (\text{or})$$



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$$\frac{\partial^2 \psi}{\partial t^2} = -\psi_0 (2\pi \nu)^2 \sin 2\pi\nu t \quad \text{(or)}$$

$$= -(4\pi^2\nu^2)(\psi_0 \sin 2\pi\nu t) \quad \text{(or)}$$

$(\because$ from eq$^n$ ③ $)$

$$\therefore \frac{\partial^2 \psi}{\partial t^2} = -4\pi^2 \nu^2 \psi \longrightarrow ④$$

(or) $\left\langle \because v = \nu\lambda \Rightarrow \nu = \frac{v}{\lambda} \right\rangle$

$$= -4\pi^2 \left(\frac{v}{\lambda}\right)^2 \psi \quad \text{(or)}$$

$$\therefore \frac{\partial^2 \psi}{\partial t^2} = -\left(\frac{4\pi^2 v^2}{\lambda^2}\right)\psi \longrightarrow ⑤$$

Substituting equation ⑤ in ①, we get

$$-\left(\frac{4\pi^2 \cancel{v^2}}{\lambda^2}\right)\psi = \cancel{v^2}\, \nabla^2 \psi \quad \text{(or)}$$

$$-\left(\frac{4\pi^2}{\lambda^2}\right)\psi = \nabla^2 \psi \quad \text{(or)}$$

$$\therefore \nabla^2 \psi + \left(\frac{4\pi^2}{\lambda^2}\right)\psi = 0 \longrightarrow ⑥$$

We have de Broglie wave length

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

$$\therefore \nabla^2 \psi + \left[\frac{4\pi^2}{\left(\frac{h^2}{m^2 v^2}\right)}\right]\psi = 0 \quad \text{(or)}$$

$$\therefore \nabla^2 \psi + \left(\frac{4\pi^2}{h^2} \cdot m^2 v^2\right)\psi = 0 \longrightarrow ⑦$$

If E be the total energy and V be the potential energies of the particle respectively. Then its kinetic energy (T) is given by

$\left\langle \because E = T + V \right.$
$\left. \text{Tot Energy} = \text{K.E} + \text{P.E} \right\rangle$

$$T = E - V$$

$$\frac{1}{2} m v^2 = E - V$$



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$$\frac{m^2 v^2}{2m} = (E-V) \quad (or)$$

$$m^2 v^2 = 2m(E-V) \longrightarrow (8)$$

Substituting eqⁿ (8) in (7) we get,

$$\nabla^2 \psi + \left[\frac{4\pi^2}{h^2} \times 2m(E-V)\right] \psi = 0 \quad (or)$$

$$\therefore \boxed{\nabla^2 \psi + \left[\frac{8\pi^2 m}{h^2}(E-V)\right] \psi = 0} \longrightarrow (9)$$

Equation (9) is known as Schrodinger time independent wave equation.

Substituting $\hbar = \frac{h}{2\pi}$ in eqⁿ (9), the Schrodinger wave equation can be written as,

$$\nabla^2 \psi + \frac{2m}{\left(\frac{h^2}{4\pi^2}\right)}(E-V)\psi = 0 \quad (or)$$

$$* \therefore ** \boxed{\nabla^2 \psi + \frac{2m}{\hbar^2}(E-V)\psi = 0} \longrightarrow (10)$$

Case(i) :- (For a Free Particle)

For a free particle P.E $V=0$, hence the Schrodinger wave equation for a free particle can be expressed as

For a free particle $\boxed{\nabla^2 \psi + \frac{2mE}{\hbar^2}\psi = 0} \longrightarrow (11)$



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Case (ii) :- <Operator Form>

Equation (10) can be written as,

$$\nabla^2\psi = -\frac{2m}{\hbar^2}(E-V)\psi \quad \text{(or)}$$

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

$$\left[-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right] = E\psi \quad \text{(or)}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi \longrightarrow (12)$$

(or)

$$** \quad \therefore \boxed{H\psi = E\psi} \longrightarrow (13)$$

is the operator form of Schrodinger time independent wave equation.

where, $H = -\frac{\hbar^2}{2m}\nabla^2 + V$ is the Hamiltonian operator

& $E$ = is the total energy operator

$\psi$ = is the wave function

# Physical significance of the wave function $\psi$ :-

<Born's Interpretation of the wave function>

The wave function $\psi$ - which is a solution of Schrodinger's equation has no physical meaning. It is a mathematical tool and is a complex quantity. $\psi^*$ is the complex conjugate of $\psi$.

Max Born suggested a new idea about the



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physical significance of $\psi$.

According to Max Born $\psi\psi^* = |\psi|^2$ gives the probability of finding the particle in the state $\psi$. i.e., $\psi^2$ is a measure of "probability density".

The probability of finding a particle in volume $d\tau = dxdydz$ is given by

$$|\psi|^2 d\tau = |\psi|^2 dxdydz$$

Now, the total probability of finding the particle is unity.

i.e., $$\boxed{\int_{-\infty}^{+\infty} |\psi|^2 dxdydz = 1} \longrightarrow (1)$$

This is known as normalization condition.

The wave function "$\psi$" must fulfil the following Requirements :-

(i). The wave function should be continuous everywhere.

(ii). The wave function should be single valued everywhere.

(iii). The wave function should be finite everywhere.

(iv). The first derivatives of the wave function with respect to space - that is $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ & $\frac{\partial\psi}{\partial z}$ should be continuous and single valued everywhere.



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# Particle in a one Dimensional potential Box:-

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(Infinite Squarewell potential)

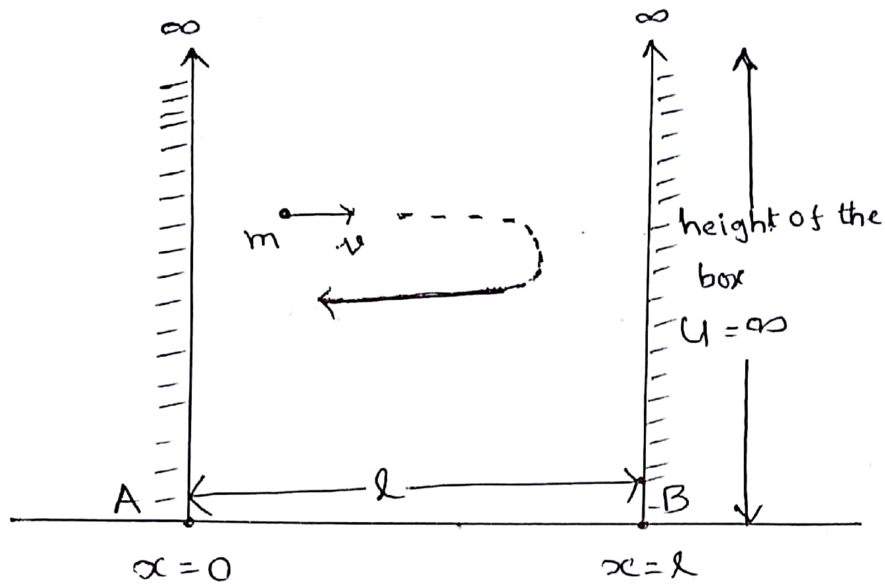


Fig (a):- One-dimensional potential well of infinite depth

Let us consider a particle of mass 'm' moving along x-axis between the two rigid walls A and B at $x = 0$ and $x = l$ as shown in fig (a).

The particle is free to move between the walls. Hence, inside the box we can take $V = 0$.

we have Schrodinger equation.

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \longrightarrow (1)$$

as potential energy $V = 0$ inside the box, along x-direction, eq$^n$ (1) reduces to,



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

Solution of equation (2) is,

$$\psi = A \sin\left(\frac{\sqrt{2mE}}{\hbar}\right)x + B\cos\left(\frac{\sqrt{2mE}}{\hbar}\right)x \longrightarrow (3)$$

where, A & B are constants

height of the box is $U=\infty$, the particle can not exist in the region $x \leq 0$ & $x \geq l$, since in this region $\psi$ is zero.

Boundary Condition :-

$\therefore \psi = 0$ for $x = 0$ & $x = l$ $\longrightarrow (4)$

is the boundary condition

Applying 1st condition (i.e., $x=0$), eq$^n$ (3) becomes,

at $x=0$ ; $\psi = 0$

$$\therefore 0 = A \cdot 0 + B \cdot \cos 0^\circ$$

$$\therefore \boxed{B = 0} \longrightarrow (5)$$

putting this value in eq$^n$ (3), we get

$$\psi = A\sin\left(\frac{\sqrt{2mE}}{\hbar}\right)x \longrightarrow (6)$$

Now applying 2nd condition,

i.e., $\psi = 0$ at $x = l$

eq$^n$ (6) $\Rightarrow$ $0 = A \sin\left(\frac{\sqrt{2mE}}{\hbar}\right)l$ (or)



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$$\sin\left(\frac{\sqrt{2mE}}{\hbar}\right)l = 0 \quad \text{(or)}$$

$$\left(\frac{\sqrt{2mE}}{\hbar}\right)l = n\pi \longrightarrow (7)$$

$n = 1, 2, 3, \ldots$ (or)

$$\left(\frac{2mE}{\hbar^2}\right)l^2 = n^2\pi^2 \quad \text{(or)}$$

$$\text{**} \quad \therefore \boxed{E_n = \frac{n^2\pi^2\hbar^2}{2ml^2}} \longrightarrow (8)$$

$n = 1, 2, \ldots$

These are the eigen values and correspond to the energies of the system.

If $n = 1$,

$$E_1 = \frac{\pi^2\hbar^2}{2ml^2} \longrightarrow (9)$$

If $n = 2$,

$$E_2 = \frac{4\pi^2\hbar^2}{2ml^2} = 4E_1 \longrightarrow (10)$$

If $n = 3$,

$$E_3 = 9\frac{\pi^2\hbar^2}{2ml^2}$$

$$= 9E_1 \longrightarrow (11)$$



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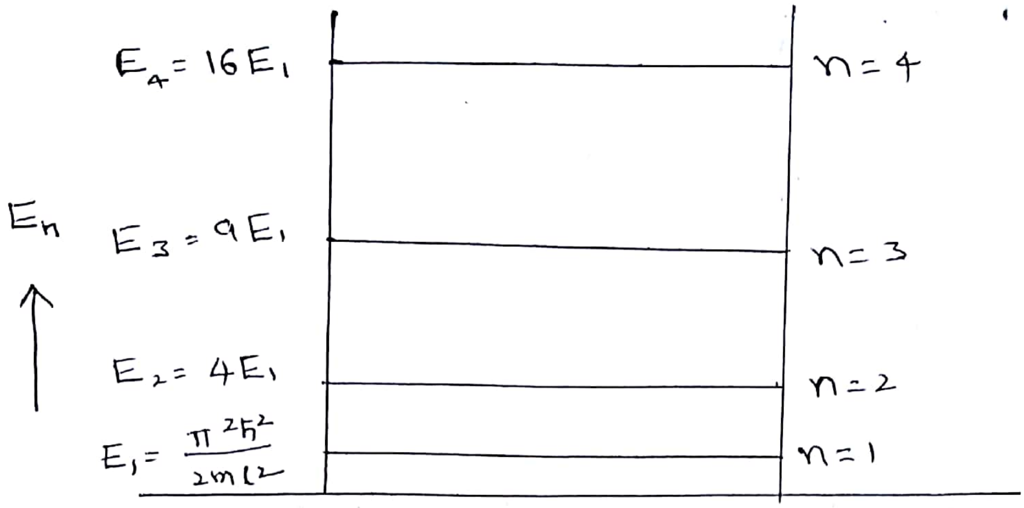
These energy levels are shown in fig (6)

'A'




Fig(6): Energy level diagram of a particle in a box

Eigen Functions :-

From eq$^n$ (6), we have

$$\psi_n = A \sin\left(\frac{\sqrt{2mE_n}}{\hbar}\right)x \longrightarrow 11(a)$$

from (7),

$$\left(\frac{\sqrt{2mE_n}}{\hbar}\right)l = n\pi \quad (or)$$

$$\frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{l} \longrightarrow (12)$$

Making this substitution in 11(a), we get

$$\therefore \boxed{\psi_n' = A \sin\left(\frac{n\pi}{l}\right)x.} \longrightarrow (13)$$



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'A' can be calculated from normalization condition,

$$\int_{-\infty}^{+\infty} |\psi_n|^2 dx = 1 \qquad \left( \because \int_{-\infty}^{+\infty} |\psi|^2 d\tau = 1 \right)$$

$x = 0$ & $x = l$ as particle move b/w 0 to $l$

$$\int_{x=0}^{x=l} |\psi_n|^2 dx = 1 \quad \text{(or)}$$

$$\int_{x=0}^{l} \left| A \sin\left(\frac{n\pi}{l}\right)x \right|^2 dx = 1 \quad \text{(or)}$$

$$\int_{x=0}^{l} \left[ A^2 \sin^2\left(\frac{n\pi}{l}\right)x \right] dx = 1$$

on simplification, we get

$$\therefore \boxed{A = \sqrt{\frac{2}{l}}} \longrightarrow (14)$$

Substituting this value in (13) we get

$$\therefore \boxed{\psi_n = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi}{l}\right)x} \longrightarrow (15)$$

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

Equation (15) represents the wave functions for a particle in a box.

These wave functions are shown in fig (c)



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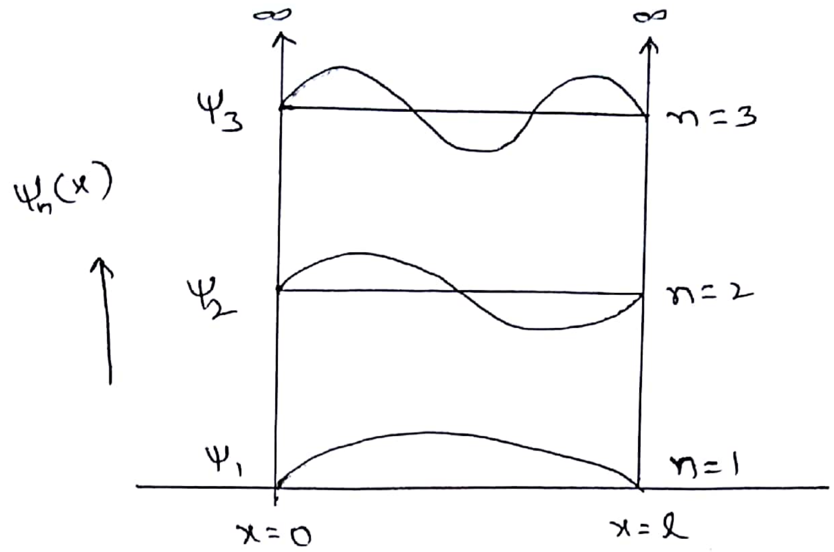


Fig (c)

Problem :-

① . An electron is bound in one-dimensional box of size $4 \times 10^{-10}$ m. What will be its minimum energy? ⟨2003, 2004⟩

Imp

Solution :- The possible energies of a particle in a one dimensional box of size 'l' is given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ml^2} \quad (\text{or}) \quad \left(\because \hbar = \frac{h}{2\pi}\right)$$

$$= \frac{n^2 \cancel{\pi^2} h^2}{2ml^2 \, 4\cancel{\pi^2}}$$

$$\therefore \boxed{E_n = \frac{n^2 h^2}{8ml^2}} \longrightarrow (1)$$

with n = 1, 2, ...

For minimum energy,

$n = 1$



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hence, $E_1 = \dfrac{h^2}{8ml^2} \longrightarrow (2)$

with, $h = 6.626\times10^{-34}$ joul-sec

$m = 9.1\times10^{-31}$ kg

$l = 4\times10^{-10}$ m (given)

$$\therefore E_1 = \frac{(6.626\times10^{-34})^2}{8\times9.1\times10^{-31}\times(4\times10^{-10})^2} \text{ jouls}$$

$$\therefore \boxed{E_1 = 0.346\times10^{-18} \text{ joules}} \quad \text{(Ans)} \rightarrow (3)$$

(2). An electron is bound in one-dimensional infinite well of width $1\times10^{-10}$ m. Find the energy values in the ground state and first two excited states. <2003, 2004, 2005>

Imp

Solution:- we have, $E_n = \dfrac{n^2h^2}{8ml^2} \rightarrow (1)$

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

For ground state $n = 1$ $E_1$

for first 2 excited states $n = 2$ & $n = 3$

with $h = 6.626\times10^{-34}$ J-sec

$m = 9.1\times10^{-31}$ kg

$l = 1\times10^{-10}$ m (given)

$\therefore$ Energy in the ground state

$$E_1 = \frac{(6.626\times10^{-34})^2}{8\times9.1\times10^{-31}\times(1\times10^{-10})^2} \approx 0.6031\times10^{-17} \text{ joules}$$

$\rightarrow$ (2) (Ans)



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Energy of the first excited state

$$E_2 = n^2 \left(\frac{h^2}{8ml^2}\right)$$

$$= 2^2 \left(0.6031\times10^{-17} \text{ joules}\right)$$

$$\therefore \boxed{E_2 = 2.4124\times10^{-17} \text{ joule}} \quad (\text{Ans}) \longrightarrow 3$$

Energy of second excited state

$$E_3 = 3^2 \left(0.6031\times10^{-17} \text{ joules}\right)$$

$$\therefore \boxed{E_3 = 5.428\times10^{-17} \text{ joule}} \quad (\text{Ans}) \longrightarrow 4$$

Imp

3. An electron is moving under a potential field of 15KV. Calculate the wavelength of the electron waves. (2001, 2003)

Sol:- de Broglie wavelength $\lambda = \frac{12.26}{\sqrt{V}}\ A^\circ$

$$= \frac{12.26}{\sqrt{15000}}\ A^\circ$$

$$= \frac{12.26}{122.47}\ A^\circ$$

$$= 0.1\ A^\circ$$

$\therefore$ Wavelength of the electron waves

$$\therefore \boxed{\lambda = 0.1 A^\circ} \longrightarrow 5$$



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4. Electrons are accelerated by 344 Volts and are reflected from a crystal. The first reflection maximum occurs when the glancing angle is 60°. Determine the spacing of the crystal. ⟨2004⟩

Imp

Sol:- we have $\lambda = \frac{12.26}{\sqrt{V}}$ A°

$= \frac{12.26}{\sqrt{344}}$ A°

$\lambda = 0.661 \times 10^{-10}$ m $\rightarrow$ (1)

According to Bragg's law,

$2d \sin\theta = n\lambda \longrightarrow$ (2) $\Rightarrow \boxed{d = \frac{n\lambda}{2\sin\theta}}$

For first order reflection maximum $n = 1$

$\sin 60° = 0.866$

$\therefore \quad 2d(0.866) = 1.\lambda$ (or) $(\because$ from (2)$)$

$= 1(0.661 \times 10^{-10}$ m$)$ (or)

$d = \frac{0.661 \times 10^{-10} \times 1}{2 \times 0.866}$ m

$= 0.3816 \times 10^{-10}$ m (or)

$\therefore \boxed{d = 0.3816 \text{ A°}}$ (Ans) $\longrightarrow$ (3)

* * *



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# Black body Radiation - Planck's Law :-

## Quantum Theory of Radiation:

As regards the black body radiation, Wien's formula agrees with experiment only on the shorter wavelength side, but disagrees at longer wavelengths.

On the other hand, Rayleigh - Jeans formula agrees with experiment only on the longer wavelengths side, but miserably fails at shorter wavelengths.

Planck observed that, by making a small modification in Wien's formula, he could derive a formula that agrees perfectly well with experimental results at all wavelengths and at all temperatures.

## Planck's Hypotheses :-

Max Planck in the year 1900 proposed that, " Radiation is by the exchange of energy between atomic systems in discrete amounts of quanta (called photons) and not by continuous way".

The assumptions made by Planck are :-

→ A black body radiator consists of tiny atomic harmonic oscillators.

→ These oscillators cannot emit or absorb energy in a continuous way.



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→ The emission or absorption of energy takes place in discrete amounts called the "Quanta". These quanta of energy are also called the "photons".

Energy of the photon is $\boxed{E = nh\nu}$ → (1)

where, $n$ → is any +ve integer

$\nu$ → is the frequency

$h$ → is the planck's const, $h = 6.63 \times 10^{-34}$ J-sec

Planck formula is,

$$\boxed{e_\lambda = \frac{2\pi c^2 h}{\lambda^5} \cdot \frac{1}{(e^{hc/\lambda KT} - 1)}} \rightarrow (2)$$

where,

$e_\lambda$ → is Monochromatic emissive power of black body radiator

$k$ → is the Boltzmann constant ($k = 1.38062 \times 10^{-23}\ JK^{-1}$)

$T$ → is the absolute temp.

Proof:- In a black body radiating energy at temp ($T$) let there be a total no. of $N$ oscillators. Let the total energy of all these oscillators be $E$. Then the average energy $\bar{E}$ per each oscillator is given by

$$\bar{E} = \frac{E}{N} \rightarrow (3)$$



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Now, among all these N oscillators, let us suppose that,

$N_0$ oscillators have, each one an amount of energy "0" (zero),

$N_1$ oscillators have, " " of energy "$\varepsilon$",

$N_2$ " ", " " of energy "$2\varepsilon$",

⋮

$N_m$ oscillators have, each one an amount of energy "$m\varepsilon$",

⋮

and so on

From these considerations we can say that,

$$N = N_0 + N_1 + N_2 + N_3 + \dots + N_m + \dots \longrightarrow (4)$$

$$E = E_0 + E_1 + E_2 + E_3 + \dots + E_m + \dots \quad (\text{or})$$

$$E = (N_0 \times 0) + (N_1 \times \varepsilon) + (N_2 \times 2\varepsilon) + (N_3 \times 3\varepsilon) + \dots$$
$$\dots + (N_m \times m\varepsilon) + \dots \longrightarrow (5)$$

According to Maxwell-Boltzmann distribution law,

we have $$N_m = N_0 e^{-m\varepsilon/kT} \longrightarrow (6)$$

$m = 0, 1, 2, \dots$

$$\left.\begin{aligned} \text{If } m=0,\quad & N_0 = N_0 (e^{-0\varepsilon/kT}) = N_0 \\ m=1,\quad & N_1 = N_0 e^{-\varepsilon/kT} \\ m=2,\quad & N_2 = N_0 . e^{-2\varepsilon/kT} \end{aligned}\right\} \rightarrow 6(a)$$

$$m=3,\quad N_3 = N_0 . e^{-3\varepsilon/kT}$$

⋮

Substituting eq$^n$ 6(a) in (4),



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Equation ④ yields,

$$N = N_0 + N_0 e^{-\varepsilon/kT} + N_0 e^{-2\varepsilon/kT} + N_0 e^{-3\varepsilon/kT} + \dots + N_0 e^{-m\varepsilon/kT} + \dots \quad (or)$$

$$= N_0 \left[ 1 + e^{-\varepsilon/kT} + e^{-2\varepsilon/kT} + \dots + e^{-m\varepsilon/kT} + \dots \right] \quad (or)$$

$$* \therefore \boxed{N = \frac{N_0}{(1 - e^{-\varepsilon/kT})}} \longrightarrow ⑦$$

Substituting eq^n 6(a) in ⑤, we get

$$E = (N_0 \times 0) + (N_0 e^{-\varepsilon/kT} \cdot \varepsilon) + (N_0 \cdot e^{-2\varepsilon/kT} \cdot 2\varepsilon) + \dots + (N_0 e^{-m\varepsilon/kT} \cdot m\varepsilon) + \dots \quad (or)$$

$$= 0 + N_0 e^{-\varepsilon/kT} \left[ \varepsilon + 2\varepsilon \cdot e^{-\varepsilon/kT} + \dots + m\varepsilon \cdot e^{-(m-1)\varepsilon/kT} + \dots \right] \quad (or)$$

$$= N_0 e^{-\varepsilon/kT} \cdot \varepsilon \left[ 1 + 2 e^{-\varepsilon/kT} + \dots + m e^{-(m-1)\varepsilon/kT} + \dots \right] \quad (or)$$

$$* \therefore \boxed{E = N_0 \cdot \varepsilon \cdot e^{-\varepsilon/kT} \left[ \frac{1}{(1 - e^{-\varepsilon/kT})^2} \right]} \longrightarrow ⑧$$

Now substituting eq^n's ⑦ & ⑧ in eq^n ③ we get,

$$\bar{\varepsilon} = \frac{E}{N} = \frac{N_0 \varepsilon e^{-\varepsilon/kT}}{(1 - e^{-\varepsilon/kT})^2} \times \frac{(1 - e^{-\varepsilon/kT})}{N_0} \quad (or)$$

$$\bar{\varepsilon} = \frac{\varepsilon}{e^{\varepsilon/kT} - 1} \quad (or) \quad \langle \because \varepsilon = h\nu \rangle$$

∴ Avg. energy of each oscillator is,

$$* \therefore \boxed{\bar{\varepsilon} = \frac{h\nu}{(e^{h\nu/kT} - 1)}} \longrightarrow ⑨$$



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From Rayleigh - Jeans formula, we have, No. of oscillators per unit volume in the wavelength region $\lambda$ & $\lambda + d\lambda$ is

$$df = \frac{8\pi}{\lambda^4}\, d\lambda \longrightarrow (10)$$

Now, the total radiant energy per unit volume within the wavelength range $\lambda$ & $\lambda + d\lambda$ as

$$\psi_\lambda \cdot d\lambda = (9) \times (10)$$

$$= \bar{E} \times df = \frac{h\nu}{(e^{h\nu/kT} - 1)} \times \frac{8\pi}{\lambda^4}\, d\lambda \qquad \left\langle \because \; \begin{array}{l} c = \nu\lambda \\ \nu = \frac{c}{\lambda} \end{array} \right\rangle$$

$$\psi_\lambda \cdot \cancel{d\lambda} = \frac{hc}{\lambda(e^{hc/\lambda kT} - 1)} \times \frac{8\pi}{\lambda^4}\, \cancel{d\lambda}$$

**

$$\therefore \boxed{\psi_\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{(e^{hc/\lambda kT} - 1)}} \longrightarrow (11)$$

where, $\psi_\lambda \rightarrow$ is the Energy density

But, we have Monochromatic emissive power $(e_\lambda)$ is

$$e_\lambda = \frac{c}{4} \times \text{Energy density}$$

Hence,

$$e_\lambda = \left[\frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1}\right] \cdot \frac{c}{4}$$

**

$$\therefore \boxed{e_\lambda = \frac{2\pi c^2 h}{\lambda^5} \cdot \frac{1}{(e^{hc/\lambda kT} - 1)}} \longrightarrow (12)$$

Either of these two Eq$^n$'s (11) (or) (12) is known as 'Planck's Eq$^n$' for spectral Energy distribution of a black body radiation.



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# Photo Electric Effect :-

The emission of electrons from a metal surface when illuminated by light of sufficiently high frequency is called "photo electric Effect". The electrons ejected out from the metal surface are called "photo electrons" and they constitute the "photoelectric current".

## Experimental Study of photoelectric Effect :-

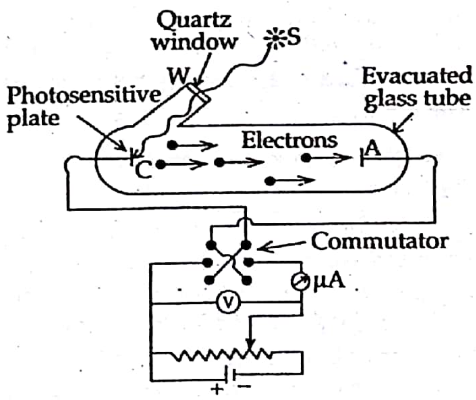


Fig (a)

It consists of an evacuated tube of glass (or) quartz, having a photosensitive metal plate "C", and another metal plate A. Monochromatic light radiation of sufficiently high frequency passes through the window W and falls on C. C acts as the cathode or emitter. The photo electrons emitted out from C are collected by the plate A which serves as anode and is called the collector.



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The potential difference between C & A can be varied by a rheostat. The commutator in the circuit allows us to invert the direction of the potential difference between C and A. The emission of photoelectrons out of C gives rise to a flow of current in the outer ckt. This photo current is measured by the microammeter μA.

Light of different wavelengths can be used by placing appropriate filters in the path of light incident on the emitter "C". The intensity of incident light can be changed by varying the distance of the light source "S" from the emitter.

(1). Effect of Intensity of Incident Light on the photoelectric current :-

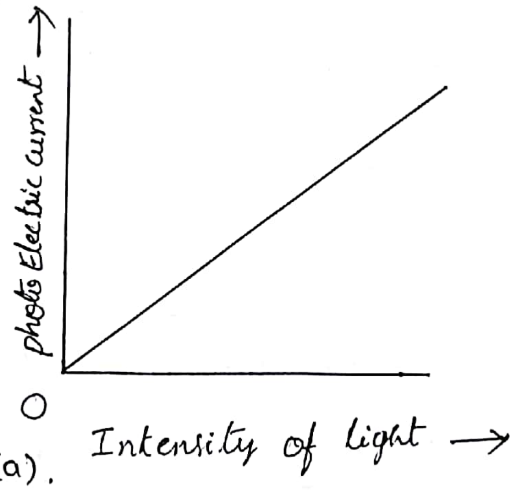


Fig (a).

The photoelectric current increases linearly with increase in the intensity of incident light.

(2). Effect of potential on photoelectric current :-



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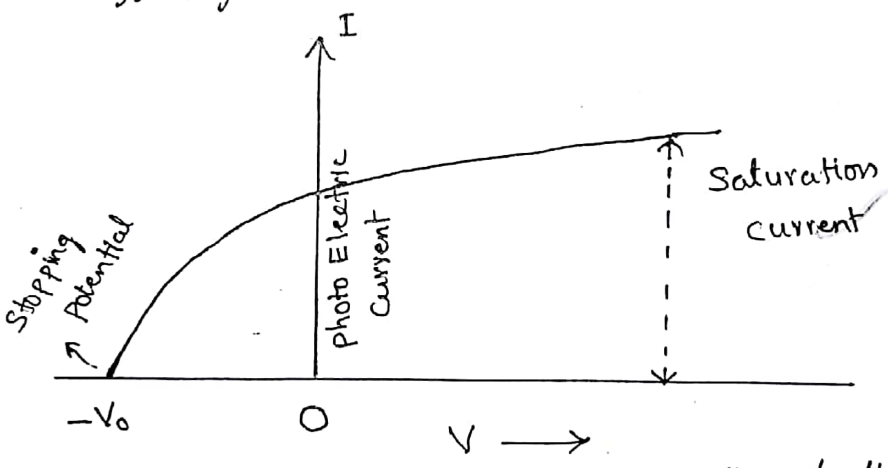
(a). Collector (A) at +ve potential relative to emitter (C):-

In this case photo current gradually increase with increase of the potential and reaches a (max.) saturation value. (see fig ↓)

(b). Collector (A) at -ve potential relative to Emitter (C):-

In this case, as we gradually increase this potential (-ve potential can be achieved with help of commutator), the photoelectric current decreases rapidly and becomes zero at a certain -ve potential "$-V_0$". This potential is called "Stopping potential ($V_0$)" or the "cut off potential.




Fig(b):- Variation of photo current (I) with potential (V)

(3). Effect of Intensity of incident light on photo current:-

The value of saturation current increases with increase in intensity of incident light.



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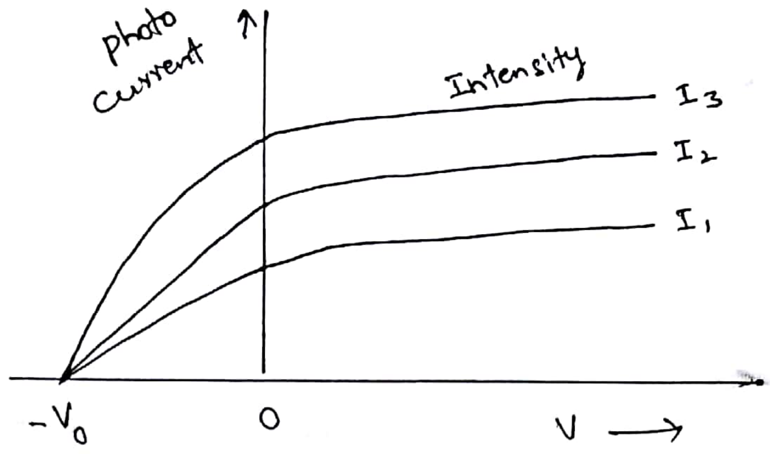


Fig (c)

From the fig (c), It is clear that, the stopping potential ($V_0$) does not depend on the intensity of incident light.

(4). Effect of Frequency of incident light on photo current :-

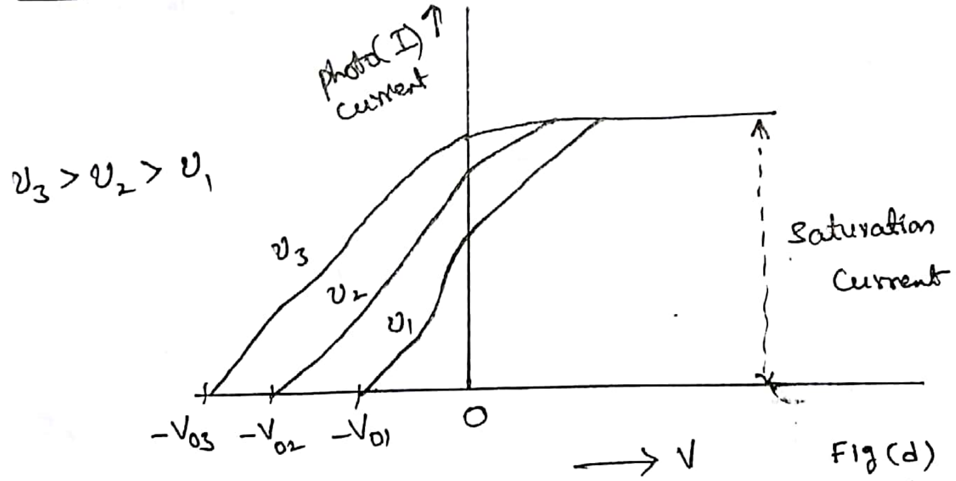


Fig (d)

→ The value of the stopping potential ($V_0$) will be different for different frequencies of incident light.

→ The value of the saturation photo electric current is the same for different frequencies of incident light.

(5). Variation of stopping potential with frequency of incident light :-



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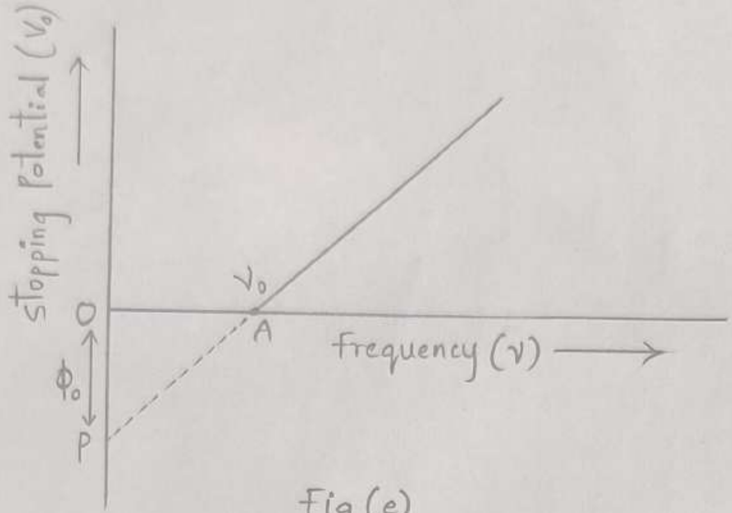



Fig (e)

From fig it is clear that only when $\nu = \nu_0$ do we get the photo electrons emitted from the surface. " This minimum Value of frequency ($\nu_0$) to get photo electrons emitted from a metal surface is called the "threshold Frequency" of the given metal.

$$\nu_0 = \frac{c}{\lambda_0} \text{ ——— } ①$$

$\lambda_0 \rightarrow$ is called "threshold wavelength"

The intercept OP on the Y-axis gives the minimum energy of the incident light required to release photo electrons from the given metal. This is called the "work function' ($\phi_0$)" of the given metal.

## Einstein's photoelectric Equation

Einstein's photoelectric equation is,

$$\therefore \boxed{h\nu = \phi_0 + k.E_{max}} \text{ ——— } ②$$

Where,

$\phi_0 = h\nu_0 = \frac{hc}{\lambda_0}$ is the work function of metal

$k.E_{max} = \frac{1}{2} m v_{max}^2$ is the k.E of the photo $e^{-1}$'s

$V_{max}$ is the max Velocity of the photo $e^{-1}$'s.

Wein's law (shorter wave length)

$\nu$ is large, $\left(\frac{h\nu}{KT}\right) >> 1$

$$e^{h\nu/KT} - 1 \cong e^{h\nu/KT}$$

According to planck's law,

$$E(\nu) = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/KT} - 1}$$

$$E(\nu) = \frac{8\pi h\nu^3}{c^3} \cdot e^{-h\nu/KT}$$

The above eq$^n$ represents wein's law

Rayleigh - Jeans law (longer wave length)

$\nu$ is small, $\left(\frac{h\nu}{KT}\right) << 1$

$$e^{h\nu/KT} - 1 \cong \frac{h\nu}{KT}$$

According to planck's law

$$E(\nu) = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/KT} - 1}$$

$$E(\nu) = \frac{8\pi \cancel{h}\nu^{\cancel{3}}}{c^3} \cdot \frac{KT}{\cancel{h\nu}}$$

$$E(\nu) = \frac{8\pi\nu^2 KT}{c^3}$$

The above eq$^n$ represents Rayleigh - Jeans law.

stefan - Boltzmann Law

According to stefan - Boltzman law area of energy spectrum in a black body is directly proportional to fourth power of temperature

$$E \propto T^4$$

$$E = \sigma T^4$$

$\sigma \rightarrow$ stefan Boltzman Constant

$= 5.673 \times 10^{-8}\ W/m^2 K^4$

# SOLIDS

## Free electron theory:-

Classical Free Electron Theory of Metals:- (Drude and Lorentz).

1. This theory was developed by Drude and Lorentz.
2. In this theory, the free electrons in a metal are treated like molecules in a gas and Maxwell-Boltzmann statistics is applied.

Assumptions:-

1. A metal is composed of positive metal ion fixed in the lattice.
2. All the valence electrons are free to move among the ionic array. such freely moving electrons contribute towards conduction (electrical and thermal) in metals.
3. There are a large number of free electrons in a metal and they move about the whole volume like the molecules of a gas.
4. The free electrons collide with the positive ions in the lattice and also among themselves; all the collisions are elastic so there is no loss of energy.
5. The electrostatic force of attraction between the free electrons and metallic ions are neglected, i.e., the total energy of free electron is equal to its kinetic energy.

6. All the free electrons in metal have wide range of energies and velocities.
7. In the absence of electric field, the random motion of free electron is equally probable in all directions, so, the net current flow is zero.

Merits:-

1. It verifies ohm's law.
2. It explains the thermal and electrical conductivities of metals.
3. It explains the optical properties of metals.

Demerits:-

1. The theoretical value obtained for specific heat and electronic specific heat of metals based on this theory is not in aggrement with the experimental value.
2. The classical free electron theory is not able to explain the electrical conductivity of semiconductors and insulators.
3. The theoretical value of paramagnetic susceptibility is greater than the experimental value; also, ferromagnetism cannot be explained.
4. The phenomena such as photoelectric effect, compton effect and black body radiation cannot be explained by this theory.

Quantum Free Electron Theory of Metals :- (sommerfeld)

To overcome the drawbacks of the classical free electron theory by applying quantum mechanical principles Arnold sommerfeld proposed a new theory in 1928 called quantum free electron theory or sommerfeld theory.

Assumption :-

1. The energy levels of the conduction electrons are quantized.
2. The distribution of electrons in the various allowed energy level occurs as per paulis exclusion principle.
3. The electrons are assumed to posses wave nature.
4. The free electrons are assumed to obey Fermi - Dirac statistics.
5. The electrons are free to move inside the metal, but confined to stay within its boundaries.
6. The potential energy of the electrons and is uniform or constant inside the metal.
7. The attraction between the electrons and the lattice ions, and the repulsion between the electrons themselves are ignored.

Merits :-

Quantum free electrons theory provides explanation for electrical conductivity, thermal conductivity, specific heat capacity of metals, electronic specific heat capacity, compton effect, photo electric effect etc.

Demerits:-

1. This theory fails to make distinction between metals, semiconductors and insultors.
2. It fails to explain the positive value of the hall coefficient and some transport properties of metals.

## Fermi Dirac Distribution

1. The probability to find an electron in an energy state of energy E can be expressed as $F(E) = \dfrac{1}{1+\exp\left(\frac{E-E_F}{K_BT}\right)}$

   Where F(E) is called the Fermi Dirac distribution function.
2. E is the energy level occupied by the electron and $E_F$ is the Fermi level and is constant for a particular system.
3. The Fermi level is a boundary energy level which separates the filled energy states and empty energy states at 0K.
4. The energy of the highest filled state at 0K is called the Fermi energy $E_F$ and the energy level is known as Fermi level.
5. It is shown in Fig. 4.2(a). Fermi-Dirac distribution curve at 0K is shown in Fig. 4.2(b).

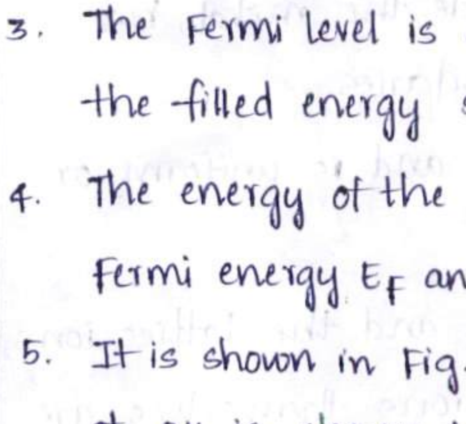


Fig. 4.2(a)

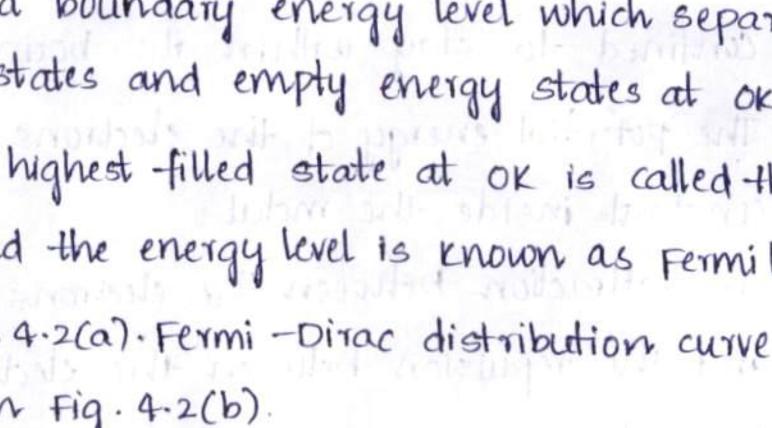


Fig. 4.2(b)

6. At 0K, the Fermi-Dirac distribution of electrons can be understood mathematically from the following two cases,

case (i) If $E > E_F$ then $F(E) = 0$

It indicates that the energy levels above the fermi level are empty.

case (ii) If $E < E_F$ then $F(E) = 1$

It indicates that the energy levels below the fermi level are ~~empty~~. full with electrons.

7. The variation of Fermi-Dirac distribution function with temperature is shown

8. It can be observed that the probability to find an electron decreases below the fermi level and increases above the fermi level as temperature increases. And there exists a two-fold symmetry in the probability curves about the fermi level.

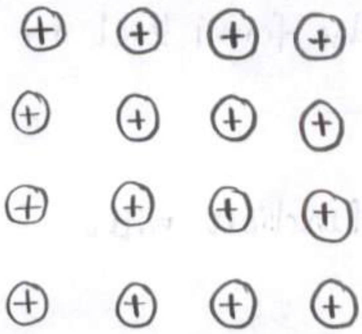
## Electron in periodic potential - Bloch Theorem:-

(Wave $eq^n$ in period potential)

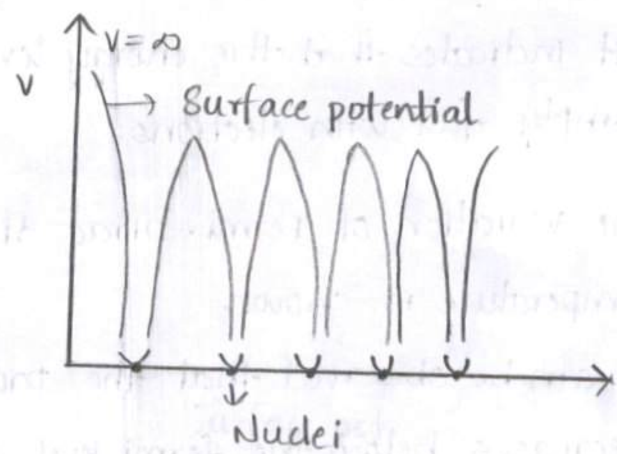
1. In order to consider the motion of an electron in a crystalline solid, we apply schrodinger equation for electrons and find its solution under periodic boundary conditions.
2. The solution of schrodinger equation was modified by scientist Bloch by considering the symmetry properties of the potential in which the electron in a crystalline solid moves.

3. Metals and alloys are crystalline in nature.

4. Instead of considering uniform constant potential (as we have done in free $\bar{e}$ theory), we have to consider the variation of potential inside the metallic crystal with the periodicity of the lattice as shown in fig.(1).



Fig(1):- periodic +ve ion cores inside Metallic crystals




Fig(2): one dimensional periodic potential in crystal.

5. The potential is minimum at the positive ion sites and maximum between the two ions. This is shown in fig.(2).

The one dimensional schrodinger equation corresponding to this can be written as,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0 \longrightarrow (1)$$

The periodic potential $v(x)$ may be defined by means of the lattice constant "a" as,

$$V(x) = V(x+a) \longrightarrow (2)$$

Block has shown that the one dimensional solution of the schrodinger equation ① is of the form,

$$\therefore \boxed{\psi_K(x) = e^{ikx} \cdot U_K(x)} \longrightarrow ③$$

$\because$ Wave vector $K = \frac{2\pi}{\lambda}$

$$\Rightarrow \hbar K = \frac{2\pi}{\lambda} \hbar \ (\text{or}) \ \hbar K = \frac{2\pi}{\lambda} \cdot \frac{h}{2\pi} = \frac{h}{\lambda} = p$$

$$\therefore p = \hbar K \ (\text{or}) \ K = \frac{p}{\hbar} \qquad \left(\because \lambda = \frac{h}{p}\right)$$

where, $K = \frac{p}{\hbar}$

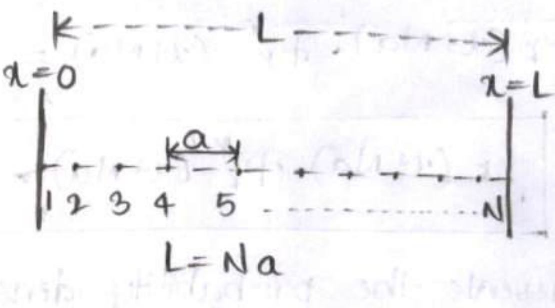
The physical meaning of $K$ is that it represents the momentum of electron divided by $\hbar$.

$U_K(x) \rightarrow$ is the periodic potential function.

In three dimensional form the above equation can be explained as

$$\therefore \boxed{\psi_K(r) = e^{ikr} \cdot U_K(r)} \longrightarrow ④$$

The above two equations ③ and ④ are known as "Bloch functions" in one dimension and three dimensions, respectively.



Let us now consider a linear chain of atoms of length L in one dimensional case with N no. of atoms in the chain. (where N is even) then,

$$\boxed{U_K(x) = U_K(x+Na)} \longrightarrow (5)$$

Where 'a' is the lattice distance

The Bloch-function $\psi_K(x) = e^{ikx} \cdot U_K(x)$ has the property,

$$\psi_K(x+Na) = e^{ik(x+Na)} \cdot U_K(x+Na)$$

$$= e^{ikx} \cdot e^{ikNa} \cdot U_K(x) \quad (\because \text{from } (5))$$

$$= e^{ikNa} \cdot \{e^{ikx} \cdot U_K(x)\}$$

$$\therefore \boxed{\psi_K(x+Na) = e^{ikNa} \cdot \psi_K(x)} \longrightarrow (6) \quad (\because \text{from } (3))$$

This is referred to as "Bloch condition".

~~Kronig - penny Model:~~

Now, the complex conjugate of equation (6) can be written as,

$$\psi_K^*(x+Na) = e^{-ikNa} \cdot \psi_K^*(x) \longrightarrow (7)$$

From equations (6) and (7), we find that

$$\psi_K(x+Na) \cdot \psi_K^*(x+Na) = e^{ikNa} \cdot e^{-ikNa} \cdot \psi_K(x) \cdot \psi_K^*(x)$$

$$\therefore \boxed{\psi_K(x+Na) \cdot \psi_K^*(x+Na) = \psi_K(x) \cdot \psi_K^*(x)} \longrightarrow (8)$$

represents the probability density $|\psi_K(x)|^2$ of the electron.

here, $e^{ikNa} = 1$

i.e., $kNa = 2\pi n$ (or)

$k = \frac{2\pi n}{Na}$ (or)

$\therefore \boxed{k = \frac{2\pi n}{L}}$ $(\because Na = L)$ $\longrightarrow$ (9)

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

$\because e^{ikNa} \cdot e^{-ikNa} = 1$ (or)

$\frac{e^{ikNa} + e^{-ikNa}}{2} = 1$ (or)

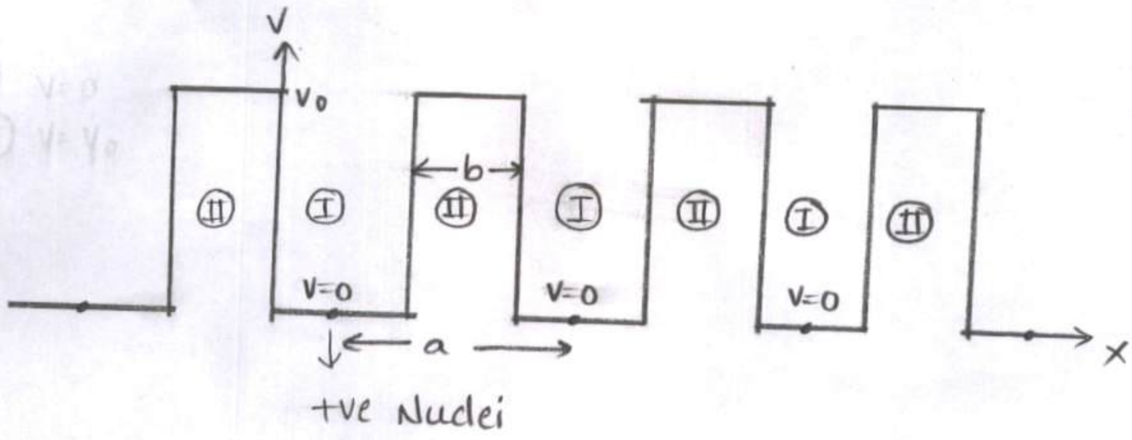
$\sin kNa = 1$

$\therefore kNa = 2\pi n$

$\left(\because \frac{e^{ix} + e^{-ix}}{2} = \sin x\right)$

Where L is the length of the chain of atoms.
Here $k=0$ is excluded as it corresponds to all the atoms at rest.

Kronig - penny Model:-




Region - I :- $V = 0$

Region - II :- $V = V_0$

1. This model illustrate behaviour of an electron in periodic potential.
2. The potential consists of infinite row of rectangular potential wells seperated by barrier width 'b' with space periodicity 'a'.
3. In this model it is assumed that P.E $(V=0)$ of electron is zero of positive ion in the lattice and maximum $(V=V_0)$ between two ions.
4. The schrondinger wave equation for region 'I' is

$$\frac{d^2\psi_1}{dx^2}+\frac{2mE}{\hbar^2}\psi_1=0 \longrightarrow (1) \qquad (V=0)$$

Region 'II' is

$$\frac{d^2\psi_2}{dx^2}+\frac{2m}{\hbar^2}(E-V_0)\psi_2=0 \rightarrow (2) \qquad (V=V_0)$$

5. Here it is assumed that energy 'E' of the electron is smaller than $V_0$. i.e., $E<V_0$ (or) $V_0>E$. so equation (2) becomes

$$\frac{d^2\psi_2}{dx^2}-\frac{2m}{\hbar^2}(V_0-E)\psi_2=0 \rightarrow (3)$$

Let

$$\left.\begin{aligned} \frac{2mE}{\hbar^2}&=\alpha^2 \\ \frac{2m(E-V_0)}{\hbar^2}&=\beta^2 \end{aligned}\right\} \rightarrow (4)$$

where $\alpha, \beta$ are constants.

Now substitute equation ④ in equation ① and ③

$$\frac{d^2\psi_1}{dx^2} + \alpha^2\psi_1 = 0 \rightarrow ⑤$$

$$\frac{d^2\psi_2}{dx^2} - \beta^2\psi_2 = 0 \rightarrow ⑥$$

According to Bloch theorem solution of equation ⑤ and ⑥ is

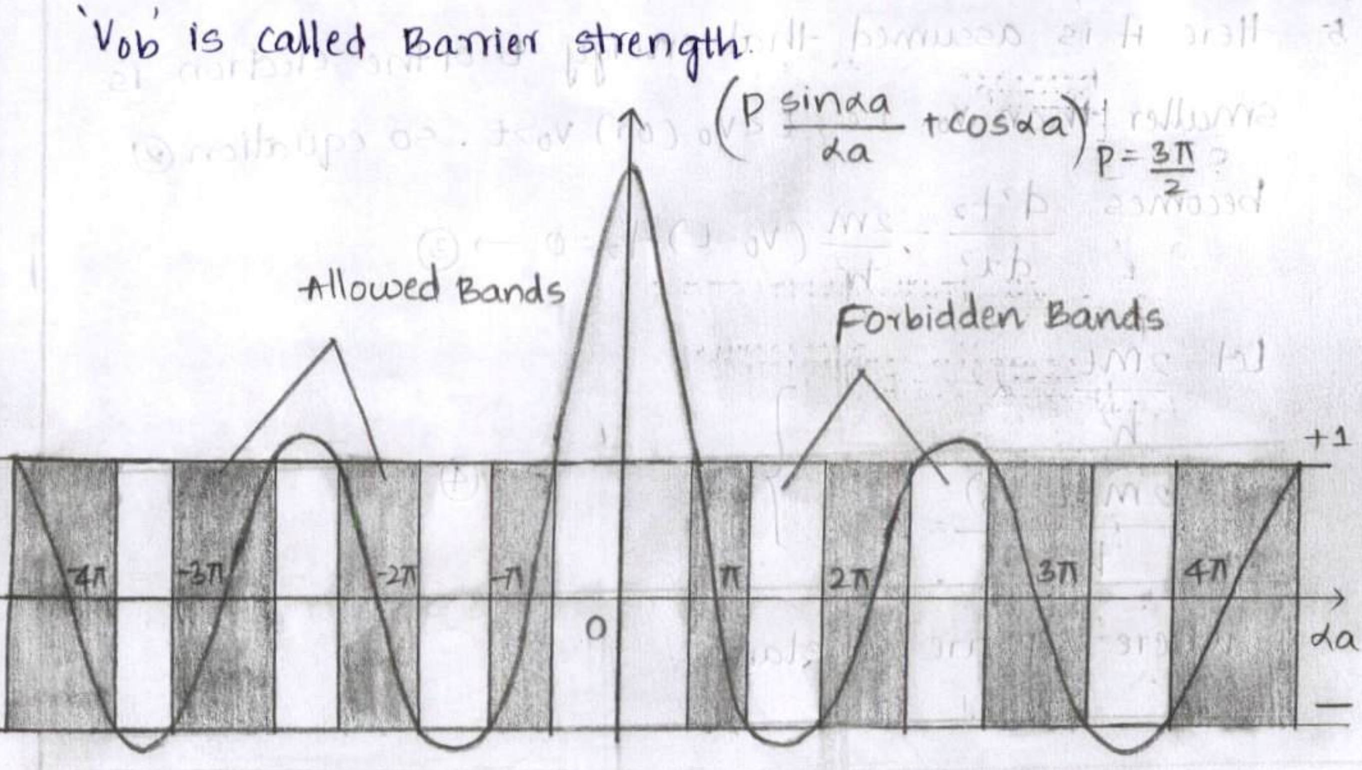
$\psi_K(x) = U_K(x) \cdot e^{iKx} \rightarrow ⑦$ where $U_K(x) = U_K(x+a)$

solving equation ⑤, ⑥ and ⑦ applying boundary conditions and on simplification we get,

$$\frac{mV_0ba}{\hbar^2} \cdot \frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos Ka$$

$$P \cdot \frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos Ka \rightarrow ⑧ \quad \left(\because P = \frac{mV_0ba}{\hbar^2}\right)$$

This 'p' is called scattering power of the potential barrier. '$V_0b$' is called Barrier strength.



The equation ⑧ has solution only when

$p \to 0$ then $\cos \alpha a = \cos ka$

$$\alpha a = ka$$

$$\alpha = k$$

$$\boxed{\alpha^2 = k^2} \longrightarrow ⑨$$

$p \to 0$ then $\sin \alpha a = 0$

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

$$\alpha = \frac{\pm n\pi}{a} = k \longrightarrow ⑩ \quad (\because \text{from } ⑨)$$

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

$$\Rightarrow \quad E = \frac{n^2\pi^2\hbar^2}{2ma^2} \longrightarrow ⑪$$

$$\Rightarrow \quad \boxed{E = \frac{k^2\hbar^2}{2m}} \longrightarrow ⑫$$

This equation represents Energy 'E' is dependent of 'k'

Energy (E) as function of 'p'.

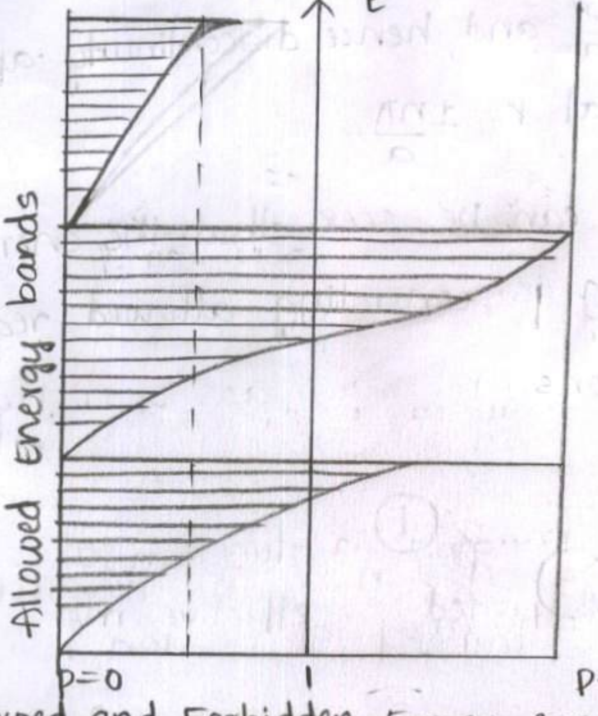


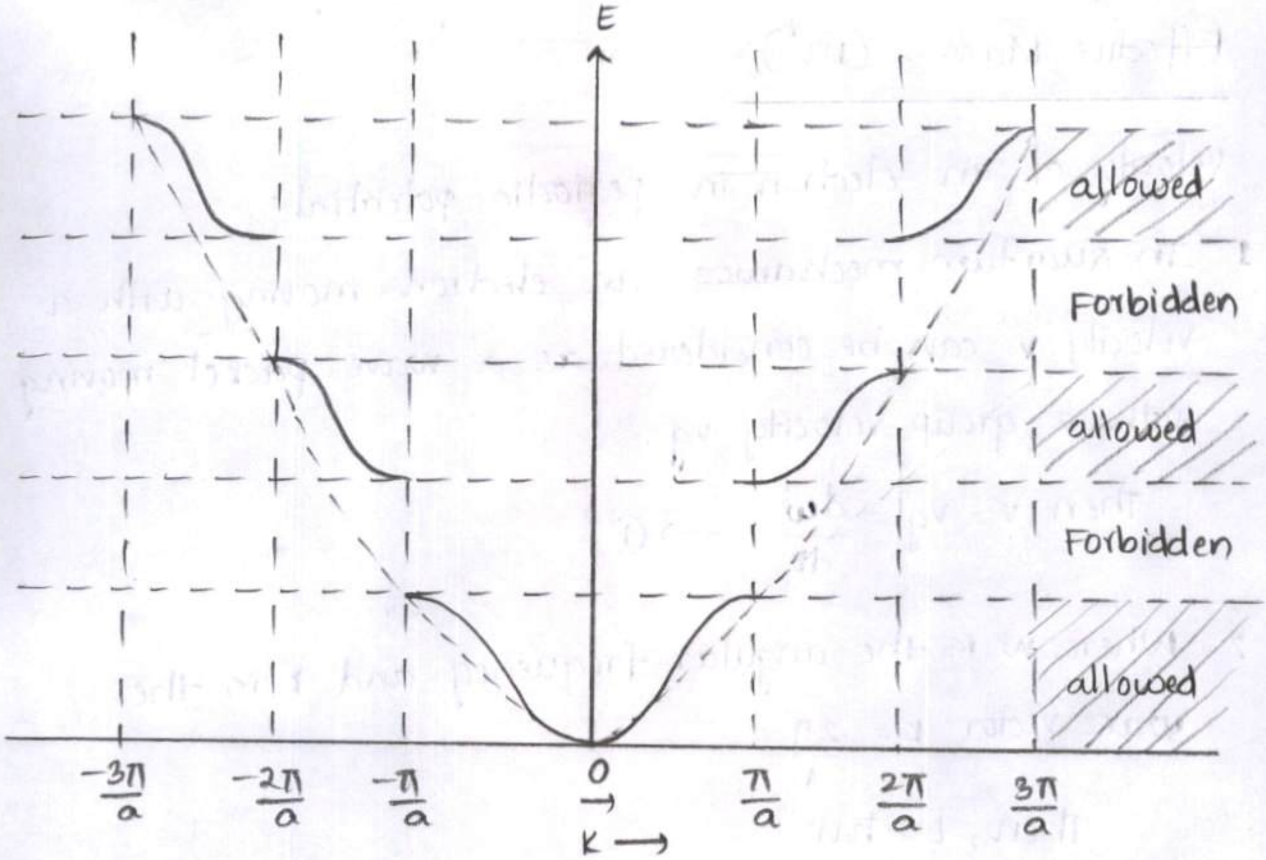

Fig: Allowed and Forbidden Energy Ranges as function of 'p'.

Conclusion:-

1. The energy spectrum consists of number of allowed and energy bands seperated by forbidden bands.
2. The width of allowed energy band Increases with increasing energy (E) values.
3. With Increasing 'P', the width of allowed energy band decreases. For $P \to \infty$, the allowed energy region becomes narrow and the energy spectrum is a line spectrum.

E-K curve :-

1. It is possible to plot a curve showing the energy E as a function of K, which is shown.
2. It is clear from the figure that the energy of electron is continuously increasing from $K=0$ to $\frac{\pi}{a}$.
3. The right-hand side of the equation becomes +1 or −1 for values of $K = \pm\frac{n\pi}{a}$ and hence discontinuity appears in the E-K graph at $K = \pm\frac{n\pi}{a}$.
4. From the graph, it can be seen that the energy spectrum of electron is consisting allowed regions and forbidden regions.




5. The allowed region or zone extended from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$.
6. This is known as first Brillouin zone.
7. After a discontinuity in energy, called forbidden gap, the another allowed region or zone extended from $-\frac{2\pi}{a}$ to $-\frac{\pi}{a}$ and $\frac{\pi}{a}$ to $\frac{2\pi}{a}$.
8. This is known as second Brillouin zone.
9. In the same way further Brillouin zones will be continued.

## Effective Mass :- ($m^*$):-

Velocity of an electron in periodic potential:-

1. In quantum mechanics, an electron moving with a velocity 'v' can be considered as a wave packet moving with a group velocity vg.

Then $v = v_g = \frac{d\omega}{dk} \longrightarrow (1)$

2. Where, w is the angular frequency and k is the wave vector $k = \frac{2\pi}{\lambda}$.

Then, $E = \hbar\omega$

Differentiating w.r.t 'k'.

$$\frac{dE}{dk} = \hbar\frac{d\omega}{dk}$$

$$\frac{1}{\hbar}\frac{dE}{dk} = \frac{d\omega}{dk} = v_g.$$

$$\therefore \boxed{v_g = \frac{1}{\hbar}\frac{dE}{dk}} \longrightarrow (2)$$

Effective mass of an electron:-

1. When an electron in a periodic potential is accelerated by an electric field then the mass of electron varies with velocity.
2. This means that mass is a function of velocity for electron and is termed as effective mass of electron ($m^*$).

3. The acceleration of electron can be taken as rate of change of velocity.

$$a = \frac{dv_g}{dt} \longrightarrow (3)$$

substituting the value of $v_g$ in 'a' we get

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

$$a = \frac{1}{\hbar}\frac{d^2E}{dk^2}\cdot\frac{dk}{dt} \longrightarrow (4)$$

But the momentum of electron, $p = \hbar k$.

Differentiating $\frac{dp}{dt} = \hbar \cdot \frac{dk}{dt}$ (since $\frac{dp}{dt} = F$)

$$\frac{dk}{dt} = \frac{F}{\hbar}$$

substitute $\frac{dk}{dt}$ value in equation (4)

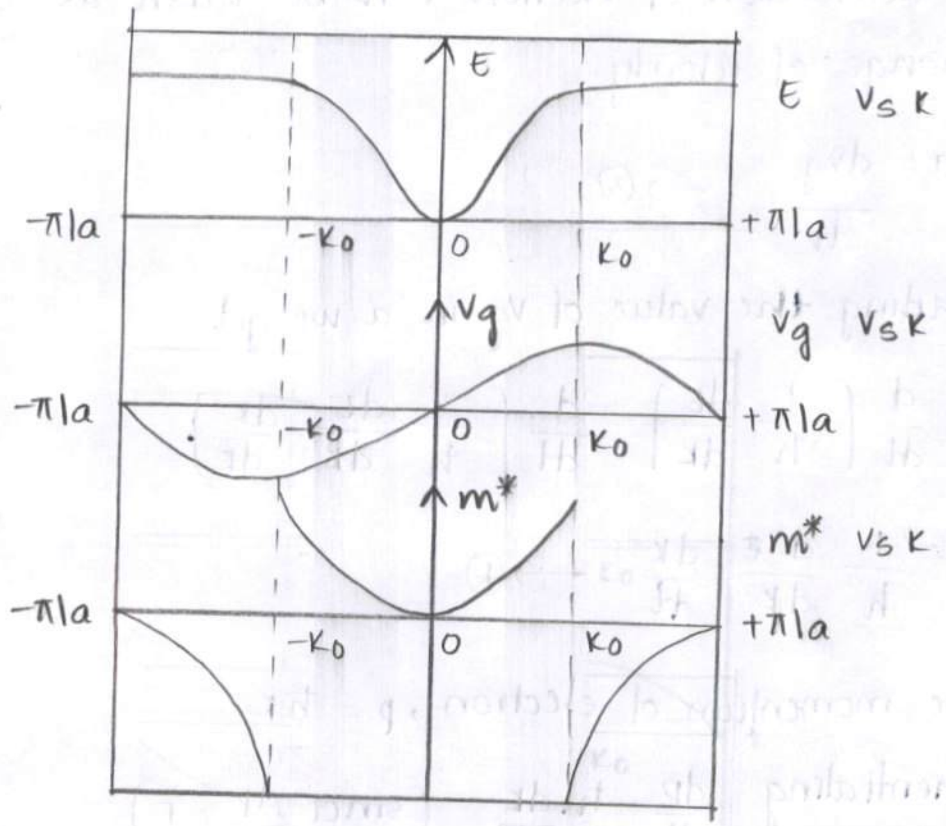
$$a = \frac{1}{\hbar}\frac{d^2E}{dk^2}\cdot\frac{F}{\hbar}$$

$$F = \left[\frac{\hbar^2}{\frac{d^2E}{dk^2}}\right]\cdot a$$

But Force = effective mass of electron $(m^*)$ x acceleration (a)

$$\boxed{m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}}}$$

This shows that the effective mass of electron is a function of k.




From Graph:-

1. Effective mass as a function of K is drawn. It says that $m^*$, is positive at the bottom of the energy band and negative at the top of the band. And it tends to zero as $\frac{d^2E}{dK^2}$ approaches to zero.

2. As the value of K increases the velocity of electron increases and reaches to maximum at $K = K_0$. Further, the increase of K, the velocity of electron decreases and reaches to zero at $K = \pi/a$ i.e., at the top of the band.

3. similarly E Vs K is drawn, using which velocity of electron can be calculated.

Band Theory of solids:-

classification of solids into Metals, semi conductors and Insulators:-

Based on the value of the energy gap (band gap). we can classify the solids into three types:-

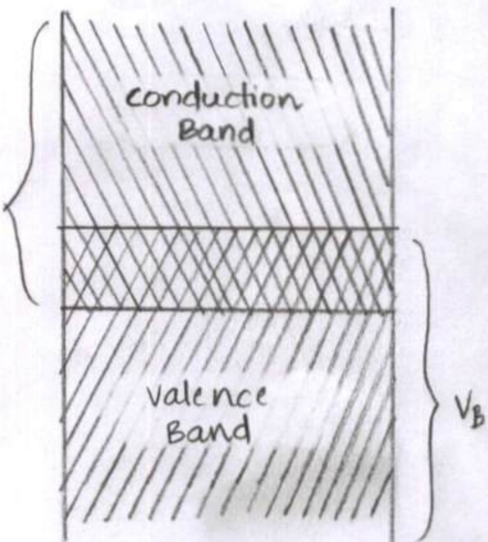
(i). Metals (conductors)

(ii). Semi conductors &

(iii). Insulators.

1 Metals (conductors):-

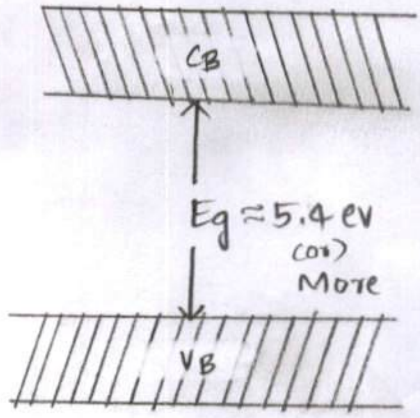
In metals like copper or silver there is no forbidden energy gap between the VB and the CB. These two bands overlap as shown in fig.(a). Hence, the free electrons require very less energy for their movement.



Fig(a)

2. Insulators (Dielectrics):-

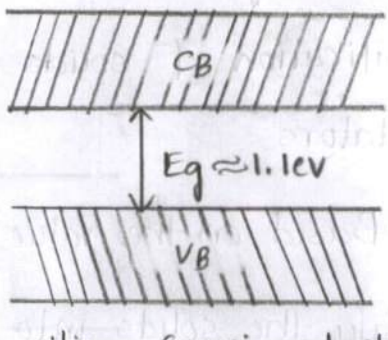
Materials like glass, rubber that do not conduct electricity are called "insulators". The forbidden energy gap for insulator will be quite wide. (5 ev or more) as shown in fig(b).



Fig(b)

3. Semiconductors :-

In the case of a semiconductor like Ge or Si the energy band gap ($E_g$) is not wide. It is quite narrow, of the order of 1eV.




silicon (semi conductor)

Fig(c)

For Germanium $E_g = 0.72 eV$.

For silicon $E_g = 1.12 eV$

Even at room temp, the heat energy will be quite sufficient to raise the electrons from VB to CB. Hence, semiconductors will conduct electric current even at room temperatures.