wave having same frequency and wavelength of original one. Hence resulting wave have periodically varying amplitude $A' = 2A\cos\left(\frac{\Delta K}{2}x - \frac{\Delta\omega}{2}t\right)$ forming the envelopes as shown in fig. below

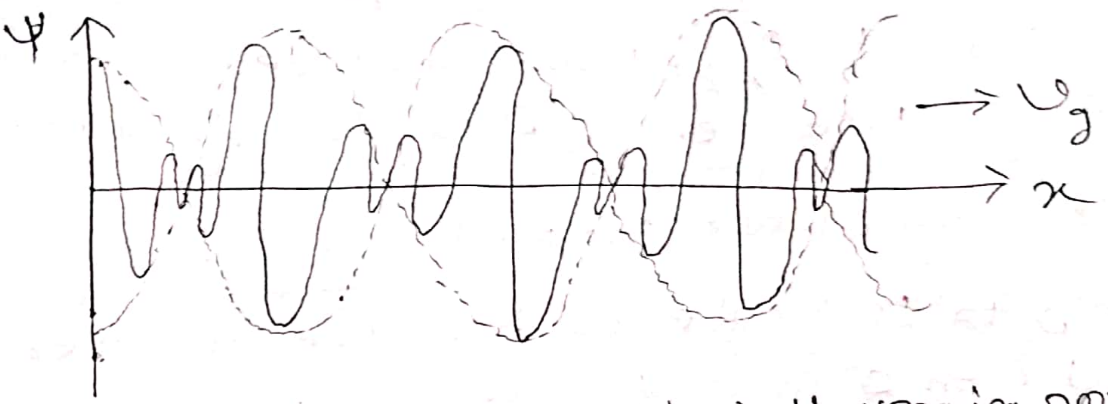


fig. wave with periodically varying amplitude

Such wave 'ψ' could be used to describe a beam of particles, with one particle in each wave packet. The velocity of wave inside the envelopes is same as velocity of individual wave $\left(v = \frac{\omega}{K}\right)$ known as phase or wave velocity. Now, velocity of envelopes or wavepackets (called group velocity) is

$$v_g = \frac{\frac{\Delta\omega}{2}}{\frac{\Delta K}{2}} = \frac{\Delta\omega}{\Delta K} = \frac{d\omega}{dK} \quad \text{(for limmitting value)}$$

$$\therefore v_g = \frac{d(\hbar\omega)}{d(\hbar K)} \quad \left\{ \text{where } \hbar\omega = \frac{h}{2\pi} \times 2\pi f = hf = E \quad \& \quad \hbar K = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \frac{h}{\lambda} = P \right.$$

$$v_g = \frac{dE}{dP}$$

$$\text{or, } v_g = \frac{d}{dP}\left(\frac{P^2}{2m}\right)$$

$$v_g = \frac{1}{2m} \times 2P = \frac{P}{m} = \frac{m v_{particle}}{m} = v_{particle} \Rightarrow \boxed{v_g = v_{particle}}$$

which shows that wave packet moves along with particle.

The salient feature of this graph is, greater the range of 'K' being mixed, the narrower the resulting wave packet. In fig. (2) 'ψ' contains only one 'K', the wave has well defined wavelength (λ) and momentum ($p = \frac{h}{\lambda}$). Also amplitude is same for all points in space i.e. particle completly unlocalized.

Velocity of wave packet (Group velocity) v_g :

According to De-Broglie, each particle of matter is associated with a group of wave differ slightly wavelength and frequency called wave packet. Velocity of such wave-packet is called group velocity. Let us consider two travelling waves of particle

$$\psi_1 = A\sin(Kx - \omega t) \quad \text{--- (1)} \quad \text{and}$$

$$\psi_2 = A\sin\{(K+\Delta K)x - (\omega+\Delta\omega)t\} \quad \text{--- (2)} \quad \text{where } \Delta K \ll K, \ \Delta\omega \ll \omega$$

On mixing such two waves, resulting wave is

$$\psi(x,t) = \psi_1 + \psi_2 = A\sin(Kx - \omega t) + A\sin\{(K+\Delta K)x - (\omega+\Delta\omega)t\}$$

$$\text{or, } \psi(x,t) = 2A\cos\left[\frac{(Kx-\omega t) - \{(K+\Delta K)x - (\omega+\Delta\omega)t\}}{2}\right]\sin\left[\frac{(Kx-\omega t) + \{(K+\Delta K)x - (\omega+\Delta\omega)t\}}{2}\right]$$

$$\text{or, } \boxed{\psi(x,t) = 2A\cos\frac{(\Delta Kx - \Delta\omega t)}{2}\sin(Kx-\omega t)} \quad \text{--- (3)}$$

$\sin A + \sin B$
$= 2\cos\frac{A-B}{2}\sin\frac{A+B}{2}$

Also $\cos(-A) = \cos A$

where we use

$2K + \Delta K \simeq 2K$

$2\omega + \Delta\omega \approx 2\omega$

Hence, resulting wave is product of two travelling wave.

The first term of equation (3) represents a wave having larger wavelength ($\lambda = \frac{2\pi}{\Delta K}$) and smaller frequency ($f = \frac{\Delta\omega}{2\pi}$). The second term of (3) represents in wavelength ($\lambda = \frac{2\pi}{k}$) and frequency ($f = \frac{\omega}{2\pi}$) by small amount from previous one. The resultant amplitude becomes function of 'λ' & 'f' i.e. $A(\lambda, f)$. Hence wave packet can be written in integral form as

$$\psi(x,t) = \int_0^\infty \int_0^\infty A(k,\omega) \sin(kx - \omega t)\, dk\, d\omega \qquad (2)$$

Such wave is known as matter wave.

The spatial variation of 'ψ' at $t=0$ when we mix various amounts of sinusoidal waves of different wavelength is shown in fig. (2) below

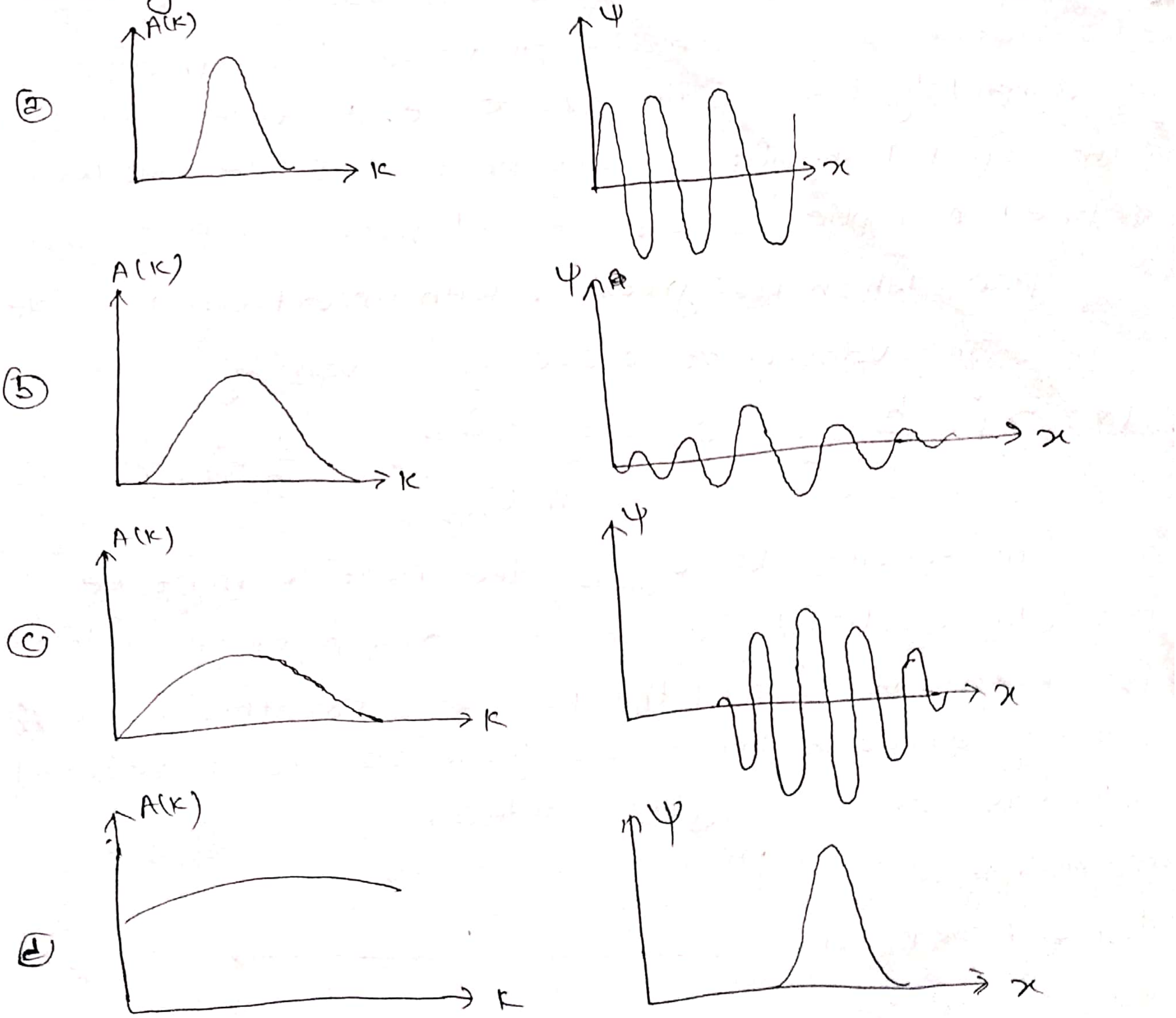


fig. (2) Wave packets obtained by mixing sinusoidal travelling waves.

Matter wave and the uncertainity Principle

The wave propagation of particle can be represented by simple sinusoidal travelling wave function as

$$\psi(x,t) = A\sin(kx-\omega t) \quad — (1)$$

this particular wave has the following properties

1. The amplitude 'A' is same at all points in space
2. It has well defined wavelength, $\lambda = \frac{2\pi}{k}$; 'K' is wave no.
3. It has well defined frequency, $f = \frac{\omega}{2\pi}$; 'ω' is angular frequency
4. It travels along +ve x-axis with velocity $v = \lambda f = \frac{\omega}{k}$

Since 'A' is same for all value of 'x' then particle is completely unlocalized ; $\Delta x = \infty$ i.e. particle can be found with equal probability at any point in space. But well defined 'A' implies a well defined momentum $(p = \frac{h}{\lambda} = \text{Const})$ i.e. $\Delta p = 0$. Which is agreement with uncertainity principle.

The velocity of wave is given by

$$v = \lambda f = \frac{h}{p} \cdot \frac{E}{h} = \frac{E}{p} = \frac{\frac{1}{2} m v^2_{particle}}{m v_{particle}} = \frac{1}{2} v_{particle}.$$

To become $v = v_{particle}$, the particle must be partially localized i.e. in small region of space, there is chance of finding the particle. For this wave of varying amplitude known as wave packet is required which is shown in fig (1) below.

Mathematically Such a wave packet is obtained by mixing large no. of sinusoidal travelling waves like eqn (1). Each of these waves differ

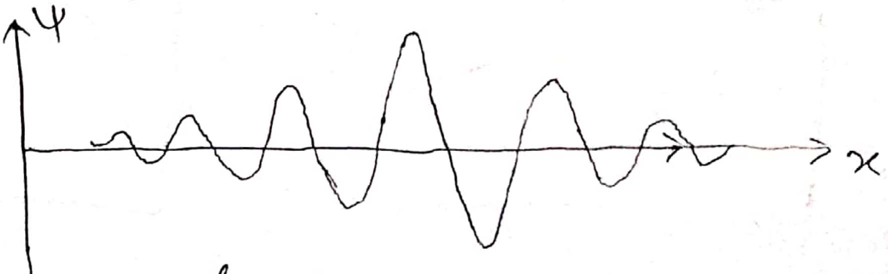


fig. (1) wave packet.

The change in x-component of momentum is

$$\Delta P_x = p\sin\phi - (-p\sin\phi) \Rightarrow \Delta P_x = 2p\sin\phi$$

$$\Delta P_x = 2\left(\frac{h}{\lambda}\right)\sin\phi \quad -(1)$$

The resolving power of microscope is given by

$$\Delta x = \frac{\lambda}{2\sin\phi} \quad -(2)$$

from (1) & (2)

$$\Delta x \cdot \Delta P_x = h$$

$$\Rightarrow \boxed{\Delta x \cdot \Delta P_x \geq \frac{h}{2\pi}}$$

According to equation (1), we could reduce the uncertainity in momentum (ΔP_x) in two ways, i.e.

(a) by reducing the angle ϕ i.e. making aperture of lens small

(b) by using the photons of longer wavelength (λ).

unfortunately, these two factors lead to an increase in the uncertainity in the position (Δx) of electron that we are trying to locate. It illustrates that the measuring process itself introduces an uncertainity.

Δx = uncertainity in position
ΔP = " " momentum
Δt = " " time
ΔE = " " Energy
$\Delta \theta$ = " " angular position
ΔJ = " " " momentum

Applications of uncertainity Principle:

1. To prove the non existance of electrons inside nucleus
2. To Determine the B.E. of electron in an atom
3. To Determine the redius of H-atom
4. To Determine the width of spectral lines
5. To Determine the stability of atom and strength of nuclear force.

Physical origin of uncertainity principle:

Let us consider any photon is scattered by an electron within angle $\phi + \phi = 2\phi$ is focused by the hypothetical microscope lenses and will be detected by eye ~~~~ as shown in fig. aside known as Bohr's gedanken experiment.

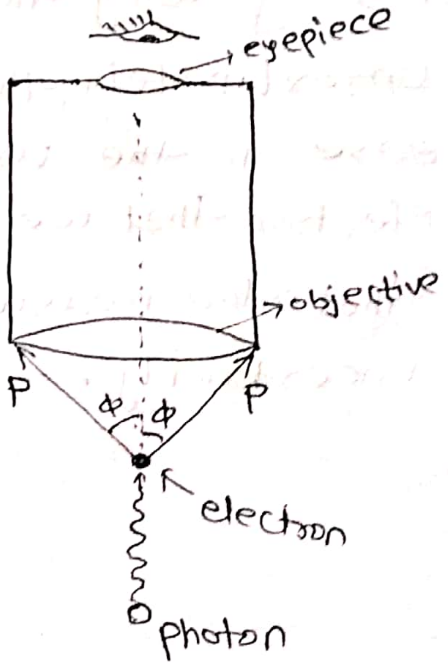


fig. Bohr's gedanken experiment.

The scattered photon may ~~be~~ enter the objective lens anywhere within the angular range $+\phi$ to $-\phi$. Hence the momentum of this photon could have any value between $-p\sin\phi$ to $+p\sin\phi$

Ni-crystal is shown in fig. (3)

From fig. (3).

$$\theta + \phi + \theta = 180^\circ$$
$$\Rightarrow 2\theta = 180^\circ - \phi$$
$$2\theta = 180^\circ - 50^\circ$$
$$2\theta = 130^\circ \Rightarrow \boxed{\theta = 65^\circ}$$

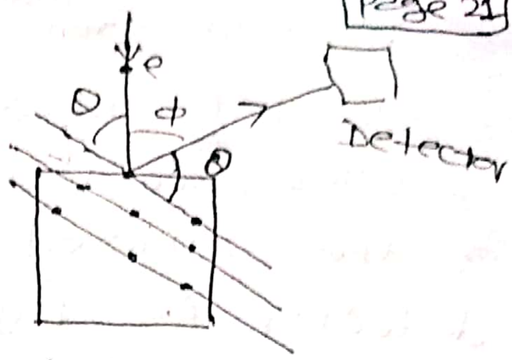


fig (3) scattering of electrons by crystal

Now, eqn (2) is

$$2 \times 0.91 \times 10^{-10} \sin 65^\circ = 1 \times \lambda \quad (n = 1)$$

$$\Rightarrow \boxed{\lambda = 1.65 \times 10^{-10} m} \quad (4)$$

which is nearly equal to the De-Broglie wavelength of electron beam. This agreement between the wavelength of electron beam and x-ray shows that, electron beam produce same type of diffraction pattern as produced by x-rays. Thus, the experiment confirms the De-Broglie Hypothesis that particle (electron) have wave nature.

Heisenberg's uncertainity principle:

The Dual nature of matter provides the difficulty to determine the precisely and simultaneously the value of canonically conjugate variable (pair of physical quantities which describe the motion of an atomic system). e.g. position & momentum, time and energy, Angular position and angular momentum. This difficulty was overcome by Heisenberg, giving a principle known as Heisenberg's uncertainity principle. According to this Principle.

$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi} \quad (1)$$

$$\Delta t \cdot \Delta E \geq \frac{h}{2\pi} \quad (2)$$

$$\Delta \theta \cdot \Delta J \geq \frac{h}{2\pi} \quad (3)$$

where Δ represents the uncertainity of measurement.

Electrons from a heated fillament are accelerated with a variable voltage V. The beam is allowed to incident on a Ni-crystal. The intensity of the scattered beam can be measured by the detector for different angle 'φ' and various voltage V. ~~If the propagation of beam is~~ While rotating, the detector observes the variation in intensity and the maximum intensity at a certain value of φ=50° & V=54V as shown in fig. (2) above.

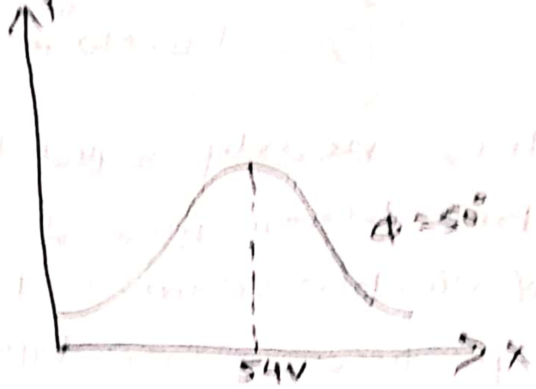


fig.(2) Variation of I(Intensity) with V at fixed φ=50°

Let us Consider, an electron of mass 'm' is accelerated ~~with~~ with velocity 'v' by accelerating potential 'V': K.E.= eV

$\frac{1}{2}mv^2 = eV$

$m^2v^2 = 2meV$

$\Rightarrow mv = \sqrt{2meV}$

∵ De-Broglie wavelength of electron $\lambda = \frac{h}{mv} \Rightarrow \lambda = \frac{h}{\sqrt{2meV}}$

or, $\lambda = \frac{6.62\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-19}\times50}}$

$\boxed{\lambda \simeq 1.67\times10^{-10}\,m}$ — (1)

Instead of electron, X-ray beam (wave nature) is incident on the crystal, the Bragg's law of diffraction is

$$2d\sin\theta = n\lambda \quad -(2)$$

For Ni-crystal, spacing of crystal planes $d = 0.91\,\text{Å}$
$= 0.91\times10^{-10}\,m$

The scattering of electrons by atomic planes in of frequency (f) is given by $E = hf = \frac{hc}{\lambda}$ —(1)

According to Einstein's mass-energy relation

$E = mc^2$ ——(2) where 'm' is mass of photon moving with velocity 'c'

from eqn. (1) & (2) $mc^2 = \frac{hc}{\lambda} \Rightarrow \boxed{\lambda = \frac{h}{mc}}$ —(3)

$\therefore \lambda = \frac{h}{p}$ —(4) where $p = mc$ is the linear momentum of photon

Now, for a particle of mass 'm' moving with velocity v, $p = mv$ $\therefore \boxed{\lambda = \frac{h}{mv}}$

De-Broglie wavelength of electron:

Let us consider an electron of mass 'm' having charge 'e' is accelerated by the potential of V volt. $\therefore$ K.E. gain by that electron is

$E = K.E. = eV$

or $\frac{1}{2}mv^2 = eV$

$\Rightarrow mv = \sqrt{2meV}$

& $mv = \sqrt{2mE}$

Now, De-Broglie wavelength of electron $\lambda = \frac{h}{mv}$

$\therefore \boxed{\lambda = \frac{h}{\sqrt{2meV}}} \rightarrow \boxed{\lambda = \frac{h}{\sqrt{2mE}}}$

Experimental verification of De-Broglie Hypothesis

In 1927, Davisson - Germer performed an experiment for the verification of De-Broglie hypothesis. Such experimental arrangement is shown in fig. (1) above

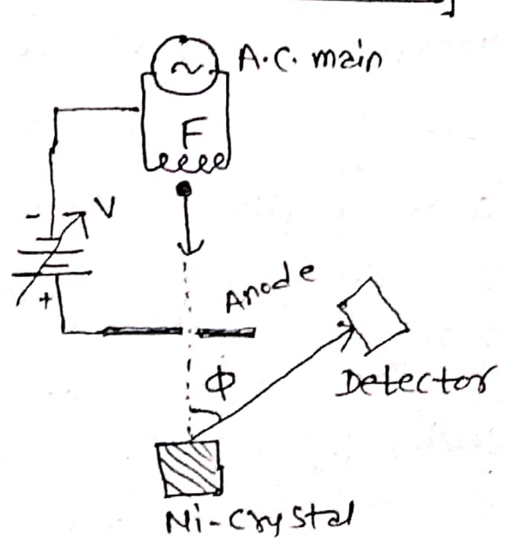


fig. (1) Darission-Germer experiment

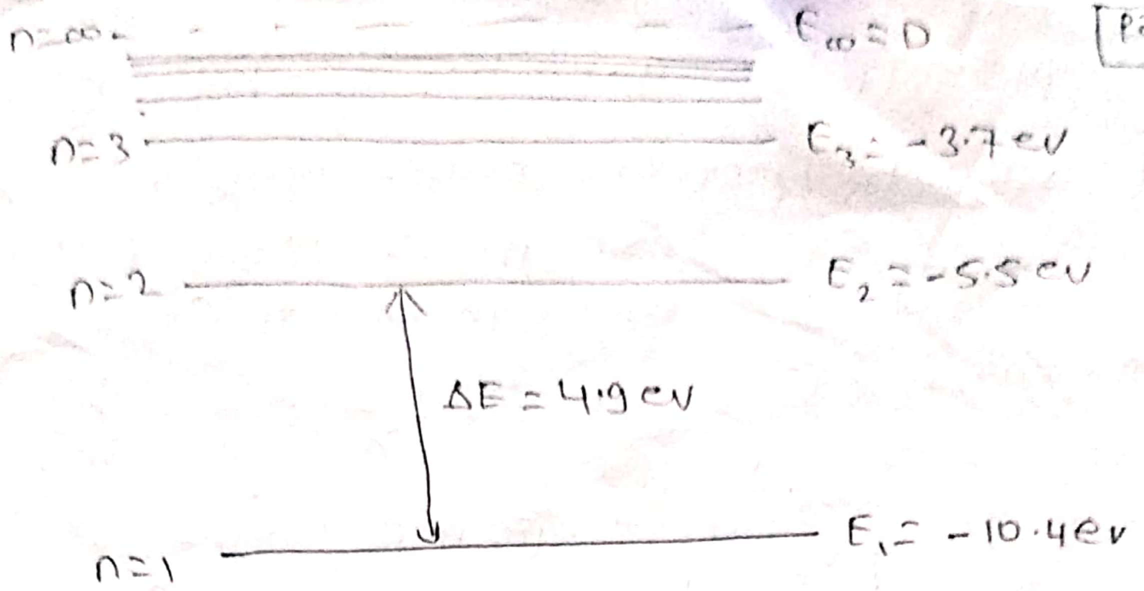


fig.(3) Atomic energy Level of Hg atom

De-Broglie Hypothesis (Theory):

The phenomenon like interference, Diffraction, Polarization etc. exhibited by em radiation (light) shows that em radiations are wave nature while the phenomenon like, photoelectric effect, campton effect exhibited by em radiation (light) shows that em radiations are particle nature. From this De-Broglie Suggest that every moving matters shows Dual nature particle as well as wave.

According to De-Broglie hypothesis every moving particle (matter) is associated with wave known as as De-Broglie wave or matter wave and corresponding wavelength is known as De-broglie wavelength which is given by $\lambda = \frac{h}{p}$. Where $p = mv$ is the linear momentum of particle of mass 'm' moving with velocity 'v'.

According to Planck's theory of quantum radiation, energy of a photon of em radiation

When $V_0 = 4.9V$, I' suddenly dips to a minimum. Again V_0 is gradually increased above 4.9V, I gradually increases, till another maximum is reached. When $V_0 = 2 \times 4.9 = 9.8V$ then current again dips steeply to another minimum. Similarly, a significant decrease in the plate current occurs each time the accelerating potential is increased by 4.9V.

Explanation:

As V_0 reaches the value of a critical potential 4.9V, an electron acquires 4.9eV of energy on reaching 'G'. The electron losses all its energy in an inelastic Collision with 'Hg' atom. Thus the electron is left with no energy to reach 'P'. Consequently the Current drops. This suggests that the 'Hg' atoms has absorbed 4.9eV energy to raise it from G.S. to a state of higher energy. This current dipping to a minimum at 4.9V does not reach zero because statistically some electron may succed in reaching 'P', avoiding an inelastic collision with 'Hg' atom.

Each time there is an inelastic collision, the 'Hg' atoms will excited and returns to G.S. by emission of photons. By using spectroscopic techniques the wavelength of the radiation comming from the tube was found to be 2530Å. Let us see what is energy of a photon of this wavelength,

$$E = hf = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{2530 \times 10^{-10}} \simeq 4.9\,eV$$

An energy level diagram for 'Hg' from spectral data is shown ~~below~~ in fig. (3) below

The arrangement of Franck-Hertz experiment is shown in fig. ① above. It consist of a glass tube 'T' filled with 'Hg' vapour at low pressure (1 mmHg). Three electrodes (Fillament 'F', Grid 'G' and a plate 'P' (collector)) are fitted inside tube. 'F' is heated by A.C. supply to produce electrons which are accelerated towards 'G' by variable potential 'V_0' (0 - 60V). A small retarding potential V_r ($\sim$ 1V) is applied between 'P' & 'G', ~~only those~~ The Electrons will reaches to 'G' with K.E. ($E_K = eV_0$). Thus, only those electrons from 'G' can go to 'P' which has K.E. greater than eV_r and contribute to the plate current (I) which is measured by milliammeter (mA).

<u>Working</u>:

Keeping 'V_r' constant, V_0 is gradually increased in small steps from zero upwards and corresponding collector (plate) current (I) is noted.

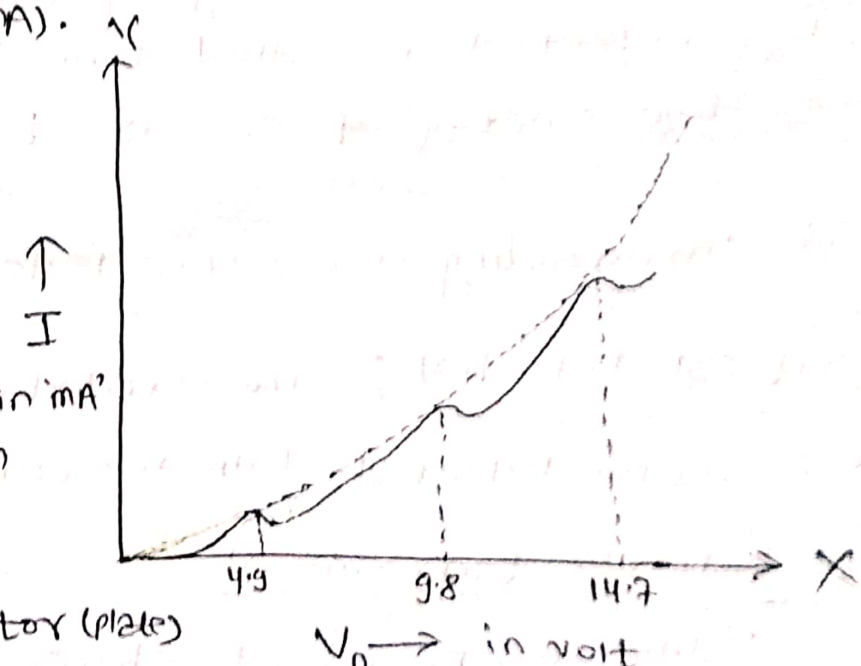


fig. ② graph of V_0 vs 'I'

If a graph is plotted by taking accelerating potential 'V_0' along X-axis and current (I) along Y-axis then the nature of graph obtained is shown in fig. ② above (solid line).

There is no plate current for $V_0 < V_r$, above this i.e. $V_0 > V_r$, 'I' is continuously increases.

Excitation Energy and Excitation Potential:

The minimum amount of energy required to shift an electron from G.S. to given excited state is called excitation energy of that state and corresponding potential is called excitation potential. e.g. Excitation energy of 1st excited state or 2nd energy state is

$E = E_2 - E_1 = -3.4 - (-13.6) = 10.2 eV$ and corresponding excitation potential is 10.2V.

Ionization energy and Ionization potential:

The minimum amount of energy required to shift an electron from given energy state to infinite state is called Ionization energy of that state and corresponding potential is called Ionization potential. e.g. Ionization energy of G.S. is $E = E_\infty - E_1$

$= 0 - (-13.6) = 13.6 eV$

and corresponding Ionization potential is 13.6V.

Critical potential: The excitation potential and Ionization potential both are called Critical potential.

Franck-Hertz Experiment:

This experiment shows the existence of discrete energy levels in the mercury atom.

Experimental arrangement:

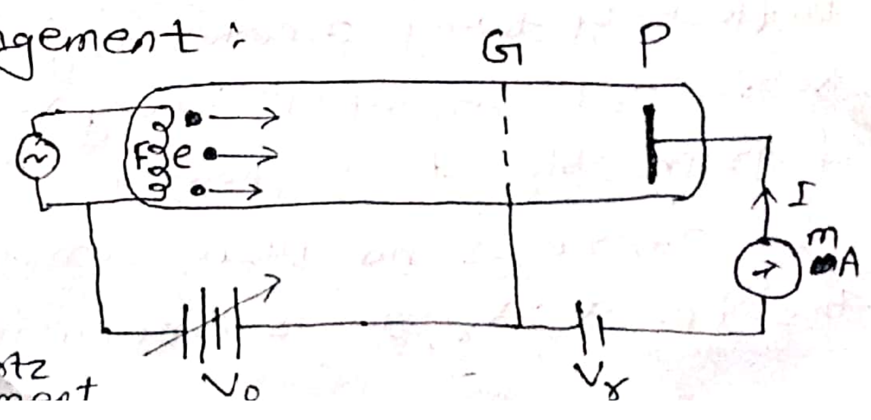
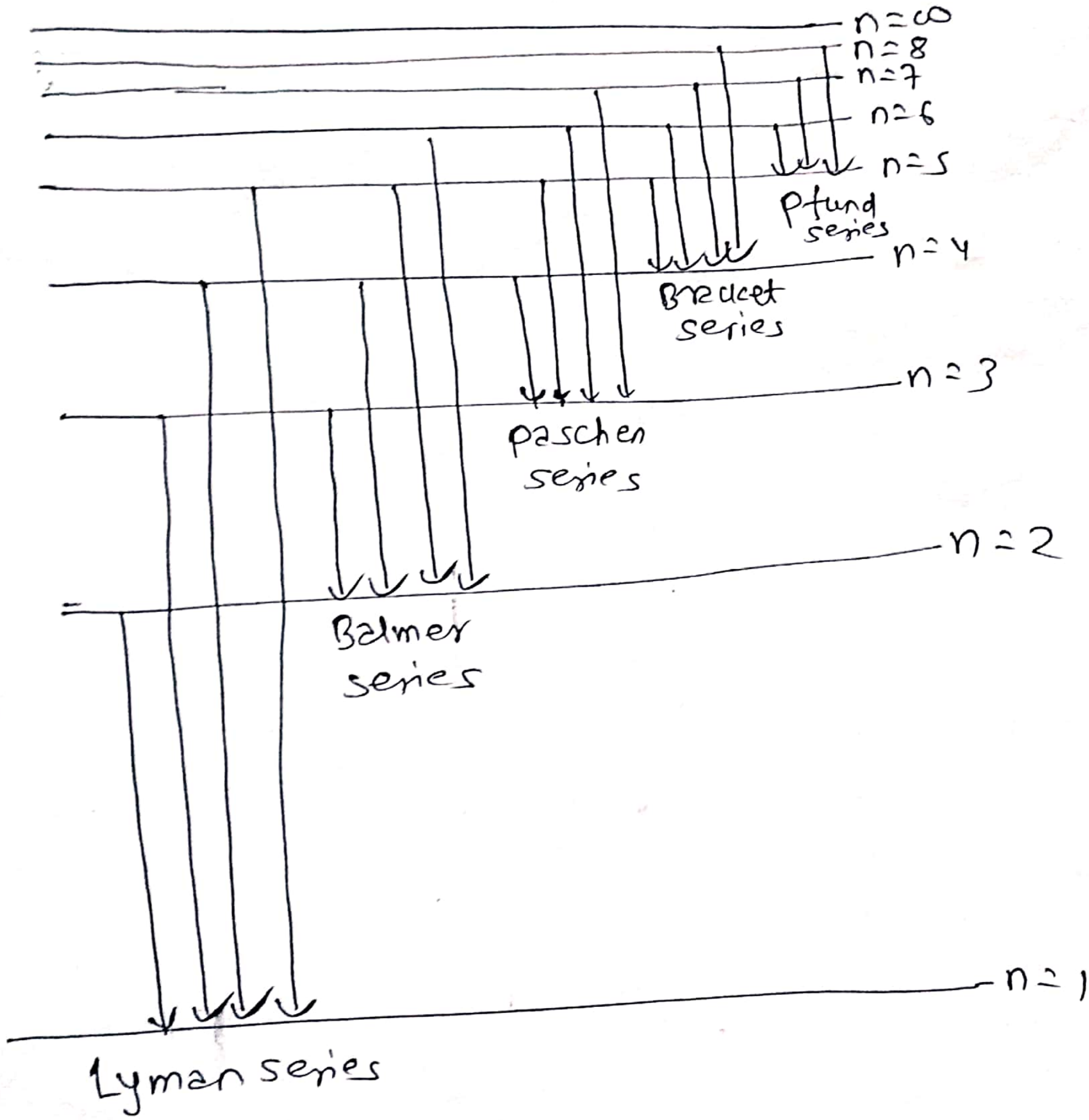


fig. ① Franck-Hertz experiment

Spectral series of H-atom is shown in fig. below



Limitations of Bohr's Theory:

(1) It is in violation of Heisenberg uncertainity principle.

(2) It can not predict the relative intensities of spectral lines

(3). It can not explain splitting of spectral line (zeemen effect)

(4) It can not account for the wave nature of electron.

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$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n_2^2}\right)$$

$n_2 = 4$

$$\frac{1}{\lambda_1} = 1.097\times10^{7}\left(\frac{1}{9} - \frac{1}{16}\right) = 1.097\times10^{7}\left(\frac{16-9}{9\times16}\right)$$

$$\Rightarrow \lambda_1 = \frac{9\times16}{7\times1.097\times10^{7}} = 18.752\times10^{-7} = 18752\times10^{-10}\ m$$

$\boxed{\lambda_1 = 18752\ \mathring{A}}$ longest wavelength of paschen series

$\lambda_2 =$

$\lambda_3 =$

$\frac{1}{\lambda_\infty} =$

$$\frac{1}{\lambda_\infty} = 1.097\times10^{7}\left(\frac{1}{9} - \frac{1}{\infty}\right)$$

$$\lambda_\infty = \frac{9}{1.097\times10^{7}} = 8.204\times10^{-7}\ m$$

$\lambda_\infty = 8204\times10^{-10}\ m$

$\therefore \boxed{\lambda_\infty = 8204\ \mathring{A}}$ shortest wavelength of paschen series.

Hence $\lambda = (8204\ \mathring{A} - 18752\ \mathring{A})$ lies in infrared region

(4) Bracket series: For this $n_2 = 5, 6, 7, 8 \ldots$
$n_1 = 4$

λ lies in infrared region

(5) Pfund series: For this $n_2 = 6, 7, 8, 9 \ldots$
$n_1 = 5$

λ lies in far infrared region.

The radiation emitted in Lyman series lies in ultraviolet region

(2) Balmer series: This series of lines is emitted when electron jumps from different higher energy level $n_2 = 3, 4, 5, 6, \ldots$ to fixed lower energy level $n_1 = 2$. The wavelength of this series of lines are given by $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$

for, $n_2 = 3$, $\frac{1}{\lambda_1} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = R\left(\frac{9-4}{4\times 9}\right) = R \times \frac{5}{36}$

$$\Rightarrow \lambda_1 = \frac{1}{R} \times \frac{36}{5} = \frac{1}{1.097\times 10^7} \times \frac{36}{5} = 6.563\times 10^{-7}\, m = 6563\times 10^{-10}\, m$$
$$= 6563\,\mathring{A}$$

$\boxed{\lambda_1 = 6563\,\mathring{A}}$ is wavelength of 1^{st} line of Balmer series which is longest wavelength of Balmer series of H-atom

Similarly, wavelength of 2^{nd} line $\lambda_2 = \ldots\,\mathring{A}$ for $n_2 = 4$

$\lambda_2 = \ldots\,\mathring{A}$ for $n_2 = 5$

For $n_2 = \infty$

$$\therefore \frac{1}{\lambda_\infty} = R\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right)$$

$$\Rightarrow \lambda_\infty = \frac{4}{R} = \frac{4}{1.097\times 10^7} = 3.646\times 10^{-7}\, m = 3646\times 10^{-10}\, m$$
$$= 3646\,\mathring{A}$$

$\boxed{\lambda_\infty = 3646\,\mathring{A}}$ is ~~longest~~ shortest wavelength of Balmer series of H-atom.

The radiation emitted in Balmer series lies in visible region.

(3) Paschen series: $n_2 = 4, 5, 6, 7 \ldots$

For this $n_1 = 3$

$\therefore$ $\boxed{R = 1.097 \times 10^{7}\ m^{-1}}$

$\therefore$ $\boxed{\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$ — (2)

This eqn. is known as Bohr's eqn.

The emission of all the spectral series of lines ~~H-atom~~ in Hydrogen spectrum are explained below.

(1) Lyman series: This series is obtain when electron jumps from different higher energy level $n_2 = 2, 3, 4, 5$ ---- to fixed lower energy level $n_1 = 1$.

The wavelength of this series of lines are given by $\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$

$n_2 = 2$, $\frac{1}{\lambda_1} = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 1.097 \times 10^{7}\left(\frac{3}{4}\right)$

$\Rightarrow \lambda_1 = \frac{1}{1.097 \times 10^{7}}\left(\frac{4}{3}\right) = 1.215 \times 10^{-7}\ m = 1215 \times 10^{-10}\ m = 1215\ \mathring{A}$

is wavelength of 1st line of Lyman series i.e. maximum wavelength (longest wavelength) of Lyman series of H-atom

Similarly, for $n_2 = 3$, $\lambda_2 =$ ----

$n_2 = 4$ $\lambda_3 =$ ----

$n_2 = \infty$ $\lambda_\infty = \frac{1}{R\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)} = \frac{1}{1.097 \times 10^{7}}$

$\Rightarrow \lambda_\infty = 0.9116 \times 10^{-7}\ m = 911.6 \times 10^{-10}\ m$

$\boxed{\lambda_\infty = 911.6\ \mathring{A}}$ is shortest wavelength of Lyman series of H-atom.

Spectral series of H-atom:

According to Bohr's second postulate, when the electron make a transition from higher energy level n_2 having energy E_{n_2} to lower energy level n_1 having energy E_{n_1} then frequency (f) of the emitted radiation is given by

$$hf = E_{n_2} - E_{n_1}$$

$$\text{or, } hf = -\frac{mz^2e^4}{8\epsilon_0^2 n_2^2 h^2} - \left(-\frac{mz^2e^4}{8\epsilon_0^2 n_1^2 h^2}\right)$$

$$\text{or, } hf = \frac{mz^2e^4}{8\epsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Rightarrow \boxed{f = \frac{mz^2e^4}{8\epsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

put $f = \frac{c}{\lambda}$

$$\therefore \frac{c}{\lambda} = \frac{mz^2e^4}{8\epsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Rightarrow \boxed{\frac{1}{\lambda} = \frac{mz^2e^4}{8\epsilon_0^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \quad \text{--- (1)}$$

Here, $\frac{mz^2e^4}{8\epsilon_0^2 h^3 c}$ = Const; $= R$, Known as Rydberg's Constant (R)

$$\therefore R = \frac{9.1\times10^{-31}(1)^2(1.6\times10^{-19})^4}{8\times8.85\times10^{-12}\times(6.62\times10^{-34})^3\times3\times10^8} \simeq 1.097\times10^{7}\,m^{-1}$$

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$$E_n = -\frac{13.6}{n^2} \times 1.6\times10^{-19} \text{ J}$$

$$\Rightarrow \boxed{E_n = -\frac{13.6}{n^2} \text{ eV}} \quad -(10)$$

eqn. (10) is required expression for the energy spectrum of H-atom i.e. ~~ea~~ Total energy of n^{th} orbit of H-atom i.e. total energy of n^{th} energy state or Level.

For, $n=1$, $E_1 = -\frac{13.6}{1^2} = -13.6\text{eV}$ is lowest energy Level called G.S. energy of atom. The higher energy Levels are

$n=2$, $E_2 = -\frac{13.6}{(2)^2} = -3.4\text{eV}$ is energy in 1^{st} excited state or 2^{nd} energy state.

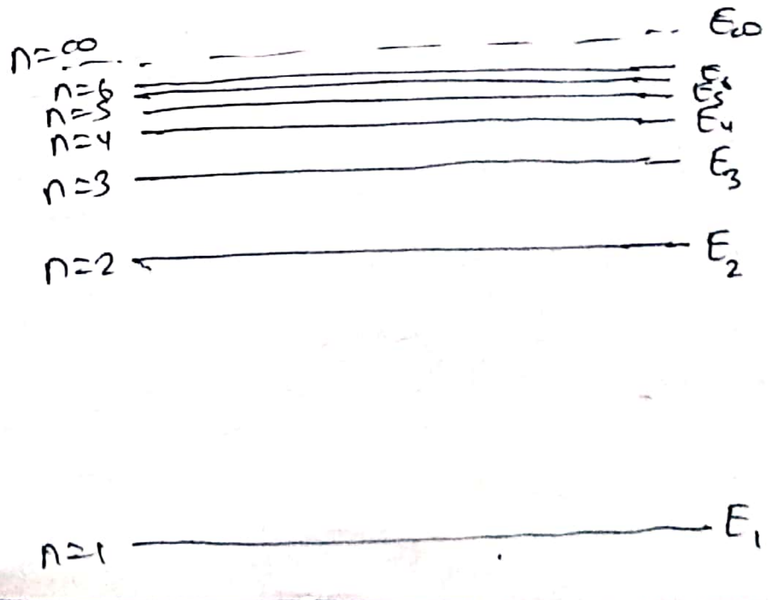
$n=3$, $E_3 = \frac{-13.6}{(3)^2} = -1.51\text{ eV}$ is " in 2^{nd} excited state or 3^{rd} energ state

Similarly,

$E_4 = \cancel{-0.8}\frac{-13.6}{(4)^2} = -0.85\text{ eV}$, $E_5 = \frac{-13.6}{(5)^2} = -0.544\text{ eV}$

$E_6 = -0.38\text{ eV}$ - - - - - - $E_\infty = \frac{-13.6}{\infty} = 0\text{ eV}$.

∴ Energy level diagramme of H-atom is shown in fig.



for n=1, $\boxed{r_1 = 0.53\text{Å}}$ called Bohr's radius

for n=2, $r_2 = 0.53(2)^2\text{Å} \Rightarrow r_2 = 4r_1$

for n=3, $r_3 = 9r_1$, for n=4, $r_4 = 16r_1$

Hence, allowed orbits are

$r_1, 4r_1, 9r_1, 16r_1$ - - - - -

Now, Kinetic energy of electron in n^{th} orbit is

$K.E. = \frac{1}{2}mv^2$ — (6)

putting value of mv^2 from eq^n (1) into eq^n (6)

$$K.E. = \frac{ze^2}{8\pi\epsilon_0 r} \quad -(7)$$

P.E. of electron in n^{th} orbit is

$$P.E. = \frac{(ze)(-e)}{4\pi\epsilon_0 r} = \frac{-ze^2}{4\pi\epsilon_0 r} \quad -(7)$$

The total energy electron in n^{th} orbit is

$E = K.E. + P.E.$

or, $E = \frac{ze^2}{8\pi\epsilon_0 r} - \frac{ze^2}{4\pi\epsilon_0 r}$

$$\Rightarrow E = \frac{-ze^2}{8\pi\epsilon_0 r} \quad -(8)$$

putting value of 'r' from eq^n. (3) to (8) we get

$$E = \frac{-ze^2}{8\pi\epsilon_0\left(\frac{\epsilon_0 n^2 h^2}{\pi m z e^2}\right)}$$

$$\therefore \boxed{E_n = \frac{-mz^2e^4}{8\epsilon_0^2 n^2 h^2}} \quad -(9)$$

-ve sign indicate that electrons are bound to the nucleus

putting value of m, z=1, e, ϵ_0 & h we get

Energy spectrum of Hydrogen Atom

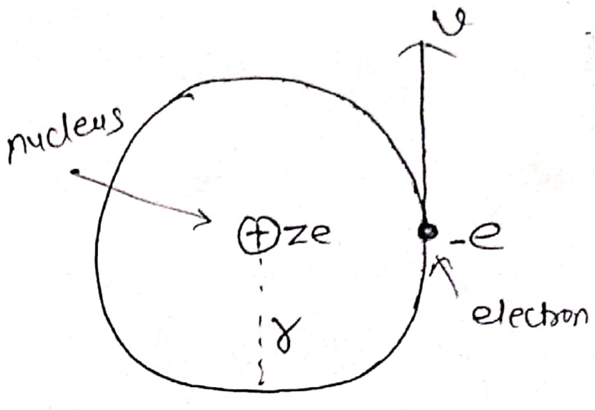


fig. H-atom

Let us consider a H-atom having a nucleus of charge (ze) around which an electron of charge 'e' having mass 'm' is revolving in the n^{th} orbit of radius 'r' with velocity 'v' as shown in fig above.

To revolve the electron in the circular orbit ~~~~ the necessary centripetal force is provided by the electrostatic force of attraction between nucleus (ze) and electron (-e). i.e.

$$\frac{mv^2}{r} = \frac{e(ze)}{4\pi\epsilon_0 r^2}$$

$$\Rightarrow mv^2 = \frac{ze^2}{4\pi\epsilon_0 r} \quad -(1)$$

According to Bohr postulate 1,

$$mvr = \frac{nh}{2\pi}$$

$$\Rightarrow v = \frac{nh}{2\pi m r} \quad -(2)$$

putting value of 'v' in equation (1) we get

$$m\cdot\left(\frac{nh}{2\pi m r}\right)^2 = \frac{ze^2}{4\pi\epsilon_0 r}$$

$$\therefore r = \frac{\epsilon_0 n^2 h^2}{\pi m z e^2} \quad -(3)$$

$\therefore$ radius of n^{th} orbit of H-atom is

$$r_n = \frac{\epsilon_0 n^2 h^2}{\pi m z e^2} \quad -(4)$$

put $\epsilon_0 = 8.85\times10^{-12}\ Fm^{-1}$

$h = 6.62\times10^{-34}\ J\ s$

$\pi = 3.14$

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

$z = 1$ for H-atom

$e = 1.6\times10^{-19}\ C$

$r_n = 0.53 n^2 \times 10^{-10}$ meter

$$\Rightarrow \boxed{r_n = 0.53 n^2\ \mathring{A}} \quad -(5)$$

Bohr's Atomic model:

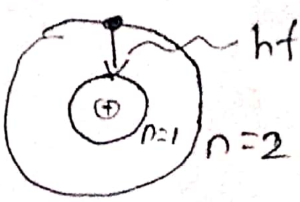
TO avoid the two problems encountered by the Rutherford model (Stability and Continuous spectrum) and to explain the spectrum of H-atom, Neils Bohr (in 1913) proposed a model of H-atom that can be summarized in two postulates.

Postulate 1: An electron cannot revolve round the nucleus in all possible orbits. It revolve only in those orbit for which angular momentum of electron is an integral multiple of $\frac{h}{2\pi}$. ~~Here h~~

i.e. $$mvr = \frac{nh}{2\pi} \quad - (1)$$

where 'm' is mass of electron
'v' " velocity " "
r " radius of n^{th} orbit.
$h = 6.62 \times 10^{-34}$ JS is plank's Constant,
$n = 1, 2, 3 ---$ are integers

Postulat 2: An accelerated electron in one of the allowed orbits doesnot radiate e.m. radiation. They emits radiation (energy) only when Jumps from higher energy state to lower energy state while they absorbed radiation (energy) when Jumps from lower energy state to higher energy state. The frequency 'f' of radiation emitted or absorbed is given by $hf = E_{n_2} - E_{n_1}$



where
E_{n_2} is energy of higher energy state.
E_{n_1} " " " lower " ".

pages

emitted or absorbed energy is given by $\Delta E = E_{n_2} - E_{n_1} = (n_2 - n_1) hf$

Using the energy spectrum for the atomic oscillators and consequently for the em. waves emitted by them, together with simple thermo-dynamic arguments, planck derive an expression for E(f) that matched the experimental data as

$$E(f) = \frac{2\pi h f^3}{c^2} \frac{1}{e^{\frac{hf}{KT}} - 1}$$

where 'c' is velocity of light,
K is Boltzmaan Constant.

planck's Theory :

Inorder to explain the distribution of energy in the spectrum of blackbody, Max-planck in 1990 introduced quantum theory of radiation. He assumed that, atoms in the blackbody have characteristic frequency and oscillates like simple harmonic oscillator called atomic oscillator. He made two assumptions.

① The atomic oscillator can not have any arbitrary values of energy but only those value of the total energy 'E' are given by

$$E = E_n = nhf \quad - (1)$$

where, $n = 0, 1, 2, 3, \ldots$ are called quantum no.
'f' is frequency of oscillation
$h = 6.62 \times 10^{-34}$ JS is planck's constant.

Hence total energy of oscillator is always quantized as shown in fig. below

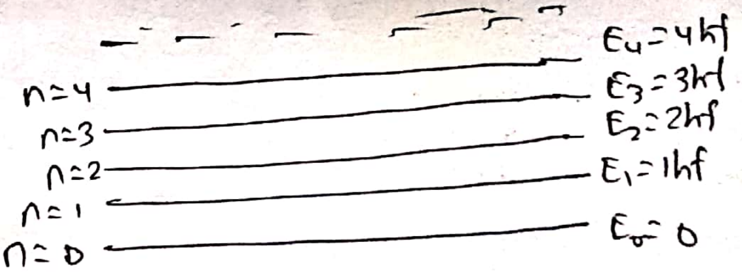


fig. quantized energy spectrum.

② The oscillator can not emit and absorb energy so, it in a stationary state ($E = nhf$). The emission and absorption of energy occurs only when the oscillator jumps from one energy state to another energy state. Energy is emitted when oscillator jumps from higher to lower state while energy is absorbed when it jumps from lower to higher energy state.

The main features of the spectrum emitted by a blackbody are

1. The spectrum is continuous with a broad maximum

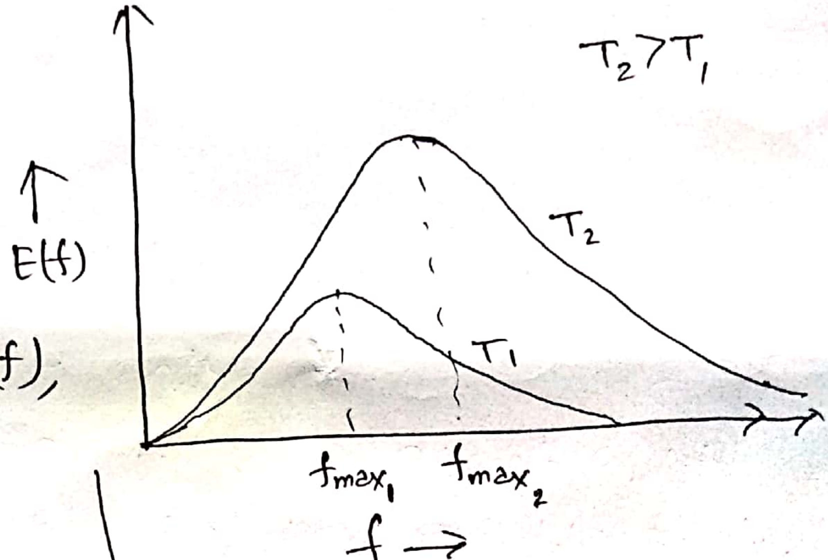


fig. spectrum of blackbody

2. The Integral of $E(f)$ over all frequency (f), called E_T, represents the energy emitted per unit area per unit time is found to be increases with the fourth power of absolute temp^r. of blackbody i.e

$$E_T = \int_0^\infty E(f)\,df = \sigma T^4 \quad -(1)$$

This rel^n is known as stefan's - Boltzmann law of blackbody radition.

$\sigma = 5.67 \times 10^{-8}\ Wm^{-2}K^{-4}$ is Stefan's Constant.

3. The spectrum shifted towards higher frequencies as the temp^r increases. Also maximum frequency $f_{max} \propto T$

or minimum wavelength $\lambda_m \propto \frac{1}{T}$

or $\lambda_m = \text{Const} \cdot \frac{1}{T}$

$\boxed{\lambda_m T = \text{Const}}$ This is known as Wien's displacement law.

~~It can absorb~~

Any radiation entering the ~~sphere~~ cavity (sphere) through hole suffers multiple reflections

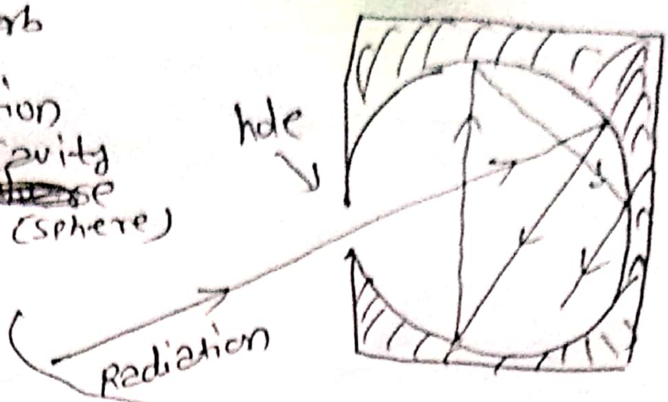


fig. metalic cavity

at the inner surface and resulting multiple absorption of radiation. It can absorb 96% to 98% of radiation, acting as perfect blackbody.

The radiation with a uniform tempr of the enclosure in equilibrium with its surroundings is called blackbody radiation at the tempr. of the enclosure. The radiation comming out from such an enclosure through an ~~opp~~ opening in it at any temperature of ~~the~~ its wall, is the blackbody radiation at that temperature.

Character of the spectrum of blackbody:

Blackbody radiation of different frequencies is called spectrum of blackbody. The amount of energy emitted by a blackbody per unit area per unit timpe is called Intensity of blackbody radiation i.e. $I = \frac{Q}{At}$.

Spectral radiancy ~~(E)~~ at each frequency is defined as the Intensity of blackbody radiation per ~~fer~~ frequency i.e. $E(f) = \frac{I}{f}$.

Unit-3 Fundamentals of Atomic Theory

(The begining of the quantum mechanics)

Most of the astronomical data about the motion of the planets, as well as the behaviour of ordinary mechanical systems, could be explained using Newton's law of motion and Newton's law of gravitation. The existence of em waves had been experimently verified by 'Heinrich Hertz'. ~~The~~ To explain the behaviour of submicroscopic objects (atom & molecules), techniques of statistical mechanics was developed. The classical as well as statistical mechanics can not explain the distribution of energy in the spectrum of blackbody. ~~which was the origin~~ To explain this quantum idea was introduced by Max. plank in 1900;

Blackbody Radiation:

All ~~the~~ substances at finite temp^r. radiate em waves. Isolated atom (in a gas) emit discrete frequencies. Molecules emits bands of frequencies and solids emits a continuous spectrum of frequencies. As the temp^r of solid increases, emitted radiation lies within visible region of the spectrum.

A body which can absorb all the radiation incident upon it is called blackbody. A body having a surface which can absorb ~~all~~ radiation of all the wavelength is called perfect blackbody. A metalic cavity with a small hole whose inner surface is coated with Lamp black or platinum black is nearest approach of perfect blackbody as shown in fig. below