Unit- 1(Part-I)
Wave Mechanics and X-Ray diffraction

Wave-Particle duality of Radiation

A particle is specified by its –
(1)- Mass (2)-Velocity (3)-Momentum (4)-Energy and is localised at a point in space. On the other hand a wave is spread out of disturbance and is specified by –
(1)-Frequency (2)-Wavelength (3)-Amplitude (4)_Intensity
Considering the above facts it appears difficult to accept the conflicting ideas that radiation has a dual nature i.e. radiation is a wave which is spread out over a large region of space and is a particle which is localised at a point in space. However this acceptance is essential because radiation sometimes behave as a wave and other times as a particle as explained below:
1. Radiation including visible light, infrared, ultra-violet & X-rays etc. behave as a wave in the experiment based on interference & diffraction etc. This is due to the fact that these phenomenon require the presence of 2 waves at the same time at the same position. It is impossible for 2 particles to occupy at the same position at the same time. That is it is impossible for two particles to fulfil the above condition of interference. Thus, we conclude that radiation behave as a wave.
2. Planck's quantum theory was successful in explaining black body radiation, photoelectric effect and Compton effect etc. and had clearly established that radiant energy in its interaction with matter behave as though it consist of corpuscles. Thus radiation interacts with matter in form of photon or quanta Therefore, it is clear that radiation behave as a particle. Thus radiation sometimes behave as a wave and other times as a particle which is known as wave particle duality of radiation and both the character i.e. wave and particle will be complementary to each other.

De-Broglie concept of matter wave

The following consideration De Broglie to the conception of matter wave**.**
(a)Nature loves symmetry: The two forms in which nature manifests itself are matter and radiation. Radiation has been shown to possess dual nature. Therefore, according to law of symmetry the matter also might possess the same dual nature.
(b) Close parallelism between optics and Mechanics: The principal of least action in mechanics states that a moving particle always chooses that path for which the action is minimum i.e. a moving particle always chooses the least path. Now according to Fermat's Principle in optics light also chooses that path for with time of transit is minimum, i.e. light also chooses the least path.

Therefore, if the light following the least path possess dual nature then a particle following the least path must possess the dual nature.

(c) Bohr's theory of atomic structure: According to Bohr's theory of atomic structure; the stable state of electrons in an atom are governed by integers rule. The only phenomenon involving integer rules are those of interference and modes of vibration in stretched string. The latter two phenomenon involving integers rule are associated with a wave nature. So the former one i.e. the revolving electron (in atomic orbit) must possess the wave nature.

In addition to above facts; matter and radiation both are forms of energy and can be transformed into each other. Also both are governed by the same space time symmetry of theory of relativity.

In view of all the above facts in 1924 Louis de Broglie put a bold suggestion that just like radiation matter should also possess the dual nature. According to de Broglie hypothesis a material particle in motion is associated with a wave which is known as known as matter wave and the wavelength of this matter wave is defined as

$$\lambda = h/mv$$

where ; h is plank`s constant, m is mass of material particle & v is velocity of material particle.

DE BROGLIE WAVE LENGTH

The expression for de Broglie wavelength can be derived with analogy of radiation. According to Planck's theory, the energy of a photon is given by

$$E = h\nu$$

or $$E = hc/\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

According to Einstein's mass energy relation

$$E = mc^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

So , from equation (1) & (2), we have

$$hc/\lambda = mc^2$$

or $$\lambda = h/mc \quad \ldots\ldots\ldots\ldots\ldots(3)$$

therefore, if we consider a material particle of mass 'm' moving with velocity 'v', then we must have

$$\boxed{\lambda = \frac{h}{mv}} \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

de Broglie wavelength corresponding to an electron

Let us consider that an electron of mass 'm' is accelerated at a potential difference of 'V' volt then we have

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

Where, e is the change of electron and v is velocity of the electron.

Multiplying by 2m both side we get

$$m^2v^2 = 2meV$$

or $$mv = \sqrt{2me\,V}$$

Thus, the wave length of matter wave corresponding to the electron is given by

$$\lambda = h/mv$$

$$\lambda = \frac{h}{\sqrt{2meV}}$$

Putting values of different constants we get

$$\lambda = \frac{6.62x10^{-34}}{\sqrt{2x9.1x10^{-31}x1.6x10^{-19}xV}}$$

or $$\boxed{\lambda = \frac{12.26}{\sqrt{V}}Å}$$

Thus, If V = 100 volt then $\lambda = \frac{12.26}{\sqrt{100}}Å = 1.226Å$

WAVE VELOCITY OF MATTER WAVE

The velocity of any wave is given by

$$u = \nu\,\lambda \qquad ……………(1)$$

Where, ν is frequency and λ is wavelength.

According to Einstein's mass energy relation

$$E = mc^2 \qquad …………..(2)$$

According to Planck's law

$$E = h\nu \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

From equation (2) & (3)

$$h\nu = mc^2$$

or $$\nu = \frac{mc^2}{h} \qquad \ldots\ldots\ldots\ldots(4)$$

According to de Broglie's hypothesis

$$\lambda = h/\,mv \qquad \ldots\ldots\ldots(5)$$

Putting value of λ & ν from eq (5) & (4) in eq (1)

We get $$u = \frac{mc^2}{h} \times \frac{h}{mv}$$

or $$\boxed{\mathbf{u} = \frac{\mathbf{c^2}}{\mathbf{v}}} \qquad \ldots\ldots\ldots\ldots\ldots(6)$$

where, c is velocity of light & v is velocity of material particle

PROPERTIES OF MATTER WAVE:

(1) From the relation $=h/mv$ it is clear that the wavelength of matter wave varies inversely with the mass and velocity of the material particle i.e.lighter is the particle greater will be the wavelength and so on.

(2) From the relation $\lambda = h/mv$, it is clear that : if $v = 0$ then $\lambda = \infty$ and if $v = \infty$ then $\lambda = 0$. Thus, matter wave will only be associated with the material particle when it will move with a definite velocity. In other words wave character will not be associated with a stationary particle.

(3) Matter waves are not electromagnetic waves because electromagnetic waves are only generated by the motion of charge particles only however matter wave can be generated by any particle whether it is charged or neutral. On the other hand the velocity of electromagnetic wave is always constant and equal to the velocity of light however the velocity of matter wave depends upon the velocity of material particle[$u = c^2/v$].

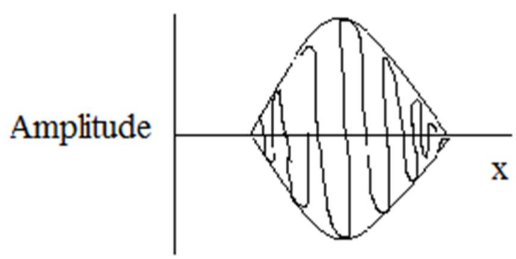
(4) Both the character i.e. wave and particle are complementary to each other what one can say is particles have wave like properties and waves have particle like properties.

Wave packet: Phase & Group velocity

Let us consider the expression of wave velocity of matter wave i.e.

$$u = \frac{c^2}{v} \qquad \text{……………(1)}$$

According to Einstein's theory of relativity, the speed of light is the maximum velocity that can be attained by a particle in nature i.e. velocity of material particle v should always be less than velocity of light c Accordingly equation (1) implies that de Broglie wave velocity (u) must be greater than c. This is an unexpected result. Furthermore according to this result, the de Broglie wave associated with material particle would travel faster than the particle itself; thus leaving the particle far behind. Thus it is clear that material particle in motion can't be equivalent to a single wave. This difficulty was resolved by Schrodinger by postulating that a material particle in motion is equivalent to a wave packet rather than a single wave. A wave packet comprises of a large no. of waves each with slightly different velocity & wavelength with phases and amplitude so chosen that they interfere constructively over only a small region of space where the particle can be located, outside of which they interfere distructively so that their amplitude reduces to zero rapidly. The amplitude of dimensional wave packet in general can be shown as below:



Two velocities are defined as ;

(1) Phase velocity (V_p):

The individual wave forming a wave packet possess an average velocity known as phase velocity. It is define as

$$V_p = \omega/k$$

Where ω is angular frequency **(**$\omega = 2\pi\upsilon$**)**

& k is wave vector ($k = 2\pi/\lambda$)

(2) Group velocity (V_g):

The wave packet moves with its own velocity known as group velocity. It is defined as

$$V_g = d\omega/dk$$

Relation between phase and group velocity: As we know that phase & group velocities are defined as

$$V_p = \omega/k \qquad \ldots \ldots (1)$$
$$V_g = d\omega/dk \qquad \ldots\ldots .(2)$$

Let us consider equation (2)

$$V_g = d\omega/dk$$

$$= d(V_p k)/dk \qquad \text{(from equation 1)}$$

$$= V_p + k\, dV_p/dk \qquad \ldots\ldots\ldots(3)$$

Since $k = 2\pi/\lambda$

So $dk = -2\pi/\lambda^2 d\lambda$

Putting both values in equation (3) we get

$$\boxed{V_g = V_p - \lambda\,(dv_p/ d\lambda)} \qquad \ldots\ldots\ldots\ldots(4)$$

Case 1: For non-dispersive medium

$$dV_p/ d\lambda = 0$$

So $V_g = V_p$

Case 2-: For a dispersive medium ($dV_p/ d\lambda > 0$)

So $V_g < V_p$

TO PROVE THAT PARTICLE VELOCITY IS SAME AS THE GROUP VELOCITY ($v = V_g$)

Let us consider two waves having some amplitude and slightly different phase velocity and frequency i.e.

$$E_1 = A\cos\omega_1 (t - x/u_1) \qquad \ldots\ldots\ldots(1)$$

$$E_2 = A\cos\omega_2 (t - x/u_2) \qquad \ldots\ldots\ldots(2)$$

Thus the resultant wave can be written as

$$E = E_1 + E_2$$

$$= A\cos\omega_1 (t - x/u_1) + A\cos\omega_2 (t - x/u_2)$$

or $E = 2A\cos\left[t\left(\frac{\omega_1+\omega_2}{2}\right) - \frac{x}{2}\left(\frac{\omega_1}{u_1} + \frac{\omega_2}{u_2}\right)\right]\cos\left[\left[t\left(\frac{\omega_2-\omega_1}{2}\right) - \frac{x}{2}\left(\frac{\omega_2}{u_2} - \frac{\omega_1}{u_1}\right)\right]\right]$ . . (3)

Let us write:

$\omega_1 = \omega$

$\omega_2 = \omega + d\omega$

$\omega_1 + \omega_2 = 2\omega$ as $d\omega << \omega$

$\omega_1/u_1+\omega_2/u_2=2\omega/u$ as $u = \frac{u_1+u_2}{2}$

$\omega_2 - \omega_1 = d\omega$

$\omega_2/u_2 - \omega_1/u_1 = d(\omega/u)$

Putting these substitutions in equation (3), we have

$$E = 2A\cos\left(t\omega - \frac{x\omega}{u}\right)\cos\left[\frac{td\omega}{2} - \frac{xd(\omega/u)}{2}\right]$$

or $$E = 2A\cos\omega\left(t - \frac{x}{u}\right)\cos\frac{d\omega}{2}\left(t - \frac{xd(\omega/u)}{d\omega}\right)$$

or $$E = 2A\cos\cos\frac{d\omega}{2}\left(t - \frac{xd(\omega/u)}{d\omega}\right)\cos\omega\left(t - \frac{x}{u}\right) \quad \text{.........(4)}$$

Here it is clear that resultant wave packet moves in the same direction with the frequency of first wave. Here it is also clear that the amplitude term i.e.

$2A\cos\cos\frac{d\omega}{2}\left(t - \frac{xd(\omega/u)}{d\omega}\right)$ in itself is a wave. Since the amplitude velocity is the signal velocity and signal velocity is termed as group velocity therefore we can write

$$2A\cos\cos\frac{d\omega}{2}\left(t - \frac{xd(\omega/u)}{d\omega}\right) = 2A\cos\cos\frac{d\omega}{2}\left(t - \frac{x}{V_g}\right)$$

Where $$V_g = \frac{d\omega}{d(\omega/u)} \quad \text{... ... (5)}$$

is known as group velocity .

Let us consider equation (5) i.e. $$V_g = \frac{d\omega}{d(\omega/u)}$$

$$= \frac{d(2\pi\nu)}{d\left(\frac{2\pi\nu}{u}\right)}$$

$$= \frac{d\nu}{d\left(\frac{\nu}{u}\right)}$$

$$= \frac{d\nu}{d\left(\frac{1}{\lambda}\right)} \qquad \text{(since } u=\nu.\lambda) \quad .....(6)$$

If E and V be the total & potential energy of a particle then its kinetic energy can be given as

$$\tfrac{1}{2} mv^2 = E - V$$

or $$v^2 = 2(E - V)/m$$

or $$v = [2(E - V)/m]^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots.(7)$$

According to de Broglie hypothesis

$$\lambda = h/mv$$

or $$1/\lambda = mv/h$$

$$\frac{1}{\lambda} = \frac{m}{h}\left[2\left(\frac{E-V}{m}\right)\right]^{1/2} \qquad \ldots\ldots\ldots\ldots(8)$$

Let us consider equation (6) $$V_g = \frac{d\nu}{d\left(\frac{1}{\lambda}\right)}$$

or $$\frac{1}{V_g} = \frac{d\left(\frac{1}{\lambda}\right)}{d\nu}$$

$$= \frac{d}{d\nu}\left[\frac{m}{h}\left\{2\left(\frac{E-V}{m}\right)\right\}^{1/2}\right]$$

or $$= \frac{m}{h}\left[\frac{d}{d\nu}\left\{\left\{2\left(\frac{E-V}{m}\right)\right\}^{1/2}\right\}\right]$$

As; E =h ν

So $$\frac{1}{V_g} = \frac{m}{h}\left[\frac{d}{d\nu}\left\{\left\{2\left(\frac{h\nu-V}{m}\right)\right\}^{1/2}\right\}\right]$$

$$= \left(\frac{1}{2}\right)\frac{m}{h}\left[\left\{\left\{2\left(\frac{h\nu - V}{m}\right)\right\}^{-1/2}\right\}2\frac{h}{m}\right]$$

or $$\frac{1}{V_g} = \left[2\left(\frac{E-V}{m}\right)\right]^{-1/2}$$

or $$\frac{1}{V_g} = \left[\frac{m}{\{2(E-V)\}}\right]^{1/2} = \frac{1}{\text{v}}$$

Thus $$\boxed{V_g = \text{v}}$$

Thus, it is clear that particle is equivalent to a wave packet. But we know that a wave packet is always dissipated with time. So the postulate was again modified & it was concluded that the particle will equivalent to a wave packet plus guiding wave. Guiding wave will never dissipate with time and the amplitude of guiding wave will represent the probability of finding the particle in any space.Thus the concept of guiding wave & wave packet completes the theory.

RELATION BETWEEN PHASE & GROUPVELOCITY FOR A NON-RELATIVISTIC FREE PARTICLE:

As we know that phase velocity of any wave is given by

$$V_p = \upsilon\,\lambda \qquad \text{..............(1)}$$

The total energy of a non- relativistic free particle [means a particle having potential energy(V) = 0] is given by

$$E = \frac{1}{2}m\text{v}^2 \qquad \text{................(2)}$$

According to Planck's law

$$E = h\upsilon \qquad \text{..................(3)}$$

From equation (2) & (3)

$$h\upsilon = \frac{1}{2}m\text{v}^2$$

$$\upsilon = \frac{m\text{v}^2}{2h} \qquad \text{................(4)}$$

According to de -Broglie's hypothesis

$$\lambda = \frac{h}{m\text{v}} \qquad \text{................(5)}$$

Putting value of υ & λ from equation (4) & (5) in equation (1) we get

$$V_p = \frac{mv^2}{2h} \times \frac{h}{mv}$$

$$V_p = \frac{v}{2}$$

$$\boxed{V_p = \frac{V_g}{2}} \qquad \text{(Since } v=V_g\text{)} \ldots\ldots\ldots\ldots(6)$$

Experimental evidence of matter wave

1. Davission – Germer's experiment

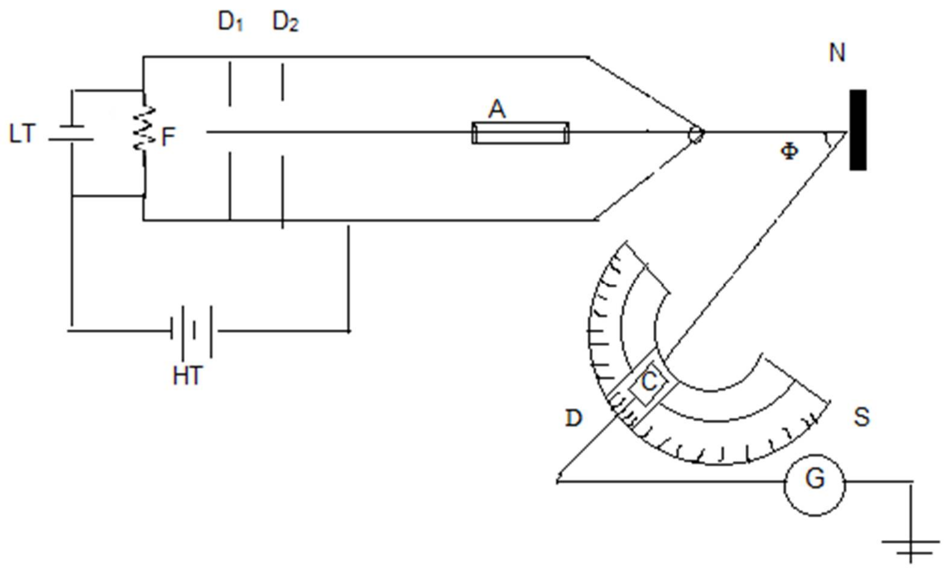
2. G.P. Thomson experiment

1. Davisson – Germer's Experiment:

The first experimental evidence of matter wave was given by two American physicist C.J. Davission and L.H. Germer in 1927. They also succeed in measuring de -Broglie wavelength associated with slow electron. Davission and Germer were studying the reflection of electron from nickel target. Accidently, the Ni target was subjected to such a heat treatment that reflections become anomalous (irregular). Now, the reflected intensity showed striking maxima & minima, thus they suspected that electrons are diffracted like X-rays i.e. they behave like wave under certain condition.

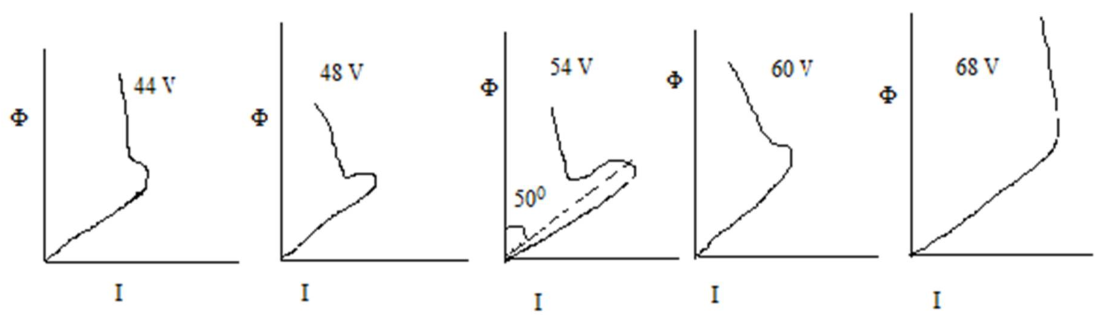
Experimental arrangement:

The electron beam falls on a Nickel crystal N and scattered in all direction by the atoms in the crystal. These scattered electrons were collected by faraday cylinder C, called collector. Collector is connected to a sensitive galvanometer G & can be moved on a graduated circular scale S. So that it is able to receive the diffracted electrons at all angles between 20^0 to 90^0. The collector has two walls C & D insulated from each other. A retarding potential is applied between the walls so that secondary electrons can't reach on C.



Experimental Procedure:

The beam of electron falls normally on the surface of Nickel crystal (N). A diffraction effect from the surface layer of the crystal acting as a plane grating is produced. The collector is moved to various positions on scale (S) & the galvanometer deflection at each position is noted. This deflection gives a measure of the intensity of the diffracted beam of electrons. The galvanometer deflection is plotted against the angle (Φ) between the incident beam and the beam entering the collector. The observations are repeated for different accelerating potential & no. of curves are drawn.



The graph remains fairly smooth till the accelerating potential become 44 V when a spur (bump) appear on the curve. As the accelerating potential is increased, the length of spur increases till it reaches a maximum at 54V at an angle of 50^0 with further increase in accelerating potential the spur decrease in length & finally disappears at 68V. This diffraction of electron beam is very much similar to Bragg's diffraction. Therefore according to Bragg's law we have

$$2d\sin\theta = n\lambda$$

$\theta=50^0$
$n=1$

So $\lambda=2.15\text{x}\ \sin50^0\ \text{Å}$

$=1.66\ \text{Å}$

According to de-Broglie's hypothesis the wavelength of matter wave associated with an electron accelerated at a potential difference of V volt is given by

$$\lambda = \frac{12.26}{\sqrt{V}}\text{Å}$$

Here V=54 Volt, so $\lambda = \frac{12.26}{\sqrt{54}}\text{Å}$

$\lambda=1.67\ \text{Å}$

Here, it is clear that the theoretically predicted value of wavelength of matter wave (λ = 1.67 Å) is very close to experimentally observed value of wavelength (λ= 1.66 Å) in this way Davisson- Germer experiment directly verifies the wave nature of electron.

Application of Matter wave:

Matter wave are valuable supplement of X-Rays and are used in surface study of material and study of nuclei.

Heisenberg's Uncertainty Principle

This principle was discovered by W. Heisenberg in 1927. According to this principle simultaneous (at the same time) & precise (accurate) measurement of position & momentum of a particle is impossible. This principle is a direct consequence of dual nature of matter.

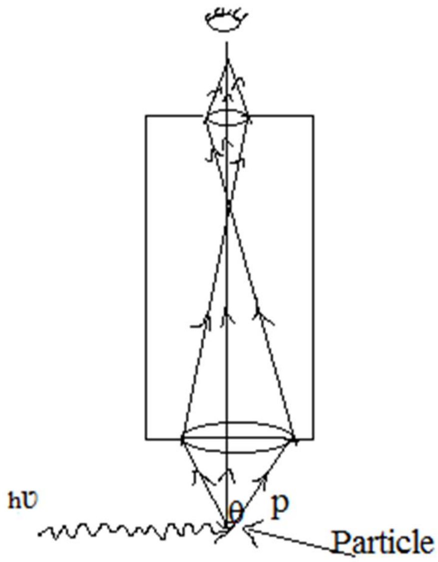
Mathematically this principle can be stated as:

$$\Delta p.\ \Delta q \geq \hbar/2$$
$$\Delta j.\ \Delta\theta \geq \hbar/2$$
$$\Delta E.\ \Delta t \geq \hbar/2$$

Where, Δp is uncertainty in momentum, Δq is uncertainty in position
Δ j is uncertainty in angular momentum, $\Delta\theta$ is uncertainty in angle
Δ E is uncertainty in energy, Δ t is uncertainty in time
$\hbar= h/2\pi$ and h is Planck's constant

Experimental illustration of Heisenberg Uncertainty Principle(HUP):

1- Determination of position of particle by a microscope: Let us consider that a particle say electron is observed by a microscope as shown below.



For the observation of electron it is required that at least one photon must strike to the eye after reflection from the particle. According to the Rayleigh criteria of resolution; the minimum distance between the two objects which can just be resolved is given by

$$\Delta x = \frac{\lambda}{2\,sin\theta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where, λ is wavelength of illuminating radiation and θ is semivetical angle.

Since, photon is travelling along the x-axis; therefore change in x component of momentum can be given as –

$$\Delta p_x = p \sin\theta - (-\,p \sin\theta)$$

$$= 2p \sin\theta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Thus from equation (1) and (2) we have

$$\Delta x.\Delta p_x = \frac{\lambda}{2\,sin\theta} x 2p\,sin\theta$$

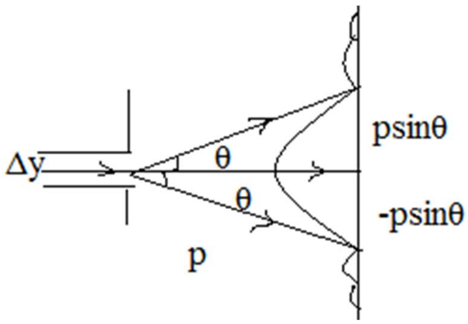
$$= \lambda p$$

$$= \frac{h}{p} xp \qquad [\text{since } \lambda = \frac{h}{p}]$$

$$= h$$

Therefore, $\Delta x.\Delta p_x \geq \hbar/2$

2- Diffraction by single slit: Let us consider that a beam of electron is diffracted by a single slit of width Δy as shown below:



As we know that diffraction from a grating is defined as

$$d \sin\theta = n\lambda$$

Here, $d = \Delta y$ and $n=1$ for single slit; so we have $\Delta y \sin\theta = \lambda$

or $$\Delta y = \frac{\lambda}{\sin\theta} \quad \ldots\ldots..(1)$$

Here, Δy is the total uncertainty in the position of entering electron.

Now change in y component of momentum can be given by

$$\Delta p_y = p \sin\theta - (-p \sin\theta)$$
$$= 2p \sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Therefore, from equations (1) and (2) we have

$$\Delta y . \Delta p_y = \frac{\lambda}{\sin\theta} \times 2p \sin\theta$$
$$= 2\lambda p$$
$$= 2\frac{h}{p} \times p \qquad [\text{since } \lambda = \frac{h}{p}]$$
$$= 2h$$

Therefore, $\Delta y . \Delta p_y \geq \hbar/2$

Note: All the calculations will be done by equating ħ.

Application of Heisenberg uncertainty principle

<u>1. Non - existence of electron in nucleus</u>:

Let us suppose that electron exists in nucleus. The total uncertainty in the position of electron will be given by

$$\Delta q = 2 \times 10^{-14} \text{ m} \qquad [\text{ as } 10^{-14} \text{ m is the radius of nucleus}] \ldots\ldots\ldots(1)$$

According to Heisenberg uncertainty principle

$$\Delta p . \Delta q = \hbar \qquad [\text{as } \hbar = h/2\pi = 1.054 \times 10^{-34} \text{ J s}]$$

$$= \frac{1.054x10-34}{2x10^{-14}}$$

$=5.27x10^{-21}$

This is uncertainty in the momentum of the electron. Therefore the momentum of the electron will be at least comparable to Δp i.e, momentum of electron (p) ≈ Δp

or $p \approx \Delta p = 5.27x10^{-21}$

So the kinetic energy (T) of the electron will be given by

$$T = \frac{p^2}{2m}$$

$$= \frac{(5.27x10^{-21})^2}{2x9.1x10^{-31}}$$

$=95.3$ Mev

Here, it is clear that if electron exists in nucleus, then it must have a kinetic energy of 95.3 MeV but experimental observations report that no particle having energy more than 4 MeV can exist in atom. Thus it is clear that electron can't exist in nucleus.

2. Radius of Bohr's first orbit:

According to Heisenberg's uncertainty principle

$$\Delta p.\Delta q = \hbar$$

or $\Delta p = \frac{\hbar}{\Delta q}$ …………………..(1)

This is uncertainty momentum therefore; uncertainty in kinetic energy (T) of the electron will be given by.

$$T = \frac{p^2}{2m}$$

$$= \frac{\hbar^2}{(\Delta q)^2 x 2m}$$

Similarly uncertainty in potential energy will be given by

$$\Delta V = \frac{-Ze^2}{\Delta q}$$

Thus uncertainty is total energy will be given by

$$\Delta E = \Delta T + \Delta V$$

$$\triangle \mathrm{E} = \frac{\hbar^2}{2m\,\mathrm{x}(\triangle \mathrm{q})^2} - \frac{Ze^2}{\triangle \mathrm{q}}$$

This is uncertainty in energy therefore, the energy of the electron will be at least comparable to $\triangle$E i.e.,

$$\mathrm{E} \approx \triangle \mathrm{E}$$

$$E = \frac{\hbar^2}{2m\,\mathrm{x}(\triangle \mathrm{q})^2} - \frac{Ze^2}{\triangle \mathrm{q}}$$

For energy to be minimum, we must have to show that

$$\frac{\partial E}{\partial(\triangle \mathrm{q})} = 0 \ \& \ \frac{\partial^2 E}{\partial(\triangle \mathrm{q})^2} = +$$

Thus let us apply first condition: $\frac{\partial E}{\partial(\triangle \mathrm{q})} = -2\frac{\hbar^2}{2m\,\mathrm{x}(\triangle \mathrm{q})^3} + \frac{Ze^2}{(\triangle \mathrm{q})^2} = 0$

or $\frac{\hbar^2}{m\,\mathrm{x}(\triangle \mathrm{q})^3} = \frac{Ze^2}{(\triangle \mathrm{q})^2}$

or $\triangle \mathrm{q} = \frac{\hbar^2}{mZe^2}$

Now applying the second condition i.e.

$$\frac{\partial^2 E}{\partial(\triangle \mathrm{q})^2} = \frac{3\hbar^2}{m(\triangle \mathrm{q})^4} - \frac{2Ze^2}{(\triangle \mathrm{q})^3}$$

$$= \frac{1}{(\triangle \mathrm{q})^3}\left[\frac{3\hbar^2}{m(\triangle \mathrm{q})} - 2Ze^2\right]$$

$$= \frac{m^3Z^3e^6}{\hbar^6}\left[\frac{3\hbar^2 mZe^2}{m(\hbar^2)} - 2Ze^2\right]$$

$$= \frac{m^3Z^4e^8}{\hbar^6} = +\mathrm{ve}$$

Thus it is clear that the value of energy is minimum & minimum value of the energy will correspond to the Bohr's first orbit.

Thus , radius of the Bohr's first orbit $\boxed{r_1 = \Delta q = \frac{\hbar^2}{mZe^2}}$

Function

The quantity whose variation makes up the matter wave is known as wave function. A wave function is a function of space and time both. It is denoted by Greek letter Ψ and generally is a complex quantity and is represented as.

$$\Psi = a + ib$$

Thus, $\Psi^* = a - ib$

Where, Ψ^* is complex conjugate of Ψ

Thus, $\Psi . \Psi^* = |\Psi^2| = a^2 + b^2$ is a real quantity & represented as probability density.

Well behaved Wave Function:

A Function is said to be well behaved when it satisfies the following condition.

1. Ψ must be continuous & single valued.
2. $\frac{\partial \Psi}{\partial x}, \frac{\partial \Psi}{\partial y}$ & $\frac{\partial \Psi}{\partial z}$ must be continuous.
3. Ψ must tends to 0 as $x \to \infty$ $y \to \infty$ $z \to \infty$.

Schrodinger Wave equation

This equation was discovered by Erwin Schrodinger in 1926. This equation is a fundamental equation of quantum mechanics and has the same sense as Newton's second Law in classical mechanics. This equation has two forms:

1. Time independent form or steady state form.
2. Time dependent form.

<u>1. Time independent form:</u> The classical differential equation for any wave in three dimensions is given by:

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2}$$

or $$\nabla^2 \Psi = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is known as Laplacean operator.

The general solution of the equation (1) can be written as:

$$\Psi(\vec{r}, t) = \Psi_o(\vec{r})e^{-i\omega t} \quad \text{……………..(2)}$$

Differentiating above equation with respect to't' we get

$$\frac{d\Psi}{dt} = (-i\omega)\Psi_o e^{-i\omega t}$$

$$\frac{d\Psi}{dt} = -i\omega\Psi \quad [\text{as } \Psi = \Psi_0 e^{-i\omega t}] \quad \text{………..(3)}$$

Again differentiating with respect to 't' we get

$$\frac{\partial^2\Psi}{\partial t^2} = (-i\omega)^2\Psi$$

$$\frac{\partial^2\Psi}{\partial t^2} = -\omega^2\Psi \quad [\text{as } i^2=-1] \quad \text{……..(4)}$$

Putting this value of $\frac{\partial^2\Psi}{\partial t^2}$ in equation (1) we get:

$$\nabla^2\Psi = \frac{-\omega^2}{v^2}\Psi \quad \text{………..(5)}$$

Since, $\omega = 2\pi\upsilon$, therefore, $\frac{\omega}{v} = \frac{2\pi\upsilon}{v}$ $(\because v = \upsilon\lambda)$

$$\frac{\omega}{v} = \frac{2\pi}{\lambda}$$

Putting this value of $\frac{\omega}{v}$ in equation (5)

$$\nabla^2\Psi = -\frac{4\pi^2}{\lambda^2}\Psi \quad \text{……….(6)}$$

According to de-Broglie relation

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

Putting this value in equation (6): we get,

$$\nabla^2\Psi = -\frac{4\pi^2}{h^2}m^2v^2\Psi \quad \text{…………(7)}$$

Let E & V be the total & potential energy of the particle, then kinetic energy of the particle will be written as:

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

Multiply by 2m both sides we get:

$$m^2\mathrm{v}^2 = 2m(\mathrm{E} - \mathrm{V})$$

Putting the values of $m^2\mathrm{v}^2$ in equation (7) we get:

$$\nabla^2\Psi = -\frac{4\pi^2}{h^2}2m(E - V)\Psi$$

or $$\nabla^2\Psi = -\frac{2m}{\hbar^2}(E - V)\Psi \qquad [\because \hbar = h/2\pi]$$

or $$\boxed{\nabla^2\Psi + \frac{2m}{\hbar^2}(E - V)\Psi = 0} \qquad \ldots\ldots\ldots(8)$$

This is Schrodinger's wave equation in the independent form.

2: <u>Time dependent form:</u> Let us consider equation (8) i.e.

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

Multiplying $\frac{\hbar^2}{2m}$ both the sides, we get:

$$\frac{\hbar^2}{2m}\nabla^2\Psi + E\Psi\text{-}V\Psi = 0$$

or $$-\frac{\hbar^2}{\mathbf{2m}}\nabla^2\Psi + V\Psi = E\Psi \quad \ldots\ldots\ldots.(9)$$

Let us consider equation (3) i.e. $\frac{d\Psi}{dt} = -i\omega\Psi$

$$= \text{-}\ i2\pi\upsilon\Psi \qquad [\text{since } \omega = 2\pi\upsilon]$$

$$= \text{-}i2\pi\frac{E}{h}\Psi \qquad [\text{since } (E = h\upsilon)]$$

or $$E\Psi = \text{-}\ \frac{h}{i2\pi}\frac{\partial\Psi}{\partial t}$$

or $$E\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Putting this values of $E\Psi$ in equation (9), we get:

$$\boxed{-\frac{\hbar^2}{\mathbf{2m}}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(10)$$

This is Schrodinger wave equation in time independent form.