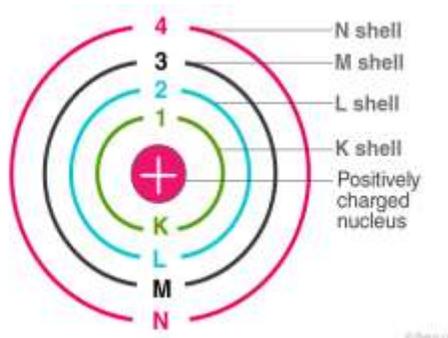


Introduction to the Bohr Model

Bohr model of the atom was proposed by Neil Bohr in 1915. It came into existence with the modification of Rutherford's model of an atom. Rutherford's model introduced the nuclear model of an atom, in which he explained that a nucleus (positively charged) is surrounded by negatively charged electrons.

Bohr modified this atomic structure model by explaining that electrons move in fixed orbital's (shells) and not anywhere in between and he also explained that each orbit (shell) has a fixed energy level. Rutherford basically explained the nucleus of an atom and Bohr modified that model into electrons and their energy levels.



Bohr's model consists of a small nucleus (positively charged) surrounded by negative electrons moving around the nucleus in orbits. Bohr found that an electron located away from the nucleus has more energy, and electrons close to the nucleus have less energy.

Postulates of Bohr's Model of an Atom

In an atom, electrons (negatively charged) revolve around the positively charged nucleus in a definite circular path called as orbits or shells.

Each orbit or shell has a fixed energy and these circular orbits are known as orbital shells.

The energy levels are represented by an integer ($n=1, 2, 3, \dots$) known as the quantum number. This range of quantum number starts from nucleus side with $n=1$ having the lowest energy level. The orbits $n=1, 2, 3, 4, \dots$ are assigned as K, L, M, N,.... shells and when an electron attains the lowest energy level it is said to be in the ground state.

The electrons in an atom move from a lower energy level to a higher energy level by gaining the required energy and an electron moves from a higher energy level to lower energy level by losing energy.

Limitations of Bohr's Model of an Atom

Bohr's model of an atom failed to explain the Zeeman Effect (effect of magnetic field on the spectra of atoms).

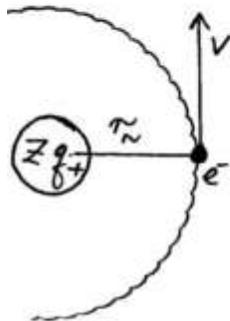
It also failed to explain the Stark effect (effect of electric field on the spectra of atoms).

It violates the Heisenberg Uncertainty Principle.

It could not explain the spectra obtained from larger atoms.

DERIVATION OF E_n and r_n FOR
HYDROGEN-LIKE ATOM (SINGLE ELECTRON SYSTEM)

$He^+ (1e^-, 2p^+)$; $Li^{2+} (1e^-, 3p^+)$; $Be^{3+} (1e^-, 4p^+)$
 $B^{4+} (1e^-, 5p^+)$; $C^{5+} (1e^-, 6p^+)$ } different Z val



$$F = \frac{(-e)(+Ze)}{4\pi\epsilon_0 r_n^2} \quad \leftarrow F = \frac{1}{4\pi\epsilon_0}$$

$$F = -\frac{Ze^2}{4\pi\epsilon_0 r_n^2} \quad \text{----- (i)}$$

$$F' = -\frac{mv^2}{r_n} \quad \text{----- (ii)}$$

(centrifugal force)

(i) = (ii) : $F = F'$

$$-\frac{Ze^2}{4\pi\epsilon_0 r_n^2} = -\frac{mv^2}{r_n}$$

$$\therefore mv^2 = \frac{Ze^2}{4\pi\epsilon_0 r_n} \quad \text{----- (ii)}$$

Total Energy, $E_n = \text{Potential Energy} + \text{Kinetic Energy}$

$$= (F \times r_n) + \left(\frac{1}{2}mv^2\right)$$

$$\begin{aligned}
 \text{Total Energy, } E_n &= \text{Potential Energy} + \text{Kinetic Energy} \\
 &= (F \times r_n) + \left(\frac{1}{2}mv^2\right) \\
 &= -\frac{e^2 Z}{4\pi\epsilon_0 r_n} + \frac{1}{2}\left(\frac{e^2 Z}{4\pi\epsilon_0 r_n}\right) \\
 E_n &= -\frac{1}{2} \frac{e^2 Z}{4\pi\epsilon_0 r_n} \dots\dots (iv)
 \end{aligned}$$

angular momentum

$$mvr_n = n \frac{h}{2\pi} \Rightarrow m^2 v^2 r_n^2 = \frac{n^2 h^2}{4\pi^2}$$

$$(mv^2)mr_n^2 = \frac{n^2 h^2}{4\pi^2}$$

$$\frac{Ze^2}{4\pi\epsilon_0 r_n} \times mr_n^2 = \frac{n^2 h^2}{4\pi^2}$$

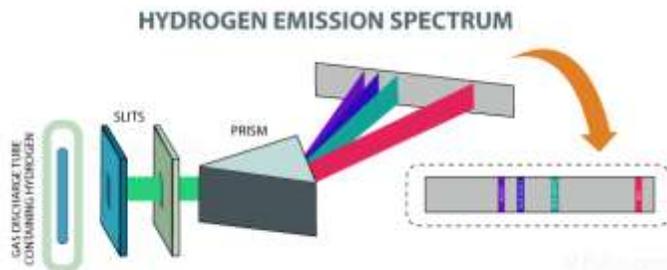
$$\therefore r_n = \frac{n^2 h^2 \epsilon_0}{\pi e^2 m Z} \dots\dots (v)$$

From eqn (iv) & (v) substitute for r_n .

$$E_n = -\frac{e^4 m Z^2}{8\epsilon_0^2 h^2 n^2} \dots\dots (vi)$$

Atomic spectrum of hydrogen atom: Rydberg Equation

We all know that electrons in an atom or a molecule absorb energy and get excited, they jump from a lower energy level to a higher energy level and they emit radiation when they come back to their original states. This phenomenon accounts for the emission spectrum through hydrogen too, better known as the [hydrogen emission spectrum](#).



In the late 1800s, it was known that when a gas is excited using an electric discharge and the light emitted is viewed through a diffraction grating; the spectrum observed consists not of a continuous band of light, but of individual lines with well-defined wavelengths. Experiments have shown that the wavelengths of the lines were characteristic of the chemical element

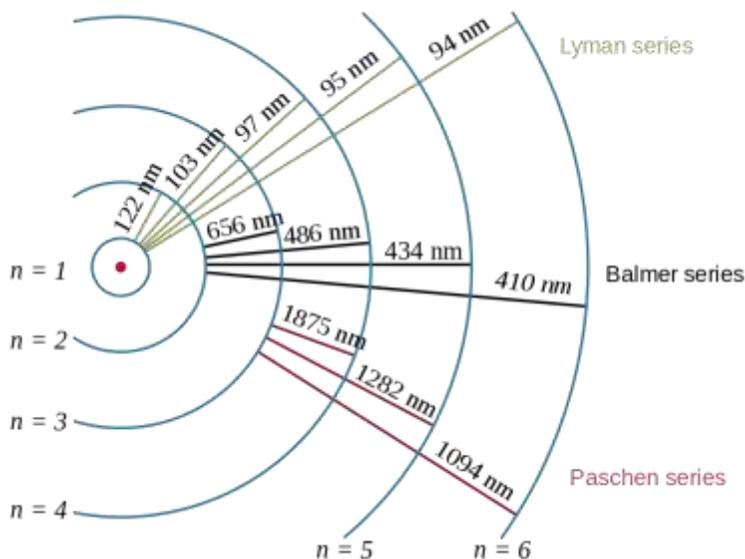
emitting the light. They were an atomic fingerprint which resulted from the internal structure of the atom.

What is Hydrogen spectrum?

The **hydrogen** spectrum is an important piece of evidence to show the quantized electronic structure of an atom. The hydrogen atoms of the molecule dissociate as soon as an electric discharge is passed through a gaseous hydrogen molecule. It results in the emission of electromagnetic radiation initiated by the energetically excited hydrogen atoms. The hydrogen emission spectrum comprises radiation of discrete frequencies. These series of radiation are named after the scientists who discovered them.

Hydrogen spectrum wavelength

When a hydrogen atom absorbs a photon, it causes the electron to experience a transition to a higher energy level, for example, $n = 1$, $n = 2$. When a photon is emitted through a hydrogen atom, the electron undergoes a transition from a higher energy level to a lower, for example, $n = 3$, $n = 2$. During this transition from a higher level to a lower level, there is the transmission of light occurs. The quantized energy levels of the atoms, cause the spectrum to comprise wavelengths that reflect the differences in these energy levels. For example, the line at 656 nm corresponds to the transition $n = 3 \rightarrow n = 2$.



Hydrogen transitions

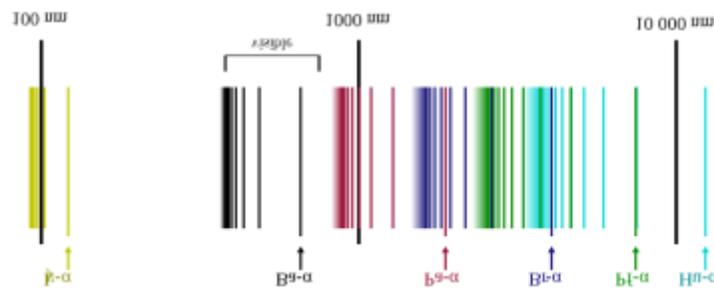
Hydrogen emission spectrum:

In the year 1885, on the basis of experimental observations, Balmer proposed the formula for correlating the wave number of the spectral lines emitted and the energy shells involved. This formula is given as:

$$\bar{\nu} = 109677 \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

This series of the hydrogen emission spectrum is known as the Balmer series. This is the only series of lines in the electromagnetic spectrum that lies in the visible region. The value, $109,677 \text{ cm}^{-1}$, is called the Rydberg constant for hydrogen. The Balmer series is basically the part of the hydrogen emission spectrum responsible for the excitation of an [electron](#) from the second shell to any other shell. Similarly, other transitions also have their own series names. Some of them are listed below,

- Transition from the first shell to any other shell – Lyman series
- Transition from the second shell to any other shell – Balmer series
- Transition from the third shell to any other shell – Paschen series
- Transition from the fourth shell to any other shell – Brackett series
- Transition from the fifth shell to any other shell – Pfund series



Hydrogen spectrum series

Johannes Rydberg, a Swedish spectroscopist, derived a general formula for the calculation of wave number of hydrogen spectral line emissions due to the transition of an electron from one orbit to another. The general formula for the hydrogen emission spectrum is given by:

$$\bar{\nu} = 109677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where,

$$n_1 = 1, 2, 3, 4 \dots$$

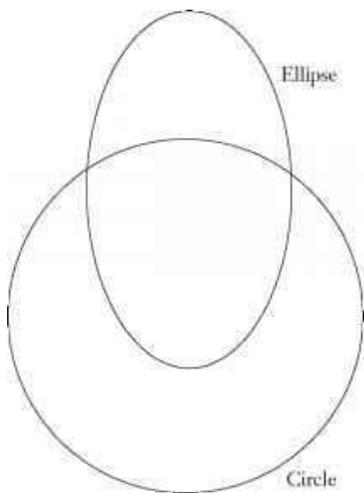
$$n_2 = n_1 + 1$$

$\bar{\nu}$ = wave number of [electromagnetic radiation](#). The value $109,677 \text{ cm}^{-1}$ is known as Rydberg constant for hydrogen.

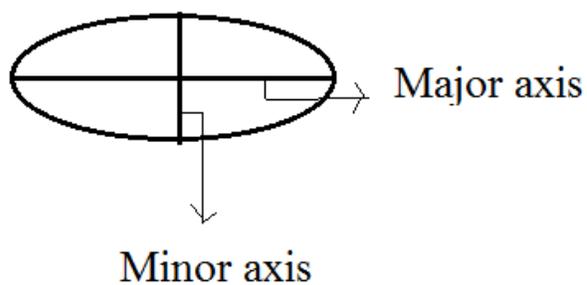
Sommerfeld atomic model –

This model explains the fine spectrum of Hydrogen atom. The important postulates of Sommerfeld atomic model are-

1) *The orbits may be both circular or elliptical.*



2) *When path is elliptical, then there are two axis – major axis & minor axis. When length of major & minor axis become equal then orbit is circular.*



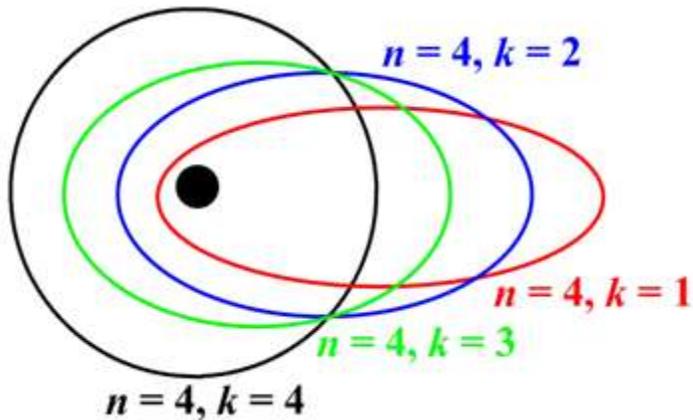
3) *The angular momentum of electron moving in an elliptical orbit is $kh/2\pi$.*

k is an integer except zero.

Value of k = 1,2,3,4.....

$n/k = \text{length of major axis} / \text{length of minor axis}$

With increase in value of k , ellipticity of the orbit decreases. When $n = k$, then orbit is circular.



source : nptel

4) Sommerfeld suggested that orbits are made up of sub energy levels . These are s,p,d,f. These sub shells possess slightly different energies.

Bohr gave a quantum number 'n', which determines the energy of electron.

Sommerfeld introduced a new quantum number called Orbital or Azimuthal Quantum number (l) which determines the orbital angular momentum of electron.

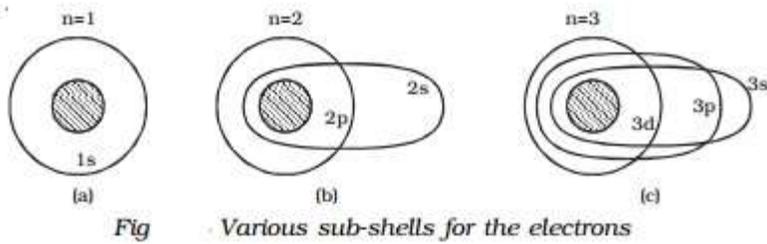
Values of $l = 0$ to $(n-1)$

For, $n=1$; $l=0$; 1s sub shell

$n=2$; $l=0,1$; 2s , 2p sub shell

$n=3$; $l=0,1,2$; 3s , 3p , 3d sub shell

$n=4$; $l=0, 1, 2, 3$; 4s , 4p , 4d , 4f sub shell



source : Readorrefer.in

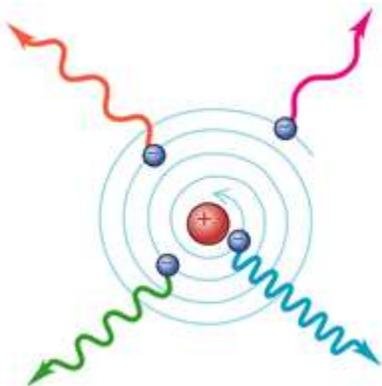
5) When an electron jumps from one orbit to another orbit, the difference of energy (ΔE) depends upon sub energy levels.

6) It explains the splitting of individual spectral lines of hydrogen & thus fine spectrum . It could not predict the exact number of lines which are actually present in the fine spectrum.

Defects of Sommerfeld atomic model-

- 1) This model does not explain the behavior of system having more than one electron.
- 2) This model does not explain the Zeeman & Stark effect.

De-Broglie Waves



Classical physics predicts electron should “spiral in” to the nucleus emitting continuous spectrum of radiation as the atom “collapses”. Classical physics can’t give us stable atoms.

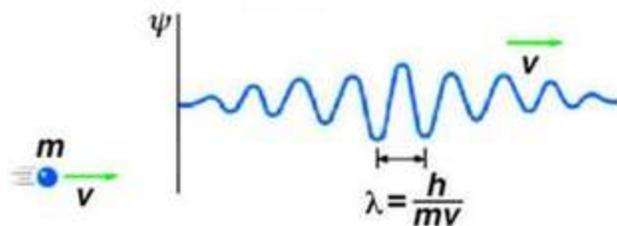
In 1924, the French physicist Louis de Broglie proposed that moving objects behave like waves; these are called Matter Waves.

De Broglie waves represent the set of waves which establish or reveal the nature and conduct of some atoms, molecules or some elementary particles under certain circumstances.

The de Broglie Wavelength is denoted by λ and is written as,

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

Here the symbols have the following meanings.



'h' stands for Planck constant

'm' denotes the mass

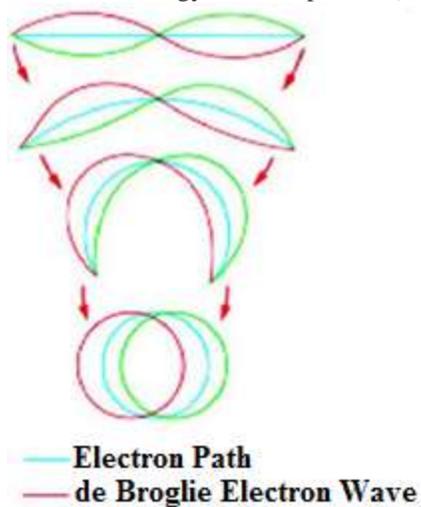
'v' is the velocity of the particle

So, the momentum of 'p' will be,

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

Hence, the De Broglie relation shows that **the wavelength is proportional to the momentum of the particle.**

The frequency of the waves has also been deduced by Broglie and he has proved it to be directly proportional to the total energy E of the particle (where E is the sum of potential and kinetic energy).

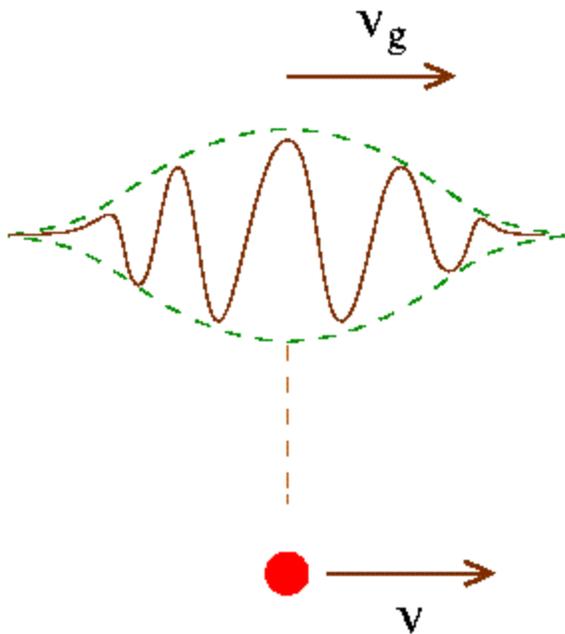


The French Physicist Louis de Broglie, in 1924 suggested that besides the particle properties, particles may also exhibit wave properties. It took around three years to spot the wave nature of electrons. These waves are also called as matter waves and they demonstrate the properties of a material object which tend to change in time or space in accordance with the mathematical equations which illustrate these waves. De Broglie waves play a vital and commendable role but only in the case of subatomic particles.

An electron can circle a nucleus only in orbits that contain a whole number of de Broglie Wavelengths. The quantum number n of an orbit is the number of electron waves that fit into the orbit.

It is only due to the Broglie waves that subatomic particles can be found in otherwise unexpected cases. The reason behind this is the ability of these waves to penetrate barriers.

The Broglie waves around a closed loop just like the waves coupled with electrons attached to the nuclei in atoms can continue to stay provided the waves fit perfectly around the loop, else they cancel out themselves. It is this necessity that forces the electrons in atoms to opt for some specific structures or arrangements out of the many which would have been there otherwise.



It was in 1925, even before the discovery of electron diffraction that De Broglie proposed the concept of wavelength λ of waves associated with particles like electrons and photons. If 'p' is the momentum of these particles then it is given by

$$\lambda = h/p = h/mv$$

The wavelength associated with an electron accelerated through a potential difference of V volt is given by

$$1/2 m_e v^2 = eV \quad \text{or} \quad v = \sqrt{2eV/m_e}$$

$$\lambda = \frac{h}{m_e v} = \frac{h}{\sqrt{2m_e eV}}$$

Problem 1

An electron and a photon have same wavelength. If p is the momentum of electron and E is the energy of photon. The magnitude of p/E in S.I unit is

- (a) 3.0×10^8
- (b) 3.33×10^{-9}
- (c) 9.1×10^{-31}
- (d) 6.64×10^{-34}

Solution:-

As we know that, for electron, $\lambda = h/p$

or, $p = h/\lambda$

and for photon $E = hc/\lambda$

Thus, $p/E = 1/c = 1/(3 \times 10^8 \text{ m/s})$

$= 3.33 \times 10^{-9} \text{ s/m}$

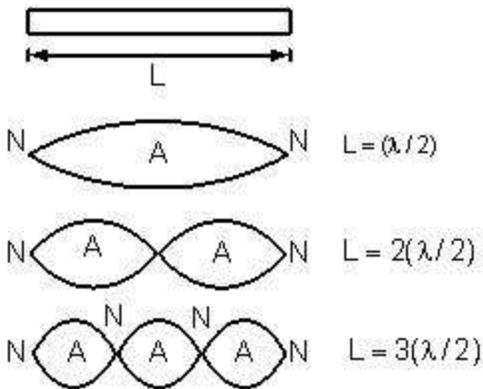
Therefore, from the above observation we conclude that, option (b) is correct.

Problem 2:-

A particle of mass m is confined to a narrow tube of length L . Find

- (a) The wavelengths of the de-Broglie wave which will resonate in the tube,
- (b) The corresponding particle momenta, and
- (c) The corresponding energies.

Solution:-



(a) The de Broglie waves will resonate with a node at each end of the tube.

A few of the possible resonance forms are listed below:

$$\lambda_n = 2L / n; \quad n = 1, 2, 3, \dots$$

(b) Since de-Broglie wavelengths are

$$\lambda_n = h / p_n$$

$$\therefore p_n = h / \lambda_n = nh / 2L \quad n = 1, 2, 3, \dots$$

$$(c) (KE)_n = P_n^2 / 2m = n^2 h^2 / 8L^2 m, \quad n = 1, 2, 3, \dots$$

Problem 3:-

What is the energy and wavelength of a thermal neutron?

Solution:-

By definition, a thermal neutron is a free neutron in a neutron gas at about 20°C (293 K).

$$KE = \frac{3}{2} kT = \frac{3}{2} (1.38 \times 10^{-23}) (293) = 6.07 \times 10^{-21} \text{ J}$$

$$\lambda = h/p = h/\sqrt{2m_0 (KE)} = 6.63 \times 10^{-34} / \sqrt{2(1.67 \times 10^{-27}) (6.07 \times 10^{-21})} = 0.147 \text{ nm}$$

Heisenberg's Uncertainty Principle

All moving objects that we see around us e.g., a car, a ball thrown in the air etc., move along definite paths. Hence their position and velocity can be measured accurately at any instant of time. Is it possible for subatomic particle also?

As a consequence of dual nature of matter, Heisenberg, in 1927 gave a principle about the uncertainties in simultaneous measurement of position and momentum (mass x velocity) of small particles.

This Principle States:

“It is impossible to measure simultaneously the position and momentum of a small microscopic moving particle with absolute accuracy or certainty” i.e., if an attempt is made to measure any one of these two quantities with higher accuracy, the other becomes less accurate.

The product of the uncertainty in position (Δx) and the uncertainty in the momentum ($\Delta p = m \cdot \Delta v$ where m is the mass of the particle and Δv is the uncertainty in velocity) is equal to or greater than $h/4\pi$ where h is the Planck's constant.

Thus, the mathematical expression for the Heisenberg's uncertainty principle is simply written as

$$\Delta x \cdot \Delta p > h/4\pi$$

Explanation of Heisenberg's uncertainty principle

Suppose we attempt to measure both the position and momentum of an electron, to pinpoint the position of the electron we have to use light so that the photon of light strikes the electron and the reflected photon is seen in the microscope. As a result of the hitting, the position as well as the velocity of the electron is disturbed. The accuracy with which the position of the particle can be measured depends upon the wavelength of the light used. The uncertainty in position is $\pm\lambda$. The shorter the wavelength, the greater is the accuracy. But shorter wavelength means higher frequency and hence higher energy. This high energy photon on striking the electron changes its speed as well as direction. But this is not true for macroscopic moving particle. Hence Heisenberg's uncertainty principle is not applicable to macroscopic particles.

What is Schrodinger wave equation?

Schrodinger wave equation describes the wave function or state function, There are two types of Schrodinger equations, time-dependent Schrodinger wave equation, and time-independent Schrodinger wave equation. These equations were presented by Ervin Schrodinger in 1925.

In classical mechanics, the motion of a body is given by Newton's second law of motion. But elementary particles like electron, protons, and photons possess wave properties as well, therefore another equation instead of Newton's second law equation ($F=ma$) is required for describing their motion.

The new equation must take into account wave properties of particles and it should, therefore, be similar to the equation describing wave on strings acoustic waves or electromagnetic waves. This equation was found in 1926 by the Austrian physicist Schrodinger and is known after his name as Schrodinger wave equation.

Schrodinger wave equation derivation

Consider a particle of mass "m" moving with velocity "v" in space. Suppose a system of stationary waves is associated with the particles at any point in space in the neighborhood of particle.

We know that:

$$\Psi = \Psi_0 \sin 2\pi vt \text{ -----(1)}$$

Where

$$\omega = 2\pi\nu, \Psi_0 = \text{amplitude} \text{ and } \nu = \text{frequency}$$

Differentiating equation (1) with respect to time we have:

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t} (\Psi_0 \sin 2\pi vt)$$

$$\frac{\partial \Psi}{\partial t} = \Psi_0 2\pi\nu \cos 2\pi vt$$

Again differentiating above equation with respect to time we have:

$$\frac{\partial}{\partial t} \left(\frac{\partial \Psi}{\partial t} \right) = \Psi_0 2\pi\nu \frac{\partial}{\partial t} (\cos 2\pi vt)$$

$$\frac{\partial^2 \Psi}{\partial t^2} = \Psi_0 2\pi\nu (-\sin 2\pi vt) 2\pi\nu$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -4\pi^2 \nu^2 \Psi_0 \sin 2\pi vt$$

Using equation (1) $\Psi = \Psi_0 \sin 2\pi vt$ the above relation will become

$$\frac{\partial^2 \Psi}{\partial t^2} = -4\pi^2 \nu^2 \Psi \text{ -----(2)}$$

Sine the general wave equation is:

$$\frac{\partial^2 \psi}{\partial t^2} = \nabla^2 v^2 \psi \quad \text{-----(3)}$$

Comparing equation (2) and (3) we get

$$\nabla^2 v^2 \psi = -4 \pi^2 v^2 \psi \quad \text{-----(4)}$$

But $v = v\lambda$

$$v = \frac{v}{\lambda}$$

$$v^2 = \frac{v^2}{\lambda^2}$$

Now equation (4) will become

$$\nabla^2 v^2 \psi = -4 \pi^2 \times \frac{v^2}{\lambda^2} \times \psi$$

$$\nabla^2 v^2 \psi = \frac{-4 \pi^2}{\lambda^2} \psi \quad \text{-----(5)}$$

According to de broglie hypothesis:

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

$$\lambda^2 = \frac{h^2}{m^2 v^2}$$

Now equation (5) will become

$$\nabla^2 \psi = \frac{-4\pi^2}{h^2} \frac{\psi}{m^2 v^2}$$
$$\nabla^2 \psi = -\frac{4\pi^2 m^2 v^2 \psi}{h^2} \text{-----(6)}$$

We know that total energy of the particle in space is the sum of its K.E and P.E, so

$$E = \text{K.E} + \text{P.E}$$

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

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

$$m^2 v^2 = 2m(E - V) \text{-----(7)}$$

Using equation (7) in equation (6) we have

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

$$\nabla^2 \psi = -\frac{8\pi^2 m(E - V)}{h^2} \psi$$

$$\nabla^2 \psi + \frac{8\pi^2 m(E - V)}{h^2} \psi = 0$$

This is the Schrodinger time-independent wave equation.

Wave function and its physical significance

WAVE FUNCTION

If there is a wave associated with a particle, then there must be a function to represent it. This function is called wave function.

Wave function is defined as that quantity whose variations make up matter waves. It is represented by Greek symbol ψ (psi), ψ consists of real and imaginary parts.

$$\Psi = A + iB$$

PHYSICAL SIGNIFICANCE OF WAVE FUNCTIONS (BORN'S INTERPRETATION):

Born's interpretation

The wave function ψ itself has no physical significance but the square of its absolute magnitude $|\psi|^2$ has significance when evaluated at a particular point and at a particular time $|\psi|^2$ gives the probability of finding the particle there at that time.

The wave function $\psi(x,t)$ is a quantity such that the product

$$P(x,t) = \psi^*(x,t)\psi(x,t)$$

Is the probability per unit length of finding the particle at the position x at time t .

$P(x,t)$ is the probability density and $\psi^*(x,t)$ is complex conjugate of $\psi(x,t)$

Hence the probability of finding the particle is large wherever ψ is large and vice-versa.

NORMALIZATION CONDITION

The probability per unit length of finding the particle at position x at time t is

$$P = \psi^*(x,t)\psi(x,t)$$

So, probability of finding the particle in the length dx is

$$Pd x = \psi^*(x,t)\psi(x,t)dx$$

Total probability of finding the particle somewhere along x -axis is

$$\int p dx = \int \psi^*(x,t)\psi(x,t) dx$$

If the particle exists, it must be somewhere on the x-axis, so the total probability of finding the particle must be unity i.e.

$$\int \psi^*(x,t)\psi(x,t) dx = 1 \quad (1)$$

This is called the normalization condition. So a wave function $\psi(x,t)$ is said to be normalized if it satisfies the condition(1)