→ Elementary quantum mechanics:→

→ Introduction:→

→ Classical mechanics:→

- The phenomenon associated with large size objects moving at speed much below the speed of light e.g., falling stones, planetary motion etc. could be explained by classical mechanics.
- Classical mechanics is also called Newtonian mechanics as it was put forward by Newton and is based on Newtons laws of motion.

→ Quantum mechanics or Wave mechanics:→

- Wave mechanics is a mathematical treatment of the behaviour of small particles and involves the application of fundamental concept in physics, namely the concept of wave.
- Two important principles laid down the foundation of wave mechanics, dual nature of matter and the Heisenberg uncertainty principles.
- Later, the mathematics of WM was developed by workers, the most popular is Schrodinger.
- The development of wave mechanics is based on the following concepts:-
  1. de-Broglie's idea of dual nature of matter.
  2. Heisenberg's uncertainty principle.
  3. Schrodinger's wave equation.
- The heart of the wave mechanics is an equation called Schrodinger wave equation. It can be derived directly or on the basis of certain postulates of quantum mechanics.

→ Failure of classical mechanics :→

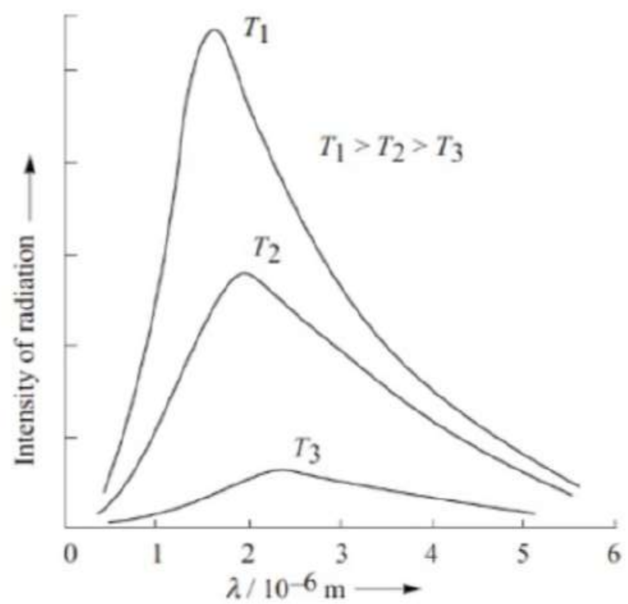
- Classical mechanics fails when applied to small particles such as electrons, atoms, molecules etc.
- According to classical mechanics it should be possible to determine simultaneously the position and velocity (or momentum) of a moving particle but this contradicted by the Heisenberg's uncertainty principle.
- Similarly classical mechanics assumes that the energy is emitted or absorbed continuously whereas Planck's quantum theory postulates that energy is emitted or absorbed not continuously but discontinuously in the form of packets of energy, called quanta.

→ In view of the failure of classical mechanics to explain the phenomenon associated with the small particles, a new mechanics has been put forward to explain these phenomenon.

- One of these is called matrix mechanics put forward by Heisenberg in 1925. It is purely mathematical and does not assume any atomic model.
- The other is called the wave mechanics put forward by Schrodinger in 1926. It is based upon de-Broglie's concept of dual nature of matter.
- However it has been shown that both mechanics are essentially equivalent so far as the basic physical concepts are concerned. Wave mechanics is comparatively simpler and more useful in applications to chemistry.
- Wave mechanics is called 'particle mechanics' or 'quantum mechanics' because it deals with the problems that arise when particles such as electrons, nuclei, atoms, molecules etc. are subjected to force.

→ Black-body radiation:→

- A black-body is one which can absorb all types of radiation that falls upon it.
- Experimentally, such a body is represented by a hollow container with a very small hole in the wall.
- When such a body is heated, it emits radiations of all types of wavelengths. The origin of radiations from a heated is the rapid vibrating particles (known as oscillators) composing the body.
- According to Maxwell's electromagnetic theory, these oscillators emit radiant energy in the form of electromagnetic waves. The frequency of the wave emitted from an oscillator is equal to the frequency of electromagnetic waves.
- At low temperatures, the emission is mainly in the infrared region, but as the temperature is raised, the wavelength at which most of the light is emitted shifts the blue region of the spectrum.
- The intensity of the emitted radiation depends on the temperature of the container as well as on the wavelength of the radiation.



→ Fundamental laws of black-body radiations:→

- These laws are base on classical theory
- These laws explain qualitative and quantitative nature of the curve shown in fig.

1. Stefan-Boltzman law.
2. Wien's displacement law.

1. Stefan - Boltzmann law :→

- This law was established experimentally by Stefan.
- According to this law, the intensity E of total radiation (the area under the curve) is proportional to the fourth power of the Kelvin temperature T, i.e.

$$E = \sigma' T^4$$

or $$E = \left(\frac{4}{c}\sigma\right) T^4$$

where σ = Stefan's constant = $5.672 \times 10^{-8}\ J\ m^{-2}\ s^{-1}\ K^{-4}$

- Subsequently, this law was derived by Boltzmann using thermodynamic principles.

2. Wien's displacement law :→

- According to this law, the wavelength λ at the maximum of the spectral distribution is inversely proportional to the temperature T.

$$\lambda_{max} = \frac{1}{T}$$

or $$\lambda_{max} T = \text{constant}$$

$$\lambda_{max} T = b$$

where b = Wien constant = 0.0029 m K.

→ Planck's radiation law: Quantum theory of radiation:→

- The energy distribution in black body radiations could not be explained by the application of classical mechanics.
- The correct expression was derived by Planck on the basis of the quantum theory of radiation. According to this theory-
  1. Radiant energy is emitted or absorbed discontinuously in the form of tiny bundles of energy known as quanta.
  2. Energy of each quanta is given by

$$E = h\nu$$

where ν = Frequency of radiation (s^{-1})
h = Fundamental constant known as Planck's constant (6.626×10^{-34} Js)

- The value of quantum of energy is also given by

$$E = hc\bar{\nu} \qquad \left[\nu = \frac{c}{\lambda}, \quad \nu = c\bar{\nu}, \quad \bar{\nu} = \frac{1}{\lambda} \right]$$

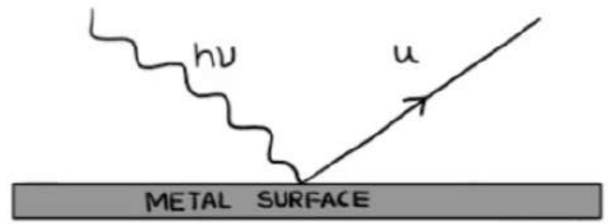
where $\bar{\nu}$ = wave number (Reciprocal of wave length)

  3. A body can emit or absord energy in whole number mulitples of quantum, i.e., $1h\nu$, $2h\nu$, $3h\nu$ ... $nh\nu$. Energy in fractions of a quantum cannot be lost or absorbed. This is known as quantization of energy.
- Based on this theory, Planck obtained the following expression for energy density of black body radiation. This expression explains all black body radiation curves at all wave lengths obtained at different temperatures. Plank was awarded Physics Nobel prize 1918 for this theory.

$$E(\nu)\,d\nu = \frac{8\pi h\nu^3}{c^3} \times \frac{d\nu}{\exp(h\nu/kT)-1}$$

→ Photoelectric effect:→

- J.J. Thomson obeserved in some experiments that when light of a certain frequency strikes the surface of a metal, electrons are ejected from the metal.
  This phenomenon is known as the photoelectric effect.
- A few metals show this effect under the action of visible light but many more show it under the action of more energetic UV light.



- Cesium, which amongst the alkali metals has lowest ionisation energy, is also the metal from which electrons are ejected most easily by light. This metal is, therefore, used largely in photoelectric cells.
- After making careful studies of photoelectric effect under different conditions, the following observation were made -

1. For each metal, a certain minimum frequency of incident light is needed to eject electrons. This is known as threshold frequency (ν_0). A light of smaller frequency than this cannot eject electrons no matter how long it falls on the metal surface or how high is its intensity. The threshold frequency is different for different metals.
2. The kinetic energy of ejected electrons is independent of the intensity of the incident light but varies linearly with its frequency.
3. The number of ejected electrons from the metal surface depends upon the intensity of the incident radiation. The greater the intensity, the larger is the number of ejected electrons.

- The photoelectric effect cannot be explained on the basis of classical wave theory of light. According to this theory, energy of light depends on its intensity. If this view is correct, then light of any frequency, if made sufficiently intense, can cause ejection of electrons. But this does not happen.
- The quantum theory of radiation gave an easy explanation for the photoelectric effect. According to this theory, light consists of bundles of energy called photons (Energy, $E = h\nu$). When a photon of light of frequency ν_0 (threshold frequency) strikes an electron in a metal, it imparts its entire energy ($= h\nu_0$) to the electron. This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus. Thus each photon can eject one electron. If the frequency of the light is less than ν_0, there will be no ejection of electron.
- Now, suppose the frequency of the light falling on a metal surface is higher than the threshold frequency. Let it be ν.

  When photon of this light strikes a metal surface, some of it energy (which is equal to the energy binding the electrons with nucleus) is consumed to separate the electron from the metal and the remaining energy will be imparted to the ejected electron to give it certain velocity u (i.e., Kinetic energy $= \frac{1}{2}mu^2$).
- Einstein, applying the quantum theory, showed that

$$h\nu = \phi + \frac{1}{2}mu^2 \quad —①$$

Where = ϕ = threshold energy (or the work function) of the metal.

$\frac{1}{2}mu^2$ = Kinetic energy imparted to the ejected electron.

Evidently $\phi = h\nu_0$ — (2)

substituting value of ϕ in eq. (1)

$$h\nu = h\nu_0 + \frac{1}{2}mu^2$$

or $$h\nu - h\nu_0 = \frac{1}{2}mu^2$$

or $$h(\nu - \nu_0) = \frac{1}{2}mu^2 \quad \text{— (3)}$$

Eq. (3) is called Einstein photoelectric equation. Albert Einstein (1879-1955), German physicist, won the Physics Nobel prize (1921) for explaining the photoelectric effect.

Eq. (3) is tested by Robert Milliken. Knowing the value of kinetic energy, ν and ν_0, value of h (6.570×10^{-34} Js) was also calculated which was found to be an excellent agreement with the value 6.626×10^{-34} Js obtained from experiments on black body radiations.

- It is evident from the above discussion that photoelectric effect can be explained only on the basis of the particle theory of light. But certain phenomenon, such as diffraction, interference and polarisation of light, can be explained on the basis of classical wave theory of light. Thus, light is considered to have a dual character. It behave as a particle and also as a wave.

→ Heat capacity of solids:→

- The amount of heat required for increasing the temperature of one mole a solid through 1°c is called molar heat capacity or heat capacity.
- If mass of the solid is 1 gm, the heat capacity is colled specific heat.
- According to Einstein, variation of heat capacity of monoatomic solids with temperature can be explained with the help of Planck's quantum theory of radiation.
- The monoatomic solid may be considered a collection of oscillators with three vibrational degrees of freedom.
- On the basis of classical law of equipartition of energy, each oscillator of such a solid possesses an average energy equal to 3kT.

Thus, for one mole of oscillators, the molar energy is

$$E = N_A(3kT) = 3RT \quad -(1) \quad [\because R = N_A k]$$

where N_A = Avogadro number

k = Boltzmann constant

T = Temperature

Since $C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad -(2)$

we have $C_V = 3N_A k = 3R \quad -(3)$

According to eq. (3), monoatomic solid have constant heat capacity equal to 3R (a value which was obtained theoretically by Dulong and Petit, $3R = 25\ J\ K^{-1}\ mol^{-1}$). Experimentally, it is found that this value of heat capacity is observed only at high temperatures.

- According to classical theory, the heat capacity of monoatomic solid should be independent of temperature. This conclusion, however, does not agree with the experimental results, according to which, the heat capacity decrease with the decrease in temperature.

→ Einstein explanation of variation of heat capacity:→

- Einstein explained the variation of heat capacity with temperature by using Planck's quantum theory of radiation.
- He assumed that the oscillator can have vibrational energy which is an integral multiple of some minimum value i.e.

$$E = n\varepsilon \quad \text{— (4)}$$

or

$$\nu = n\nu_0 \quad \text{— (5)}$$

where ν = frequency of oscillator

ν_0 = smallest allowed frequency

Thus, all oscillators are not vibrating with the same frequency but have values which are simply on integral of the smallest frequency ν_0. The number of oscillators possesing the frequency ν can be determined from equation of Blotzmann law.

$$N_i = n_0 \exp(-\varepsilon_i / kT) \quad \text{— (6)}$$

where = ε_i = energy of ith oscillator

n_0 = Constant

- The average energy of the oscillator is given by

$$\bar{E} = \frac{\varepsilon}{\exp(\varepsilon/kT) - 1} \quad \text{— (7)}$$

where ε = minimum energy of the oscillator

Substituting $\varepsilon = h\nu_0$, we get

$$\bar{E} = \frac{h\nu_0}{\exp(h\nu_0/kT) - 1} \quad \text{— (8)}$$

- The molar energy of a solid is

$$E = N_A(3\bar{E}) = N_A\left\{3\frac{h\nu_0}{\exp(h\nu_0/kT) - 1}\right\} \quad \text{— (9)}$$

and the corresponding value of molar heat capacity is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N_A k\left(\frac{h\nu_0}{kT}\right)^2 \frac{\exp(h\nu_0/kT)}{\{\exp(h\nu_0/kT) - 1\}^2} \quad \text{— (10)}$$

Eq. (10) is known as an Einstein equation.

→ Limiting value of C_V at lower temperatures.

- At low temperature, we have $h\nu_0 >> kT$

and thus $\exp(h\nu_0/kT) >> 1$, under these conditions, Eq. (10) will reduce to

$$C_V = 3N_A k\left(\frac{h\nu_0}{kT}\right)^2 \exp(-h\nu_0/kT) \quad \text{— (11)}$$

On decreasing the temperature, the exponential factor decreases much faster than the corresponding increase in the factor $(h\nu_0/kT)^2$. Consequently, C_V decreases with decrease in temperature. Einstein suggested that the above decrease is basically due to the lesser absorption of energy by the oscillators at low temperatures.

→ Limiting value of C_V at higher temperatures :→

— At high temperatures $h\nu_0 << kT$

— Eq. (10) is

$$C_V = 3N_A k\left(\frac{h\nu_0}{kT}\right)^2 \frac{\exp(h\nu_0/kT)}{\{\exp(h\nu_0/kT)-1\}^2}$$

Expanding the exponential factor, we have

$$C_V = 3N_A k\left(\frac{h\nu_0}{kT}\right)^2 \left[\frac{1+(h\nu_0/kT)+\dots}{\{1+(h\nu_0/kT)+\frac{1}{2}(h\nu_0/kT)^2+\dots-1\}^2}\right]$$

or $$C_V = 3N_A k \frac{(h\nu_0/kT)^2+(h\nu_0/kT)^3+\dots}{\{(h\nu_0/kT)+\frac{1}{2}(h\nu_0/kT)^2+\dots\}^2}$$

At sufficiently high values of T, $h\nu_0/kT$ is very small and the terms with power higher than two can be neglected. Thus, we have

$$C_V = 3N_A k = 3R$$

→ Bohr's model of hydrogen atom :→

- Niels Bohr, a Danish physicist, proposed this model in 1913.
- He retained the Rutherford's model of very small positively charged nucleus at the center which contains all the protons and neutrons present in an atom.
- Bohr also agreed that negatively charged electrons are revolving round the nucleus in the same way as the planets are revolving round the sun.
- Bohr explained the revolution of electron round the nucleus on the basis of Planck's quantum theory.

→ Postulates of Bohr's model :→

1. The electrons in an atom revolve around the nucleus only in certain selected circular orbits.
2. As long as the electron remains in a particular orbit, it neither loses or gains energy. In other words, the energy of electron remains constant in a particular orbit.
3. The orbit is associated with a definite energy, i.e. with a definite whole number of quanta of energy. These orbits are also called energy levels or energy shells.

Energy levels or energy shells	K	L	M	N	....
Principal quantum number (n)	1	2	3	4	....

$$n \propto \text{Energy of shell/level}$$

4. The energy of an electron cannot change continuously. It changes only when the electron jumps from one energy level to another.

5. The angular momentum of an electron moving round the nucleus is quantised. The angular momentum of moving electron in a circular orbit is given by mur.

where m = mass of electron
u = linear velocity of electron
r = radius of orbit

According to Bohr, the angular momentum of an electron in an atom can have only definite or discrete value given by the expression

$$\text{Angular momentum} = mur = \frac{nh}{2\pi}$$

where n = any integer (1, 2, 3.... etc.)

Thus, the angular momentum of an electron may be $h/2\pi$ or a simple whole number multiple of $h/2\pi$ such as $2h/2\pi$, $3h/2\pi$ .... $nh/2\pi$. This principle is known as quantisation of angular momentum.

6. Radius of orbit is given by

$$r \equiv r_n = \frac{n^2h^2}{4\pi^2 Zme^2} \quad \text{or} \quad r \equiv r_n = \frac{(4\pi\varepsilon_0)n^2h^2}{4\pi^2 Zme^2} \text{ (In SI system)}$$

where Z = Atomic number

Since, for hydrogen atom, $Z = 1$, hence,

$$r \equiv r_n = \frac{n^2h^2}{4\pi^2 me^2}$$

For hydrogen atom in the ground state ($n=1$), the radius of the orbit (r_1) is designated as the Bohr radius, a_0. Thus

$$r \equiv a_0 = \frac{h^2}{4\pi^2 me^2} = 0.529\ \text{A}^\circ$$

7. The energy of electron in n^{th} orbit is given by

$$E_n = -\frac{2\pi^2 z^2 me^4}{n^2 h^2} \quad \text{or} \quad E_n = -\frac{2\pi^2 z^2 me^4}{(4\pi\varepsilon_0)^2 n^2 h^2} \ (\text{In SI system})$$

The factor $4\pi\varepsilon_0$ is called the permittivity factor ($1.11264 \times 10^{-10}\ C^2 N^{-1} m^{-2}$)

This is famous Bohr equation applicable to hydrogen and hydrogen-like atoms.

The energy of electron in hydrogen atom ($z=1$) in ground state, i.e., when it revolving in the first orbit is

$$E_1 = -1312.19\ \text{kJ mol}^{-1} \ \text{or} \ -13.6\ \text{eV (per atom)}$$

The energy of electron in excited state can be obtained by putting $n = 2, 3, 4$ etc.

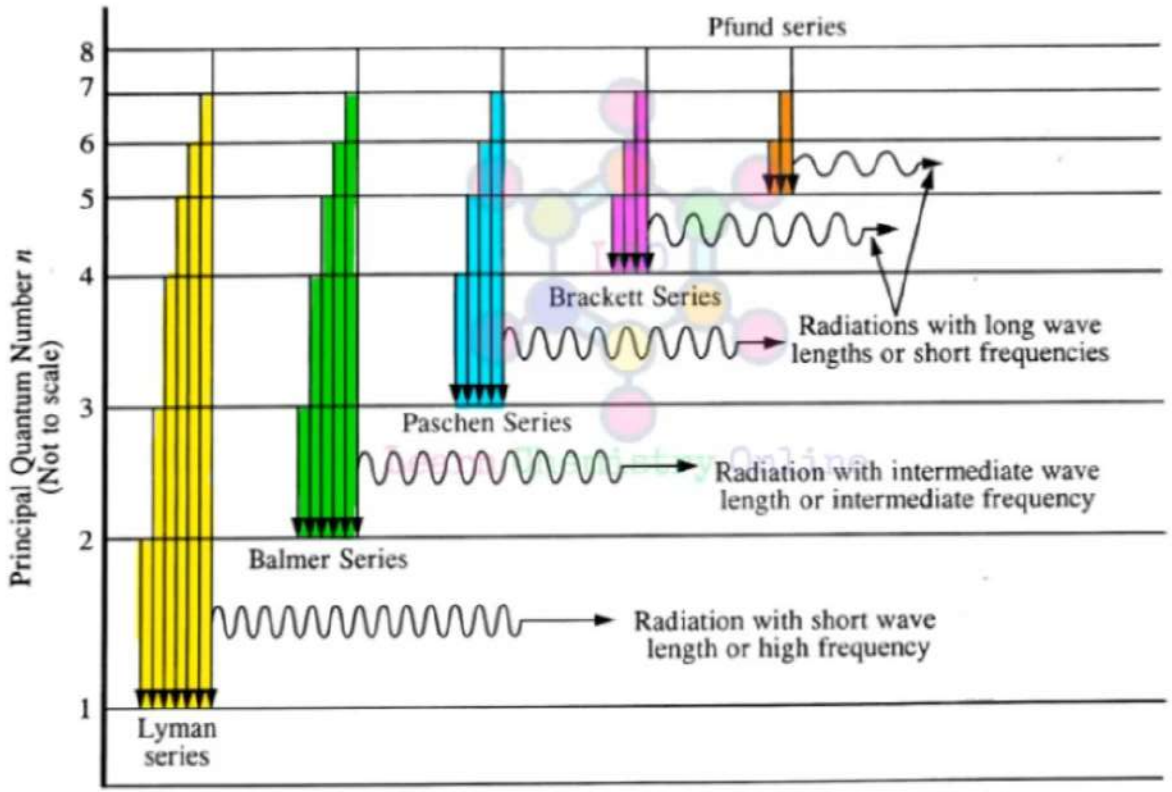
8. The velocity of electron is given by

$$u = \frac{nh}{2\pi mr}$$

The velocity of electron, in the first orbit of hydrogen atom is given by-

$$u_1 = \frac{(1)(6.626 \times 10^{-34}\ Js)}{2\pi(9.109 \times 10^{-31}\ kg)(0.529 \times 10^{-10}\ m)} = 2.188 \times 10^6\ ms^{-1} \quad (J = kg\ m^2 s^{-2})$$

9. Bohr also explain spectrum of hydrogen atom. Hydrogen atom contains only one electron but its spectrum consists of a large number of lines. A given sample of hydrogen contains large number of atom. Different atom will absorb different amounts of energy. Therefore electrons of different atoms will jump into different energy levels. So, spectrum consists of large number of lines.



The origin of the hydrogen spectrum.

- The difference in energy of levels is given by

$$\Delta E = E_2 - E_1 = h\nu$$

- The frequency of the spectral lines is given by

$$\nu = \frac{\Delta E}{h} = \frac{2\pi^2 m e^4}{(4\pi\varepsilon_0)^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

- The wave number of the spectral lines is given by

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{2\pi^2 m e^4}{(4\pi\varepsilon_0)^2 h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \left[\because \nu = \frac{c}{\lambda} \text{ or } \lambda = \frac{c}{\nu} \text{ or } \frac{1}{\lambda} = \frac{\nu}{c}\right]$$

$$\text{or} \quad \bar{\nu} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where R_H = Rydberg constant of the hydrogen atom

$$R_H = \frac{2\pi^2 m e^4}{(4\pi\varepsilon_0)^2 h^3 c}\ \text{cm}^{-1} = \frac{2\pi^2 m e^4}{(4\pi\varepsilon_0)^2 h^2}\ \text{J}$$

(Frequency in cm^{-1} is multiplied by hc to get energy in joules)

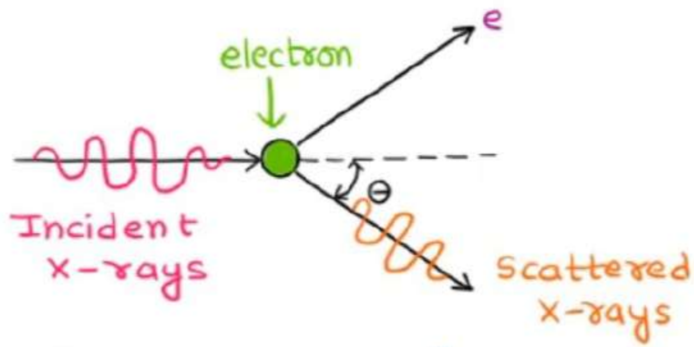
Numerical value of R_H = $109690.8\ cm^{-1} = 21.79 \times 10^{-19}\ J = 13.6\ eV$

→ Defects of Bohr's model :→

- It failed to explain spectra of atoms other than hydrogen.
- If failed to explain Zeeman effect and Stark effect.
- Bohr assumed that the nucleus is staitionary and only electrons are revolving around. But detailed facts have revealed that both nucleus and the electrons move in closed orbits around their center of mass.
- If failed to explain distribution and arrangement of electrons in atoms.
- Bohr used two theories which opposed to each other i.e. he used quantum mechanics to explain existence of staitionary orbits and used law of classical mechanics to explain frequencies of radiation emitted while motion of electron in orbit.
- Bohr model is also against to the Heisenberg's uncertainty principle.

→ Compton effect :→

- Arthur Compton found that if monochromatic x-rays (i.e., x-rays having one particular wavelength) are allowed to fall on carbon or some other light element, the scattered x-rays have wave-lengths larger than the incident rays.



- In other words, the scattered X-rays have lower frequency, i.e., lower energy than the incident x-rays.
- Since scattering is caused by electrons, it is evident that some interaction between X-rays and electrons has taken place and this has resulted in decrease in energy of the X-rays.
- This decrease in energy or increase in wavelength of x-rays after scattering from the surface of an object is known as the Compton effect.
- By applying law of conservation of energy and the law of conservation of momentum and assuming x-rays to consist of photons, each possessing energy equal to $h\nu$, Compton showed that

$$\Delta\lambda = \left(\frac{2h}{mc}\right)\sin^2\left(\frac{\theta}{2}\right) \quad - \quad (1)$$

where $\Delta\lambda$ = Increase in wave length (termed as Compton shift)
m = Rest mass of the e^-
c = velocity of light
θ = Angle between the incident and the scattered x-rays.

- Arthur Compton (1892-1962), the American physicist, shared the 1927 Physics Nobel Prize with C.T.R. Wilson.
- The Compton equation ① can also be written as

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{mc}(1-\cos\theta) \quad -② \qquad \because \quad 1-\cos\theta = 2\sin^2\left(\frac{\theta}{2}\right)$$

- The wave length λ' of scattered x-rays is always greater than the wave length λ of the incident x-rays. The wave length shift is independent of the nature of the substance and the wave length of incident x-rays. It depends only on the scattering angle θ. The following case may be considered -

1. Case-1 :→ $\theta = 0°$, i.e., the scattered radiation is parallel to the incident radiation.
   $\cos 0° = 1$, $\Delta\lambda = \frac{h}{mc}(1-1)$, $\Delta\lambda = 0$, i.e., no change in wavelength.

2. Case-2 :→ $\theta = 90°$, i.e., the scattered radiation is perpendicular to the incident radiation.
   $\cos 90° = 0$, $\Delta\lambda = \frac{h}{mc}(1-0)$, $\Delta\lambda = \frac{h}{mc}$, $\Delta\lambda = \frac{6.626 \times 10^{-34}\ Js}{(9.109 \times 10^{-31}\ kg)(3 \times 10^{8}\ m\,s^{-1})} = 0.02422 \times 10^{-10}\ m$

   * In this case, $\Delta\lambda$ is called Compton wave length.

3. Case-3 :→ $\theta = 180°$, i.e., the scattered radiation is in a direction opposite to the incident radiation.
   $\cos 180° = -1$, $\Delta\lambda = \frac{h}{mc}[1-(-1)]$, $\Delta\lambda = \frac{2h}{mc}$, $\Delta\lambda = 0.0484 \times 10^{-10}\ m$
   * This the twice the value of Compton wave length.

- Compton effect also explains about uncertainty principle. Suppose x-rays are used to determine the position and momentum of an electron. As a result of mutual interaction of x-rays and the electron, the wave length of X-rays increases, i.e., frequency or energy of the x-rays decreases. This energy must have been transferred to the electron and, therefore, the momentum of the electron must have changed during the process. Consequently, the momentum of the electron cannot be determined with certainty
- Compton effect also provides evidence for the photon nature of radiation.

→ de Broglie hypothesis :→

- Einstein had suggested, in 1905, that light has dual character; as wave and also as 'particle'.
- The French physicist Louis de Broglie (1892-1987) proposed that matter also has a dual character; as wave and as particle. The name wavicle was suggested for such a particle.
- de Broglie was awarded the physics Nobel Prize in 1929.
- In Bohr's theory, electron is treated as a particle. But, de Broglie's theory suggested that matter, and, therefore, electron also, has a dual character, both as a material particle and as a wave.
- de Broglie derived an expression for calculating the wave length λ of a particle of mass m moving with velocity u according to which

$$\lambda = \frac{h}{mu} \quad \text{— (1)}$$

where h = Planck's constant

Eq. (1) is known as the de Broglie equation.

→ Derivation:→

- The de Broglie equation can be easily derived by using the Einstein's mass-energy relation-ship -

$$E = mc^2 \quad \text{— (2)}$$

where c = velocity of light

- Energy of a photon having frequency ν is given by

$$E = h\nu \quad \text{— (3)}$$

From eq. (2) and (3) we have

$$h\nu = mc^2$$

or $$\frac{hc}{\lambda} = mc^2 \qquad \because \nu = \frac{c}{\lambda}$$

or $$\frac{h}{\lambda} = mc$$

or $$\lambda = \frac{h}{mc} \quad \text{— (4)}$$

Replacing c by the velocity of the electron, u, we have

$$\lambda = \frac{h}{mu} = \frac{h}{p} \quad \text{— (5)}$$

where p = the linear momentum of the particle

Eq. (5) can be written as

$$\lambda \propto \frac{1}{p} \quad \text{— (6)}$$

According to eq. (6), the momentum of moving particle is inversely proportional to the wave length of wave associated with it.

→ de-Broglie relationship and Bohr's model: Derivation of the Bohr angular momentum postulate from de-Broglie's relation :→

- Cosider an electron moving in a circular orbit of radius r around a nucleus. The wave train (non-energy radiating motion) would be as shown in figure.
- If the wave is to remain continually in phase (fig a), the circumference of the circular orbit must be an integral multiple of wave length λ, that is,

$$2\pi r = n\lambda \quad — (1)$$

where r = Radius of the orbit, n = Whole number

The de-Broglie relationship is

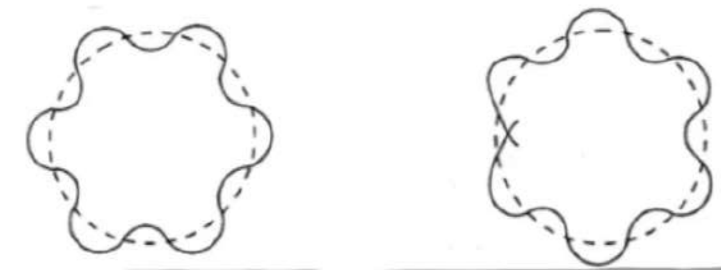
$$\lambda = \frac{h}{mu} \quad — (2)$$

Substituting value of λ in eq. (1) we have

$$2\pi r = \frac{nh}{mu} \quad \text{or} \quad mur = \frac{nh}{2\pi} \quad — (3)$$

Eq. (3) represents the Bhor's postulate, according to which, " electron can move only in such orbits for which the angular momentum must be an integral multiple of $h/2\pi$.

- If the circumference is bigger or smaller than the value given by eq. (3), it means that the wave will no longer remain in phase (fig b).



(a) Wave continually in phase (b) Wave not in phase

→ Experimental verification of de-Broglie's equation: →

- Let an electron of charge e be accelarated by a potential V. Then its kinetic energy is eV.
- The kinetic energy is also equal to $\frac{1}{2}mu^2$ where u is the velocity of the electron. Thus,

$$\frac{1}{2}mu^2 = eV \quad \text{— (1)}$$

or $$u^2 = \frac{2eV}{m}$$

or $$u = \left(\frac{2eV}{m}\right)^{1/2} \quad \text{— (2)}$$

de Broglie equation is

$$\lambda = \frac{h}{mu} \quad \text{— (3)}$$

substituting value of u in eq. (3), we have

$$\lambda = \frac{h}{m(2eV/m)^{1/2}}$$

$$\lambda = \frac{h}{(2meV)^{1/2}} \quad \text{— (4)}$$

Substituting the numerical values of various quantities, we have

$$\lambda = \frac{6.626 \times 10^{-34}\ Js}{[(2)(9.109 \times 10^{-31} kg)(1.602 \times 10^{-19} C)(V\ volt)]^{1/2}} \qquad (J = kg\ m^2 s^{-2})$$

$$\lambda = 12.26 \times 10^{-10} (V\ volt)^{-1/2}\ m \quad - \quad 5$$

- If an electron is accelerated through a potential of 100 volts, then the wave length is

$$\lambda = 12.26 \times 10^{-10} (100)^{-1/2}\ m$$

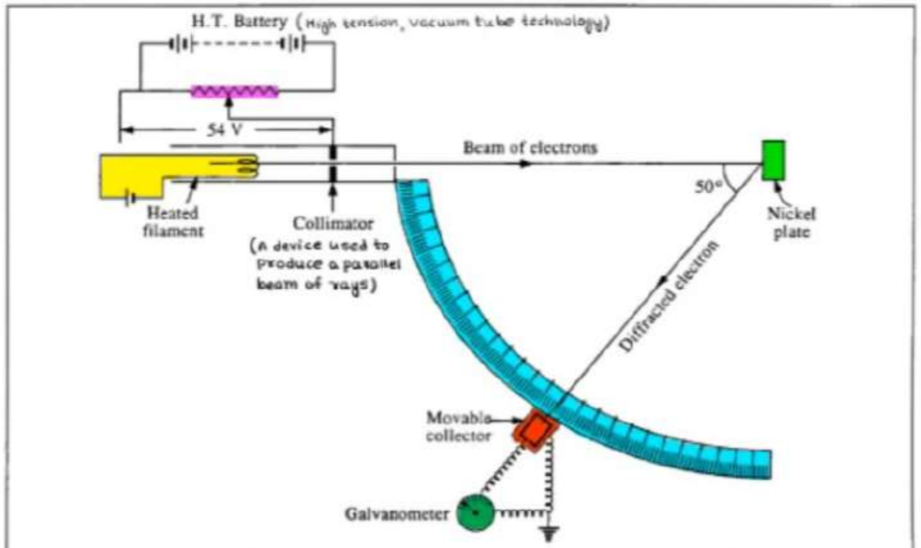
$$\lambda = 1.226 \times 10^{-10}\ m.$$

- If potentials are varied between 10 and 10,000 volts, λ should vary between 3.877×10^{-10} m and 0.1226×10^{-11} m.
- It is well known that x-rays have wave lengths of this order. i.e. of above wavelengths.
- It is also well known that crystalline solids can acts as diffraction gratings for x-ray having wavelengths of the above order.

Therefore, if de Broglie's view regarding wave-particle duality of electron is correct, the crystalline solids should act as diffraction gratings for a beam of electron as well. This has been verified experimentally.

→ Davisson-Germer experiment :→

- The de Broglie hypothesis regarding wave character of electron received first experimental support from C.J. Davisson and L.H. Germer.



The Davisson–Germer experiment for verification of de Broglie's equation.

- In their experiment, electrons were emitted from hot filament and accelerated by a potential ranging between 40 and 68 volts before striking a nickel plate.
- They found that the impact of electrons resulted in the production of diffraction patterns which were similar to those given x-rays under similar conditions. Since x-rays possess wave character, the experiment gave direct evidence for wave character of electrons as well.
- The intensities of electrons waves scattered by the nickel plate at different angles were measured. It was found that the reflection was most intense and took place at an angle of 50° when electrons were accelerated through 54 volts. On substituting value of volts in following equation –

$$\lambda = 12.26 \times 10^{-10} (V\ \text{volt})^{-1/2}\ m$$

Value of λ, the wavelength of the electron wave, comes out to be 1.668×10^{-10} m or 1.668 Å. This wave length also lies in the range of x-rays. This is another point of similarity between electron waves and x-rays.

- It should be possible, therefore, to apply the Bragg equation derived for x-ray diffraction, to electron diffraction as well. According to this equation-

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

where n = whole number (1, 2, 3 etc.)

λ = wave length

d = distance between successive lattice planes of the crystal (Nickel crystal in the present case).

θ = grazing angle of the waves.

This provided an independent experimental method for determining wave length of electron waves.

- Davisson and Germer found the value of λ to be very close to that obtained by de Broglie equation.
- The Davisson - Germer experiment thus offered full support to de-Broglie's views and his equation.
- The American physicist C.J. Davisson (1881-1958) shared the 1937 Physics Nobel prize with the British physicist G.P. Thomson (1892-1975) for investigation of electron diffraction by crystals.
- J.J. Thomson was awarded the Nobel Prize for showing that the electron is a particle and G.P. Thomson, his son, was awarded the Nobel prize for showing that the electron is a wave.

→ Heisenberg uncertainty principle :→

- According to this principle, " It is not possible to determine precisely both the position and the momentum (velocity) of a small moving particle.
- Consider a photon incident on a particle. If the particle is of reasonable size, its position or velocity will not be altered by the impact of light photons. Hence it will be possible to know exactly both the position and velocity of the particle.
- When the particle is extremely minute, such as an electron. It will suffer a change in its velocity and path due to the impact of even a single photon of light used to observe it.
- The path and velocity of an electron, after the impact of light photons, may be quite different from the original path and velocity.
- For an electron moving in x-direction, the Heisenberg uncertainty principle is expressed mathematically as

$$(\Delta x)(\Delta p_x) \geq \frac{h}{4\pi} \quad \text{— (1)}$$

where h = Planck's constant

Δx = Uncertainty in position

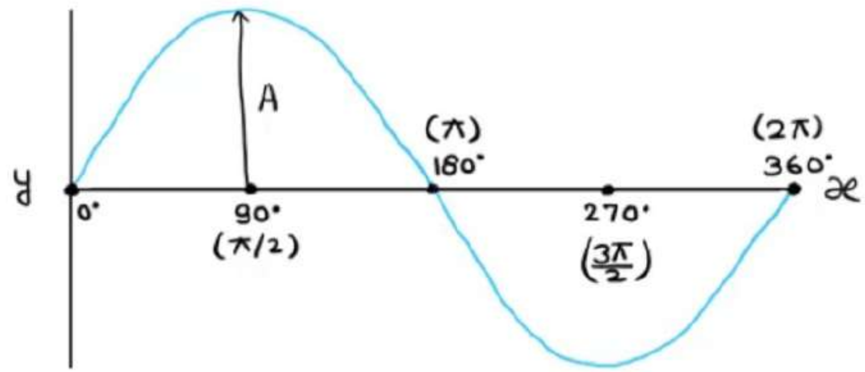
Δp_x = uncertainty in momentum

- Evidently, if Δx is very small, i.e, position of a particle is known more or less exactly, Δp would be large, i.e., uncertainty with regard to momentum will be large. Similarly, if an attempt is made to measure exactly the momentum of particle, the uncertainty with regard to position will become large.
- Werner Heisenberg (1900-1976), the German physicist, won the Physics Nobel prize in 1932.

→ Sinusoidal wave equation :→

– Sinusoidal wave / sine wave equation can be represented by following equation –

$$y(x,t) = A\sin(kx - \omega t + \phi) \quad \text{— (1)}$$



Where
y = Vertical position
x = Horizontal position
A = Amplitude (m)
k = Angular wave number = $\frac{2\pi}{\lambda}$ (rad/m)
ω = Angular frequency = $2\pi\nu$ or $\frac{2\pi}{T}$ (rad/s)
t = time variable
ϕ = phase

– Eq. (1) can also be written as

$$y(x,t) = A\sin\left(\frac{2\pi}{\lambda}x - \frac{2\pi}{T}t + \phi\right) \quad \text{— (2)} \quad \text{or} \quad y(x,t) = A\sin\left(\frac{2\pi}{\lambda}x - 2\pi\nu t + \phi\right) \quad \text{— (3)}$$

– A wave traveling in the negative direction :-

$$y(x,t) = A\sin(kx + \omega t + \phi) \quad \text{— (4)}$$

– Cosine wave equation is represented by

$$y(x,t) = A\cos(kx \pm \omega t + \phi) \quad \text{— (5)}$$

→ Schrodinger wave equation: →

- Erwin Schrodinger, in 1926, gave a wave eq. to describe the behaviour of electron waves in atoms and molecules.
- In Schrodinger's wave model of an atom, the discrete energy levels or orbit proposed by Bohr are replaced by mathematical functions, ψ, which are related to the probability of finding electrons at various places around the nucleus.

→ Derivation: →

- The equation for a standing sine wave of wavelength λ is given by

$$\psi = C \sin \frac{2\pi}{\lambda} x \quad — \quad (1)$$

where ψ = Wave function (Amplitude of the wave varying sinusoidally along x)

C = Maximum amplitude

Double differentiating eq (1) with respect to x

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} C \sin \frac{2\pi}{\lambda} x$$

or

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad — \quad (2)$$

$$\left[\because \psi = C \sin \frac{2\pi}{\lambda} x \right]$$

Differentiation w.r.t. x

$$\frac{\partial \psi}{\partial x} = C \cos\left(\frac{2\pi x}{\lambda}\right) \cdot \frac{2\pi}{\lambda}$$

Further differentiation w.r.t. x

$$\frac{\partial^2 \psi}{\partial x^2} = -C \sin\left(\frac{2\pi x}{\lambda}\right) \cdot \left(\frac{2\pi}{\lambda}\right)^2$$

$$\frac{\partial^2 \psi}{\partial x^2} = -C \sin \frac{2\pi x}{\lambda} \cdot \frac{4\pi^2}{\lambda^2}$$

- According to de Broglie relationship

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

or $$\lambda^2 = \frac{h^2}{m^2 u^2} \quad — (3)$$

Substitute the value of eq. (2),

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2 m^2 u^2}{h^2}\psi \quad — (4)$$

- The kinetic energy of a moving particle of mass m and velocity u is given by -

$$K.E. = \frac{1}{2} mu^2 \quad — (5)$$

- Total energy of a moving particle is given by

$$E = K.E. + V \quad — (6)$$ where V = Potential energy

or $$E = \frac{1}{2}mu^2 + V$$

or $$mu^2 = 2(E - V)$$

or $$m^2u^2 = 2m(E-V) \quad — (7)$$

Substitute value of m^2u^2 from eq. (7) into eq. (4)

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

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

or
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{— (8)}$$

Eq. (8) is called Schrodinger's equation (time independent) for a particle in one dimension.

- For three dimensions Schrodinger equation (time independent) is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{— (9)}$$

* E. Schrodinger (1887–1961), Austrian physicist, shared the 1933 Physics Nobel prize with P.A.M. Dirac (1902–1984) for the discovery of new productive forms of atomic theory.

→ Importance of Schrodinger wave equation:→

- Being a differential equation of second order, Schrodinger equation has several solution for ψ but many of these are imaginary and hence are not valid. Only those values of ψ are valid which satisfy the following conditions.

(i) The wave function must be finite and continuous.

(ii) The solution must be single valued i.e. at a given point there can never be more than one value for the amplitude, ψ.

(iii) $\frac{\partial\psi}{\partial x}$, $\frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ must be continuous functions of x, y and z respectively.

(iv) The solutions must be normalised. i.e. they must satisfy the relation.

$$\int_0^{+\infty} \psi^2 \, d\tau = 0 \quad \text{where } d\tau = \text{small volume element}$$

Value of ψ which satisfy the above conditions and hence valid are called Eigen-functions and the values of E corresponding to these valid values of ψ are called Eigen-values.

The eign function for an electron is called an atomic orbital. As the eign-values (i.e. E values) correspond very nearly to the energy levels associated with different Bohr orbits, the occurance of definite energy levels in an atom follows directly from the wave mechanical concept.

→ Laplacian and Hamiltonian operators :→

→ Operators:→

- An operator is a mathematical instruction or procedure to be carried out on a function.
- It is written in the form

(operator) . (function) = (Another function)

- The function on which the operation is carried out is called an operand.
- The left hand side of the above equation does not mean that the function is multiplied with the operator. Evidently, an operator written alone has no significance.

Example:-

(i) $\frac{d}{dx}(x^3) = 3x^2$. Here $\frac{d}{dx}$ which stands for differentiation w.r.t. x is the operator, x^3 is the operand and $3x^2$ is the result of the operation.

- Taking the square or taking the square root or multiplication by a constant k etc. are different operations which can be carried on any function (i.e. the operand)
- In case the symbol used for the operator is not self-explanatory, a suitable letter or some symbol for the operator is used with the symbol ^ over it.

→ Laplacian and Hamiltonian operators:→

- Schrodinger wave equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad - (1)$$

or $$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

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

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

Eq. (2) can be written as

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

Multiply both sides by $-\frac{h^2}{8\pi^2 m}$

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

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

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

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

or $$\left[-\frac{h^2}{8\pi^2 m}\nabla^2+V\right]\psi = E\psi$$

or $$\hat{H}\psi = E\psi \quad \text{— (3)}$$

Eq. (3) is another form of Shrodinger wave equation.

where ψ is eigen function

E is eigen value

$\hat{H}$ is Hamiltonian operator ($\hat{H}$, $\check{H}$ or H)

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V$$

or $$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \qquad \left[\because \hbar = \frac{h}{2\pi}, \ \hbar^2 = \frac{h^2}{4\pi^2}\right]$$

where $\hbar$ is reduced Planck's constant or Dirac constant.

→ Physical interpretation of wave function:→

→ First interpretation of wave function(ψ):→

- Schrodinger interpret the wave function in terms of charge density.
- In any electromagnetic wave system,

$$\text{the energy density} \propto A^2$$

where energy density = the energy per unit volume
A = amplitude of the wave.

- The number of photons per unit volume is called the photon density.

$$\text{Photon density} = \frac{\text{Energy density}}{h\nu} = \frac{A^2}{h\nu}$$

Thus, we conclude that photon density is proportional to A^2 since $h\nu$ is constant, i.e.

$$\text{Photon density} \propto A^2$$

- Similary, if ψ is the amplitude of the matter wave at any point in space, we may consider the particle density (number of particles per unit volume at that point) to be proportional to ψ^2. Hence square of ψ is a measure of the particle density.
- If we multiply the particle density by electric charge (e) of the particle, we get the charge density. Therefore, the quantity ψ is also the measure of charge density.

- Above interpretation gave satisfactory results when wave mechanics was applied to the stable states of the Bohr theory. But certain difficulties arises against this interpretation of ψ.

→ Second interpretation of wave function: →

- Born, Bohr and Heisenberg put forward the interpretation of ψ.
- According to them, ψ^2 does not measure the particle density or charge density at any point but it is related to the probability of finding the particle at that point at any given moment.
- The probability 'P' of finding the electron at the point (x, y, z) is given by

$$P = \psi(x,y,z)\,\psi^*(x,y,z)$$

where ψ^* = complex conjugate of ψ.

As ψ may have imaginary values one must multiply it by complex conjugate in order to make P real.

- The probability of finding the electron or particle at any point, may be large, small or zero, but it cannot be imaginary. Of course, if ψ is real, $\psi^* = \psi$, and the probability P equals to the square of ψ. Thus, we conclude that ψ must satisfy the following conditions -

(i) it must be single valued at each and every point.

(ii) it must have finite value at any point

(iii) its absolute values at all points must be such that

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \psi(x,y,z)\psi^*(x,y,z)\,dx\,dy\,dz = \int \psi\psi^* d\tau = 1$$

τ is the general symbol for all coordinates. As there is one electron, it means that the total probability must be one.

→ Postulates of quantum mechanics :→

- The formulation of quantum mechanics or wave mechanics for the wave mechanical treatment of the structure of atom depends upon a few postulates which, for a system moving in one dimension, say, along the x - coordinate, are given below -

→ First postulate :→

- The physical state of a system at time t is described by the wavefunction $\psi(x, t)$.

→ Second postulate :→

- The wave function $\psi(x,t)$ and its first and second derivatives $\partial\psi(x,t)/\partial x$ and $\partial^2\psi(x,t)/\partial x^2$ are continuous, finite and single valued for all values of x. Also, the wave function $\psi(x,t)$ is normalised, i.e.,

$$\int_{-\infty}^{+\infty} \psi(x,t)\,\psi^*(x,t)\,dx = 1 \quad - (1)$$

where ψ^* is the complex conjugate of ψ formed by replacing i with $-i$ wherever it occurs in the function ψ $(i = \sqrt{-1})$.

→ Third postulate :→

- A physically observable quantity can be represented by an Hermitian operator. An operator $\hat{A}$ is said to be Hermitian if it satisfies the following condition:

$$\int \psi_i^* \hat{A} \psi_j \, dx = \int \psi_j (\hat{A}\psi_i)^* dx \quad - (2)$$

where ψ_i and ψ_j are the wavefunctions representing the physical state of the quantum system such as a particle, an atom or molecule.

→ **Fourth postulate :→**

- The allowed values of an observable A are the eigenvalues, a_i, in the operater equation.

$$\hat{A}\psi_i = a_i\psi_i \quad \text{— (3)}$$

Eq. (3) is known as an eigenvalue equation. Here $\hat{A}$ is the operator for the observable (physical quantity) and ψ_i is the eigenfunction of $\hat{A}$ with eigenvalue a_i, In other words, measurment of the observable A yields the eigenvalue a_i.

→ **Fifth postulate :→**

- The average value (or, the expectation value), $\langle A \rangle$, of an observable A, corresponding to the operator $\hat{A}$, is obtained from the relation.

$$\langle A \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{A} \psi \, dx$$

Where the function ψ is assumed to be normalised in accordance with eq. (1). Thus, the average value of x - coordinate is given by

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{x} \psi \, dx$$

→ **Sixth postulate :→**

- The quantum mechanical operators corresponding to the observables are constructed by writing the classical expression in terms of the variables and converting the expression to the operators.

Wave Mechanical Operators for Evaluating Various Classical Variables

Classical variable	Quantum mechanical operator	Operator	Operation
x	$\hat{x}$	x	Multiplication by x
p_x	$\hat{p}_x$	$-i\hbar \frac{\partial}{\partial x}$	Taking derivative with respect to x and multiplying by $-i\hbar$
x^2	$\hat{x}^2$	x^2	Multiplication by x^2
p_x^2	$\hat{p}_x^2$	$-\hbar^2 \frac{\partial^2}{\partial x^2}$	Taking second derivative with respect to x and multiplying by $-\hbar^2$
t	$\hat{t}$	$\hat{t}$	Multiplying by t
E	$\hat{E}$	$i\hbar \frac{\partial}{\partial t}$	Taking derivative with respect to t and multiplying by $i\hbar$

→ Seventh postulate :→

- The wave function $\psi(x,t)$ is a solution of the time-dependent Schrodinger equation.

$$\hat{H}\,\psi(x,t) = i\hbar \frac{\partial \psi(x,t)}{\partial t}$$

where $\hat{H}$ = Hamiltonian operator.

$\hbar$ = Reduced Planck's constant.

→ Particle in a one-dimensional box :→

- This is the simplest quantum mechanical problem which represents translational motion.
- Here a particle of mass m is confined to move in a one dimentional box of width a, having infinitely high walls.
- It is assumed, for the sake of simplicity, that the potential energy of the particle is zero anywhere inside the box, that is

$$V(x) = 0 \quad \text{— (1)}$$

The Schrodinger equation for one dimension is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \text{— (2)}$$

Thus, inside the box the Schrodinger equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

or

$$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0 \quad \text{— (3)}$$

Where k^2 is constant, independent of x.

$$\because \quad k^2 = \frac{8\pi^2 mE}{h^2}$$

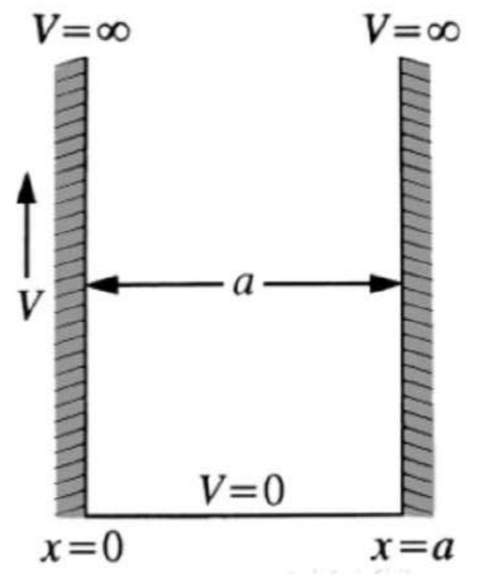


Fig: Particle in one dimensional box

Eq. (3) is an ordinary second order differential equation which has solution of the form

$$\psi = A\cos kx + B\sin kx \quad - (4)$$

where A and B are constants.

- Outside the box, where $V(x) = \infty$, the Schrodinger eq. is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-\infty)\psi = 0 \quad - (5)$$

This equation satisfied if ψ is zero everywhere outside the box. This is another way of saying that the particle cannot be found outside the box; it is confined within the box. This implies that ψ must be zero at the walls of the box, i.e. at $x=0$ and at $x=a$.

At $x = 0$, $\psi = 0$

from eq. (4)

$$0 = A\cos k0 + B\sin k0$$

$$0 = A\cos 0 + B\sin 0 \qquad \{\sin 0 = 0 \text{ and } \cos 0 = 1\}$$

$$0 = A + 0$$

or $A = 0$

Substitute value of A in eq. (4), we get

$$\psi = B\sin kx \quad - (6)$$

At $x = a$, $\psi = 0$

$$0 = B\sin ka$$

or $B \sin ka = 0$

But since $B \neq 0$

$$\sin ka = 0$$

or $\sin ka = \sin n\pi \qquad \because \sin n\pi = 0$

or $ka = n\pi$

or $k = \frac{n\pi}{a}$ — (7)

where $n = 1, 2, 3, 4 \ldots$ is quantum number

Substitute value of k in eq. (6)

$$\psi \equiv \psi_n = B \sin \frac{n\pi x}{a} \quad \text{— (8)}$$

– Energy of particle in one dimensional box

from eq. (7)

$$k^2 = \frac{n^2\pi^2}{a^2} \quad \text{— (8)}$$

and $k^2 = \frac{8\pi^2 mE}{h^2}$ — (9)

from eq. (8) and (9)

$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{a^2}$$

$$E \equiv E_n = \frac{n^2 h^2}{8ma^2} \quad - (10)$$

or $$E \equiv E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2} \quad - (11) \quad \because \hbar = \frac{h}{2\pi} \text{ and } \hbar^2 = \frac{h^2}{4\pi^2}$$

where $\hbar$ = Reduced Planck's constant or Dirac's constant

- In any atom which is regarded as a type of potential box there are several energy levels corresponding to $n = 1, 2, 3 \ldots$

where $n = 1$, $E_1 = \frac{h^2}{8ma^2}$

$n = 2$, $E_2 = \frac{4h^2}{8ma^2}$

$n = 3$, $E_3 = \frac{9h^2}{8ma^2}$

$$E_2 - E_1 = \frac{3h^2}{8ma^2}$$

$$E_3 - E_2 = \frac{5h^2}{8ma^2}$$

This suggests that difference between consective energy levels is not constant.

- The energy levels, wavefunction (a) and probability densities for the particle in one dimensional box are given in figure.
- 'n' is the typical quantum number, which represents the nodes in the electron waves. As n increases, the number of nodes varies in the following manner,

$n = 1$	no node
$n = 2$	1 node
$n = 3$	2 node
$n = 4$	3 node

and so on

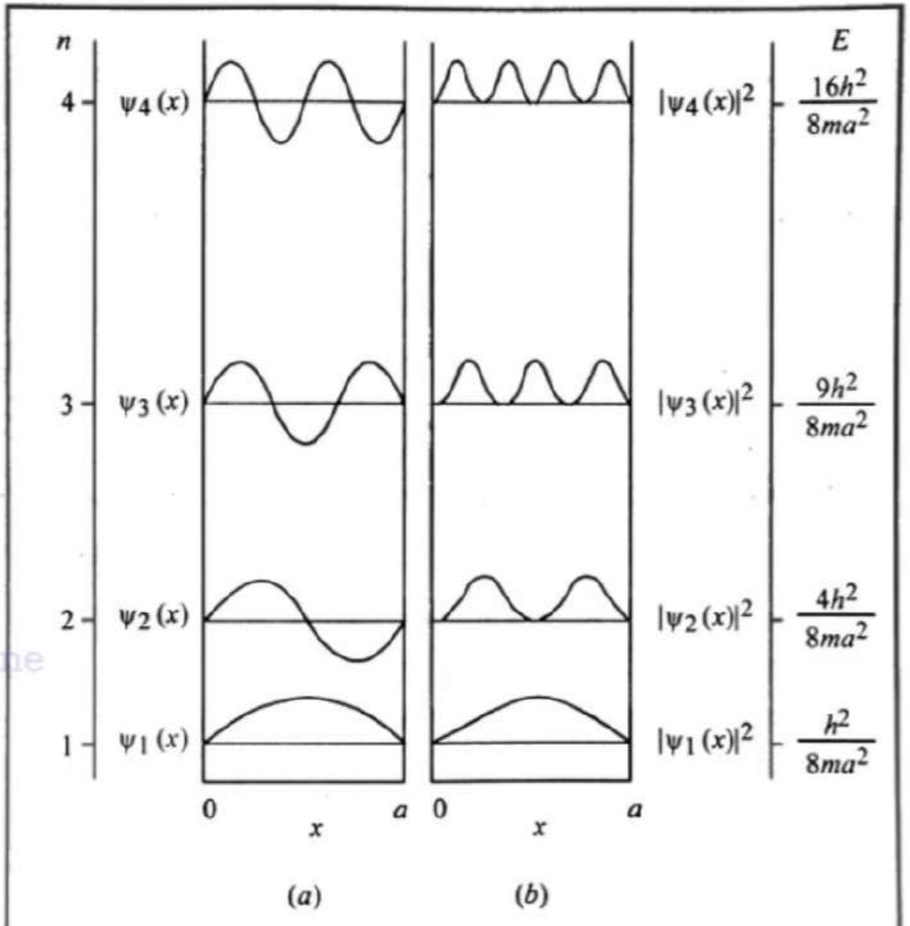


Fig. The energy levels, wavefunctions (a) and (b) probability densities for the particle in a one-dimensional box.

→ Value of coefficient B :→

- This can be done by normalizing the wave function.
- Since the total probability of finding the particle within the box is 1,

$$\int_0^a \psi_n^2 \, dx = 1 \quad — (12)$$

$$\int_0^a (B \sin n\pi x/a)^2 \, dx = 1 \quad \because \psi \equiv \psi_n = B \sin \frac{n\pi x}{a}$$

or $$B\int_0^a \sin^2(n\pi x/a)\,dx = 1$$

since $$\sin^2\theta = \frac{1}{2}(1-\cos 2\theta)$$

hence

$$\int_0^a \psi_n^2\,dx = B^2\left[\frac{1}{2}\int_0^a dx - \frac{1}{2}\int_0^a \cos\left(\frac{2n\pi x}{a}\right)dx\right]$$

$$= B^2\left[\frac{a}{2} - 0\right] = 1$$

Hence $$B = (2/a)^{1/2} = \sqrt{\frac{2}{a}} \quad — (13)$$

Thus, the normalised wave functions for the particle are:

$$\psi_n(x) = (2/a)^{1/2}\sin\left(\frac{n\pi x}{a}\right); \quad n = 1,2,3\ldots \quad — (14)$$

→ Schrodinger wave equation for H- atom :→

- Hydrogen atom is the simplest of all atoms. It is three dimensional system and the Schrodinger equation for this system is -

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad - (1)$$

where ∇^2 is Laplacian operator in Cartesian coordinates is given by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad - (2)$$

- The potential energy of interaction between the electron and the nucleus is given by

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad - (3)$$

where Z = Atomic number
e = charge on electron
ε_0 = Permittivity factor
r = radius

From eq. (1), (2) and (3)

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = 0 \quad - (4)$$

- Since the attractive potential has spherical symmetry depending only upon r, it is convenient to express the Schrodinger equation in terms polar coordinates (r, θ, ϕ), rather than Cartesian coordinates (x, y, z).
- The Cartesian coordinates are related to polar coordinates (see fig.) as follows:

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$

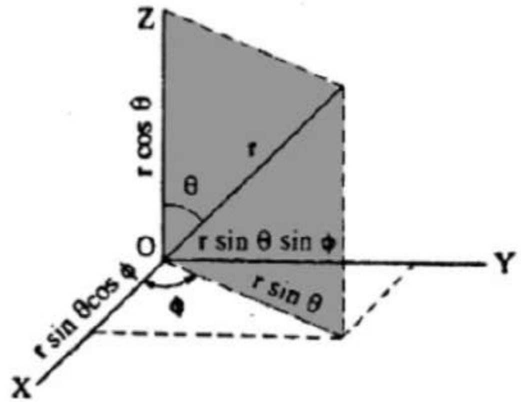


Fig :- Polar coordinate system

- The transformed Schrodinger equation is given by (complete solution on next slides)

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi=0 \quad — (5)$$

or

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi=0 \quad — (6)$$

- If mass m is replaced by reduced mass then. (Because H-atom is two body system i.e. 1 nucleus and 1 electron)

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi+\frac{8\pi^2 \mu}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi=0 \quad — (7)$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi=0 \quad — (8)$$

where $\mu = \dfrac{m_e m_n}{(m_n+m_e)}$ $\qquad m_e$ = mass of electron

m_n = mass of nucleus

- These equation can also be write in the form of reduced Planck's constant or Dirac's constant.

$$\hbar = \frac{h}{2\pi}$$

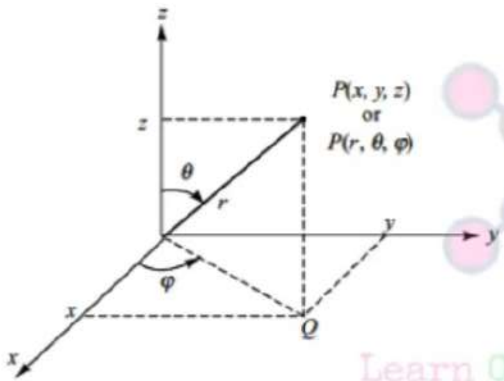
$$\text{or} \quad \hbar^2 = \frac{h^2}{4\pi^2}$$

→ Complete solution of Schrodinger wave equation for H-atom: →

→ Angular momentum operators in spherical polar coordinates: →

The Cartesian coordinates (x, y, z) of a point are related to its spherical polar coordinates (r, θ, φ) by the expressions

$$z = r\cos\theta$$
$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$



The transformations from Cartesian coordinates to spherical polar coordinates can be carried over by using the expressions

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x}\right)\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial x}\right)\frac{\partial}{\partial \varphi} \quad \text{— (1)}$$

$$\frac{\partial}{\partial y} = \left(\frac{\partial r}{\partial y}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial y}\right)\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial y}\right)\frac{\partial}{\partial \varphi} \quad \text{— (2)}$$

$$\frac{\partial}{\partial z} = \left(\frac{\partial r}{\partial z}\right)\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial z}\right)\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial z}\right)\frac{\partial}{\partial \varphi} \quad \text{— (3)}$$

Using the fact that $r^2 = x^2 + y^2 + z^2$, we get

(i) $$\frac{\partial r}{\partial x} = \frac{x}{r} = \frac{r\sin\theta\cos\varphi}{r} = \sin\theta\cos\varphi$$

(ii) $$\frac{\partial r}{\partial y} = \frac{y}{r} = \frac{r\sin\theta\sin\varphi}{r} = \sin\theta\sin\varphi$$

(iii) $$\frac{\partial r}{\partial z} = \frac{z}{r} = \frac{r\cos\theta}{r} = \cos\theta$$

From the expression $\cos\theta = \frac{z}{r} = \frac{z}{(x^2+y^2+z^2)^{1/2}}$, we get

(iv) $$-\sin\theta \frac{\partial\theta}{\partial x} = -\frac{1}{2}\frac{z}{(x^2+y^2+z^2)^{3/2}}\,(2x)$$

i.e. $$\frac{\partial\theta}{\partial x} = \frac{zx}{\sin\theta(x^2+y^2+z^2)^{3/2}} = \frac{(r\cos\theta)(r\sin\theta\cos\varphi)}{(\sin\theta)r^3} = \frac{\cos\theta\,\cos\varphi}{r}$$

(v) $$-\sin\theta \frac{\partial\theta}{\partial y} = -\frac{1}{2}\frac{z}{(x^2+y^2+z^2)^{3/2}}\,(2y)$$

i.e. $$\frac{\partial\theta}{\partial y} = \frac{zy}{\sin\theta(x^2+y^2+z^2)^{3/2}} = \frac{(r\cos\theta)(r\sin\theta\sin\varphi)}{(\sin\theta)r^3} = \frac{\cos\theta\,\sin\varphi}{r}$$

(vi) $$-\sin\theta \frac{\partial\theta}{\partial z} = \frac{1}{(x^2+y^2+z^2)^{1/2}} + \left(-\frac{1}{2}\right)\frac{z}{(x^2+y^2+z^2)^{3/2}}\,(2z)$$

i.e. $$\frac{\partial\theta}{\partial z} = \left(-\frac{1}{\sin\theta}\right)\left(\frac{1}{r} - \frac{r^2\cos^2\theta}{r^3}\right) = \left(-\frac{1}{\sin\theta}\right)\left(\frac{1}{r}\right)(1-\cos^2\theta)$$

$$= -\frac{\sin\theta}{r}$$

Finally, from the expression $\tan\varphi = y/x$, we get

(vii) $$\sec^2\varphi \frac{\partial\varphi}{\partial x} = -\frac{y}{x^2}$$

i.e. $$\frac{\partial\varphi}{\partial x} = -\left(\frac{1}{\sec^2\varphi}\right)\left(\frac{y}{x^2}\right) = -(\cos^2\varphi)\left(\frac{r\sin\theta\,\sin\varphi}{r^2\sin^2\theta\,\cos^2\varphi}\right) = -\frac{\sin\varphi}{r\sin\theta}$$

(ix) $$\sec^2\varphi \frac{\partial\varphi}{\partial y} = \frac{1}{y}$$

i.e. $$\frac{\partial\varphi}{\partial y} = \left(\frac{1}{\sec^2\varphi}\right)\left(\frac{1}{x}\right) = (\cos^2\varphi)\left(\frac{1}{r\sin\theta\,\cos\varphi}\right) = \frac{\cos\varphi}{r\sin\theta}$$

(x) $$\frac{\partial\varphi}{\partial z} = 0$$

With these derivatives, Eqs 1 – 3 become

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)\frac{\partial}{\partial r} + \left(\frac{\partial\theta}{\partial x}\right)\left(\frac{\partial}{\partial\theta}\right) + \left(\frac{\partial\varphi}{\partial x}\right)\frac{\partial}{\partial\varphi}$$

$$= (\sin\theta\cos\varphi)\frac{\partial}{\partial r} + \left(\frac{\cos\theta\cos\varphi}{r}\right)\frac{\partial}{\partial\theta} + \left(-\frac{\sin\varphi}{r\sin\theta}\right)\frac{\partial}{\partial\varphi} \quad \text{— 4}$$

$$\frac{\partial}{\partial y}=\left(\frac{\partial r}{\partial y}\right)\left(\frac{\partial}{\partial r}\right)+\left(\frac{\partial \theta}{\partial y}\right)\left(\frac{\partial}{\partial \theta}\right)+\left(\frac{\partial \varphi}{\partial y}\right)\left(\frac{\partial}{\partial \varphi}\right)$$

$$=(\sin\theta\sin\varphi)\frac{\partial}{\partial r}+\left(\frac{\cos\theta\sin\varphi}{r}\right)\frac{\partial}{\partial \theta}+\left(\frac{\cos\varphi}{r\sin\theta}\right)\frac{\partial}{\partial \varphi} \quad — ⑤$$

$$\frac{\partial}{\partial z}=\left(\frac{\partial r}{\partial z}\right)\frac{\partial}{\partial r}+\left(\frac{\partial \theta}{\partial z}\right)\frac{\partial}{\partial \theta}+\left(\frac{\partial \varphi}{\partial z}\right)\frac{\partial}{\partial \varphi}$$

$$=(\cos\theta)\frac{\partial}{\partial r}+\left(-\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta} \quad — ⑥$$

→ Transformation of Laplacian Operator from Cartesian Coordinates to Spherical polar coordinates →

The Laplacian operator is

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \quad — ⑦$$

From eq. ④, ⑤ and ⑥

$$\frac{\partial}{\partial x}=(\sin\theta\cos\varphi)\frac{\partial}{\partial r}+\left(\frac{\cos\theta\cos\varphi}{r}\right)\frac{\partial}{\partial \theta}+\left(-\frac{\sin\varphi}{r\sin\theta}\right)\frac{\partial}{\partial \varphi}$$

$$\frac{\partial}{\partial y}=(\sin\theta\sin\varphi)\frac{\partial}{\partial r}+\left(\frac{\cos\theta\cos\varphi}{r}\right)\frac{\partial}{\partial \theta}+\left(\frac{\cos\varphi}{r\sin\theta}\right)\frac{\partial}{\partial \varphi}$$

$$\frac{\partial}{\partial z}=(\cos\theta)\frac{\partial}{\partial r}+\left(-\frac{\sin\theta}{r}\right)\frac{\partial}{\partial \theta}$$

We now derive the expressions of $\partial^2/\partial x^2$, $\partial^2/\partial y^2$ and $\partial^2/\partial z^2$.

$$\frac{\partial^2}{\partial x^2}=\left[\sin\theta\cos\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right]$$

$$\left[\sin\theta\cos\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right]$$

$$=\sin\theta\cos\varphi\left[\sin\theta\cos\varphi\frac{\partial^2}{\partial r^2}-\frac{\cos\theta\cos\varphi}{r^2}\frac{\partial}{\partial\theta}\right.$$

$$\left.+\frac{\cos\theta\cos\varphi}{r}\frac{\partial^2}{\partial r\partial\theta}+\frac{\sin\varphi}{r^2\sin\theta}\frac{\partial}{\partial\varphi}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial^2}{\partial r\partial\varphi}\right]$$

$$+\frac{\cos\theta\cos\varphi}{r}\left[\cos\theta\cos\varphi\frac{\partial}{\partial r}+\sin\theta\cos\varphi\frac{\partial^2}{\partial\theta\partial r}-\frac{\sin\theta\cos\varphi}{r}\frac{\partial}{\partial\theta}\right.$$

$$\left.+\frac{\cos\theta\cos\varphi}{r}\frac{\partial^2}{\partial\theta^2}+\frac{\sin\varphi\cos\theta}{r\sin^2\theta}\frac{\partial}{\partial\varphi}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial^2}{\partial\theta\partial\varphi}\right]$$

$$-\frac{\sin\varphi}{r\sin\theta}\left[-\sin\theta\sin\varphi\frac{\partial}{\partial r}+\sin\theta\cos\varphi\frac{\partial^2}{\partial\varphi\partial r}-\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}\right.$$

$$\left.+\frac{\cos\theta\cos\varphi}{r}\frac{\partial^2}{\partial\varphi\partial\theta}-\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}-\frac{\sin\varphi}{r\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

$$=\sin^2\theta\cos^2\varphi\frac{\partial^2}{\partial r^2}+\frac{\cos\theta}{r^2}\left(\frac{\sin^2\varphi}{\sin\theta}-2\sin\theta\cos^2\varphi\right)\frac{\partial}{\partial\theta}$$

$$+\frac{2\sin\theta\cos\theta\cos^2\varphi}{r}\frac{\partial^2}{\partial r\partial\theta}+\frac{\sin\varphi\cos\varphi}{r^2}\left[1+\frac{\cos^2\theta}{\sin^2\theta}+\frac{1}{\sin^2\theta}\right]\frac{\partial}{\partial\varphi}$$

$$-\frac{2\cos\varphi\sin\varphi}{r}\frac{\partial^2}{\partial r\partial\varphi}+\frac{1}{r}(\cos^2\theta\cos^2\varphi+\sin^2\varphi)\frac{\partial}{\partial r}$$

$$-\frac{2\cos\theta\cos\varphi\sin\varphi}{r^2\sin\theta}\frac{\partial^2}{\partial\theta\partial\varphi}+\frac{\cos^2\theta\cos^2\varphi}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{\sin^2\varphi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Similarly, we can proceed to show that

$$\frac{\partial^2}{\partial y^2}=\sin^2\theta\sin^2\varphi\frac{\partial^2}{\partial r^2}+\frac{\cos\theta}{r^2}\left[\frac{\cos^2\varphi}{\sin\theta}-2\sin\theta\sin^2\varphi\right]\frac{\partial}{\partial\theta}$$

$$+\frac{2\cos\theta\sin\theta\sin^2\varphi}{r}\frac{\partial^2}{\partial r\partial\theta}-\frac{\sin\varphi\cos^2\varphi}{r^2}\left[1+\frac{\cos^2\theta}{\sin^2\theta}+\frac{1}{\sin^2\theta}\right]\frac{\partial}{\partial\varphi}$$

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

$$+\frac{2\cos\theta\cos\varphi\sin\varphi}{r^2\sin\theta}\frac{\partial^2}{\partial\theta\,\partial\varphi}+\frac{\cos^2\theta\sin^2\varphi}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{\cos^2\varphi}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

$$\frac{\partial^2}{\partial z^2}=\cos^2\theta\frac{\partial^2}{\partial r^2}+\frac{2\sin\theta\cos\theta}{r^2}\frac{\partial}{\partial\theta}-\frac{2\cos\theta\sin\theta}{r}\frac{\partial^2}{\partial r\partial\theta}$$

$$+\frac{\sin^2\theta}{r}\frac{\partial}{\partial r}+\frac{\sin^2\theta}{r^2}\frac{\partial^2}{\partial\theta^2}$$

With these derivatives, Eq. 7 becomes

$$\nabla^2=\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\left(\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{1}{r^2}\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

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

→ Schrodinger wave equation for H- atom:→

→ Separation into three equations (without derivation):→ (complete solution on next slides).

— Schrondinger equation for H-atom is -

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi=0 \quad — (1)$$

Eq. (1) is a second order partial differential equation. Thus, the Schrodinger wave equation for the hydrogen like species has been separated into three equations, These are :-

- Equation involving only r

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)=l(l+1) \quad — (2)$$

- Equation involving only θ

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)\sin^2\theta=m^2 \quad — (3)$$

- Equation involving only ϕ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2 \quad — (4)$$

→ Complete solution: →

Rearranging the equation 1 we get

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

$$+\frac{8\pi^2\mu}{h^2}\left(\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right)\psi=0$$

Multiplying throughout by r^2 and rearranging the resultant expression, we get

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{8\pi^2\mu r^2}{h^2}\left\{\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right\}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi=0 \quad — 5$$

Since the operator is made up of two terms, one depending on the variable r and the other on the variables θ and φ taken together, we can write the wave function ψ as the product of two functions—one depending on r and the other on θ and φ. Hence, we can write

$$\Psi_{r,\theta,\varphi}=R_rY_{\theta,\varphi} \quad — 6$$

The function Y is known as spherical harmonics. Substituting Eq. 6 in Eq. 5 we get

$$Y_{\theta,\varphi}\frac{d}{dr}\left(r^2\frac{d}{dr}R_r\right)+\frac{8\pi^2\mu r^2}{h^2}\left[\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right]R_r\,Y_{\theta,\varphi}$$

$$+R_r\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y_{\theta,\varphi}=0 \quad — 7$$

Dividing throughout by $R_rY_{\theta,\varphi}$, we get

$$\left[\frac{1}{R_r}\frac{d}{dr}\left(r^2\frac{d}{dr}R_r\right)+\frac{8\pi^2\mu r^2}{h^2}\left\{\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right\}\right]$$

$$=-\left[\frac{1}{Y_{\theta,\varphi}}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\theta,\varphi}\right] \quad — 8$$

Equality shown in Eq. 8 holds good only when both sides are equal to a constant, say, $l(l+1)$. Thus Eq. 8 separates into two equations, one depending only on r and the other on θ and φ. These are:

Equation involving the variable r

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)=l(l+1)} \quad — 9$$

Equation involving the angles θ and φ

$$\frac{1}{Y_{\theta,\varphi}}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\theta,\varphi}=-l(l+1) \quad — 10$$

Multiplying Eq. 10 by $\sin^2\theta$ and rearranging the resultant expression, we get

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+l(l+1)\sin^2\theta+\frac{\partial^2}{\partial\varphi^2}\right]Y_{\theta,\varphi}=0 \quad — 11$$

Since the operator in Eq. 11 consists of two terms, one depending on θ and the other on φ, we can write the wave function $Y_{\theta,\varphi}$ as

$$Y_{\theta,\varphi}=\Theta_\theta\,\Phi_\varphi$$

With this, Eq. (11) becomes

$$\Phi_\varphi \sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta_\theta}{d\theta}\right) + l(l+1)\sin^2\theta\, \Theta_\theta\, \Phi_\varphi + \Theta_\theta \frac{d^2}{d\varphi^2}\Phi_\varphi = 0$$

Dividing throughout by $\Theta_\theta \Phi_\varphi$ and rearranging, we get

$$\frac{\sin\theta}{\Theta_\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta_\theta}{d\theta}\right) + l(l+1)\sin^2\theta = -\frac{1}{\Phi_\varphi}\frac{d^2\Phi_\varphi}{d\varphi^2} \quad \text{— (12)}$$

The two sides of Eq. (11) must be equal to a constant, say m^2. Thus, we have

$$\boxed{\frac{\sin\theta}{\Theta_\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta_\theta}{d\theta}\right) + l(l+1)\sin^2\theta = m^2} \quad \text{— (13)}$$

and

$$\boxed{\frac{1}{\Phi_\varphi}\frac{d^2\Phi_\varphi}{d\varphi^2} = -m^2} \quad \text{— (14)}$$