

Topic on Chemistry

STRUCTURE OF ATOM

Introduction :

The atomic concept of matter was put forth by **John Dalton** (1808) to explain the laws of chemical combination. He considered atoms as structureless indivisible particles. The inner structure of atom was first proposed by **Rutherford** (1911). He proposed that atom consists of two parts—

- A positive centre known as **nucleus**, holding most of the mass of an atom, is the key component of an atom.
- The extranuclear part of an atom is occupied by light weight negatively charged electrons revolving in circular paths.

By carefully measuring the fraction of α -particles, deflected through large angles, Rutherford was able to estimate the size of nucleus. According to his calculations, the radius of the nucleus is atleast $\frac{1}{10000}$ of radius of the atom. The vast majority of volume of an atom is, therefore, empty space. Radius of nucleus of an atom is of the order of 10^{-13} cm, whereas, radius of atom is of the order of 10^{-8} cm. The density of nucleus is of the order of 10^{14} g/cm³ or 10^6 tonnes/cm³.

Electronic structure of atom emerged in 1832, when Michael Faraday through his experiments on electrolysis showed that a chemical change takes place, when electricity is passed through a solution of an electrolyte. He indicated some relations between atom and electricity. Moreover, the laws of electrolysis indicate that atom involves discrete units of electricity.

Discovery of Electron :

Electron was discovered by **Sir J. J. Thomson** in 1897, from the studies carried out on cathode rays in the discharge tube. The cathode rays consist of stream of negatively charged particles known as **electrons**.

Properties of Electron :

An electron is a universal particle of all matters which has following properties :

- The charge on an electron is -1.602×10^{-19} coulombs or -4.8003×10^{-10} e.s.u. as estimated by **Millikan**.
- Mass of electron can be calculated from the experimental observations of **Thomson** and **Millikan**, as—

Thomson's experiment :

$$e/m = 1.76 \times 10^8 \text{ coulombs/g}$$

Millikan's experiment (Oil-drop) :

$$e = 1.602 \times 10^{-19} \text{ coulombs/electron}$$

Mass of electron

$$\begin{aligned} m &= \frac{e}{e/m} \\ &= \frac{1.602 \times 10^{-19} \text{ coulombs/electron}}{1.76 \times 10^8 \text{ coulombs/g}} \\ &= 9.108 \times 10^{-28} \text{ g} \end{aligned}$$

Value 9.108×10^{-28} g is known as the rest mass of the electron.

The mass of electron in kg

$$= 9.108 \times 10^{-31} \text{ kg/electron}$$

● Molar mass of electron

$$\begin{aligned} &= 9.108 \times 10^{-28} \times \text{Avogadro number} \\ &= 9.108 \times 10^{-28} \times 6.023 \times 10^{23} \\ &= 5.486 \times 10^{-4} \text{ g/mole.} \end{aligned}$$

- Mass of electron is about 1/1837 times the mass of hydrogen atom.
- Electron is responsible for all the chemical reactions of a matter.

Discovery of Proton :

Goldstein in 1886 discovered existence of positively charged rays in the discharge tube by using perforated cathode. These rays were named as **anode rays** or **cannal rays**. The positively charged particles constituting these rays were named as **protons**.

Properties of Proton :

Like electron, proton is also a universal particle of all matters. Proton is characterised by following properties :

- The charge on proton is $+1.602 \times 10^{-19}$ coulombs or $+4.8003 \times 10^{-10}$ e.s.u.
- Mass of proton is 1.672×10^{-24} gm or 1.672×10^{-27} kg.
- Charge to mass ratio for proton was found to be 9.58×10^4 coulombs per gm.
- On atomic mass scale, the mass of proton is 1.00728. The proton is 1837 times heavier than electron.
- Protons are the major constituents of nucleus of an atom. Proton is thus, a universal particle of matter.
- Since, an atom is electrically neutral and hence the number of protons is always equal to the number of electrons outside the nucleus.
- Proton does not participate in **chemical reactions**, however, it plays an important role in **nuclear reactions**.
- Proton is symbolised as ${}_1p^1$.

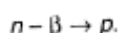
Discovery of Neutron :

Rutherford in 1911 established that whole of the mass of an atom is concentrated in its nucleus. When the total number of protons in the nucleus could not account for the total mass of an atom, scientists engaged in discovering other particles in the nucleus.

James Chadwick in 1932 discovered a new particle, when he bombarded beryllium foil with alpha (α) particles. In his experiment he found that penetrating rays consisting of neutral particles are produced. He named these particles as **neutrons**.

Properties of Neutron :

- Neutron is electrically neutral *i.e.*, it carries no charge.
- The mass of neutron is 1.672×10^{-24} gm or 1.672×10^{-27} kg. On atomic mass scale, the mass of neutron is 1.00866.
- Neutron is symbolised as ${}_1^0n$.
- Neutron is found in the nucleus of an atom. **Except lightest isotope *i.e.*, protium** all atoms have neutrons in their nuclei.
- Neutron contributes to the mass of an atom and it takes part in nuclear reactions.
- Neutron is unstable as compared to proton. It decays by emission of β -particles and gets converted into proton. The half-life of neutron is 12.8 minutes.

**Atomic Number and Mass Number :**

In 1913 H.G. J. Moseley discovered that the number of unit positive charges on the nucleus of an atom of the element is called **atomic number** of the element. Thus :

$$\begin{aligned} \text{Atomic number (Z)} &= \text{Number of protons} \\ &= \text{Number of electrons} \end{aligned}$$

The total number of protons and neutrons in the nucleus, is called mass number of the atom. Thus :

$$\begin{aligned} \text{Mass number (A)} &= \text{Number of protons} + \text{Number} \\ &\quad \text{of neutrons} \\ &= \text{Number of nucleons} \end{aligned}$$

Nuclear particles are generally referred to as **nucleons**.

Atomic Weight :

Elements have different isotopes. Therefore, the percentage of atoms in natural sample of pure element represented by a particular isotope is called isotope's per cent abundance.

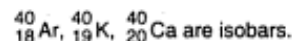
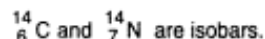
Per cent abundance

$$= \frac{\text{No. of atoms of given isotope}}{\text{Total number of atoms of all isotopes}} \times 100$$

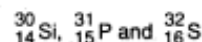
When per cent abundance is determined for each isotope then the average mass can be calculated. Such determination is done with the help of **mass spectrometer**. The average mass of representative sample of atoms is known as 'atomic weight'.

Points to Remember

- All atoms of a particular element have same number of protons, however, the number of neutrons may be different. Such atoms of same element which have same atomic number but different mass number, are known as **isotopes**. As ${}_1^1\text{H}$, ${}_1^2\text{D}$, ${}_1^3\text{T}$, are three isotopes of hydrogen having varying number of neutrons in their nuclei *i.e.*, 0, 1 and 2 respectively.
- It is also mentioned here that atoms of different elements having same mass number but different atomic numbers are called **isobars**. For example—



- Atoms of different elements which have equal number of neutrons in their nuclei are known as **isotones**. For example—



- Atoms of different elements having same difference in number of neutrons and the number of protons are known as **isodiapheres**. For example—



The natural sample of chlorine consists of two isotopes. One has mass 35 and other 37 amu. The per cent abundance of Cl^{35} is 75 and that of Cl^{37} is 25.

Average atomic mass

$$= (\text{Fractional abundance of } \text{Cl}^{35} \times \text{mass of the isotope}) + (\text{Fractional abundance of } \text{Cl}^{37} \times \text{mass of the isotope})$$

$$\text{Fractional abundance} = \frac{\text{Percentage abundance}}{100}$$

$$\begin{aligned} \text{Fractional abundance of } \text{Cl}^{35} \\ &= \frac{75}{100} = \frac{3}{4} \end{aligned}$$

$$\begin{aligned} \text{Fractional abundance of } \text{Cl}^{37} \\ &= \frac{25}{100} = \frac{1}{4} \end{aligned}$$

Hence average atomic mass of Cl

$$\begin{aligned} &= \frac{3}{4} \times 35 + \frac{1}{4} \times 37 \\ &= \frac{105}{4} + \frac{37}{4} = \frac{142}{4} = 35.5 \end{aligned}$$

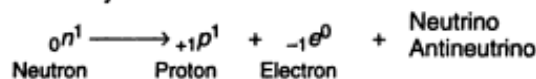
Hence atomic weight of Cl is 35.5

Other Particles :

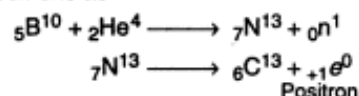
In addition to electron, proton and neutron-following atomic particles have also been discovered. A brief account is given below :

Neutrino—In 1927, **Pauli** postulated that a undetectable particle with zero mass and zero charge is simultaneously formed during neutron decay (half life of neutron = 12.8 min.) **Fermi** named this particle as **neutrino**. In 1952, **Allen** and **Rodeback** demonstrated the free existence of neutrino. Fermi in 1934 indicated the existence of **antineutrino** as well. Antineutrino is particle identical to

neutrino but has opposite spin. According to Fermi neutron decays as—



Antielectron or Positron—In 1932 Anderson, a physicist discovered this particle. The bombardment of light elements like boron with α particles resulted in the emission of positrons as—



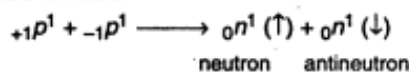
Positron has same negligible mass and same amount of charge as the electron. However, the charge on positron is positive. Positron has transitory existence of about 10^{-8} second. They quickly unite with electron producing γ rays, photons.



Antiproton—In 1955 Segre and his associates at university of California produced antiproton by bombarding a copper target with accelerated protons. The mass and spin of antiproton were found identical with protons but the charge was opposite *i.e.*, -1

Antineutron—In 1956 Cork and associates produced antineutrons. The antiparticles are identical with neutrons except that their spin is opposite.

When a proton strikes an antiproton, a neutron and an antineutron are emitted.



Meson—Hideki Yukawa, a Japanese physicist in 1935 predicted the existence of another nuclear particle called meson. Three kinds of mesons are found in cosmic rays and in laboratory.

- (i) μ mesons : having mass 206 times that of electron and charge which may be negative or positive.
- (ii) π mesons : having mass about 270 times that of electron and charge which may be negative or positive.
- (iii) K mesons : having mass 970 times that of electron and charge that may be negative, positive or zero.

Note—Nuclear particles with mass larger than proton have also been discovered. These are called **hyperons**. Mesons and **hyperons** are very short lived. **Hyperons** break down to other **hyperons**, mesons, neutrons and protons.

Planck's Quantum Theory :

Rutherford model failed in view of electromagnetic theory given by Maxwell. According to this theory a charged particle when accelerated emits energy in the form of electromagnetic radiations. According to Rutherford's model electrons revolving around the nucleus should continuously emit radiations. As a result of this it would slow down and would finally fall in the nucleus by following a spiral path. Thus Rutherford model failed to explain stability of atom.

Rutherford's model also failed to explain the existence of certain definite lines in the hydrogen spectrum. If the electron were to continuously lose energy, as discussed, the atomic spectrum of hydrogen would have been continuous. The failure of the classical electromagnetic theory of radiation to explain the phenomenon of **Photoelectric effect** led **Max Planck (1901)** to propose a new theory known as **quantum theory of radiation**. The main postulates of this theory are—

- (1) The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small packets known as **quanta**. Each wave packet or **quantum** is associated with definite amount of energy. In case of light the quantum of energy is often known as **photon**.
- (2) The amount of energy associated with a quantum of radiation is proportional to the frequency of radiation and is expressed as—

$$E \propto \nu$$

$$E = h\nu$$

{ Where h is constant known as
Planck's constant and is equal
to 6.625×10^{-34} joule-sec }

The energy of a photon of light in terms of **wavelength, λ** and **velocity of light, c** is given by—

$$E = h\nu$$

$$E = h \cdot \frac{c}{\lambda}$$

{ c = Velocity of light
= 3×10^8 m/sec }

- (3) A body can emit or absorb energy only in terms of the integral multiples of quantum *i.e.*,

$$E = nh\nu \quad \text{where } n = 1, 2, 3, 4, 5, \dots$$

Note—A body can emit or absorb energy as $h\nu, 2h\nu, 3h\nu, 4h\nu$ but cannot emit or absorb energy in fractional values of $h\nu$ as $0.5h\nu, 1.5h\nu, 2.5h\nu$.

Dual Nature of Radiation :

The **photoelectric effect** could be explained considering that radiations consist of small energy packets or quanta.

Kinetic energy of photoelectrons emitted from a metal surface is independent of intensity of radiation because increase in intensity does not effect the energy of photons rather it simply increases the number of photons and hence increases the number of photoelectrons, not energy. **Kinetic energy of photoelectrons is directly proportional to the frequency or the velocity of radiation**. On the other hand radiations exhibit phenomenon of the **interference** and **diffraction** which indicate that they have wave nature. Therefore, it may be concluded that radiation possesses **dual nature**.

Einstein (1905) calculated the mass of the photons associated with a radiation of frequency, ν . Thus

$$E = h\nu \quad \text{(Planck's equation)}$$

$$E = mc^2 \quad \text{(Einstein's equation)}$$

(m = mass of photon)

Hence, combination of two equations gives—

$$h\nu = mc^2$$

$$m = \frac{h\nu}{c^2} \text{ or } m = \frac{h}{c^2} \times \frac{c}{\lambda} \text{ or } m = \frac{h}{c\lambda} \left(\text{As } \nu = \frac{c}{\lambda} \right)$$

Points to Remember

- Moseley in 1913 studied the frequency of X-rays using different elements as anti-cathode. He postulated that the **Square root** of the frequency (ν) of X-rays is directly proportional to the nuclear charge (Z) i.e., atomic number.

$$\sqrt{\nu} = a(Z - b) \quad (a \text{ and } b \text{ are constants})$$

- **Wavelength (λ)** is distance between two nearest crests or troughs is expressed in metres, picometres (pm), nanometres (nm) or Angstrom (\AA) units.

$$1 \text{ pm} = 10^{-3} \text{ nm} = 10^{-2} \text{ \AA} = 10^{-10} \text{ cm} = 10^{-12} \text{ m}$$

- **Frequency (ν)** is the number of times a wave passes a given point in one second. It is expressed in **hertz (Hz)**.

$$1 \text{ cycle per second (1 cps)} = 1 \text{ Hz}$$

$$1 \text{ KHz} = 10^3 \text{ Hz}$$

$$1 \text{ MHz} = 10^6 \text{ Hz}$$

- **Velocity (c)** is the distance travelled by a wave in one second. It is expressed in ms^{-1} .

- The frequency (ν) wavelength (λ) are related to velocity as—

$$c = \nu\lambda$$

$$\nu = \frac{c}{\lambda}$$

- **Wave number ($\bar{\nu}$)** is reciprocal of wavelength i.e., the number of waves per meter.

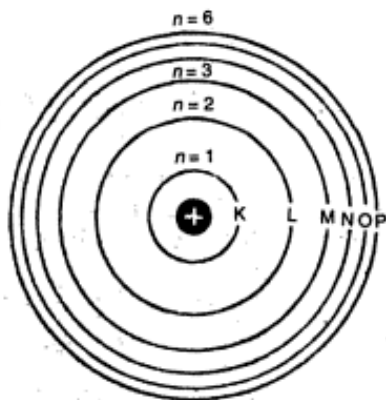
$$\bar{\nu} = \frac{1}{\lambda}$$

Bohr's Model of Atom :

In order to remove the drawbacks of Rutherford's atomic model, **Niels Bohr a Danish Physicist** (1913) proposed a new model of atom based upon quantum theory of radiations. The salient points of this model are—

(1) The electrons in an atom revolve around the nucleus only in certain circular orbits. These orbits are associated with definite energies and these are called **energy shells** or the **energy levels**. Orbits are numbered as 1, 2, 3, 4 etc. or designated as K, L, M, N ... etc.

(2) Only those orbits are permitted in which angular momentum of an electron is a whole number multiple of $\frac{h}{2\pi}$, where h is planck's constant.



Orbit like representation of various energy levels

Angular momentum of electron

$$mvr = n \frac{h}{2\pi}$$

In other words the angular momentum of an electron in an atom is quantized.

where, $n = 1, 2, 3, \dots$

m = Mass of electron

v = Velocity of electron

r = Radius of orbit

(3) As long as the electron remains in a particular orbit, it does not lose or gain energy. This is the reason that these orbits are called **stationary states**.

(4) When energy from external source is supplied to the electron, it may jump to some higher energy levels by absorbing energy (equal to the difference in energy between two energy levels). When electrons jump back to the lower energy level, it radiates some amount of energy in the form of photons of radiation.

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

$$\nu = \frac{E_2 - E_1}{h}$$

Bohr's Equation for Energy of Electron :

According to laws of classical mechanics, the centripetal force acting on electron is given by $\frac{Ze \times e}{r^2}$ tends to pull the electron towards the nucleus. The centrifugal force acting on the electron is given by $\frac{mv^2}{r}$ tends to take the electron away from its orbit.

Two forces balance each other

$$Ze^2/r^2 = mv^2/r$$

$$v^2 = Ze^2/mr \quad \dots(1)$$

According to Bohr postulate the angular momentum mvr is an integral multiple of $(h/2\pi)$ i.e., $mvr = n(h/2\pi)$

$$mvr = n \left(\frac{h}{2\pi} \right)$$

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

$$\therefore v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

and $v^2 = Ze^2/mr$

$$\therefore \frac{Ze^2}{mr} = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$

$$Ze^2 = \frac{n^2 h^2}{4\pi^2 mr}$$

From this equation the radius (r_n) of the n th orbit is obtained

$$r_n = \frac{n^2 h^2}{4\pi^2 Zme^2}$$

(As $Z = 1$ for hydrogen atom)

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

For hydrogen atom in ground state ($n = 1$), the radius r_1 is designated as the **Bohr's radius**.

$$r_1 = \frac{h^2}{4\pi^2 m e^2}$$

Total energy (E) of an electron revolving in the n th orbit is equal to sum of **Kinetic energy** ($\frac{1}{2} mv^2$) and the **Potential energy** ($-Ze^2/r_n$).

$$\therefore E = \frac{1}{2} mv^2 - Ze^2/r_n$$

From equation (1)

$$Ze^2/r^2 = mv^2/r_n$$

$$mv^2 = Ze^2/r_n$$

$$\therefore E = \frac{Ze^2}{2r_n} - \frac{Ze^2}{r_n} = -\frac{Ze^2}{2r_n}$$

$$E = -\frac{Ze^2}{2r_n}$$

Putting the value of r , we get

$$E = -\frac{Ze^2}{2} \times \frac{4\pi^2 Z m e^2}{n^2 h^2}$$

$$E_n = -\frac{2\pi^2 Z^2 m e^4}{n^2 h^2} \quad \dots(A)$$

This is famous Bohr equation applicable to hydrogen like atoms or ions as He^+ , Li^{2+} , Be^{3+} .

$$\pi = 3.14; m = 9.109 \times 10^{-28} \text{ gm}$$

$$e = 4.8003 \times 10^{-10} \text{ e.s.u.}$$

$$h = 6.626 \times 10^{-27} \text{ erg-second}$$

Therefore,

$$E = -21.80 \times 10^{-12} \times \frac{Z^2}{n^2} \text{ erg/atom}$$

$$E = -13.60 \times \frac{Z^2}{n^2} \text{ eV/atom}$$

In S.I. System equation (A) takes the form as :

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

(Factor $4\pi\epsilon_0$ is known as permittivity factor. Its numerical value is $1.1126 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$)

Therefore,

$$E_1 = -\frac{(2\pi^2) (1)^2 (9.109 \times 10^{-31} \text{ kg}) \times (1.602 \times 10^{-19} \text{ C})^4}{(1.1126 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})^2 (1)^2 (6.626 \times 10^{-34} \text{ Js})^2}$$

$$E_1 = -2.179 \times 10^{-18} \text{ J per atom}$$

$$= -1312.19 \text{ kJ Mol}^{-1}$$

Now since,

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$\text{Hence, } E_1 = -\frac{2.179 \times 10^{-18} \text{ J}}{1.602 \times 10^{-19} \text{ J/eV}}$$

$$= -13.6 \text{ eV}$$

Points to Remember

- $E = -313.6 \times \frac{Z^2}{n^2} \text{ K cal/atom}$
- Energy of electron in an atom is always negative.
- The electron present in an orbit at a infinite distance from nucleus has zero energy.
 $E_\infty = 0$.
- Lower the energy of electron or greater the -ve value of energy of electron, higher will be the attraction of the nucleus and more will be the stability of electron. The sequence of energy of energy levels is as :
 $E_1 < E_2 < E_3 < \dots \dots E_\infty = 0$.
- $E \propto -\frac{1}{n^2}$
As the value of n increases, the energy of electron also increases.
- $E \propto -Z^2$
With the increase in the value of atomic number (Z), the energy of electron decreases.
For example—Sequence of energy of 1st shell of H, He^+ , Li^{2+} , Be^{3+} will be as :
 $H > \text{He}^+ > \text{Li}^{2+} > \text{Be}^{3+}$
- $E_1 = \frac{n_2^2}{n_1^2}$
 $E_1 : E_2 = 4 : 1$
 $E_3 : E_2 = 4 : 9$

Bohr's Radius :

- $r = \frac{n^2 h^2}{4\pi^2 m e^2}$
 $\pi = 3.142, h = 6.626 \times 10^{-27} \text{ erg-sec.}$
 $m = 9.109 \times 10^{-28} \text{ gm}; e = 4.8003 \times 10^{-10} \text{ e.s.u.}$
 $\therefore r = \frac{(1)^2 (6.626 \times 10^{-27} \text{ erg-sec})^2}{(4) (3.142)^2 (9.109 \times 10^{-28} \text{ gm}) \times (4.8003 \times 10^{-10})^2 \text{ e.s.u.}}$

Hence $r = 0.529 \text{ \AA}$ for hydrogen atom for which $n = 1$, $Z = 1$.

General equation is—

$$r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

$$r = 0.529 \times 10^{-8} \times \frac{n^2}{Z} \text{ cm}$$

$$r = 0.529 \times 10^{-10} \times \frac{n^2}{Z} \text{ m}$$

- $r \propto n^2$. The value of radius of different orbits of same atom increases with the increase in value of 'n'.
- $r \propto \frac{1}{Z}$. The value of radius of same orbit of different atoms of different elements decrease with the increase in atomic number (Z).
For example—The values of radii of 1st orbit of H, He^+ , Li^{2+} and Be^{3+} have following sequence :
 $H > \text{He}^+ > \text{Li}^{2+} > \text{Be}^{3+}$
- **Circumference of Bohr's orbit** = $2\pi r$
According to Bohr's postulate
 $mvr = \frac{nh}{2\pi}$

Hence, $2\pi r = \frac{nh}{mv}$
 As, $v = \frac{2\pi e^2}{nh}$
 Hence, $2\pi r = \frac{nh}{m \times \frac{2\pi e^2}{nh}}$
 $= \frac{n^2 h^2}{m \times 2\pi e^2}$

Points to Remember

- The ratio of radii of different orbits have the relation as :

$$\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}$$
 For example—The ratio of radii of 1st orbit of H, He⁺ and Li²⁺ will be as :

$$H_{r_1} = 0.529 \times \frac{1^2}{1} \text{ \AA}$$

$$He^+_{r_1} = 0.529 \times \frac{1^2}{2} \text{ \AA}$$

$$Li^{2+}_{r_1} = 0.529 \times \frac{1^2}{3} \text{ \AA}$$

$$H_{r_1} : He^+_{r_1} : Li^{2+}_{r_1}$$

$$\frac{1}{1} : \frac{1}{2} : \frac{1}{3}$$

$$6 : 3 : 2$$
- The ratio of radii of second or third or *n*th orbits of H, He⁺ and Li²⁺ will be always 6 : 3 : 2.
- The distance between two consecutive orbits decreases as the value of Z increases. The value of Z is lowest for H atom and hence, the distance between two consecutive orbits will be maximum.

Velocity of Electron in Bohr's Orbit :

As we know that

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

or, $mv^2 = \frac{Ze^2}{r}$... (i)

Angular momentum of electron (*mvr*)
 $= \frac{nh}{2\pi}$... (ii)

Dividing equation (i) by (ii), we get

$$\frac{mv^2}{mvr} = \frac{Ze^2 \times 2\pi}{r \times nh}$$

∴ $v_n = \frac{Ze^2 \times 2\pi}{nh}$
 $= \frac{Z}{n} \times \frac{2\pi e^2}{h} \text{ cm/sec}$

Putting the values of Z, n, h, e and π in above equation, we get,

$$v_n = 2.188 \times 10^8 \text{ cm/sec}$$

or, $2.188 \times 10^6 \text{ m/sec.}$

- According to above equation one can conclude that $v \propto Z$. For the atoms of different elements, the velocity of electron in a particular orbit increases with the increase in the value of atomic number, Z.

For example—The velocity of electron in 1st orbits of H, He⁺, Li²⁺ and Be³⁺ will follow the following sequence :

$$H < He^+ < Li^{2+} < Be^{3+}$$

Velocity of electron in 1st orbit of H atom will be lowest and that in 1st orbit of Be³⁺ will be highest.

- $v \propto \frac{1}{n}$. For same atom Z is same. Hence, velocity of electron decreases when the value of n increases.

$$\frac{v_1}{v_2} = \frac{n_2}{n_1}$$

- v_1 = Velocity of electron in first orbit
- v_2 = Velocity of electron in second orbit
- n_1 = First orbit
- n_2 = Second orbit

Hence, $v_1 : v_2 = 2 : 1$

$$v_1 : v_3 = 3 : 1$$

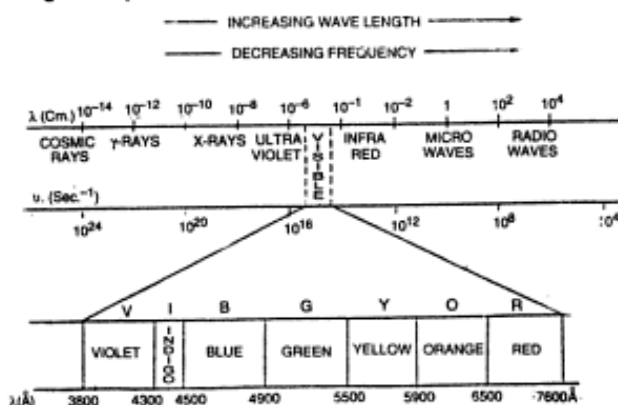
$$v_3 : v_1 = 1 : 3$$

Points to Remember

- Velocity of electron in a Bohr orbit of hydrogen atom can be determined by following formulae :
 (1) $v = \frac{Ze^2 \times 2\pi}{nh} \text{ cm/sec}$
 $v = \frac{2\pi e^2}{h}$
 (2) $mv^2 = \frac{Ze^2}{r}$
 $v^2 = \frac{Ze^2}{mr}$
 $v = \sqrt{\frac{Ze^2}{mr}}$
 (3) $mvr = \frac{nh}{2\pi}$
 $v = \frac{nh}{2\pi mr}$
- Radius (*r*₁) of first orbit of hydrogen atom is given as :
 $r_1 = \frac{h^2}{4\pi^2 m e^2}$
 ∴ The radius of *n*th orbit is given by
 $r_n = r_1 \times n^2$
- Energy (*E*₁) of the first orbit of hydrogen atom is given as:
 $E_1 = -\frac{2\pi^2 Z^2 e^4 m}{h^2}$
 ∴ Energy of *n*th orbit is given by
 $E_n = -\frac{E_1}{n^2}$
- The velocity of electron (*v*₁) of the first orbit of hydrogen atom is given as :
 $v_1 = \frac{2\pi Ze^2}{h}$
 ∴ The velocity of electron in *n*th orbit is given by
 $v_n = \frac{v_1}{n}$
- The radii of various nuclei can be determined by following relation
 $r = r_0 A^{1/3}$
 where *r*₀ is constant which is equal to $1.4 \times 10^{-13} \text{ cm}$ and A is the mass number of given nucleus.

Bohr's Theory and Origin of Hydrogen Spectrum :

Arrangement of all electromagnetic radiations in increasing order of their wavelengths or the decreasing order of their frequencies is known as **electromagnetic spectrum**. Different regions of electromagnetic spectrum are identified by different names. A complete electromagnetic spectrum is shown as :

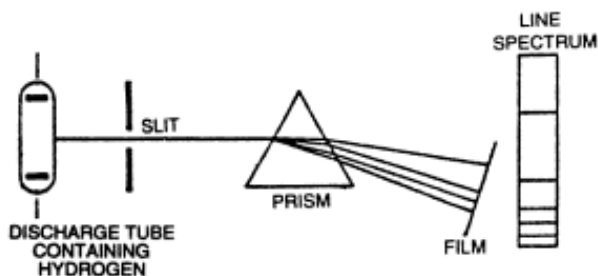


When discharge is passed through hydrogen gas at low pressure, some hydrogen atoms are formed, which emit light in the visible region. The light can be studied with spectrometer and is found to comprise a series of lines of different wavelengths. Four lines can be seen by eye, but many more lines are observed photographically in ultraviolet region. The lines become increasingly closer as the wavelength (λ) decreases, until the continuum is reached. The wavelengths, in metres are related to frequency, ν in hertz (cycles/second) by equation

$$\nu = \frac{c}{\lambda}$$

In spectroscopy frequencies are generally expressed as wave number,

$$\bar{\nu} = 1/\lambda \text{ m}^{-1}$$

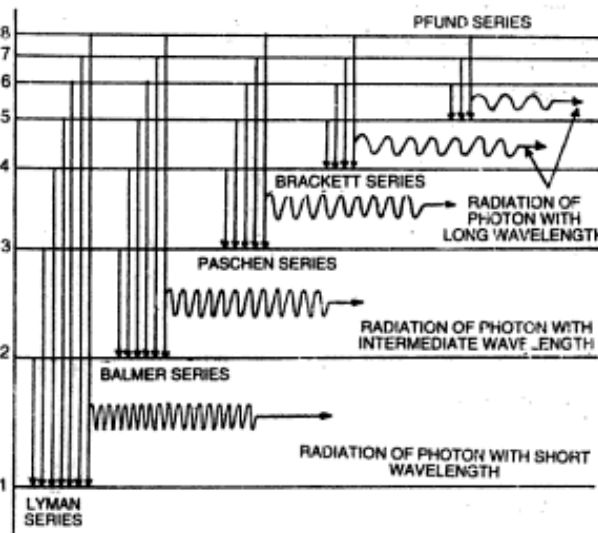


Emission spectrum of hydrogen

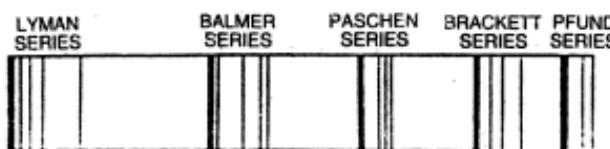
The lines in the emission spectrum of hydrogen are classified into five series as follows :

- (i) **Lyman Series**—Ultraviolet region (Wavelength less than 4000 Å)
 - (ii) **Balmer Series**—Visible region (Wavelength between 4000 – 7000 Å)
 - (iii) **Paschen Series**
 - (iv) **Brackett Series**
 - (v) **Pfund Series**
 - (vi) **Humphries Series**
- } Infra-red region (Wavelength greater than 7000 Å)

The complete spectrum of hydrogen is shown below :



The origin of hydrogen spectrum



Atomic spectrum of hydrogen

Balmer showed in 1885 that if the spectral lines are expressed in terms of wave numbers (inverse of wavelengths), then the lines in the visible region (Balmer series) obey the formula

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

{ R = Rydberg constant }
{ R = 109677 }

where, n is the integer equal to or greater than 3 i.e.,

$$n = 3, 4, 5 \dots$$

Later on, Rydberg gave a more general formula which is applicable to all the series in the hydrogen spectrum

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

where, n_1 and n_2 are integers, such that $n_2 > n_1$. For a particular series n_1 is constant.

- For Lyman Series $n_1 = 1, n_2 = 2, 3, 4, \dots$
- For Balmer Series $n_1 = 2, n_2 = 3, 4, 5 \dots$
- For Paschen Series $n_1 = 3, n_2 = 4, 5, 6 \dots$
- For Brackett Series $n_1 = 4, n_2 = 5, 6, 7 \dots$
- For Pfund Series $n_1 = 5, n_2 = 6, 7, 8 \dots$

Frequencies in Wave Numbers (m^{-1}) of Various Lines of Hydrogen Spectrum

Lyman Series		Balmer Series		Paschen Series	
Experimental Values	Calculated Values	Experimental Values	Calculated Values	Experimental Values	Calculated Values
82.2×10^5	82.2×10^5	15.20×10^5	15.21×10^5	5.32×10^5	5.30×10^5
97.5	97.5	20.60	20.60	7.79	7.80
102.8	102.7	23.00	23.05	9.13	9.12
105.2	105.2	24.30	24.35	9.95	9.95
106.3	106.2	25.20	25.18	10.50	10.45
107.2	107.1	25.70	25.55		
108.0	107.9				

The agreement between the experimental and the calculated values is **excellent**. This offered a very strong support to Bohr's theory of the hydrogen atom.

Limitations of Bohr's Model :

Bohr's theory of hydrogen atom enabled calculations of atomic radii and energies of permissible orbits in hydrogen atom. The calculated values were in agreement with the experimental values. Bohr's theory could explain successfully the position of various series of lines in the hydrogen spectrum. The theory was, therefore, largely accepted and Bohr was awarded nobel prize for this work.

On the basis of research work on structure of atom, several discrepancies were noticed in the Bohr's model of atom. Some important limitations are listed as below :

(1) Bohr model of atom could not explain the spectra of multielectron atoms.

(2) It was found that each spectral line gets split up into more hyperfine lines in the presence of external magnetic field. This is known as **Zeeman effect**. Bohr's model could not explain this phenomenon.

(3) de Broglie, a French Physicist (1923), postulated that like radiation, electron also has dual nature *i.e.*, it has particle as well as wave nature. Bohr has treated electron only as a particle.

(4) Bohr's model faced a serious set back, when Heisenberg put forth his famous **uncertainty principle**. According to Heisenberg's uncertainty principle, it is impossible to determine simultaneously the exact position and momentum of a small moving particle like electron. The postulate of Bohr, that electron moves in well defined orbits around the nucleus, is not valid.

Dual Nature of Particle :

Louis de Broglie (1924) propounded that just as radiations have particle nature, the matter particles are also associated with wave nature.

He gave following relation for calculating the wavelength of the wave associated with a particle of mass, m moving with a velocity of v .

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

Derivation of de Broglie relation. Energy of photon is given by

$$E = h \nu \text{ (Planck's equation)}$$

$$E = mc^2 \text{ (Einstein's equation)}$$

m is mass of photon

From two equations, we get

$$mc^2 = h \nu$$

$$mc^2 = h \cdot \frac{c}{\lambda} \quad \left(\text{As } \nu = \frac{c}{\lambda} \right)$$

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

de Broglie pointed out that the same equation might be applied to material particle by using m for mass of particle, instead the mass of photon and replacing c , the velocity, by v the velocity of the particle.

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

$$\text{or, } \lambda = \frac{h}{p} \quad (p \text{ is momentum})$$

This equation is known as **de Broglie equation**.

Points to Remember

- The waves associated with material particles in motion are called **matter waves** or **de Broglie waves**. These waves are distinctively different from the electromagnetic waves.
- | Electromagnetic Waves | Matter Waves |
|--|---|
| 1. These waves are associated with electrical and magnetic field. | 1. These waves are not associated with electrical and magnetic fields. |
| 2. Electromagnetic waves can be emitted or radiated in space | 2. Matter waves are neither radiated in the space nor emitted by the particles. These are simply associated with the particles. |
| 3. The velocity of all electromagnetic waves is equal to that of light <i>i.e.</i> , $3 \times 10^8 \text{ ms}^{-1}$ | 3. The velocity of matter wave is different from that of light. |
- If the electron of hydrogen atom is excited to n th energy orbit, the number of lines in different series will be as follows :
 - $(n - 1)$ lines in Lyman Series
 - $(n - 2)$ lines in Balmer Series
 - $(n - 3)$ lines in Paschen Series
 - $(n - 4)$ lines in Brackett Series
 - $(n - 5)$ lines in Pfund Series
 - de Broglie's concept of wave nature of electron was experimentally verified by **Davisson and Germer**.
 - Scintillation** produced by electron on zinc sulphide screen, shows the particle nature of electron.
 - de Broglie concept finds application in the construction of electron microscope and in study of surface structure of solids by **electron diffraction**.

Heisenberg's Uncertainty Principle :

The position and velocity of bodies can be determined precisely at a particular time. Hence, the paths or the **trajectories** of such bodies can be predicted. However, in case of small particles such as electron it is impossible to determine simultaneously its position and velocity at a given moment with certainty. Hence, it is not possible to talk of trajectory of an electron.

Werner Heisenberg (1927) put forth in the form of principle known as **Heisenberg's uncertainty principle**. Mathematically, uncertainty principle may be expressed as :

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

Δx = Uncertainty in position

Δp = Uncertainty in momentum

h = Planck's constant

The sign \geq means that the product of Δx and Δp can neither be greater than or equal to $\frac{h}{4\pi}$. It can never be less than $\frac{h}{4\pi}$, since the minimum product of Δx and Δp is constant. It means that

$$\Delta x \propto \frac{1}{\Delta p}$$

If uncertainty Δx is less, then uncertainty in Δp will be large and vice-versa.

Scientists Associated with Development of Atomic Structure

- (1) **Dalton** (1808)—Discovery of atom.
- (2) **Julius Plucker** (1859)—First discoverer of cathode rays.
- (3) **Sir J. J. Thomson** (1897)—Discovered **electron**.
- (4) **Sir J. J. Thomson and Millikan**—Determined the mass and charge on electron.
- (5) **Goldstein** (1886)—Discovered **anode rays and proton**.
- (6) **Rutherford** (1911)—Proposed atomic model (Discovered nucleus)
- (7) **H. G. J. Moseley** (1913)—Discovered **atomic number**.
- (8) **James Chadwick** (1932)—Discovered **neutron**.
- (9) **Max Planck** (1901)—Proposed **quantum theory of radiation**.
- (10) **Niel's Bohr** (1913)—Proposed new model of atom.
- (11) **de Broglie** (1923)—Established wave nature of particle.
- (12) **Werner Heisenberg** (1927)—Uncertainty principle.
- (13) **Davisson and Germer**—Experimental verification of wave nature of particle.
- (14) **Pauli** (1927)—Discovered Neutrino
- (15) **Allen and Rodeback** (1952)—Proved free existence of neutrino.
- (16) **Fermi** (1934)—Discovered antineutrino.
- (17) **Anderson** (1932)—Discovered antielectron or positron.
- (18) **Segre** (1955)—Discovered antiproton.
- (19) **Cork and associates** (1956)—Discovered antineutron.
- (20) **Hideki Yukawa** (1935)—Discovered mesons.
- (21) **Clark Maxwell's** (1921)—Electromagnetic wave theory.
- (22) **Sir. J. J. Thomson and P. Lenard**—Photoelectric effect.

It can be concluded that the position of electron cannot be known exactly at a particular moment, as postulated by Bohr. Instead it is possible to predict the probable region in a given space, where one can find the electron. Thus, Heisenberg replaced the **concept of definite orbits** by the **concept of probability**.

QUANTUM MECHANICAL MODEL OF ATOM

Introduction :

After world war I, Niels Bohr assembled a group of physicists in Copenhagen to derive a comprehensive theory for the behaviour of electron in atom from the view point of electron as a particle. Independently, **Erwin Schrodinger** (1887–1961), an Austrian, worked towards the same goal, but he used de Broglie's hypothesis that an electron in atom could be described by equations appropriate to **wave motion**. While both Bohr and Schrodinger were successful in predicting some aspects of electron behaviour, Schrodinger's approach gave correct results for some properties, where Bohr failed, so theoreticians today primarily use Schrodinger's concept. In any event, the general theoretical approach to understand atomic behaviour developed by Bohr, Schrodinger and their associates have come to be known as **quantum mechanics** or **wave mechanics**.

On the basis of Heisenberg's idea, **Máx Born** proposed that the results of quantum mechanics should be interpreted as : If we choose to know the energy of an electron in an atom with only a small uncertainty; then we must accept a correspondingly large uncertainty about its position in the space about the nucleus of atom. In practical terms, it means that only we can do, is to calculate the probability of finding the electron (for a given energy) within a given space.

The Wave Mechanical View of The Atom :

Erwin Schrodinger combined de Broglie equation with classical equations for wave motion. From these and other ideas then he derived a new equation called the **wave equation** or the **Schrodinger's equation** to describe the behaviour of an electron in the hydrogen atom.

Solving Schrodinger's wave equation leads to a set of functions called **wave functions**, symbolised by the Greek letter Ψ (Psi). There are several important points to be mentioned about these wave functions, which characterise the electron as a **matter-wave**. The Schrodinger wave equation is as follows :

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

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

Where, x , y and z are three space co-ordinates.

m is mass of electron

h is Planck's constant

E is total energy and V is potential energy of electron

Ψ is amplitude of the electron wave and is called wave function

$\frac{\partial^2 \Psi}{\partial x^2}$ refers to as second derivative of Ψ with respect

to x and so on. ∇^2 is Laplacian operator.

The solutions of Schrodinger's wave equation for hydrogen atom are numerous. Out of which only certain solutions are permissible. Each permitted solution or wave function corresponds to a definite energy state and is called **eigen function** or **orbital**.

Significance of Ψ —As a moving electron is associated with a wave and, a wave is completely defined by its amplitude, therefore, Ψ refers to the amplitude of electron wave. It has got no physical significance. However, the square of Ψ i.e. Ψ^2 has a physical significance. Just as light radiation where square of amplitude gives the intensity of light, similarly, in case of electron wave Ψ^2 gives the intensity of electrons. In other words, the knowledge of Ψ^2 is helpful in assessing the probability of electron in a particular region in the space.

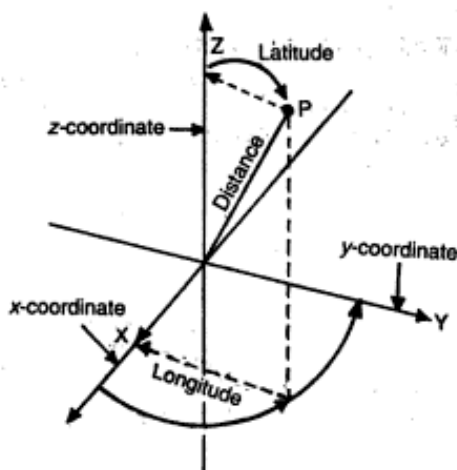
Thus, an orbital may be defined as the region of space around the nucleus where the probability of finding an electron is maximum.

Difference between Orbit and Orbital

Orbit	Orbital
1. Orbit is a well defined circular path followed by revolving electrons around the nucleus.	1. Orbital is a region of space around the nucleus of an atom where the electron is most likely to be found.
2. It represents planar motion of electron.	2. It represents three dimensional motion of electron around nucleus.
3. Orbits are circular in shape.	3. Orbitals have different shapes.
4. Orbit can accommodate $2n^2$ electrons, where n is the number of orbit.	4. An orbital can accommodate only two electrons.
5. Orbits are non-directional in nature.	5. Orbitals (except s-orbital) are directional in nature.
6. Concept of orbits does not comply with Heisenberg's principle.	6. Concept of orbitals is in accordance with Heisenberg's principle.

Quantum Numbers and Atomic Orbitals :

In three dimensional world, three numbers are required to describe the location of an object in space. For the wave description of the electron in hydrogen atom, this requirement leads to the existence of three quantum numbers.



The position of a point P in space can be specified by giving the x, y and z-coordinates or by giving the distance of point from the centre of the coordinate system and its latitude and longitude. In both cases three numbers are needed.

In an atom a large number of electron orbitals are permissible. These orbitals are designated by a set of quantum numbers. In order to specify, energy, shape and orientations of orbitals, three quantum numbers are required. These are **principal quantum number, angular momentum or azimuthal quantum number and magnetic quantum number**. These follow directly from solution of Schrodinger equation. In order to designate the electron fully, an additional quantum number known as **spin quantum number** is required to specify the spin of the electron.

Thus, each orbital in an atom is designated by three quantum numbers and each electron by a set of four quantum numbers. Three quantum numbers which designate an orbital are integers but their values cannot be selected randomly. The value of principal quantum number (n) limits the possible values of azimuthal quantum number (l), which in turn limits the values of magnetic quantum number (m). These quantum numbers are discussed below :

(1) Principal Quantum Number (n) = 1, 2, 3, ...—

This quantum number was introduced by Bohr and is denoted by n . The principal quantum number (n) can have any integer value from 1 to infinity. As the name implies it is the most important quantum number, because the value of n determines the total energy of electron.

$$E_n = -\frac{2\pi^2 Z^2 m e^4}{n^2 h^2}$$

This relation is similar to the expression given by Bohr.

Where,

- m = Mass of electron
- e = Charge on electron
- h = Planck's constant
- E_n = Energy of electron in n th shell
- n = Principal quantum number
- Z = Atomic number

Points to Remember

- The energy levels or energy shells corresponding to integers 1, 2, 3, 4, ... are designated as K, L, M, N, ...
- As the value of n increases, the electron gets farther away from the nucleus and energy increases.
- The higher the value of n , the higher is the electronic energy.
- The value of n , gives a measure of the most probable distance of electron from nucleus.
- Radius of an orbit can be evaluated as

$$r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$
- Maximum number of electrons in a shell = $2n^2$, where n is the value of principal quantum number.

(2) Angular Momentum Quantum Number or Azimuthal Quantum Number (l) = 0, 1, 2, ..., ($n - 1$)—Azimuthal quantum number was first proposed by **Sommerfeld**. This quantum number determines angular momentum of the electron as

$$\text{Angular momentum} = \sqrt{l(l+1)} \times \frac{h}{2\pi}$$

The principal quantum number gives total energy and position of an electron in general. A part of this energy, however, must be associated with the **orbital motion** of electron. This orbital motion is described by the orbital angular momentum of the electron. Therefore, it is known as orbital angular quantum number.

This quantum number accounts for the appearance of a group of closely spaced lines in hydrogen spectrum. The energy associated with angular momentum of an electron must be well within its total energy determined by n . Thus, electrons in an atom are grouped not only in main energy levels given by, n but also into energy sub-levels given by l .

The value of l gives sub-levels or sub-shells in which electron is located. The number of sub-levels within a principal shell is determined by value of n for that principal energy level. Thus, l may have all possible whole number values from 0 to ($n - 1$) i.e., $l = 0, 1, 2, \dots (n - 1)$.

The values of l quantum number are usually coded by letters according to scheme below :

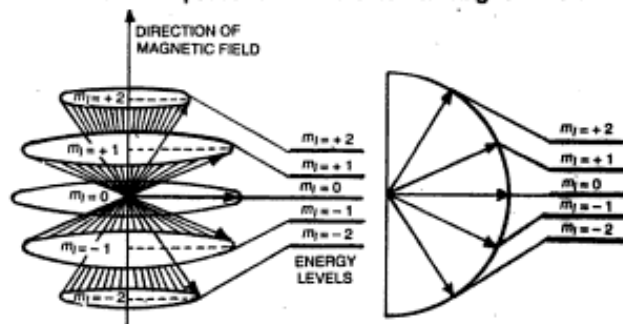
Value of l	Corresponding sub-levels/sub-shells
0	s
1	p
2	d
3	f
4	g

(3) Magnetic Quantum Number = 0, $\pm 1, \pm 2, \pm 3, \dots \pm l$ —Magnetic quantum number is denoted by m_l and refers to the different orientations of electron cloud in a particular sub-shell. These different orientations are called **orbitals**. The number of orbitals in a particular sub-shell within a principal energy level is given by the number of values allowed to m_l , which in turn depends on the value of l . The possible values of m are all integral values from $+l$ through 0 to $-l$ making a total of $(2l + 1)$ values.

Points to Remember

- Electrons of a given shell (n) can be grouped into sub-shells.
- Each sub-shell is characterised by certain wave shape.
- For a given shell, there are n different values of the quantum number l .
- Each value of l corresponds to a different orbital shape or orbital type.
- The value of n for a shell limits the number of sub-shells (shapes) that are possible within that shell. That is l can be no larger than $n - 1$.
- For $n = 1$, the rule tells that l must equal to 0 and only 0, since l has only one value when $n = 1$, only one orbital shape or type is possible for an electron assigned $n = 1$.
- When $n = 2$, however, l can be either 0 or 1. Since, 2 values of l are possible, there are two types of orbitals or sub-shells in $n = 2$ shell of electrons.

Let us consider the example of a d -orbital whose orbital angular momentum is $\sqrt{2(2+1)} \times \frac{h}{2\pi}$. It has five orientations of different energies in the presence of external magnetic field. Each orientation has a different Z component whose value ranges from $+2h/2\pi$ to $-2h/2\pi$. Thus, a spectral line obtained in the absence of external magnetic field due to the shift of electron from a higher orbital to the lower d -orbital of an atom will be split up into five lines in the presence of the external magnetic field.



Five different space orientations corresponding to $l = 2$.

The possible orientations after the energy relations of the electrons are given by magnetic quantum number proposed by Lande in 1921.

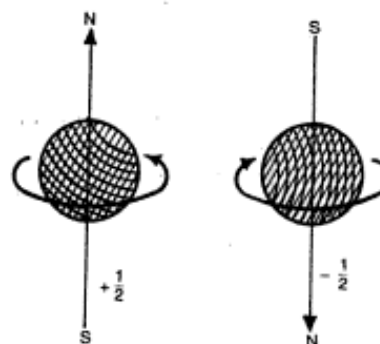
Points to Remember

- For $l = 0$ (s -sub-shell), $m_l = 1$ value i.e., 0. Hence, there is only one orientation for the s -sub-shell.
- For $l = 1$ (p -sub-shell), $m_l = 3$ values i.e., $-1, 0, +1$. Hence, three orientations are possible for p -sub-shell. Three corresponding orbitals are p_x, p_y and p_z .
- For $l = 2$ (d -sub-shell) $m_l = 5$ values i.e., $-2, -1, 0, +1, +2$. Hence, d sub-shell can have five orientations and orbitals corresponding to these are $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ and d_{z^2} .
- For $l = 3$ (f sub-shell), $m_l = 7$ values i.e., $-3, -2, -1, 0, +1, +2, +3$. Hence, seven f orbitals are possible in f sub-shell.

(4) Spin Quantum Number $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ —Spin quantum number was introduced by Uhlenbeck and Goudsmit in 1925.

This quantum number denoted by m_s , does not follow from wave mechanical treatment but arises from the spectral evidences, that the electron in its motion around the nucleus also rotates or spins about its own axis. The spin can be either clockwise or anticlockwise. The spin quantum number can have only two values which are $+\frac{1}{2}$ and $-\frac{1}{2}$. The $+\frac{1}{2}$ value indicates clockwise spin, generally shown by an arrow pointing upwards (\uparrow) and $-\frac{1}{2}$ indicates anticlockwise spin, represented by an arrow pointing downwards (\downarrow).

The spinning of an electron generates a magnetic moment which combines with magnetic moment generated due to orbital angular momentum of the electron. This combination of magnetic momenta modifies the energy of electron in a orbital and as a result of which electron can spin clockwise or anticlockwise.



Spin of electron on its own axis

Summary Points on Quantum Numbers :

- **Principal Quantum Number :**
Symbol = n
Values = 1, 2, 3,.....
Explains orbital size, energy and distance from nucleus.
No. of orbitals in a shell = n^2
No. of maximum electrons in a shell = $2n^2$
- **Angular Momentum Quantum Number or Azimuthal Quantum Number**
Symbol = l
Values = 0, 1, 2, 3, , $n - 1$.
Explains shape of orbitals
- **Magnetic Quantum Number**
Symbol = m_l
Values = $-l, \dots, 0, \dots, +l$
No. of values of m_l for a sub-shell = $2l + 1$
No. of orbitals in a sub-shell = $2l + 1$
No. of electrons in a sub-shell = $2(2l + 1)$
Explains orbital orientations and number of orbitals in a sub-shell.
- Only certain combinations of n and l are allowed as :

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

Allowed combinations

Relationship among the values of n , l and m_l

Energy level	Principal quantum number (n)	Azimuthal quantum number (l)	Designation of sub-shell	Magnetic quantum number (m_l)	Number of orbitals	
					In a given sub-shell ($2l + 1$)	In a given energy level (n^2)
K	1	0	1s	0	1	1
L	2	0	2s	0	1	4
		1	2p	-1, 0, +1	3	
M	3	0	3s	0	1	9
		1	3p	-1, 0, +1	3	
		2	3d	-2, -1, 0, +1, +2	5	
N	4	0	4s	0	1	16
		1	4p	-1, 0, +1	3	
		2	4d	-2, -1, 0, +1, +2	5	
		3	4f	-3, -2, -1, 0, +1, +2, +3	7	

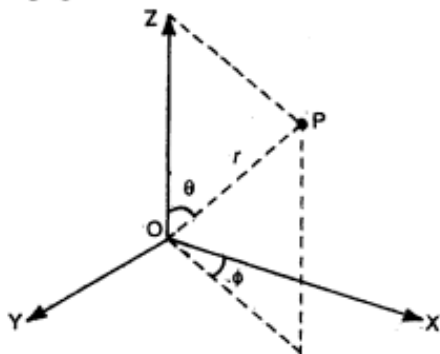
Orbital-Wave Function, Probability Distribution and Shapes of Atomic Orbitals :

In order to understand the distribution of electrons in a given volume of space about the nucleus we are required to know about the wave functions. An orbital-wave function (Ψ) can be written as product of two functions, the **radial function** and **angular function**. The radial function, Ψ_r , is the function of distance only and angular function is function of two angle variables.

Hence,

$$\Psi = \Psi_r \cdot \Psi(\theta, \phi)$$

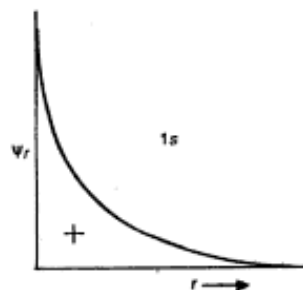
Here, r , θ and ϕ are spherical polar coordinates. Since, the Schrodinger wave function equation has more validity in the form of spherical coordinates instead of cartesian coordinates, therefore, the location of a point P in spherical coordinate system is represented in the following figure :



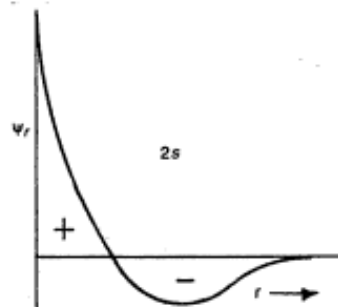
r is the length of the line between origin and point P. The angle between line and Z axis is θ . Angle ϕ is projection of this line in xy plane makes with x axis.

The complete wave function represents an orbital in which radial part (Ψ_r), depends upon quantum number n and l and tells about the size of the orbital, whereas angular part, (Ψ_θ, ϕ) depends upon quantum number l and m and tells about the shape of the orbital.

Since, three variables are involved, it is difficult to plot variation of Ψ with these variables in single diagram. In order to overcome this difficulty, the distance variation and angular variation are plotted in separate diagrams. The variation of radial part of the orbital wave function for 1s and 2s orbitals is given as :



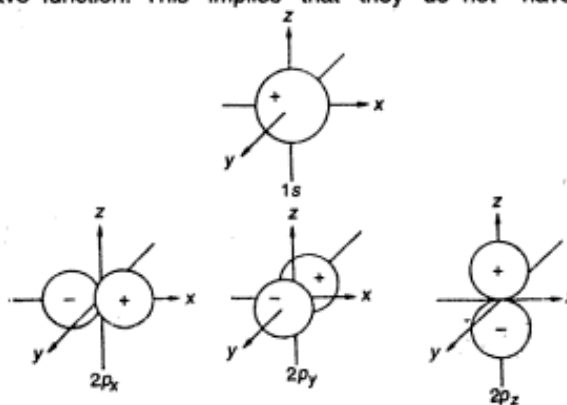
Variation of 1s orbital wave function with distance from nucleus



Variation of 2s orbital wave function with distance from nucleus

As Ψ has no significance, therefore, above plots are also meaningless except that the plots give the sign of wave function.

It has been found that s -orbitals are independent of angular wave function, but simply depend on radial part of wave function. This implies that they do not have

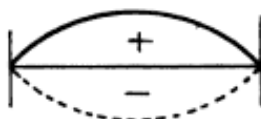


directional dependence. All *s*-orbitals, therefore, are **spherically symmetrical**, *p* and *d* orbitals, however, depend upon radial as well as angular wave functions, which means they show directional dependence. The angular dependence of 1*s*, 2*s* and 2*p* orbitals wave functions has been shown in the figure.

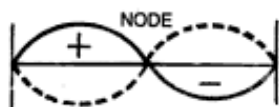
Key Fact

The positive and negative signs indicate whether the orbital wave function is +ve or -ve in a particular region. These signs do not represent +ve or -ve charges.

They are just analogous to the signs of amplitude in case of plane waves. It may be noted that 1*s* orbital wave function has same sign everywhere. This is equivalent to the wave produced by plucking the string **between the two points in the middle** as :



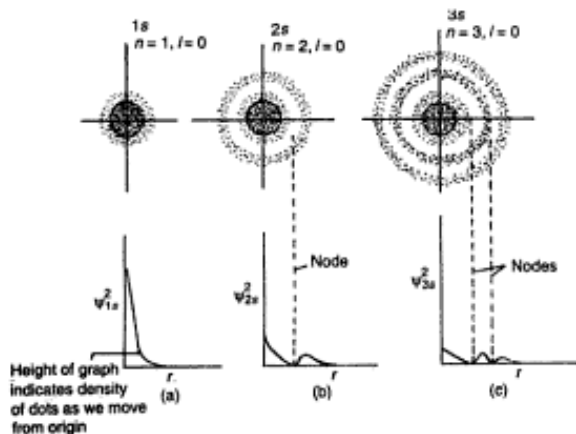
On the other hand, 2*s* orbital wave function can be +ve or -ve depending upon the distance. In fact sign of wave function changes after the node. This is equivalent to the wave produced when the string between the two points is plucked at $\frac{1}{4}$ th of a distance as :



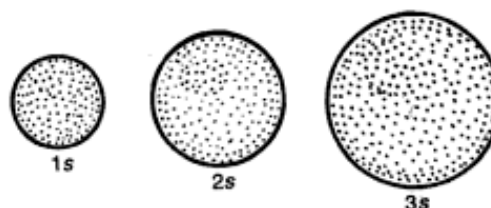
Probability Density (Ψ^2) :

The orbital wave function Ψ , as such has no physical significance. It represents amplitude of electron wave. However, square of wave function, Ψ^2 , is the measure of probability of finding the electron in a given volume around the nucleus is called **probability density**.

s-Orbitals—A graph of Ψ^2 as a function of distance from the nucleus is called probability density curve. The probability density curves for 1*s*, 2*s* and 3*s* are given as :



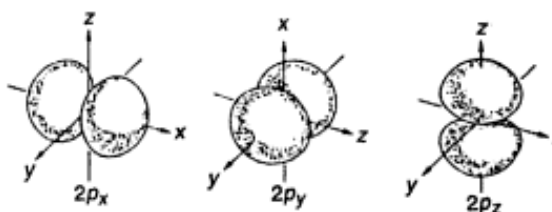
Electron density distribution in 1*s*, 2*s*, and 3*s* orbitals. The lower part of the figure shows how the electron density represented by Ψ^2 , varies as a function of distance *r* from the nucleus. In the 2*s* and 3*s* orbitals the electron-density function drops to zero at certain distances from the nucleus. The spherical surfaces around the nucleus at which Ψ^2 is zero are called nodes.



Contour representations of the 1*s*, 2*s*, and 3*s* orbitals. The relative radii of the spheres correspond to a 90 per cent probability of finding the electron within each sphere.

1*s*, 2*s* and 3*s* orbitals have same shape but they differ in size. The intermediate regions where Ψ^2 goes to zero are called **nodes**. The number of nodes increases with increasing value of principal quantum number, *n*. The size of orbital increases as *n* increases. The 2*s* orbital has one node and 3*s* has two nodes. In the *ns* orbital, the number of nodes is (*n* - 1). *s*-orbitals have spherical nodes. They do not have any nodal plane.

p-Orbitals— For *p*-orbitals there are three possible orientations of electron cloud. These three orientations or orbitals of *p*-subshell are designated as *p_x*, *p_y* and *p_z* or *p₊₁*, *p₋₁*, and *p₀* respectively. Each *p*-orbital has two lobes which are separated by a plane of zero probability called nodal plane. Each *p*-orbital is, thus, **dumb-bell shaped**. The spatial distributions of 2*p* orbitals are shown below :



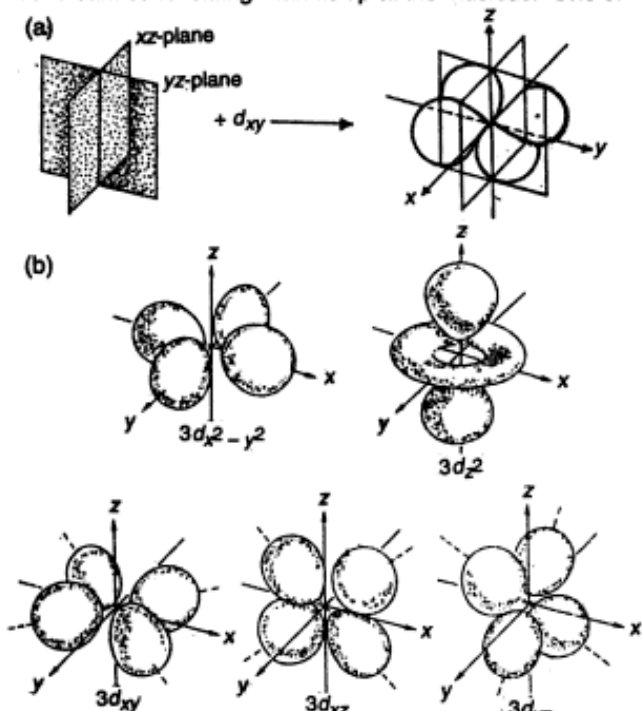
Electron-density distribution of a 2*p* orbital and Representations of the three *p* orbitals. Note that the subscript on the orbital label indicates the axis along which the orbital lies.

d-Orbitals—There is direct relation between value of *l* and the number of nodal planes, that slice through the nucleus. The *s*-orbitals for which *l* = 0 have no nodal planes. The *p*-orbitals for which *l* = 1 have one nodal plane. It follows that the five *d* orbitals, for which *l* = 2 have two nodal planes that slice the electron cloud into four sections.

The quartering of the electron cloud to give the five orientations of the *d*-orbitals is more complex. Three of the orientations are quite logical. We imagine a horizontal plane to halve space and either of two vertical planes to halve it again. This gives orientations levelled *d_{xz}* and *d_{yz}*. These orbitals lie in planes defined by *x* - *z* and *y* - *z* axes, respectively. If the electron cloud is sliced by two vertical planes, we have the *d_{xy}* orbital, where orbit lies in *x* - *y* plane.

Of the two remaining *d*-orbitals, the *d_{x2-y2}* orbital is easier to visualize. Like the *d_{xy}* orbital, *d_{x2-y2}* orbital results from two vertical planes slicing the electron cloud into quarters. Now, however, the planes bisect the *x* and *y* axes, so the regions of electron density lie along the *x* and *y* axes.

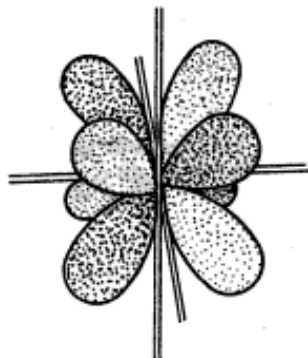
The final d orbital, d_{z^2} has two main regions of electron density along z axis but there is also a 'donut' of electron density in the xy plane. This orbital also has two nodal surfaces but the surfaces are not flat. Think of an ice cream cone sitting with its tip at the nucleus. One of



The d atomic orbitals. (a) The xz and yz nodal planes of the d_{xy} orbital. The subscript xy on the orbital label means that the orbital lies in the xy plane. (b) All d orbitals have $l = 2$, so all have two nodal planes. The 'planes' for the d_{z^2} orbital are actually conical.

the electron cloud along the z axis will sit inside the cone. If we use another cone pointing in opposite direction from first one, again with its tip at the nucleus, another electron density will fit inside this second cone. The region outside both cones defines remaining donut-shaped region of electron density.

f-Orbitals—Seven f -orbitals all have $l = 3$, meaning that there are three nodal surfaces slicing through the nucleus and carving up the electrons cloud into eight regions of probability. This makes these orbitals less easily visualised than the ones we have seen so far but one example of f -orbital is illustrated as follow :



One of seven possible f -electron orbitals. Notice the presence of three nodal planes (xy , xz and yz) as required by an orbital with $l = 3$.

Points to Remember

- **Zeeman Effect**—Zeeman in 1896, found that when a strong magnetic field is applied to a system, whose spectrum is being recorded each spectral line gets split up into a number of spectral lines. This phenomenon is known as **Zeeman effect**.
- **Compton Effect**—Compton found that if **monochromatic** X-rays are allowed to fall on carbon or some other light-element, the scattered X-rays have wavelength larger than incident X-rays. This decrease in energy or increase in wavelength of X-rays caused by interaction of X-rays and electron of element surface is known as **Compton effect**. By applying the law of conservation of energy and the law of conservation of momentum and assuming X-rays to be consisted of particles (photons) each possessing energy equal to $h \nu$, compton derived the following equation :

$$\Delta\lambda = (2h/mc) \sin^2 \theta/2.$$
 where, $\Delta\lambda$ is the increase in wavelength known as **Compton shift**, produced as a result of collision, m is the rest mass of electron, c is velocity of light and θ is angle between incident and the scattered X-rays.
- **Experimental Evidence of Electron Spin**—In 1921 **Otto Stern and Walter Gerlach** succeeded in separating a beam of neutral atoms into two groups. An inhomogenous magnetic field affected neutral atoms. The magnetic field arising from electron's spin interacts with magnetic field, deflecting the atoms from straight line path, suggesting there are two equivalent values for the electrons own magnetic field. Thus, it was realised that there are exactly two values for the spin of the electron. These values will produce equal magnetic fields that are opposite in direction.
- **Photoelectric Effect**—In 1905 Albert Einstein used Planck's quantum theory to explain Photoelectric effect. When the photons of sufficiently high energy strike a metal surface, electrons are emitted from metal. The photoelectric cells are based on this principle. The emitted electrons are drawn towards the +ve terminal, as a result current flows in the circuit.
- **Laplacian Operator**—In 1929, Schrodinger independently laid the foundation for distinctly new mechanics which is expression of wave-particle duality of matter. Schrodinger equation is expressed as :

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$
 This equation implies that a moving particle of mass m , total energy E and potential energy V has a wave associated with it of an amplitude given by wave function Ψ . ∇^2 is known as **Laplacian operator**. A particular value of Ψ is called **eigen function**. The values of energy which correspond to **eigen functions** are known as **eigen values**. Eigen function for an electron is called an atomic orbital.
- **Stark Effect**—The splitting of atomic spectral lines due to an electrical field was originally observed by **J. Stark** and the phenomenon is known as **Stark effect**.
- **Degenerate Orbitals**—When the orbitals are of equal energy they are said to be **degenerate orbitals**.
- **Nodal Plane**—A question students often ask is how electron in a p , d , or f orbitals move across the **nodal plane**. The question is not meaningful given the view that an electron behaves as a wave. If we treat the electron according to the physics of wave, then we can no longer think of it as particle moving about in space. The **standing waves** have nodes but it does not mean that string does not exist at that point, it simply means that there is no amplitude at that node. The same is true of the electron wave.
- **s, p, d, f**—These are spectroscopic notations and are first letters of sharp, principal, diffuse and fundamental respectively.

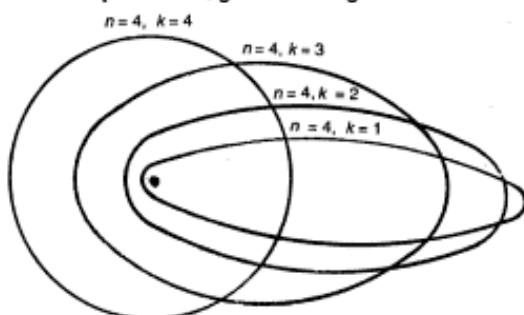
Elliptical Orbits :

According to Sommerfeld an electron revolving around the nucleus is so influenced by the nuclear charge that it is set into motion in the elliptical orbits with the nucleus situated at one of the foci. The angular momentum, according to quantum theory, must be quantised and thus, can have limited values given by a factor $kh/2\pi$, where k is an integer known as azimuthal quantum number. It should be remembered that n , is principal quantum number used by Bohr and k , the azimuthal quantum number, used by Sommerfeld.

They are related with each other as :

$$\frac{n}{k} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

Thus, for any given value of n (except $n = 1$) k can have more than a single value, when $n = k$, the orbit becomes **circular**. But when k becomes smaller, the orbit becomes **elliptical** with greater and greater **eccentricity**.



Sommerfeld's elliptical electron orbits for $n = 4$

Scientists associated with quantum mechanical or wave mechanical development of atomic structure

1. James Maxwell (1864)—Developed elegant mathematical theory to describe all forms of radiations in terms of oscillating or wave like electrical and magnetic fields in space.

2. Max Karl Ludwig Planck (1900)—Gave revolutionary scientific thought that there is minimum amount of energy that can be gained or lost by an atom and all energy gained or lost must be some integer multiple n , of that minimum.

$$\text{Energy} = n(h\nu)$$

Awarded nobel prize in 1918.

3. Albert Einstein (1900)—Explained the phenomenon of photoelectric effect on the basis of quantum theory of radiations.

4. de Broglie (1925)—He proposed that a free electron of mass m moving with velocity v should have an associated wavelength given by equation.

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

This is famous de Broglie equation.

5. Erwin Schrodinger (1926)—Gave wave equation to describe the behaviour of electron wave in atom

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

6. Niel Bohr (1913)—A Danish physicist proposed principal quantum number (n) represented by 1, 2, 3, 4, ... or K, L, M, N, ... shells.

7. Sommerfeld—Introduced concept of elliptical orbits and azimuthal quantum number.

8. Werner Heisenberg (1927)—Gave the principle of uncertainty which led to the concept of **probability** of finding electron in a given space (orbital).