CHAPTER - 02
STRUCTURE OF ATOM

The word atom has been derived from the Greek word ‘atomio’ which means uncuttable or non-divisible(400 BC). The atomic theory of matter proposed on the firm scientific basis by John Dalton(1808). Dalton’s atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion.

Dalton’s atomic theory failed to explain generation of electric charge when glass or ebonite rubbed with silk or fur. Particulate nature of electricity made clear by Faraday’s experiment(passing current through electrilyte solution.)

In mid 1850s many Scientists(Julius Plucker Crooks, J.J. Thomson, Faraday -----) mainly Faraday began to study electrical discharge in partially evacuated tubes. When sufficiently high voltage is applied across the electrodes, Current starts flowing through a stream of particles from negative electrode to positive electrode.These were called cathode rays or cathode ray particles.

Characteristic features of cathode rays

1. These rays are negatively charged and move along straight line
2. They are massive particles and deflect in magnetic and electric field.
3. They affect photographic plate
4. These rays ionise gases, which kept inside the discharge tube.
5. They produce heat and light, when hit on the tungsten filament.
6. They produce X-rays, when it hit on the tungsten metal.
7. They produce fluorescence and phosphorescence, when it hit on the corresponding material.
8. The e/m value of cathode rays doesn’t depend on the nature of the gas.

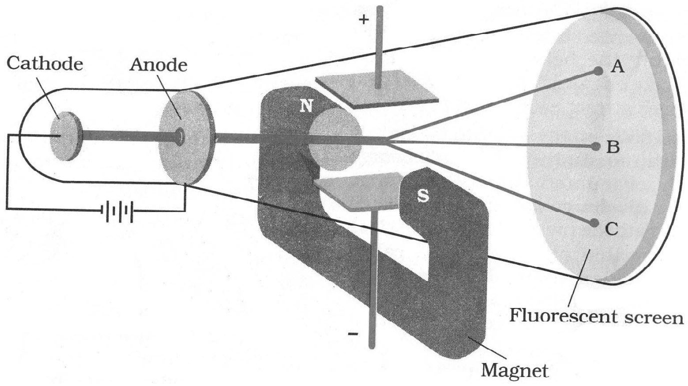
Thus we can conclude that electrons are basic constituent of all the atoms

J.J. Thomson experiment to determine the specific charge of electron (e/m)

CHARGE TO MASS RATIO OF ELECTRON

In 1897, British physicist J.J. Thomson measured the ratio of charge (e) to mass of electron(m_e) using cathode ray tube by applying electrical and magnetic fields perpendicular to each other and the path of the electrons. He observed that deviation of the particles from their path depended on the magnitude of negative charge on the particle, mass of the particle and strength of the electrical or magnetic field.

1. Greater the magnitude of charge, greater is the interaction with the field and hence higher the deviation.
2. Heavier the particle lesser the deviation
3. Greater the strength of the magnetic field or the voltage applied, greater will be the deviation.



Apparatus to determine charge to mass ratio of electron

The magnetic and electric fields deflect the beam in opposite directions (A and C) from point B. From the amount of charge required to balance the effect of the magnetic field, Thomson calculated the e/m_e of cathode ray particle as 1.758820×10^{11} C kg^{-1}.

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \mathrm{C\,kg^{-1}}$$

The e/m_e ratio for cathode rays was found to be the same irrespective of the nature of the cathode or the gas taken in the discharge tube, thus indicating that electrons are basic constituents of all atoms.

R.A. Millikan(1868 - 1953) devised a method known as oil drop experiment(1906 - 14), to determine the charge on the electrons. He found that the charge on the electron to be -1.6×10^{-19}C. The present accepted value of electrical charge is -1.6022×10^{-19}C. The mass of the electron(m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19}\mathrm{C}}{1.758820 \times 10^{11}\mathrm{C kg^{-1}}} = 9.1094 \times 10^{-31}\mathrm{kg}$$

1. Properties of subatomic particles

Particle	Electric charge (C)	Mass		Symbol	Discoverer	Location
		Kilograms (kg)	Atomic mass units (u)			
Electron	-1.60×10^{-19}	$9.109\,382 \times 10^{-31}$	5.485799×10^{-4}	e^-	J.J. Thomson	Outside the nucleus
Proton	$+1.60 \times 10^{-19}$	$1.672\,622 \times 10^{-27}$	1.007276	p	Goldstein	Inside the nucleus
Neutron	0	$1.674\,927 \times 10^{-27}$	1.008665	n	Chadwick	Inside the nucleus

Atomic models

(a) Thomson model of atom

(i) In this model of the atom, the electrons are negatively charged particles embedded in the atomic sphere of approximate radius 10^{-10}m

(ii) The sphere also contains an equal number of positive charges to make atom electrically neutral

(iii) The positive charge was assumed to be spread throughout the atom, forming a kind of pudding in which the negative electrons were suspended like plums

Limitation

The model could not account for the distribution of mass

Ruthefords nuclear model of atom

(i) The positive charge and most of the mas of the atom is concentrated in a small region of the atom and vast majority of the volume of an atom is therefore emty space

(ii) The electrons surround the nucleus and move around the nucleus in circular paths called orbits.

(iii) The electrons and nucleus are held together by the electromagnetic forces.

Limitations

It could not explain the stability of the atom

It was not able to explain the line spectra for various elements

This model was unable to explain the energies of electrons and their distribution around the nucleus.

ISOTOPES, ISOBARS AND ISOTONES

Isotopes: All atoms of an element have the same number of protons in their nuclei, however, the number of neutrons may vary. Atoms having same atomic number but different mass numbers are known as isotopes. For example, hydrogen has three isotopes namely protium $\left({}_{1}^{1}H\right)$, deuterium $\left({}_{1}^{2}D\right)$ and tritium $\left({}_{1}^{3}T\right)$.

Similarly, the three isotopes of carbon are ${}_{6}^{12}C$, ${}_{6}^{13}C$ and ${}_{6}^{14}C$. Chlorine has two isotopes, ${}_{17}^{35}Cl$ and ${}_{17}^{37}Cl$.

Chemical properties of atoms are controlled by the number of electrons and therefore, all isotopes of a given element exhibit same chemical behaviour.

Isotones: Sometimes atoms of different elements contain the same number of neutrons. Such atoms are known as isotones. Thus, isotones are atoms of different elements containing the same number of neutrons. E.g. ${}_{6}^{13}C$ and ${}_{7}^{14}N$; ${}_{14}^{30}Si$, ${}_{15}^{31}P$ and ${}_{16}^{32}S$.

Isodiaphers: They are atoms of different elements which have the same difference between the number of neutrons and protons (same n - p value). Eg. ${}_{5}^{11}B$ and ${}_{6}^{13}C$, ${}_{7}^{15}N$ and ${}_{9}^{19}F$

Isosters: Molecules which have the same number of atoms and electrons are alled isosters. E.g. CO and N_2O, CaO and KF, OF_2 and HClO.

<u>LIGHT</u>

I. **<u>Newtons Corpusular Theory :</u>** Particle nature could clearly explained by Newtons corpusular theory.

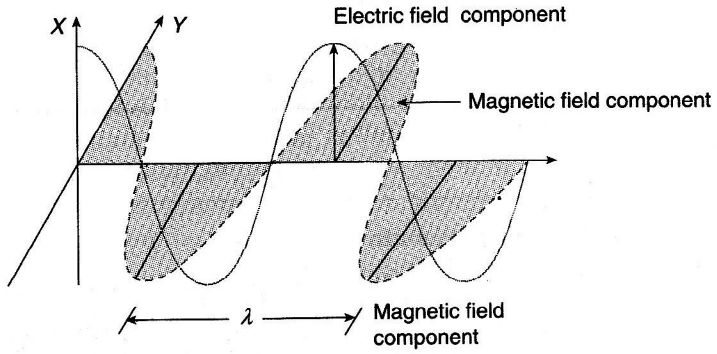
♦ *Limitations of Newtons corpusular theory*

Diffraction, Interference etc could not clearly explained.

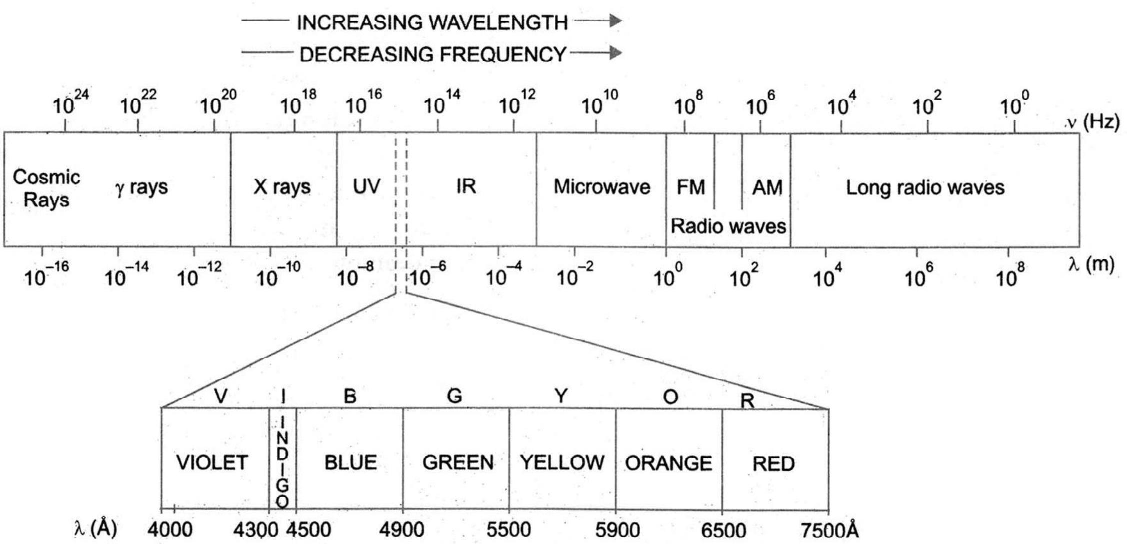
II. Wave theory

Electromagnetic wave theory :

Accelerated charged particles like electron which emit radiation/energy in the form of wave component. Which resolve into two component, ie., electrical component wave and magnetic component wave. Those waves are mutually particular to each other and are perpendicular to the propagation.



The electric and magnetic field components of electromagnetic wave



The electromagnetic spectrum (visible region is only a small part of the spectrum)

Characteristic features of wave

1. Wavelength (λ) : Distance between the two consecutive crests or troughs

2. Frequency (υ) : Number of waves passing through a point per second.

$\upsilon = \frac{c}{\lambda}$; c is the velocity of light, $\upsilon = \frac{1}{T}$

3. Amplitude A : The maximum height of crests or the maximum depth of trough.

$\upsilon = 1/T$, T = Time in second.

4. Wave number $\bar{\upsilon}$ = Number of waves passing per unit length .

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

Relation between υ and $\bar{\upsilon}$

$\upsilon = c\bar{\upsilon}$

2. **Plancks quantum theory**

Postulate

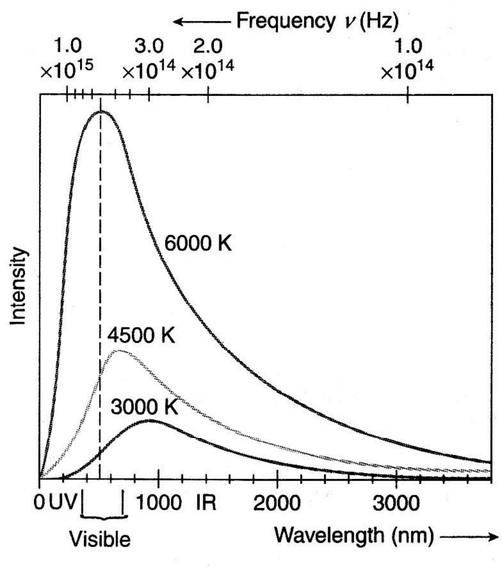
1. Atom and nucleus absorbs and liberate energy not continuously discontinuously in the form of small packets called quanta (photon)
2. E = $h\upsilon$ - (1 photon or 1 quanta)
3. E = $\frac{hc}{\lambda}$
4. E = n $\frac{hc}{\lambda}$ n = no. photons

Limitations of wave theory

1. **Black body radiation**

An ideal black body is expected to absorb completely the radiant energy falling on it is known as a black body. The radiation emitted by a black body kept at high temperature is called black body radiation. A black body radiation is the visible glow that the solid object gives off, when heated.

A graph is obtained by plotting the intensity of radiation against wave length gives the following details.

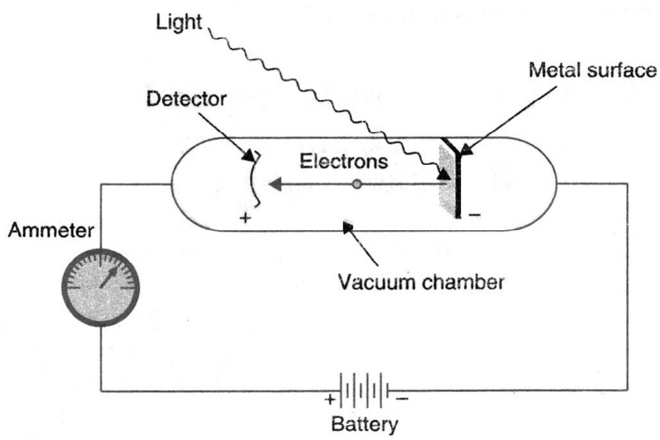


It is observed that

1. The naure of the radiation depends upon the Temperature of the black body.
2. At given temperature, the intensity of radiation increases with the wavelength, reaches maximum and then decreases.
3. As the temperature increases peak of maximum intensity shifts towards the shorter wavelength.

Photo electric effect

Electrons are ejected from certain metals like K, Rb Cs---- when they are exposed to a beam of light.



Equipment for studying photoelectric effect.

$\left(E_0 = h\upsilon_0\right)$ υ_0 = Threshold frequency

$E_1 = E_0 \rightarrow$ photoelectric effect is formed

$E_1 < E_0 \rightarrow$ No photo electric effect

$E_1 > E_0 \rightarrow$ K.E. of photoelectrons are present

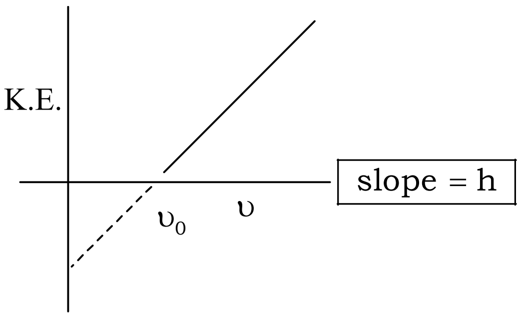
$$\Delta E = E_1 - E_0 = KE = h\upsilon - h\upsilon_0$$

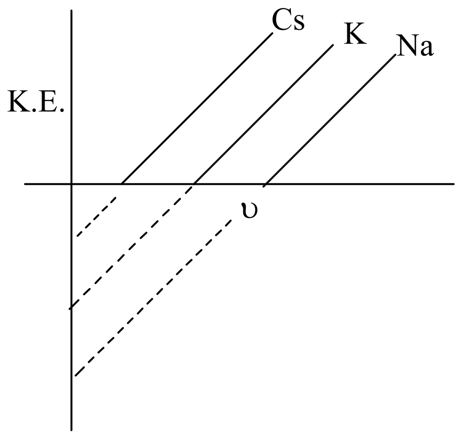
$$KE = h\left(\upsilon - \upsilon_0\right)$$

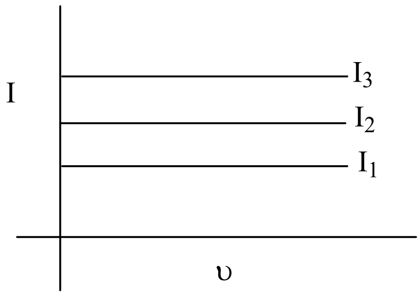
$$\boxed{KE \ \alpha \ \upsilon}$$

$$\boxed{I_{\text{incident light}} \ \alpha \ \text{no ejected electrons}}$$

Graphical explanation of photoelectric effect







Stopping potential :

The external potential is required to stop the K.E. of ejected electrons.

KE = $h\upsilon - h\upsilon_0$

eV = $h\upsilon - h\upsilon_0$

$$V = \frac{h\upsilon}{e} - \frac{h\upsilon_0}{e}$$

$$y = mx + c$$

Where V is the stopping potential.

Bohr atomic model

Bohr's atomic theory

Postulates

1. Electron is revolving round the nucleus in a circular stationary energy path called **Orbit.**
2. As long as electron revolve round the nucleus in a circular path, it neither loose energy nor absorb.
3. Angular momentum of an orbit is quantised. It is integral multiple of some constant values $mvr_n = \frac{nh}{2\pi}$

   or $mVr_n = n\hbar$

4. When an electron absorb energy from external source, it get excited to the higher energy level. That electron has no stability, it de-excited to lower levels by releasing absorbed energy. That energy corresponds to the spectrum.

MERITS

1. He could clearly derived the relations of K.E., P.E., E_n (total) velocity of electron in the n^{th} Bohr orbit and radius of n^{th} Bohr orbit.

1. Relation of KE and PE

1. $\text{K.E.} = \frac{KZe^2}{2r_n},\ K = \frac{1}{4\pi\varepsilon_0};\ \varepsilon_0 \rightarrow$ permitivity in free space

2. P.E. = $\frac{-KZe^2}{r_n}$

If KE is x, PE = –2x.

♦ Hydrogen like species are He^{+1}, Li^{+2}, Be^{+3} . Those species contain one electron in ground state.

2 Relation of Radius of Bohr orbit

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

$$r_n = 0.529\frac{n^2}{Z}A^0 \text{ or } r_n = 52.9\frac{n^2}{Z}\text{pm}$$

$$\boxed{r_{nx} = r_1H \times \frac{n^2x}{Zx}}$$ x = Hydrogen like species

3. Relations of total energy of Bohr orbit

K.E. + P.E. = E_n

$$E = \frac{-2\pi^2me^4z^2k^2}{n^2h^2}$$

$$E_n = -1312\frac{Z^2}{n^2}\text{kJ/mol}$$

$$E_n = -13.6\frac{Z^2}{n^2}\text{eV/atom}$$

$$E_n = -2.18 \times 10^{-18}\frac{Z^2}{n^2}\text{J/atom}$$

$$E_n = -313.6\frac{Z^2}{n^2}\text{Kcal/mol}$$

$$\boxed{E_n x = E_1 H \times \frac{Z^2 x}{n^2 x}}$$; Where x is the hydrogen like species.

4. Relation of velocity of Bohr orbit

V = $\frac{nh}{2\pi m r_n}$; $V_n = \frac{2\pi KZe^2}{nh}$

$$\boxed{V_n = 2.18 \times 10^6 \frac{Z}{n} m/s}$$

$$\boxed{V_{nx} = V_1 H \times \frac{Z_x}{N_x}}$$; where x is the Hydrogen like species

Ionisation energy

The energy required to eject electron from the outermost shell of neutral gaseous atom in a ground state.

5. Relations of ionisation energy of Bohr orbit

$$E_\infty - E_1 = \Delta E = -(-E_1) = +E$$

$$E_n = 1312 \frac{Z^2}{n^2} kJ/mol$$

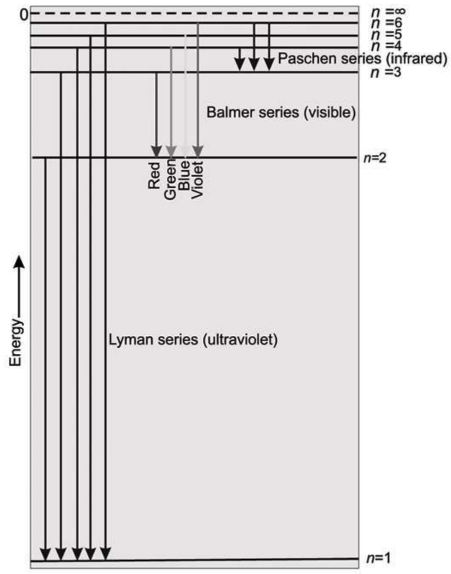
$$E_n = 13.6 \frac{Z^2}{n^2} eV/atom$$

$$E_n = 2.18 \times 10^{-18} \frac{Z^2}{n^2} J/atom$$

$$E_n = 313.6 \frac{Z^2}{n^2} Kcal/mol$$

$$\boxed{I.E_{nx} = I.E_{1H} \times \frac{Z_x^2}{n_x^2}}$$ where x is the H like species.

HYDROGEN SPECTRUM



1. Number of possible spectral lines obtained from the de excitation of electron from excited (n) level to ground level = $\dfrac{n(n-1)}{2}$
2. Number of possible spectral lines obtained from the de excitation of electron from excited (n) level to lower level other than the ground level = $\dfrac{(n_2-n_1)(n_2-n_1+1)}{2}$
3. Number of spectral lines obtained from the excited level (n) to
   1. U.V. region only = n – 1
   2. Visible region only = n – 2
   3. I.R. region only = $\dfrac{(n-3)(n-3+1)}{2}$

Rydberg equation (Ritz combination principle)

1. The principle states that, spectral lines of any element include frequencies that are either the sum or the difference of the frequencies of two other lines.

$$\bar{\upsilon} = 1/\lambda = R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]Z^2$$; n_1 = 1; n_2 = 2, 3, 4 etc

$R_H = 109677\ cm^{-1}$ or $1.09677\times10^7 m^{-1}$; n_1 = 1; n_2 = 1, 2, 3 etc

♦ Ionisation energy in terms of R_H

$\boxed{I.E. = R_H.hc\times Z_x^2}$; x = H like species

Limitations of Bohr Atom model

1. Fine spectrum could not clearly explained.

   Fine spectrum is the normal spectral line split in several by observing the spectrum through fine spectro scope.
2. Multi electron spectrums could not clearly explained
3. Zeeman effect and Stark effect could not clearly explained.

   Zeeman effect - Splitting of spectral line, when magnetic field is introduced.

   Stark effect - Splitting of spectral line, when electric field is introduced.
4. Dualism of sub-atomic particle could not clearly explained.
5. Uncertainities are the inherent property of the system that results from the dualism of matter. Those uncertainities could not clearly explained.

De-brogle relation

According to Einstein's mass energy relation and Planck's quantum theory . He derived a relation

$\lambda = \frac{h}{mc}$............(1) for light wave

$\lambda = \frac{h}{mv}$............(2) for matter wave

Relation between KE and λ

$$\boxed{\lambda = \frac{h}{\sqrt{2mKE}}}$$

- Number of waves or wavelength produced by an electron when it is revolve round the nucleus in the n^{th} Bohr orbit is equal to its principle quantum number $\frac{2\pi rn}{\lambda} = n$
- Number of revolutions made by electron in the n^{th} orbit per sec $\upsilon = \frac{V_n}{2\pi rn}$
- The time required for the revolution of electron in the n^{th} Bohr orbit T = $1/\upsilon = \frac{2\pi rn}{V_n}$
- Relation between λ and potential = $\lambda_{\mathring{A}} = \sqrt{\frac{150}{V}}$

Heinsenbergs uncertainity principle

It is impossible to determine both position and momentum of sub atomic particles simultaneously with accuracy.

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

$\Delta x.m\Delta v \geq \frac{h}{4\pi}$; where Δx and Δp are uncertainity position and uncertainity momentum respectively.

$\Delta E.\Delta t \geq \frac{h}{4\pi}$; where ΔE uncertainity energy and Δt uncertainity in time

Quantum mechanical model of an atom (Erwin Schrodinger)

Based on De-Broglie relation and Heisenberg uncertainity principle, Erwin Schrodinger put forward an equation,. Through that equation he could clearly explained the quantum mechanical model of an atom.

Schrodinger wave equation

$$\hat{H}\psi = E\psi$$

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

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

$$\left.\begin{array}{l}\hat{H} - \text{Hamiltonion} \\ \nabla^2 - \text{Laplacian}\end{array}\right\} \text{Mathematical operator}$$

Significance of ψ

ψ has no independent significance. ψ is a solution of Schrodinger equation. ψ is a wave function only.

ψ^2 has significance, it is the region in space where the probability of finding electron is maximum.

ie orbital.

ie. $\psi = \psi_{radial} \cdot \psi_{angular}$; $\psi_{(nlm)} = \psi_r \cdot \psi_{(\theta.\phi)}$

	Orbit	Orbital
1	Electrons revolving round the nucleus in a stationary circular path	It is the region in space where the probability of finding of electron is maximum
2	It is 2-Dimensional	It is 3-Dimensional
3	It is circular in shape	Orbitals have:- S-orbital - spherically symmetrical P-orbital - dumb bell d-orbital - double dumb bell f - Three dimensional complicated structure
4	It doesn't obey Heisenberg's uncertainity principle	It obeys Heisenberg's uncertainity principle

Quantum numbers

These are the numbers which designate size/energy of orbit, shape of orbitals, orientation /direction of orbitals and spinning of electrons in its own axis.

Mainly three quantum number n, *l*, m are used to construct an orbital.

I. Principal quantum number (n) Bohr

It gives the size or energy of shell or orbit

It denoted by the letter n

n can have values 1, 2, 3, 4 etc represents K, L, M, N shells.

- Maximum number of subshells present in shell = n
- Maximum number of orbitals present in shell = n^2
- Maximum number of electrons can occupy in the shell = $2n^2$

II. Azimuthal Quantum number / Subsidiary quantum number - Angular Quantum Number (Somerfield)

- It gives shapes of sub shells
- Its value is obtained by l = 0 to n – 1
- It denoted by l

l = O - s = subshell

l = 1 - p - subshell

l = 2 - d - subshell

l = 3 - f - subshell

- If n = 1, K shell; l = 0 1s subshell
  n = 2, L shell; l = 0 2s subshell
  l = 1 2p subshell

So on

Angular momentum of orbital = $\sqrt{\ell(\ell+1)}\ {}^{h}\!/_{2\pi}$

III. Magnetic Quantum Number (m_ℓ) Lande / Zeeman

- It gives orientation or direction of orbitals
- Its value obtained by the relation $-\ell, 0, +\ell$
- It denoted by the letter m_ℓ

$n = 1$ K shell $\ell = 0$ 1s subshell $(l = 0)$ 1s orbital $(m_l = 0)$

$n = 2$ $\ell = 0$ 2s subshell $m_\ell = 0$ 2s orbital

$\ell = 1$ 2p subshell $m_\ell = $

-1	0	+1
P_x	P_z	P_y

$n = 3$ $l = 0$ s subshells $m_l = 0$ 3s orbital

$l = 1$ p subshell $m_l = $

-1	0	+1
$3P_y$	$3P_z$	P_x

$l = 2$ d $m_l = $

-2	-1	0	+1	+2
3dxy	3dyz	$3dz^2$	3dxz	$3dx^2$-y^2

- Maximum number of orbitals in subshell = $(2\ell+1)$
- Maximum number of electron can occupy the sub shell = $2(2\ell+1) = 4\ell+2$

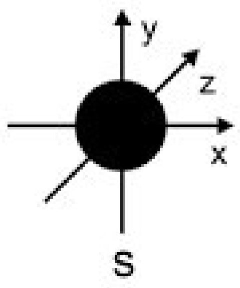
IV. Spin quantum number $(m_{(s)})$ (Uhlenbeck Goudsmit)

- It gives the spinning of electron in its own axis
- Its values are –1/2, +1/2
- Maximum two electrons with opposite spin can be placed in an orbital.

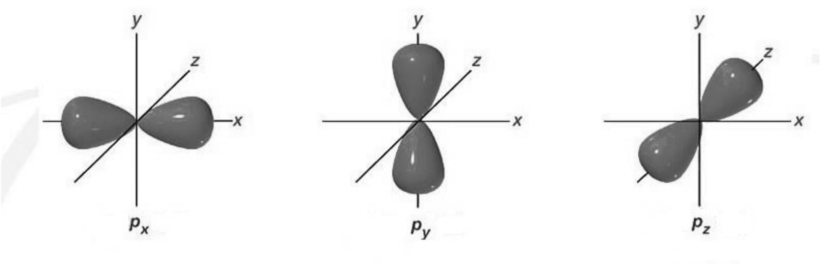
$\boxed{\uparrow\downarrow}$

SHAPES OF SUB SHELLS

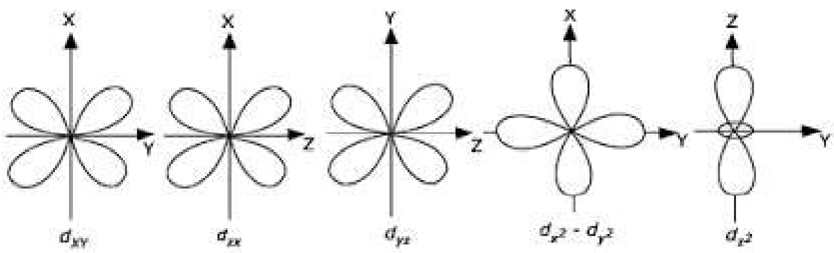
S-orbital



p-orbital



d-orbital



Node:

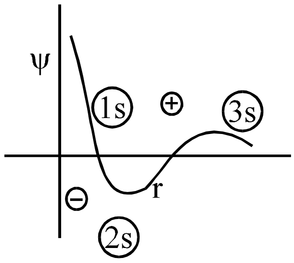
The region space where the probability of finding electron is zero. There are two types of nodes:-

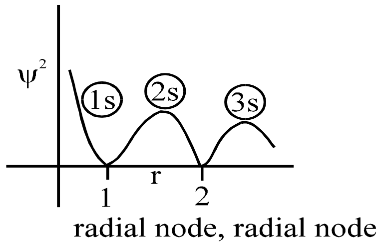
1. Radial node / spherical node
2. Nodal plane / angular node

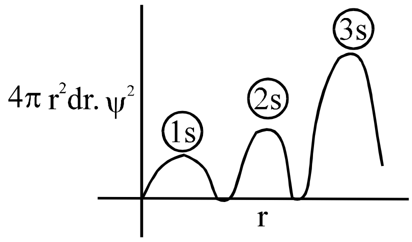
- ♦ Radial node or spherical node = $n - \ell - 1$
- ♦ Angular node/nodal plane = ℓ value
- ♦ Total number of nodes = n – 1

Radial Probability Distrubution Curves

ψ = radial wavefunction, ψ^2 radial probability density $4\pi r^2dr\ \psi^2$ -radial probability function







Number of minima = no.of radial node = $n-\ell-1$

Number of maxima = no.of radial node + 1 = $n-\ell$

Rules for writing the electronic configuration

1. **Pauli's exclusion principle :** No two electrons in an atom can have same set of 4 quantum numbers.
2. **Aufbau principle:** Electrons are filling in the increasing order of energy of atomic orbitals. It is based on $(n+\ell)$ rule

   Rule-I : The orbitals having higher $(n+\ell)$ value higher will be the energy.

   Rule-II : If the orbitals having same $(n+\ell)$ value, higher the n value orbital higher will be the energy.

   In single electron system (Orbit is considered) : 1s < 2s = 2p < 3s = 2p = 3d

   In multiple electron system : 1s < 2s < 2p < 3s < 3p < 3d (orbital is considered)

Hunds rule of maximum multiplicity

In a degenerate orbitals like p, d and f, electrons are filling first singly occupied after that pairing will occur.

For example : p^4 | ↑↓ | ↑ | ↑ |

Exceptional configuration

Cr = $24\ \underset{18}{[Ar]}4s^1 3d^5$

$Cu = 29\underset{18}{[Ar]}4s^1 3d^{10}$

This is due to half filled and fully filled stable configuration

Reason for half filled and fully filled stable configuration

The extrastability of half-filled and completely filled subshell is due to

(i) relatively small shielding

(ii) Smaller coulombic repulsion energy

(iii) Larger exchange energy