ATOMIC MODEL AND ELECTROMAGNETIC WAVE THEORY

Dalton in 1808 proposed that matter was made up of extremely small indivisible particles called ATOM. But in early 20th century various experiments established that atom was not the smallest indivisible particle but made up of still smaller few fundamental particles like electrons, protons and neutrons.

FUNDAMENTAL PARTICLES

Electron, proton and neutron are regarded as the fundamental particles.

Electrons

Electron was discovered in cathode-ray experiment.

The charge on an electron (-1.602 x 10-^{19} coulomb or - 4.8 x 10-^{10} esu) was determined by R.A. Millikan with his oil drop experiment.

Charge/mass *(elm)* ratio of the electron was determined by J. J. Thomson as

elm = 1.76 x 10^8 coulombs/g.

The *elm* ratio of electron was found to be independent of nature of gas and electrodes used.

Mass of electron is calculated as : 9.11 × 10^{-28} g

This is the rest mass of electron and it is 1 /1837 times mass of a hydrogen atom.

The mass of electron moving with velocity v is given as

$$m = \frac{m_{rest}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

Where c is the velocity of light

Mass of one mole of electrons is nearly 0.55 mg

Charge of electron (1.6 x 10-^{19} coulomb) is the smallest measurable quantity and is called one unit.

Radius of electron = 42.8 x 10-^{15} m

Density of electron = 2.17 x 10^{17} g/cm^3

Charge on one mole of electron ≈ 96500 coulomb or I Faraday

Protons

Proton was discovered in anode-ray experiment. Anode rays also called as canal rays or positive rays discovered by E. Goldstein contain positive ions produced as a result of knock out of electrons from the gaseous atom or molecule.

When hydrogen gas is taken in the discharge tube the positive particles (H^+) produced in the anode rays are called protons. Mass of proton was found to be 1.673 x 10-^{24} g

The magnitude of charge on a proton was found to be same as that on the electron but with opposite sign (positive) *i. e.* $e = +1.6 \times 10^{-19}$ coulomb. Charge/mass *(elm)* ratio of proton

was found to be 9.58 x 10^4 coulombs per gram

Mass of 1 mole of protons = 1.007 g"

Charge on 1 mole of protons'" 96500 coulombs or 1 Faraday

Neutrons

Neutron was discovered in scattering experiment by James Chadwick in 1932.

Mass of neutron was found to be 1.675 x 10^{-24} g or 1.008665 amu. It is slightly heavier (0.18%) than proton.

Neutron is a neutral particle with density = 1.5 x 10^{14} g/cm^3 Mass of one mole of neutron is 1.0087 g

Besides these three fundamental particles 35 different subatomic particles are also known like positron, neutrino, antineutrino, mesons, etc.

Cathode rays consist of negatively charged electrons with negligible mass. These are emitted from cathode itself.

Where as ***anode rays*** consist of positively charged ions *produced by the removal of one or more electrons from the gaseous atom or* molecule*.* It shows that anode rays are not emitted from anode but produced in the space between the anode and cathode. Thus *elm* of anode rays depends on the nature of gas taken in discharge tube whereas *elm* of cathode rays is constant and independent of nature of gas and electrodes.

RUTHERFORD'S ATOMIC MODEL (NUCLEAR MODEL)

Rutherford explained the structure of atom on the basis of his scattering experiment in which thin foil of metals like gold, silver, platinum, etc. was bombarded with fast moving a-particles. Various postulates of this model are:

Atom is spherical and consists of two parts, nucleus and extranuclear part.

Nucleus is very small in size. It is a positively charged highly dense central core in which entire mass of the atom is concentrated.

Extra nuclear part is an empty space around nucleus where *electrons* are *revolving* in a *circular orbit with very high* speed. This nuclear model is comparable to our solar system in which planets are revolving around sun. This model however fails to explain the stability of atom and line spectrum of hydrogen.

Atomic Number

Number of protons present in an atom is known as its atomic number. In a neutral atom,

Atomic number = Number of protons *(n_p)* = Number of electrons present

It is represented as *'Z'.*

Mass Number

Mass of an atom is concentrated in centrally located nucleus only. The sum of number of protons and neutrons in an atom is known as its mass number.

Mass number = Number of protons *(n_p)* + Number of neutrons *(n_e)*

Since it is the sum of number of protons and number of neutron in nucleus, mass number is always a whole number. It is represented by *'A'.*

An element *X* is represented as : ${}^{A}_{Z}X$

Different types of atomic species

(i) Isotopes

Atoms of same element having same atomic number but different mass number are called isotopes. *e.g.* : ${}^{1}_{1}H$ and ${}^{2}_{1}H$, ${}^{30}_{15}P$ and ${}^{31}_{15}P$

(ii) Isobars

Atoms of different elements having same mass number but different atomic number are called isobars. *e.g.* ~ ${}^{40}_{19}K$ and ${}^{14}_{6}C$ and ${}^{14}_{7}N$

(Hi) Isotones

Atoms of different elements having same number of neutrons are called isotons

e.g ${}^{14}_{6}C$ and ${}^{16}_{8}O$, ${}^{39}_{19}K$ and ${}^{40}_{20}Ca$

(iv) Isoelectronics

The chemical species having same number of electrons are called isoelectronics. *e.g.* 0^{2-}, F^{-}, Na^{+}, Mg^{2+}, etc.

(v) lsodiaphers

The chemical species having same isotopic number

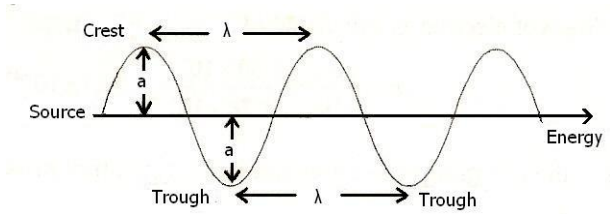
i.e. Number of neutrons - Number of protons *(n_n - n_p)* are called isodiapher

${}^{235}_{92}U$ and ${}^{231}_{90}Th$

ELECTROMAGNETIC WAVE THEORY

According to electromagnetic wave theory, energy is emitted continuously from a source in the form of radiation (or wave) and is called radiant energy. The radiations consist of both electric and magnetic field oscillating perpendicular to each other and to the direction of propagation. These radiations associated with both electric and magnetic field possess wave character and travel with speed of light. Hence these are known as *electromagnetic radiations* or *electromagnetic wave.* Electromagnetic waves do not require a *material* medium for propagation.

Characteristics of a wave



(i)Wavelength (λ)

Distance between two consecutive crests or troughs is known as wavelength. It is expressed in centimetres, nanometres (nm) or angstrom (Å)

1nm = 1O-^{9}m = 10-^{7} cm 1 Å = 10^{-10} m,= 10-^{8} cm

(ii) Frequency (v)

It is the number of waves passing through a given point in one second. It is expressed as cycles per second or hertz (Hz).

1 Hz = 1 cps.

Frequency is inversely proportional to wavelength of the wave

i.e. $\nu \propto 1 / \lambda$ or c = λ

where c is velocity of the wave.

(iii) Velocity *(c)*

It is defined as the distance travelled by a wave in one second.

Electromagnetic radiations travel with velocity of light *i. e. c* = 3 x 10^{8} *m/s.*

(iv) Wave Number (k) or $\bar{\nu}$

It is the number of waves present in one cm length. *i.e.* $\bar{\nu} = 1 / \lambda$

(v) Amplitude *(a)*

It is defined as the height of crest or depth of trough. It gives the intensity or brightness of the beam of light.

PLANCK'S QUANTUM THEORY

According to this theory, emission or absorption of radiant energy is not a continuous process but takes place discontinuously in the form of small discrete packets of energy. Such packets of energy are called ' quanta' , in case of light they are known as 'photons' Energy of each quantum is directly proportional to the frequency of radiation it is given by equation E = hu where h is constant of proportionality known as Planck's constant. Its value = 6.626 × 10^{-34} J-sec or 6.626 × 10^{-27} erg-sec

The total amount of energy emitted or absorbed is measured in terms of number of quanta.

i.e. Total energy, *E* = *n*hu

where *n* is number of quanta (any integer).

PHOTOELECTRIC EFFECT

It is the ejection of electrons from metal surface when a beam of light of certain minimum frequency is allowed to strike the metal surface in vacuum. The electrons so ejected are called as photoelectrons.

Energy of photoelectron $\propto$ Frequency of incident radiation and

Number of photoelectrons $\propto$ Intensity of incident radiation emitted per second

Few important facts about photoelectric

i) Only radiation striking the metal surface with certain minimum frequency have certain minimum energy are able to eject the electron. This minimum value of frequency known as Threshold Frequency v_0> If frequency is less than threshold frequency , no electron is ejected

(ii) The minimum energy required to eject the called the work function (ϕ).

(iii) If the frequency of incident light is more than threshold frequency then some of the energy gets consumed to eject the electron from atom and the extra energy enders the electron with kinetic energy $\frac{1}{2} mv^2$

i.e. Total energy *(E) = I.E. + K.E.*

where *I.E.* is the ionisation energy require to knock out the electron and *K.E.* is the kinetic energy of electron It can be written as

$hv = h v_0 + \frac{1}{2} mv^2$

by substituting value of v from equation $c = v\lambda$ we can get above equation in terms of λ

iv)The number of photoelectrons ejected is proportional to intensity of incident radiation *i.e.* an increase in intensity of incident radiation increases the rate of energy of photoelectrons. Not the energy of photo electrons

v) Alkali metals having lower ionization energy readily show the photoelectric effect. Caesium having lowest ionization energy, shows this effect in a best way. Hence it is used in photoelectric cells.

Compton effect

When monochromatic X-rays are allowed to fall on lighter elements like carbon, they suffer an increase in wavelength after scattering, *i.e.*

Wave length of scattered X-rays > Wave length of incident X-rays

Thus Energy of scattered X-rays < Energy of incident X-rays

or Frequency of scattered X-rays < Frequency of incident X-rays

This phenomenon of increase in wavelength of X-rays after scattering from the surface of lighter elements is known as *Compton effect.* The scattering of X-rays is due to interaction of photon (X-rays) and electrons.

BOHRS MODEL AND HYDROGEN SPECTRUM

When a radiation is analysed through the prism it produces particular pattern on photographic film. This pattern of radiation is known as spectrum. Spectra are classified in two types

1)Emission Spectra: When an excited electron returns back from higher energy level to ground state, it emits energy in the form of radiations. The spectrum produced by these emitted radiations is known as Emission Spectrum. It is further of two types

i) Continuous spectra. It consist of continuous bans of radiations corresponding to different wave length

ii) Line spectra

This spectrum consists of isolated coloured lines on photographic plate separated from each other by dark space.

2) Absorption Spectra

When white light from a source is first passed through a solution of a chemical substance, then radiation of particular wave length is absorbed by the solution of a particular wavelength is absorbed by the solution depending upon the nature of chemical substance. Now if the light coming out from the solution is analyzed by spectroscope, we get some dark lines in the otherwise continuous spectrum corresponding to the absorbed wavelength. It is observed that these dark lines appear at the same place where colored lines appeared in the emission spectrum of same substance. Absorption spectrum is always a discontinuous spectrum consisting of dark lines

HYDROGEN SPECTRUM

When electric discharge is passed through hydrogen gas taken in a discharge tube at low pressure, some radiations are emitted. These radiations on spectroscopic analysis give emission spectrum of hydrogen. The spectrum consists of number of lines in UV, visible and Infra red region each line corresponds to very particular wave length. These lines are grouped into fivr different series named after the discoverers.

Though a large number of lines appear in the hydrogen spectrum, their wave length can be measured by calculating their wave number given by Rydberg Formula

$\bar{v} = \frac{1}{\lambda} = R\left[\frac{1}{n^2} - \frac{1}{m^2}\right]$ n and m are the energy levels involve din transition

Here energy of energy level m > energy of energy level n

R is a constant known as Rydberg constant value is 13.6eV

By using equation c = vλ we can get above equation in terms of v

BOHR'S ATOMIC MODEL

To explain the stability of atom and line spectrum of hydrogen, Neil Bohr in 1913 proposed

a model of atom. His theory was based on Planck's quantum theory and some postulates of classical physics. The various postulates of the model are as fol1ows :

(i) An atom consists of highly dense positively charged nucleus at the centre and electrons revolving around nucleus in circular orbits.

(ii) Angular momentum of an electron in an atom is quantized.

$mvr = nh/2\pi$

where m = mass of electron, v = velocity of electron

r = radius of orbit, n = number of orbit in which electron is present

Out of numerous possible circular orbits, an electron can revolve only in that orbit for which n is a whole number.

(iii) Orbits in which electrons are revolving have fixed value of energy. These orbits are called *energy levels* or *stationary states.* As long as electrons are revolving in these orbit, they neither lose nor gain energy and hence explain the stability of atom. The energy of a stationary state of hydrogen atom is given as

$E_n = -\frac{2\pi^2 me^4}{n^2h^2}$ where n is the n^{th} energy level

Putting the value of m and e

$E_n = -\frac{21.8\times10^{-19}}{n^2}$ J/ atom OR $E_n = -\frac{13.6}{n^2}$ eV/atom OR $E_n = -\frac{1312}{n^2}$ kJ /mole

Energy of n^{th} orbit of other hydrogen-like one electron species is given as

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

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

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

$= -\frac{21.8\times10^{-19}}{n^2}Z^2$ J / atom where Z is atomic number

iv) Lowest energy state of electrons in an atom is the most stable state and is known as *Ground state or Normal state.* Electrons keep on revolving in this state without absorption or emission of energy.

v) Absorption or emission of energy takes place during the transition of electron from lower to higher energy level or vice-versa respectively. Energy absorbed or released in an electronic transition is given as

$\Delta E = E_2 - E$

where ΔE is energy absorbed or emitted E_2 is energy at final state E_1 is energy at initial state of transition

On the basis of Bohr's Theory, radius of *nth* orbit of anyone electron system with atomic number Z is derived as

$r = \frac{n^2h^2}{4\pi^2 mZe^2k}$ here k = 1/4πε$_0$, ε$_0$ is absolute permittivity of vacuum.

Its value is 9×10^9 Nm^2 / C^2,

Substituting values of h, m, e, etc we get radius of electron of hydrogen atom

r = 0.529 × n^2 Å

For nth orbit of any one electron species with atomic number Z

$R_n = \frac{0.529 \times n2}{Z}$

Velocity of an electron in an orbit

Velocity with which an electro is revolving in an orbit is calculated using Bohr's theory as v $= \frac{2\pi e^2}{nh} Z$ substituting value of e , h ,π we get

V $= \frac{2.19\times10^6}{n} Z$ m/s

We can observe from above equation that velocity decreases at higher energy lelvels

Velocity of electron in 1st orbit is also known as Bohr's velocity. It is calculated that Bohr's Velocity = 1/138 of velocity of light

Advantages of Bohr's Theory

i) It explain the stability of atom

ii) Line spectrum of hydrogen can be explained with Bohr's theory

iii) Using the concept of Bohr's theory radius and velocity of electron in various orbits can be calculated

Drawbacks of Bohr's Theory

i) Bohr's theory donot explain the spectrum of multielectron atom. It can only explain the spectrum of single electron species like H-atom He$^+$, Li^{2+}

ii) It does not explain the splitting of spectral lines under the influence of magnetic effect.

iii) Bohr's theory does not justify the principle of quantization of angular momentum

iv) Bohr's theory gave two dimensional model of atom by saying that electron revolves in circular orbit around nucleus in one plane. Whereas it is now established that atom has three dimensional structure

v) Bohr's Model fails to explain de Broglie concept of duel character and Heisenberg's principle of uncertainty.

CONCEPT OF DUAL CHARACTER

According to de Broglie's concept, moving matter *i.e.* moving material objects possess dual character *viz.* wave nature and particle nature (like radiations). de Broglie wavelength of material particles is given as

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

This concept of dual character gave rise to the wave mechanical theory according to which

electrons, protons and even atoms possess wave properties in motion.

This concept of duality is applicable only in case of microscopic particles like atom, electron, etc. The wave character associated with macroscopic objects is of no significance.

This concept justify the quantization of angular momentum.

Construction of electron microscope and study of surface structure of solids by electron diffraction are few important applications of this concept.

de-Broglie's wavelength can also be calculated from kinetic energy of the particle using following expression

$\lambda = \frac{h}{\sqrt{2mE}}$ here E is the kinetic energy

de-Broglie concept applies quantitatively to the particles in force-free environment.

Therefore, it cannot be applied directly to an electron in an atom, where the electron is subjected to the attractive forces of the nucleus.

HEISENBERG"S UNCERTAINTY PRINCIPLE

The principle states that, "it is impossible to measure position and momentum of any microscopic particle (subatomic particles) simultaneously with absolute accuracy". It has been seen that product of uncertainty in position (Δx) and uncertainty in momentum (Δp) is always constant and is equal to or greater than h/4π i.e Δx Δp ≥ h/4π value of h/4 π is 5.25×10^{-35}

ATOMIC ORBITALS AND ELECTRONIC CONFIGURATION

QUANTUM NUMBERS

Quantum numbers are the set of four numbers which explain the state of electron *i.e.* location, energy, type of orbital, orientation of orbital, etc. in an atom. Various quantum numbers are as follows:

1. Principal Quantum Number *(n)*

It represents the principal shell of an atom. It can have integral values except zero like 1**,** 2, 3, ... also denoted as *K, L, M,* .... etc.

Maximum number of electrons in a principal shell can be $2n^2$ where *n* is principal quantum number.

This quantum number gives information about

distance of electron from nucleus *i.e.* size of electron cloud·

energy of electron in any shell

$E_n = \frac{1312}{n^2}Z^2$ kJ mol^{-1} where Z is atomic number and n is principle quantum number

Azimuthal or Subsidiary or Angular Quantum Number (I)

Azimuthal quantum number represents the subshell or sub energy shell in an atom.

This quantum number renders following information's:

The number of subshells present in a principal shell:

For a principal shell *'n', 'l'* can have values starting from 0 to *(n* - I) *i.e.* a total of *n* values where *n* is principal quantum number.

Subshell notations *ares,p, d,fetc.*

for'l' values 0, 1, 2, 3 respectively.

Values of'n'	Values of'/'	Subshell notation
1	0	s
2	0 1	s *P*
3	0 1 2	s *p* *d*
4	0 1 2 3	s *p* *d* f

The maximum number of electrons present in a subshell is given by *2(2l* + 1).

Subshell	l	Number of electrons
s	0	2
P	1	6
d	2	10
f	3	14

Orbital angular momentum of electron is given as

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi}$$

Value of *l* gives an idea about shape of orbital.

Relative energy of different subshells belonging to same principal shell is s < *P* < *d* < *f*

3) **Magnetic Quantum Number *(m)***

It was given by Lande. Magnetic quantum number represents the orbital's present in a subshell. In a given sub-shell values of *m* are *(2l* + 1) ranging from - *l* to + *l* including zero. Each value of *m* corresponds to an orbital. Splitting of spectral lines in magnetic field (Zeeman effect) or in electric field (Stark effect) can be explained with this quantum number.

Subshell	/	*m*
s	0	0
P	1	-1,0,+1
d	2	-2,-1,0,+1,+2
/	3	-3,-2,-1,0, + 1, +2,

Thus we can say that

s-subshell has only one orbital,

p subshell has 3 orbitals P_X P_Y and P_Z

d-subshell has 5 orbitals d_{XY}, d_{YZ}, d_{xz}, dz^2 $d(z^2 - y^2)$ and

f subshell has 7 orbitals.

In general, for p-subshell

m = 0 is taken for P_z and m = ± 1is taken for Px and Py

Similarly, for d-subshell

m = 0 is taken for dz^2

m = ± 2 is taken for $d(z^2 - y^2)$ and d_{XY}

and m = ± 1 is taken for d_{xz} and d_{YZ}

Magnetic quantum number gives information about

Orientation of orbital in space around the nucleus.

Maximum number of electrons in an orbital can be two.

Number of orbitals in a shell = n^2.

4) **Spin Quantum Number *(s)***

It was given by Uhlenbeck and Goldschmidt. Spin quantum number gives information about spinning of electron on its own axis in an orbital. Electron in an orbital can spin either clockwise or anti clock wise. Thus an electron can have only two possible values of this quantum number, either +1/2 or -1/2 respectively.

Spin angular momentum (S) of an electron is given as

$$= \sqrt{l(l+1)}\frac{h}{2\pi}$$

A spinning electron acts like a micromagnet with a definite magnetic moment. In an orbital containing two electrons the two magnetic moments oppose each other and thus cancelled out. Thus in an atom if all the electrons are paired, the net magnetic moment is zero and the substance is known as *diamagnetic* (repelled by external magnetic field). However if any unpaired electron is present, the atom has a net magnetic moment and substance is known as *paramagnetic* (attracted by external magnetic field).

Net magnetic moment of an atom is given as $\mu = \sqrt{n(n+2)}$ where n is number of unpaired electrons.

Filling of Orbitals/Rules for writing electronic Configuration

There are few rules governing the filling of electrons in various orbitals which ultimately give electronic configuration.

1. Aufbau Principle

According to this rule, "orbitals are filled in the increasing order of their energies starting with the orbital of lowest energy". Energy of various orbitals are compared with *(n +l)* rule. The orbital having lower value of *(n + l),* has lower energy.

e.g. *3p* and *3d*

n=3	*n=3*
l=1	l=2
n+l=4	*n+l=5*

Thus, energy of *3p* is lower than that of *3d.*

If value *of(n + I)* is same for two orbitals, then orbital with lower value of *'n'* would have lower energy and filled first.

e.g. *4p* and *3d*

n=4	*n=3*
l=1	l=2
n+l=5	*n+l=5*

3d with lower value of *'n'* would be having lower energy than *4p.*

Increasing order of energy of various orbitals is given as

Is < 2s < *2p* < 3s < *3p* < 4s < *3d* < *4p* < 5s < *4d* < *5p* < 6s < *41*< *5d* < *6p* < 7s < 5/< *6d* and so on.

2. Pauli's exclusion Principle

The principle states that, "no two electrons in an atom can have same set of four quantum numbers". This shows that no two electrons in an atom are alike or an orbital can accommodate a maximum of two electrons that too with opposite spin.

3. Hund's Rule

According to this rule, "pairing of electrons in an orbital can not take place until each orbital of the same sub-shell is occupied by a single electron with parallel spin".

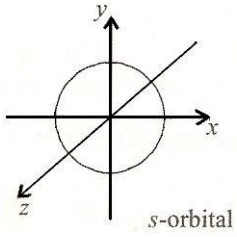
However some exceptions are found to this rule like Cr *($3d^5$)* and Cu *($3d^{10}$ $4s^1$)*, etc. owing to the extra stability of half- filled and full-filled orbitals.

SHAPES OF ORBITALS

Shape of an orbital is given by total probability density \jf2 including both radial part as well as angular part.

Shape of s-orbital

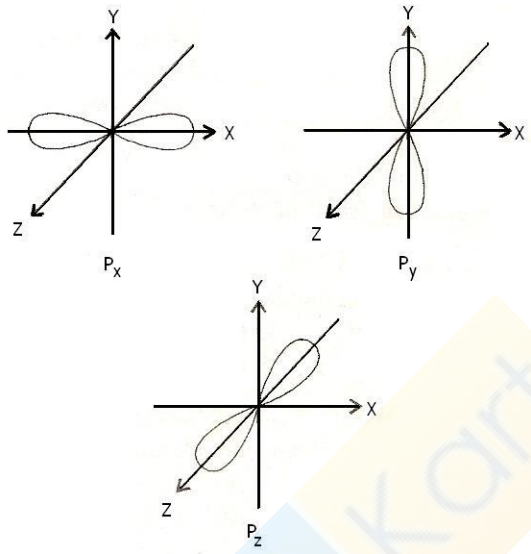
Shape of s-orbital must be spherical since probability of finding electron is equal in all directions at a distance from nucleus.



s-orbital

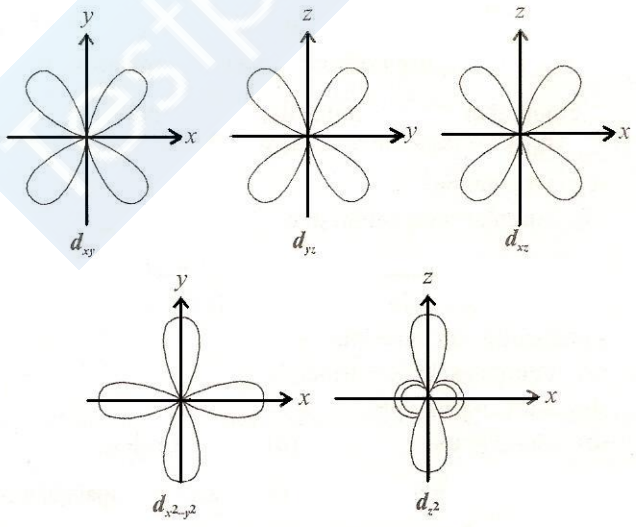
Shape of p-orbitals

The probability of finding *p-electron* is maximum in two dumb bell type lobes on the two opposite sides of nucleus. Thus, p-orbital has dumb-bell shape. In the three *p-orbitals* ,p_X,p_Y and p_Z the probability lies maximum along x-axis, y-axis and z-axis respectively. p-orbitals possess one nodal plane passing through the nucleus.



Shape of d-orbitals

Depending on the probability, d-orbitals have clover-leaf shape. There are five d-orbitals, d_{XY}, d_{YZ}, d_{xz}, dz^2 $d(z^2 - y^2)$. dz^2 has exceptionally doughnut shape. Each d-orbital has two nodal planes.



Number of radial node for orbit = (n- l -1)