Atomic Structure

DALTON'S THEORY OF ATOM

John Dalton developed his famous theory of atom in 1803. The main postulates of his theory were :

- Atom was considered as a hard, dense and smallest indivisible particle of matter.
- Each element consists of a particular kind of atoms.
- The properties of elements differ because of differences in the kinds of atoms contained in them.
- This theory provides a satisfactory basis for the law of chemical combination.
- Atom is indestructible, i.e., it cannot be destroyed or created.

Drawbacks

- It fails to explain why atoms of different kinds should differ in mass and valency etc.
- The discovery of *isotopes* and *isobars* showed that atoms of same elements may have different atomic masses (*isotopes*) and atoms of different kinds may have same atomic masses (*isobars*).
- The discovery of various sub-atomic particles like X-rays, electrons, protons etc. during late 19th century lead to the idea that the atom was no longer an indivisible and smallest particle of the matter.

DISCOVERY OF CATHODE RAYS & POSITIVE RAYS

Cathode Rays

Sir William Crooks studied various gases in a *gas discharge tube* (a glass tube with a very high potential applied to its ends) at low pressures. If the pressure in the tube is lowered to about 10^{-4} atm, glass begins to fluoresce (glow) faintly. It was established that the glow was due to bombardment of the glass by a certain kind of rays emerging from cathode (negative electrode) which travel in a straight line until they strike the anode (positive electrode). These rays were called as *cathode rays*.

Sir J. J. Thomson demonstrated that when cathode rays were deflected on to an electrometer, it acquired negative charge. He also showed that the rays were deflected on application of an electric field. The cathode ray beam was deflected away from the negatively charged plate. These results were found to be identical, irrespective of the gas taken in the discharge tube. He concluded that the cathode rays were a stream of fast moving negatively charged particles called electrons (named by Stoney). He also calculated the velocity and specific charge for an electron. The *specific charge* is the ratio of charge to the mass of an electron, denoted as e/m ratio. The e/m ratio was found to be same for all gases. This led to the conclusion that the electron must be a fundamental or universal particle common to all kinds of the atoms. The e/m ratio (for an electron) = 1.758×10^{11} C/Kg.

Note : (i) J. Millikan determined the value of the charge on an electron with the help of famous *Oil drop experiment*. The magnitude of the charge on an electron = 1.60206×10^{-19} C and the mass of an electron = 9.1×10^{-31} kg.

(ii) You will be studying the details of Thomson's calculations of e/m ratio and Millikan's oil drop experiment for the determination of electronic charge later in *Modern Physics* in the Module of Physics.

Positive Rays

Since the atom as a whole is neutral, it means that an equal amount of positive charged particle should also be there in the atom. Goldstein, by carefully experimenting with the discharge tube consisting of perforated cathode, showed the presence of another type of rays. These rays emanating from anode passed through the perforations in the cathode. These carried *positive* charge and were called as *positive or anode rays*. It was established that these rays consist of *positively* charged particles called as protons. The magnitude of charge on a proton is same as that on an electron, but its mass was found to be 1837 times the mass of an electron. The mass of a proton = 1.6735×10^{-27} kg.

Since the electron has negligible mass (as compared to the proton), so it was assumed that whole mass of an atom is associated with the protons. Later in 1932, with the discovery of neutron as IIIrd fundamental particle (*Ist and IInd being electron and proton*), it was established that the mass of an atom is the total mass of protons and neutrons taken together.

MODELS OF ATOM

Thomson's Model

Putting together all the facts known at that time, Thomson assumed that an atom is a sphere of positive charges uniformly distributed, with the electrons scattered as points throughout the sphere. This was known as *plum-pudding model* at that time. However this idea was dropped due to the success of α–*scattering experiments* studied by Rutherford and Mardson.

Rutherford's Model

Rutherford studied the scattering of α particles (doubly ionised Helium atom) by the thin metallic foils (of gold, platinum etc.). A narrow pencil beam of fast moving α - *particles* were struck on a thin metal foil ($\approx 10^4$ atoms thick). The angular deflections of scattered α particles were studied with the help of a moving microscope.

Observations of the Rutherford's experiment :

- Most of the α–particles passed through the foil undeflected, i.e., went straight through the foil.
- Some of them were deflected, but only at small angles.
- A very few (1 in 20,000) were deflected at large angles ($\approx 180°$).

Conclusions :

- As most of the α-particles passed undeflected, it was concluded by Rutherford that the atom must be predominantly empty.
- α-Particles are positively charged with appreciable mass (4 amu) and were moving high kinetic energy. In order to produce deflections, there must be some enormous positively charged body inside the atom.
- Only a few received large deflections. This led to the conclusion that enormous charge must be confined to a very small region. This small region was given the name nucleus.
- Rutherford then proposed that an atom is composed of a dense positive nucleus, thinly surrounded by the electrons. The mass and the positive charge of the nucleus are confined in a very small region of space. The electrons are outside the nucleus, so that an atom is almost entirely empty space.
- From stability point of view, the electrons cannot be stationary otherwise they would be drawn into the nucleus. So Rutherford assumed that electrons were moving in circles around the nucleus; the necessary centripetal force being provided by the electrostatic attraction between nucleus and the electrons. He gave no further justification for this assumption.

Note :

- From experiments, it was confirmed that with in the nucleus, the distribution of positive charge is uniform and atomic nuclei are spherical in shape.
- Later with the discovery of the neutrons (In 1932 by Chadwick), it was established that these also occupy the place in the nucleus bonded along with the protons by a very complex type of forces called as *Nuclear Forces*.
- Now the constituents of the nucleus, i.e., Protons and Neutrons are called as *Nucleons* and the number of nucleons in a particular atom is called as *Mass Number* denoted by **A**. The number of protons is known as *Atomic Number* denoted by **Z.**
- The order of the diameter of an atom is 10^{-10} m or 1 Å (1 Å $= 10^{-10}$ m) and the order of the diameter of the nucleus is 10^{-15} m or 1 *fm* (*fm* is called as Fermi and 1 *fm* $= 10^{-15}$ m).
- Radius of the nucleus of an atom is proportional to the cube root of the mass number of an atom (i.e., the number of nucleons in the atom). If r_0 denotes the radius of the nucleus then,

$$r_0 = (1.2 \times 10^{-15})\, A^{1/3}\ \text{m.} \qquad (A = \text{mass number})$$

Failure of Rutherford's Model

According to *Classical Theory of Electromagnetism*, whenever a charge is subjected to acceleration around an opposite charge, it emits radiation continuously. Hence the electron in Rutherford's atom will loose energy and will not be able to stay in a circular path around the nucleus and should ultimately go into a spiral motion. Such an electron will fall into the nucleus. This, of course, does not happen for electrons in an atom and the discrepancy could not be explained at that time.

Note : Later Niel Bohr, a student of Rutherford analysed atomic spectra of Hydrogen atom in terms of *Quantum Theory of Radiation* and applied the results of *Photoelectric Effect* to it and developed a model of atom which was widely accepted at that time.

NATURE OF CHARACTERISTICS OF RADIANT ENERGY

Newton was first person to comment on the nature of light in terms of *Corpuscular Theory of Light*. According to this theory, light is a stream of particles commonly known as *corpuscles of light*. He was able to explain *reflection* and *refraction*, the most common phenomenon of light. But the other phenomenon like *diffraction* and *interference* could not be explained on the basis of this theory.

Maxwell, in 1870 proposed that radiant energy (light) has wave characteristics. Light according to him is *Electromagnetic Wave* arising due to the disturbance created by electric and magnetic fields oscillating perpendicular to each other in space. Like all other mechanical waves, it is characterised by velocity, c ; frequency, ν and wavelength, λ which are related as :

$$c = \nu\lambda \qquad \text{[value of } c \text{ is constant and equal to } 3 \times 10^8 \text{ m/s]}$$

Electromagnetic Spectrum

- Electromagnetic wave or radiation is not a single wavelength radiation, but a mixture of various wave length or frequencies. All the frequencies have same speed (= c).
- If all the components of *Electromagnetic Radiation* (EMR) are arranged in order of decreasing or increasing wavelengths or frequencies, the pattern obtained is known as *Electromagnetic Spectrum*. The following table shows all the components of light.

Wavelength, λ (in Å)		0.01		1.0		150		3800		7600		6×10^6		3×10^9	
	Cosmic-rays		γ rays		X-rays		UV rays		Visible light		Infra-red		Micro waves		Radio waves
Frequency, ν (in Hz)						10^{17}		10^{15}		10^{14}		10^{11}		10^9	

Continuous Spectrum :

When sunlight (*white light*) is passed through a prism, it is dispersed or resolved into continuous spectra of colours. It extends from *Red* (7600 Å) at one end to the *Violet* (3800 Å) at other end. In this region, all the intermediate frequencies between red and violet are present. This type of spectrum is known as Continuous Spectrum. Hence continuous spectrum is one, which contains radiation of all the frequencies.

Note : A similar spectrum is produced when a rainbow forms in the sky.

Discontinuous Spectrum :

Light emitted from atoms heated in a flame or excited electrically in gas discharge tube, does not contain a continuous spread of wavelengths (or frequencies). It contains only certain well-defined wavelengths (or frequencies). The spectrum pattern appears as a series of bright lines (separated by gaps of darkness) and hence called as *Line Spectrum*.

One notable feature observed is, that each element emits a characteristic spectrum, suggesting that there is direct relation between the spectrum characteristics and the internal atomic structure of an atom.

The Quantum Theory of Radiation

In 1901, Max Planck studied the distribution of the frequencies of radiations emitted from the hot bodies. He proposed a bold hypothesis that the radiant energy such as heat or light, is not emitted continuously but discontinuously in the form of small packets called as quanta. According to him, the energy of the electromagnetic radiation is directly proportional to the frequency of the radiation. The proportionality constant is called as *Planck's constant* (h). If energy of the radiation is E, and the frequency of the radiation is ν, then we have :

$E = h\,\nu$ (The value of h is 6.626×10^{-34} J–s)

If n is the number of quanta of a particular frequency and TE be the total energy, then :

$$\text{TE} = n\,(h\nu)$$

Illustration - 1 *Find the ratio of frequencies of violet light ($\lambda_1 = 4.10 \times 10^{-5}$ cm) to that of red light ($\lambda_2 = 6.56 \times 10^{-5}$ cm). Also determine the ratio of energies carried by them.*

SOLUTION :

Using $c = \nu\lambda$

where c: speed of light; ν: frequency;
λ : wavelength

$$\frac{\nu_1}{\nu_2} = \frac{\lambda_2}{\lambda_1} \quad [1 : \text{violet and } 2 : \text{red}]$$

$$\Rightarrow \quad \frac{\nu_1}{\nu_2} = \frac{6.56 \times 10^{-5}}{4.10 \times 10^{-5}} = 1.6 : 1$$

Now the energy associated with electromagnetic radiation is given by $E = h\nu$

$$\Rightarrow \quad \frac{E_1}{E_2} = \frac{\nu_1}{\nu_2} = \frac{\lambda_2}{\lambda_1} = 1.6 : 1$$

Hence the ratio of energies is same as that of frequencies.

Illustration - 2 *A 100 W power source emits green light at a wavelength λ = 5000 Å. How many photons per minute are emitted by the source ?*

SOLUTION :

Energy given out by the source per sec

= Power (P)

$\Rightarrow$ Energy given by source in t sec = P × t

As λ = 5000 Å, the energy per photon of green light is given by : $h\nu = \dfrac{hc}{\lambda}$

$\Rightarrow$ Number of photons (n) emitted in time t sec is given by : $n = \dfrac{Pt}{(hc/\lambda)} = \dfrac{Pt\lambda}{hc}$

Using P = 100 J/s, $\lambda = 5000 \times 10^{-10}$ m and t = 60 s

$\Rightarrow$ Number of photons (n) :

$$= \frac{100(60)\left(5000 \times 10^{-10}\right)}{\left(6.626 \times 10^{-34}\right)\left(3 \times 10^{8}\right)} = 1.5 \times 10^{22}$$

Photoelectric Effect

It was observed by Hertz and Lenard around 1880 that when a clean metallic surface is irradiated by monochromatic light of proper frequency, electrons are emitted from it. This phenomenon of ejection of the electrons from metal surface was called as *Photoelectric Effect*.

- It was observed that if the frequency of incident radiation is below a certain minimum value (*threshold frequency*), no emission takes place however high the intensity of light may be.
- Another important feature observed was that the kinetic energy of the electrons emitted was independent of the intensity of the light. The kinetic energy of the electrons increase linearly with the frequency of incident light radiation. This was highly contrary to the laws of Physics at that time i.e. *the energy of the electrons should have been proportional to the intensity of the light, not to the frequency*.

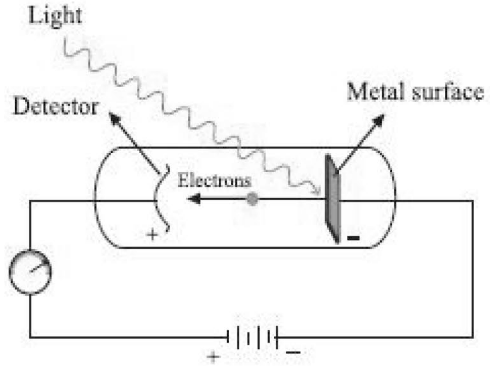
These features could not be properly explained on the basis of Maxwell's concept of light i.e. light as electromagnetic wave.

In 1905, Einstein applied Planck's quantum theory of light to account for the extraordinary features of the photoelectric effect. *He introduced a new concept that light shows dual nature. In phenomenon like reflection, refraction and diffraction, it shows wave nature and in phenomenon like photoelectric effects, it shows particle nature.* According to the particle nature, the energy of the light is carried in discrete units whose magnitude is proportional to the frequency of the light wave. These units were called as *photons* (or *quanta*).

According to Einstein, when a quantum of light (photon) strikes a metal surface, it imparts its energy to the electrons in the metal. In order for an electron to escape from the surface of the metal, it must overcome the attractive force of the positive ions in the metal. So a part of the photon's energy is absorbed by the metal surface to release the electron, this is known as *work function* of the surface and is denoted by W_0. The remaining part of the energy of the photon goes into the kinetic energy of the electron emitted. If E_i is the energy of the photon, KE is the kinetic energy of the electron and W_0 be the work function of the metal then we have ;

$E_i = KE + W_0$ (This is known as *Einstein's photoelectric equation*)

For each metal, there is a characteristic minimum frequency known as the *threshold frequency* (ν_0) below which the photoelectric effect does not occur. Electrons are emitted only after the frequency of light is equal to or above the threshold frequency. The threshold frequency is proportional to the work function of the metal. If ν_0 be the threshold frequency and ν the frequency of incident light, E is energy of incident light, then we have :



$$W_0 = h\nu_0 \qquad \text{and} \qquad E_i = h\nu$$

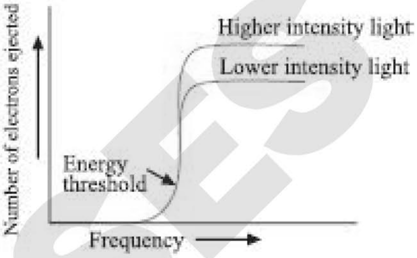
$$\Rightarrow \quad KE = E_i - W_0 \text{ or } \qquad KE = h\nu - h\nu_0 = h(\nu - \nu_0)$$

Also, if *m* be the mass and *v* be the velocity of the electron ejected then

$$KE = \frac{1}{2}mv^2 = h(\nu - \nu_0)$$

Note :

- The Electromagnetic radiation (or wave) now emerges as an entity which shows dual nature i.e. sometimes as *Wave* and sometimes as *Particle* (quantum aspect).
- The energy of an individual photon depends only on its frequency and not on the intensity of the light beam. The intensity of a light beam is a measure of the number of photons in the beam and not of the energies of those photons. A low-intensity beam of high-energy photons might easily knock out electrons from a metal but a high intensity beam of low energy photons might not be able to knock out a single electron.



- Sometimes, it is convenient to calcualte energy (in eV) of a photon in short form using:

$$E_P = \frac{hc}{\lambda} = \frac{12400}{\lambda(in\,Å)}eV = \frac{1240}{\lambda(in\,nm)}eV$$

Illustration - 3 *Calculate the velocity of electron ejected from platinum surface when radiation of 200 nm falls on it. Work function of platinum is 5 eV.* $(1eV = 1.6\times10^{-19}J)$

SOLUTION :

Using Einstein's photoelectric equation :

$$E_i = KE + W_0$$

where E_i : energy of incident radiation ;

KE : kinetic energy of ejected electron

W_0 : work function of metal

$$E_i = \frac{1240}{200}eV = 6.2\,eV;\ \text{and}\ W_0 = 5\,eV$$

$$\Rightarrow \quad KE = E_i - W_0 = (6.2 - 5)\ eV = 1.2\ eV$$
$$= 1.2 \times 1.6 \times 10^{-19}\ J = 1.94 \times 10^{-19}$$

Now, $KE = \frac{1}{2}mv^2 \Rightarrow v = \sqrt{\frac{2KE}{m}}$

$$\Rightarrow \quad v = \sqrt{\frac{2(1.94\times10^{-19})}{(9.1\times10^{-31})}} = 6.52 \times 10^5\ m/s$$

Illustration - 4 *A photon of light with* $\lambda = 400$ *nm falls on a metal surface. As a result, photoelectrons are ejected with a velocity of* 6.4×10^5 *m/s. Find :*

(*a*) *the kinetic energy of emitted photoelectrons,* (*b*) *the work function (in eV) of the metal surface.*

SOLUTION :

(a) Kinetic energy of electron = $\frac{1}{2}mv^2$

$$\Rightarrow \quad KE = \frac{1}{2}(9.1 \times 10^{-31})(6.4 \times 10^5)^2$$

$$= 1.86 \times 10^{-19}\ J = 1.16\ eV$$

(b) From Einstein's photoelectric equation :

$$E_i = KE + W_0 \quad \Rightarrow \quad W_0 = E_i - KE$$

$$\Rightarrow \quad W_0 = \frac{1240}{400} - KE = 3.1 - 1.16 = 1.94eV$$

$$\Rightarrow \quad W_0 = 1.94eV$$

ATOMIC SPECTRA OF HYDROGEN AND BOHR'S MODEL

It is observed that the atoms of hydrogen in gas discharge tube emit radiations whose spectrum shows line characteristics (line spectra). The line spectra of hydrogen lies in three regions of Electromagnetic Spectrum: *Infra-red, Visible and UV* region. In all there are five sets of discrete lines.

The set of lines in the *Visible* region are known as *Balmer Series*, those in *Ultra-Violet* as *Lyman series* and there are three sets of lines in *Infra-red* region : *Paschen*, *Brackett* and *Pfund series*. Balmer and Rydberg gave an empirical relation to define the wavelength of the lines in each series in terms of a parameter called as *Wave Number* denoted by $\bar{\nu}$. The wave number is defined as reciprocal of the wavelength

i.e., $\bar{\nu} = \frac{1}{\lambda}$; $\quad \bar{\nu} = RZ^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$

where *n* and *m* are whole numbers; λ : wavelength of spectral line ; $\bar{\nu}$: wave number of spectral line

R : Rydberg constant. The values of *n* and *m* for different spectral lines for each series are listed below.

Region	Spectral line	*n*	*m*
UV	*Lyman Series*	1	2, 3, 4, . . .
Visible	*Balmer Series*	2	3, 4, 5, . . .
Infra-red	*Paschen Series*	3	4, 5, 6, . . .
Infra-red	*Brackett Series*	4	5, 6, ...
Infra-red	*Pfund Series*	5	6, 7, ...
	Humphry Series	6	8, 7, 8 . . .

In Hydrogen atom spectra :

- Intermediate frequencies were emitted i.e. only specific spectral lines are there in the spectrum (Planck's quantum theory).
- Lines observed were characteristic of Hydrogen atom only.

These observations led Bohr to conclude that electrons in an atom are not randomly distributed, but were arranged in definite energy states. The energy of each state (or level) was fixed or quantised (from characteristic nature of H-atom spectra). The complete theory developed by him is organised in his postulates.

Bohr's Postulates

Bohr's theory was based on the application of Planck's Quantum theory on the atomic spectra of Hydrogen atom. The fundamental postulates of his theory are discussed below :

- The electron in an atom has only certain definite stationary states of motion allowed to it, called as *energy levels*. Each energy level has a definite energy associated with it. In each of these energy levels, electrons move in circular orbit around the positive nucleus. The necessary centripetal force is provided by the electrostatic attraction of the protons in the nucleus. As one moves away from the nucleus, the energy of the states increases.
- These states of allowed electronic motion are those in which the angular momentum of an electron is an integral multiple of $\frac{h}{2\pi}$ or one can say that the angular momentum of an electron is quantised.

$\Rightarrow$ Angular momentum $= mvr = n\left(\frac{h}{2\pi}\right)$ Angular momentum = moment of Inertia × angular velocity

$$= mr^2 \times \frac{v}{r} = mvr$$

where *m* is the mass of the electron, v is the velocity of the electron, *r* is the radius of the orbit, h is Planck's constant and *n* is a positive integer.

- When an atom is in one of these states, it does not radiate any energy but whenever there is a transition from one state to other, energy is emitted or absorbed depending upon the nature of transition.

When an electron jumps from higher energy state to the lower energy state, it emits radiations in form of photons or quanta. However, when an electron moves from lower energy state to a higher state, energy is absorbed, again in form of photons.

The energy of a photon emitted or absorbed is given by using Planck's relation ($E = h\nu$). If E_1 be the energy of any lower energy state and E_2 be the energy of any higher energy state, then the energy of the photon (emitted or absorbed) is given as ΔE (i.e., the difference in the energies of two states) :

$$\Delta E = E_2 - E_1 = h\nu = h\frac{c}{\lambda}$$

where *h* : Planck's constant and ν : frequency of radiation emitted or absorbed.

Additional Information :

Coulomb's Law of Electrostatic force of attraction or repulsion (F) between two charges q_1 & q_2 separated by a distance 'r' is given by :

$$\text{Force (F)} = \frac{K\,|q_1|\,|q_2|}{r^2}$$

where $$K = \frac{1}{4\pi \in_0} = 9 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$$

Note that charge on any particle can only be an integral multiple of charge on an electron (e).

Electrostatic Potential energy (E.P.E.) of a system of two charges separated by a distance 'r' is given by :

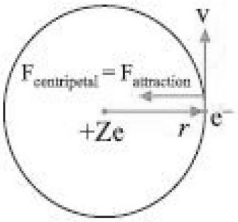
$$\text{E.P.E.} = \frac{Kq_1q_2}{r}$$

Note : E.P.E. is +ve when charges are like and –ve when charges are opposite.

Electrostatic force (F) is repulsive when both q_1 and q_2 are of same sign (i.e. either both are positive or both are negative) and is attractive when q_1 and q_2 are of different signs.

Bohr Model :

Consider a species of atomic number (Z) containing single electron revolving around its nucleus at a distance of 'r' as shown in the figure.



Note : Atomic number ≡ Number of protons on the nucleus = Z

$\Rightarrow$ Charge on the nucleus = + Ze

[As charge on each proton is +e and neutrons don't have any charge]

Electrostatic force of attraction (F) between the nucleus of charge + Ze and electron (–e) is given by :

$$F = \frac{K|Ze||-e|}{r^2} = \frac{K\,Ze^2}{r^2} \quad \ldots \text{(i)}$$

The centrifugal forces acting on the electron is $\dfrac{m_e v^2}{r}$ . . . (ii)

[Assuming uniform circular motion]

This centrifugal force must be provided by the electrostatic force of attraction (F).

$\Rightarrow$ From (i) and (ii), we have :

$$\frac{K\,Ze^2}{r^2} = \frac{m_e v^2}{r} \quad \ldots \text{(iii)}$$

Also, according to Bohr's postulate of quantization of angular momentum, we have :

Angular momentum of electron about the nucleus $= m_e vr = \dfrac{nh}{2\pi}$ . . . (iv)

where '*n*' is a positive integer
($n = 1, 2, 3, \ldots . \infty$)

Solve (iii) and (iv) to get :

$$v = \frac{2\pi K Ze^2}{nh} \quad \text{and} \quad r = \frac{n^2h^2}{4\pi^2 K m_e e^2 Z}$$

Put $K = 9 \times 10^9$ Nm^{2}C^{-2}, $e = 1.6 \times 10^{-19}$ C and $h = 6.626 \times 10^{-34}$ Js in the above expressions to get :

Velocity of an electron in *n*th Bohr orbit $\equiv v_n = 2.18 \times 10^6 \dfrac{Z}{n}$ ms^{-1}

and Radius of the *n*th Bohr orbit

$$\equiv r_n = 0.529 \times 10^{-10} \frac{n^2}{Z} \text{m} \equiv 0.529 \frac{n^2}{Z} \text{Å} \equiv 52.9 \frac{n^2}{Z} \text{pm} \left[1\text{pm} = 10^{-12} \text{m}\right]$$

Now, the Total Energy of the electron moving in *n*th orbit $\equiv$ K.E.$_n$ + E.P.E.$_n$

$$\text{T.E.}_n = \frac{1}{2} mv_n^2 + \frac{K(Ze)(-e)}{r} \qquad \left[\because \text{ E.P.E.} \equiv \frac{Kq_1q_2}{r}\right]$$

$$\Rightarrow \quad \text{T.E}_n = \frac{1}{2}\left(\frac{KZe^2}{r_n}\right) + \frac{K(Ze)(-e)}{r_n} \qquad \text{[Using (iii)]}$$

$$\Rightarrow \quad E_n \equiv \text{T.E.}_n = \frac{-KZe^2}{2r_n}$$

It can be shown from the above expressions that :

$$\text{K.E.}_n = \frac{1}{2}\frac{KZe^2}{r_n}, \quad \text{P.E.}_n = \frac{-KZe^2}{r_n} \quad \text{and} \quad E_n = \frac{-KZe^2}{2r_n}$$

or K.E.$_n$ = $-$ E$_n$ and E.P.E.$_n$ = 2E$_n$

Using the value of r_n in the expression of E_n, we get :

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

$$E_n = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{J / atom} = -13.6 \frac{Z^2}{n^2} \text{ eV / atom} \qquad \left[\because \ 1\text{eV} = 1.6 \times 10^{-19} \text{J}\right]$$

$$= -2.18 \times 10^{-18}\,\frac{Z^2}{n^2} \times 6.02 \times 10^{23}\ \text{J / mole} = -1312\,\frac{Z^2}{n^2}\ \text{kJ / mole}$$

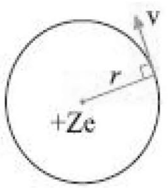
Note : ➤ Bohr's Model is applicable only to one-electron atoms like : He^+, Li^{2+}, Be^{3+} apart from H-atom.

Illustration - 5 *Determine the frequency of revolution of the electron in 2nd Bohr's orbit in hydrogen atom.*

SOLUTION :

The frequency of revolution of electron is given by :

$$\text{Frequency} = \frac{1}{\text{time period}}$$



Time period

$$= \frac{\text{Total distance covered in 1 revolution}}{\text{velocity}}$$

$$= \frac{2\pi r}{v}$$

$$\text{Hence frequency} = \frac{v}{2\pi r}$$

Calculate velocity (v_2) and radius (r_2) for electron in 2nd Bohr orbit in H-atom ($Z = 1$)

$Z = 1$ for H-atom.

Using $r_n = 0.529\,\frac{n^2}{Z}\,\text{Å}$

$$r_2 = 0.529 \times 10^{-10}\,\frac{(2)^2}{1}\,\text{m} = 1.12 \times 10^{-10}\ \text{m}$$

$$v_n = 2.18 \times 10^6\,(1/n)\ \text{m/s}$$

$$v_2 = 2.18 \times 10^6\,(1/2) = 1.09 \times 10^6\ \text{m/s}$$

$$\text{Hence frequency} = \frac{v_2}{2\pi r_2} = \frac{1.09 \times 10^6}{2(\pi)(2.12 \times 10^{-10})}$$

$$\nu = 8.18 \times 10^{14}\ \text{Hz.}$$

Note : Frequency of revolution (f) = 1/T where $T = \frac{2\pi r}{v} \propto \frac{n^3}{Z^2}\left[\because r \propto \frac{n^2}{Z} \text{ and } v \propto \frac{Z}{n}\right]$

$$\Rightarrow \quad f \propto \frac{Z^2}{n^3}$$

What does the negative electron energy (E_n) means ?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits. What do this negative sign convey ? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. An electron in an atom is because of attractive force due to protons in the nucleus. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting *n* equal to infinity in the equation so that $E_\infty = 0$. As electron gets closer to the nucleus, E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by $n = 1$ which corresponds to the most stable orbit.

When an electron jumps from an outer orbit (higher energy) n_2 to an inner orbit (lower energy) n_1, then the energy emitted in form of radiation is given by :

$$\Delta E = E_{n_2} - E_{n_1} = \frac{2\pi^2 K^2 me^4 Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \Rightarrow \Delta E = 2.18 \times 10^{-18} \times Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Also, $\Delta E = 13.6 \times Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ eV/atom

As we know that : $E = h\nu$; $\bar{\nu} = \frac{1}{\lambda}$ $\Rightarrow$ $\bar{\nu} = \frac{\Delta E}{hc} = \frac{2\pi^2 K^2 me^4 Z^2}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

The above equation can be represented as :

$$\bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{where} \quad R = \frac{2\pi^2 K^2 me^4}{ch^3}$$

R is known as Rydberg constant. Its value to be used is = 109677 cm^{-1} = 10967700 m^{-1}

Note : (i) The value of $\frac{1}{R} \approx 911.5$ Å is sometimes useful.

(ii) This relation exactly matches with the empirical relation given by **Balmer** and **Rydberg** to account for the spectral lines in H-atom spectra. In fact the value of Rydberg constant in the empirical relation is approximately the same as calculated from the above relation (**Bohr's Theory**). This was the main success of Bohr's Theory i.e. to account for the experimental observations by postulating a theory.

(iii) The maximum number of lines that can be emitted when an electron in an excited state $n = n_2$ de-excites to a state $n = n_1$ $(n_2 > n_1)$ is given by : $\frac{(n_2 - n_1 + 1)(n_2 - n_1)}{2}$

Illustration - 6 *Determine the maximum number of lines that can be emitted when an electron in H atom in n = 6 state drops to the ground sate. Also find the transitions corresponding to the lines emitted.*

SOLUTION :

The maximum number of lines can be calculated by using the above formula with $n_2 = 6$ and $n_1 = 1$ are 15.

The distinct transitions corresponding to these lines are:

$6 \rightarrow 1$

$6 \rightarrow 2,\ 2 \rightarrow 1$

$6 \rightarrow 3,\ 3 \rightarrow 2,\ 3 \rightarrow 1$

$6 \rightarrow 4,\ 4 \rightarrow 3,\ 4 \rightarrow 2,\ 4 \rightarrow 1$

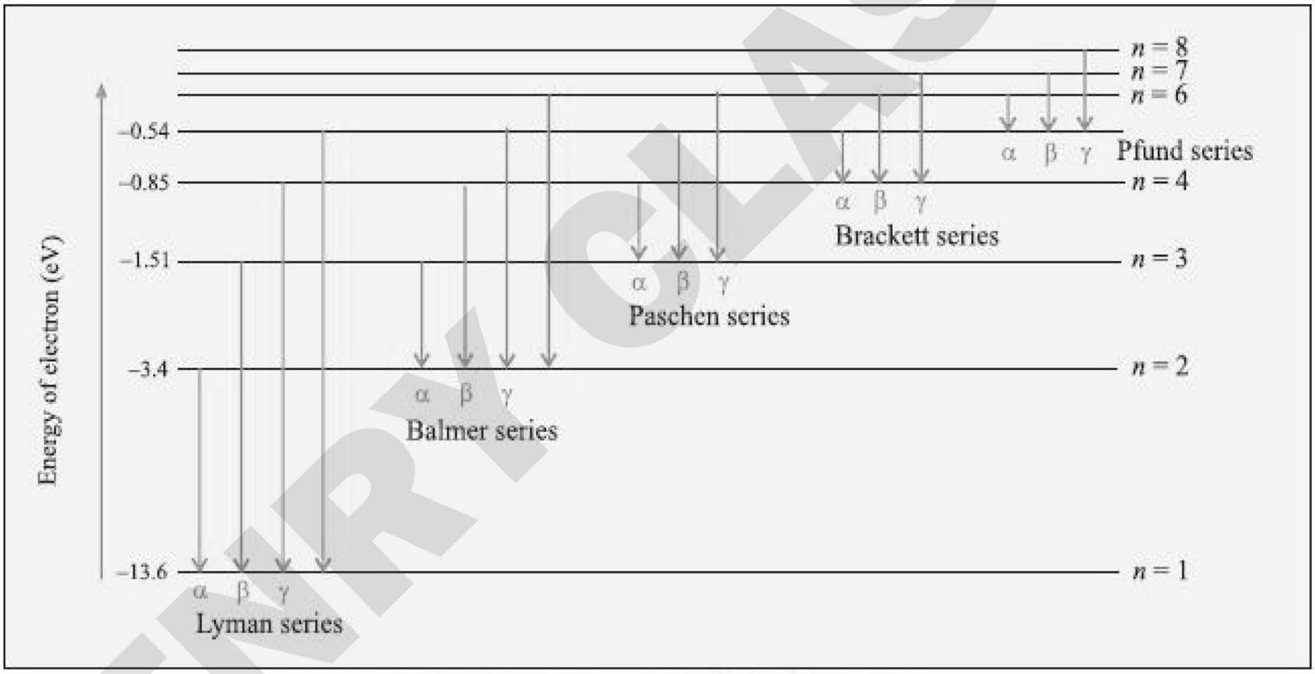
$6 \rightarrow 5,\ 5 \rightarrow 4,\ 5 \rightarrow 3,\ 5 \rightarrow 2,\ 5 \rightarrow 1$

Note : Each line (in emission spectra) corresponds to a particular photon emitted. The photon with shortest wavelength is corresponding to the largest energy difference ($6 \rightarrow 1$) and with longest wave length is corresponding to minimum energy difference ($6 \rightarrow 5$).

ENERGY LEVELS OF HYDROGEN ATOM

The spectrum of H-atom studied by *Lyman*, *Balmer*, *Paschen*, *Brackett* and *Pfund* can now be explained on the basis of Bohr's Model.

It is now clear that when an electron jumps from a higher energy state to a lower energy state, the radiation is emitted in form of photons. The radiation emitted in such a transition corresponds to the spectral line in the atomic spectra of H-atom.



Spectral Lines and Energy Levels of Hydrogen atom

Lyman Series

When an electron jumps from any of the higher states to the ground state or Ist state ($n = 1$), the series of spectral lines emitted lies in *ultra-violet region* and are called as *Lyman Series*. The wavelength (or wave number) of any line of the series can be given by using the relation :

$$\bar{\nu} = R\,Z^2\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right) \qquad n_2 = 2, 3, 4, 5, \ldots.$$

Note : For H-atom, $Z = 1$; He^+ ion, $Z = 2$ and Li^{2+}, $Z = 3$

Balmer Series

When an electron jumps from any of the higher states to the state with $n = 2$ (IInd state), the series of spectral lines emitted lies in *visible region* and are called as *Balmer Series*. The wave number of any spectral line can be given by using the relation :

$$\bar{\nu} = R Z^2 \left(\frac{1}{2^2} - \frac{1}{n_2^2}\right) \qquad n_2 = 3, 4, 5, \ldots.$$

Paschen Series

When an electron jumps from any of the higher states to the state with $n = 3$ (IIIrd state), the series of spectral lines emitted lies in *near infra-red region* and are called as *Paschen Series*. The wave number of any spectral line can be given by using the relation :

$$\bar{\nu} = R Z^2 \left(\frac{1}{3^2} - \frac{1}{n_2^2}\right) \qquad n_2 = 4, 5, 6. \ldots.$$

Brackett Series

When an electron jumps from any of the higher states to the state with $n = 4$ (IVth state), the series of spectral lines emitted lies in *far infra-red region* and called as *Brackett Series*. The wave number of any spectral line can be given by using the relation :

$$\bar{\nu} = R Z^2 \left(\frac{1}{4^2} - \frac{1}{n_2^2}\right) \qquad n_2 = 5, 6, 7. \ldots$$

Pfund Series

When an electron jumps from any of the higher states to the state with $n = 5$ (Vth state), the series of spectral lines emitted lies in *far infra-red region* and are called as *Pfund Series*. The wave number of any spectral line can be given by using the relation :

$$\bar{\nu} = R Z^2 \left(\frac{1}{5^2} - \frac{1}{n_2^2}\right) \qquad n_2 = 6, 7 \ldots.$$

Note that Lyman series in UV region, Balmer series in visible region and Paschen, Brackett & Pfund series in Infra-red region are only for H-atom ($Z = 1$).

Note : In a particular series, First $[(n_1 + 1) \rightarrow n_1]$, second $[(n_1 + 2) \rightarrow n_1]$, third $[(n_1 + 3) \rightarrow n_1]$ . . . . lines are called as $\alpha, \beta, \gamma, \ldots$ .lines respectively. For example β–line in Balmer series corresponds to $(2 + 2) \rightarrow 2$ i.e., $4 \rightarrow 2$. In Lyman series : α – line $\equiv 2 \rightarrow 1$; β – line $\equiv 3 \rightarrow 1$; γ – line $\equiv 4 \rightarrow 1$.

The energy required to remove the electron from the outermost orbit of the atom in gaseous phase is called as *Ionisation energy*. Here, since we are considering only one electron species, Ionisation energy $(IE) = -E_1 = +13.6\, Z^2$ eV.

Illustration - 7 *The Lyman series of Hydrogen spectrum can be represented by the equation :*

$$v = 3.28 \times 10^{15}\left[\frac{1}{1^2} - \frac{1}{n^2}\right] s^{-1}$$

. *Calculate the maximum and minimum frequency in this series.*

SOLUTION :

Lyman frequency will be maximum corresponding to maximum energy transition. i.e. $1 \rightarrow \infty$

$$\Rightarrow \quad v_{max} = 3.28 \times 10^{15}\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] s^{-1} = 3.28 \times 10^{15}\ s^{-1}$$

Note that corresponding wavelength will be shortest wavelength.

And Lyman frequency will be minimum corresponding to minimum energy transition. i.e. $1 \rightarrow 2$

$$\Rightarrow \quad v_{min} = 3.28 \times 10^{15}\left[\frac{1}{1^2} - \frac{1}{2^2}\right] s^{-1} = 2.46 \times 10^{15}\ s^{-1}$$

Note that corresponding wavelength will be longest wavelength.

Illustration - 8 *The wavelength of second line (also called as β–line) in Balmer series of hydrogen atom is :*

(A) 656.28 Å (B) 4872 Å (C) 6562.8 Å (D) 486.2 Å

SOLUTION :

The transition responsible for second Balmer (β–line) line is $4 \rightarrow 2$. In H-atom, $n_1 = 2$ for Balmer series.

$$\Rightarrow \quad \Delta E = 13.6\,(1)^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 2.55\ \text{eV}$$

Now $$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{2.55 \times 1.6 \times 10^{-19}}$$

$$\Rightarrow \quad \lambda = 4.872 \times 10^{-7}\ \text{m} = 4872\ \text{Å}$$

Hence correct option is **(B)**.

Illustration - 9 *A spectral line in the spectrum of H-atom has a wave number of* $15222.22\ cm^{-1}$*. The transition responsible for this radiation is :* (*Rydberg constant* $R = 109677\ cm^{-1}$).

(A) $2 \rightarrow 1$ **(B)** $4 \rightarrow 2$ **(C)** $3 \rightarrow 2$ **(D)** $2 \rightarrow 3$

SOLUTION :

$$\lambda = 1/\bar{v} = 1/15222.22 = 6.569 \times 10^{-5}\ \text{cm} = 6569\ \text{Å}$$

Clearly, it lies in Visible region i.e, in Balmer series.

Hence $n_1 = 2$

Using the relation for wave number for H-atom:

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

$$15222.22 = 109677\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$$

$\Rightarrow$ $n_2 = 3$

$\Rightarrow$ the required transition is $3 \rightarrow 2$

Hence (C) is correct.

Note : (D) is wrong, since $2 \rightarrow 3$ will absorb radiation.

Drawbacks of Bohr model :

Bohr's model was successful in explaining the spectra and hence the structure of Hydrogen atom; still many questions were not answered.

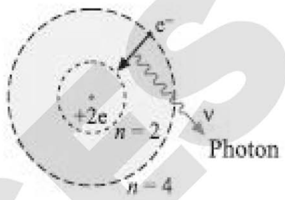
- His postulates combined two different concepts : one from classical physics and second from modern theory of quantization.
- It could not explain the spectrum of atoms or ions having two or more electrons. It accounted only for the spectra of H-atom, He^+ ion and Li^{++} ion.
- There was no justification for the quantization of angular momentum of an electron, though this was a correct assumption.
- His model could not provide a satisfactory picture of Chemical Bond.
- It also failed to account for the brightness of the spectral lines, splitting spectral lines in electric field (Stark Effect) and in magnetic field (Zeeman Effect).

Illustration - 10 *Calculate the wavelength of light radiation that would be emitted, when an electron in the fourth Bohr's orbit of He^+ ion falls to the second Bohr's orbit. To what transition does this light radiation correspond in the H-atom ?*

SOLUTION :

First calculate the energy difference (ΔE) between 4th and 2nd Bohr orbit using :

$$\Delta E_{(4\to 2)} = 13.6\ Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)eV$$



Substituting $n_1 = 2$ and $n_2 = 4$, $Z = 2$ we get ;

$$\Delta E = 10.2\ eV$$

This energy difference (energy lost by the electron) will be equal to the energy of the emitted photon.

Using : $\lambda = \dfrac{12400}{E_{Photon}(eV)}\text{Å} = \dfrac{12400}{10.2}\text{Å} = 1215.7\text{Å}$

Note : The emitted radiation is in UV region which implies that, in H-atom this transition would lie in Lyman Series ($n_1 = 1$). Hence our aim is now to find the transition : $n_2 \to 1$

Use : $\Delta E_{(n_2\to 1)} = 13.6\times\ 1^2\left(\dfrac{1}{1^2}-\dfrac{1}{n_2^2}\right)eV$

$\Rightarrow \quad 10.2 = 13.6\left(1-\dfrac{1}{n_2^2}\right)eV$

$\Rightarrow \quad n_2 = 2$

Hence the corresponding transition in H-atom is 2 → 1

***Note* :** This concept can be applied only for H-atom.

Alternate Approach :

As discussed above : $\Delta E_{(4\to 2)}\ (\text{in }He^+) = \dfrac{hc}{\lambda_{Photon}} = 13.6\times 2^2\times\left(\dfrac{1}{2^2}-\dfrac{1}{4^2}\right)eV \qquad \ldots.(i)$

$\Delta E_{(n_2\to n_1)}\ (\text{in H}) = \dfrac{hc}{\lambda_{Photon}} = 13.6\times 1^2\left(\dfrac{1}{n_1^2}-\dfrac{1}{n_2^2}\right)eV \qquad \ldots.(ii)$

Try to convert equation (ii) in the form given in equation (i) and compare it with equation (i) as below :

$\Rightarrow \quad \Delta E_{(4\to 2)}\ (\text{in }He^+) = \dfrac{hc}{\lambda_{Photon}} = 13.6\times 1^2\times\left(\dfrac{1}{1^2}-\dfrac{1}{2^2}\right)eV \qquad [2^2 \text{ shifted inside}]$

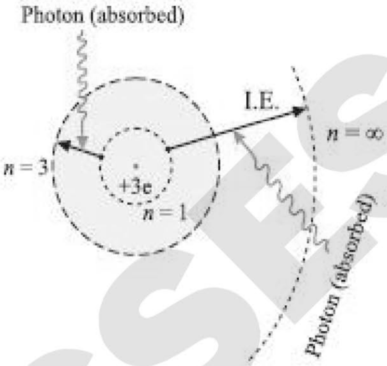
On comparing the above equation with equation (i), we get :

$n_1 = 1$ and $n_2 = 2$

***Note* :** This concept can be applied for any H-like species.

Illustration - 11 *Find the wavelength of radiation required to excite the electron in ground level of* Li^{++} *($Z = 3$) to third energy level. Also find the ionisation energy of* Li^{2+}. ($R = 109, 677\ cm^{-1}$)

SOLUTION :



Ground level : n = 1

$$\text{Use : } \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Putting the values : $n_1 = 1, n_2 = 3, Z = 3$

$$\text{We get : } \frac{1}{\lambda} = 109677 \times 3^2 \times \left(\frac{1}{1^2} - \frac{1}{3^2}\right)$$

$$\Rightarrow \frac{1}{\lambda} = 877416\text{cm}^{-1} \qquad \Rightarrow \lambda = \frac{1}{\bar{v}} = 113.97\ \text{Å}$$

Ionisation energy is the energy required to remove the electron from ground state to infinity i.e. corresponding transition responsible is $1 \rightarrow \infty$.

$$\text{i.e.} \qquad \Delta E_{(1 \rightarrow \infty)} = 13.6 \times 3^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)\text{eV}$$

Ionisation energy $= \Delta E_{(1 \rightarrow \infty)} = 122.4\ \text{eV} = 1.95 \times 10^{-17}\ \text{J} \quad \left[\because 1\text{eV} = 1.6 \times 10^{-19}\ \text{J}\right]$

***Note*:** Ionisation Energy (IE) $= -E_1 = +\,13.6\ Z^2$ eV

Illustration - 12 *Find the energy released (in ergs) when 2.0 gm atom of Hydrogen atoms undergo transition giving spectral line of lowest energy in visible region of its atomic spectra.*

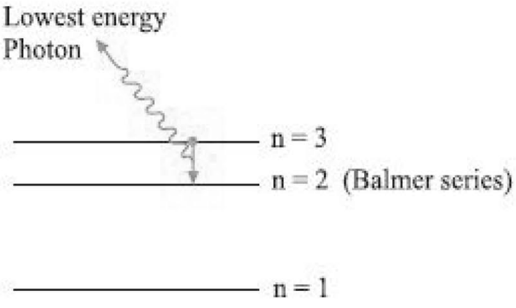
SOLUTION :

For H–atom, the spectral lines in visible region correspond to Balmer Lines ($n_1 = 2$). Now for lowest energy photon, the required transition will be from $3 \rightarrow 2$.

Using the relation for ΔE :

$$\Delta E = 2.18 \times 10^{-18}\ (1)^2 \left(\frac{1}{2^2} - \frac{1}{3^2}\right)\ \text{J / atom}$$

$$= 3.03 \times 10^{-19}\ \text{J}$$



Now for 2.0 *gm–atoms*, the energy released will be

$$E = (2 \times 6.023 \times 10^{23}) \times 3.03 \times 10^{-19}\ \text{J}$$

$$= 3.65 \times 10^5\ \text{J} \equiv 3.65 \times 10^{12} \quad [1\text{J} \equiv 10^7\ \text{ergs}]$$

WAVE NATURE OF PARTICLES

We have studied that light shows dual nature i.e. wave nature (*Electromagnetic Radiation*) and particle nature (*photons*). In the following article we will see that not only light but *matter also shows dual nature*.

In 1923, de Broglie suggested that, since light is dualistic in nature: behaving in some aspects as waves and in others like particles, the same might be true of matter. According to him, every form of matter (electron or proton or any other particle) behaves like waves in some circumstances. These were called as *matter waves* or *de Broglie waves*. de Broglie postulated that a particle of mass *m* moving with a velocity v should have a wavelength λ given by :

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad (p = \text{linear momentum} = mv)$$

Now we can think of a model of atom where moving electrons (obviously around the nucleus) should behave like waves. The wave hypothesis of de Broglie was later developed by Heisenberg, Schrödinger, Fermi and many others in modern atomic theory and is known as *wave mechanics* or *quantum mechanics*.

In new theory, electrons in an atom are visualised as diffused clouds surrounding the nucleus. The idea that the electrons in an atom move in definite orbits (*Bohr's model*) is now abandoned. The new theory assigns definite energy states to an atom but discards a definite path for movement of an electron.

Due to wave nature of electron in an atom, it is now highly impossible to ascertain the exact whereabouts of an electron. This idea is defined by Heisenberg's Uncertainty Principle as :

" It is impossible to specify at any given instant, both the momentum and the position of a sub-atomic particle like electron."

Whenever there is an attempt to specify the position of electron precisely, an uncertainty is introduced in its momentum and vice-versa. If Δx is the uncertainty in position and Δp be the uncertainty in its momentum, then according to Heisenberg, these quantities are related as follows :

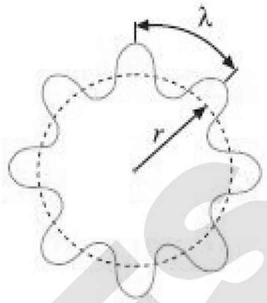
$$\Delta x \,.\, \Delta p \geq \frac{h}{4\pi}$$

In other words, it can be defined as :

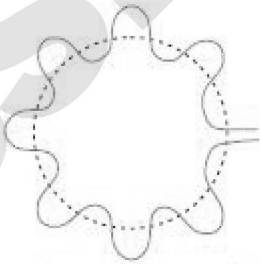
An expression of limits set by the wave nature of matter (electron) on finding the position and the state of motion of moving body (momentum) such that the product of uncertainties in simultaneous measurements of the position and momentum of a sub-atomic particle cannot be less than $h/4\pi$.

Hence, in new atomic theory, an electron can not be regarded as having a fixed (definite) path around the nucleus, called orbits. It is a matter of probability that an electron is more likely to be found in one place or the other. So we can now visualise a region in space (diffused cloud) surrounding the nucleus, where the probability of finding the electron is maximum. Such a region is called as an orbital. It can be defined as :

" The electron distribution described by a wave function and associated with a particular energy."



Electron wave in phase



Electron wave out of phase

- The new theory still defines a definite energy to an orbital in an atom (*a remarkable and accepted feature of Bohr's model*). The new theory abandons the concept of sharply defined paths.
- If we consider an electron moving in a circular orbit around the nucleus, then the wave train associated with the electron is shown in the figure.

  If the two ends of the electron wave meet to give a regular series of crests and troughs, the electron wave is said to be *in phase*.

$$n'\lambda = 2\pi r$$

where n' is the number of waves made by an electron in that Bohr orbit

$\Rightarrow$ The number of waves made by the electron

$$= \frac{\text{circumference of the orbit}}{\text{wavelength}}$$

Thus, $$n' = \frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} \qquad \left[\because \lambda = \frac{h}{mv}\right]$$

$$= \frac{2\pi}{h}(mvr) = \frac{2\pi}{h}\left(\frac{nh}{2\pi}\right) = n \qquad \left[\because mvr = \frac{nh}{2\pi}\right]$$

Hence the number of waves (n') made by an electron in an orbit is equal to principal quantum number (n)

Illustrating the concept :

Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

Using the above result, the number of waves made by the electron in 3rd Bohr orbit is 3 (i.e. $n' = 3$).

Illustration - 13 *An electron is accelerated through a potential difference of V volts. Find the de Broglie wavelength associated with the electron.*

SOLUTION :

When the electron is accelerated through a potential difference of V volts, it acquires a kinetic energy given by E = qV, where q is the charge on the electron. Also, if *m* be its mass and v be the velocity then, $E = \frac{1}{2}mv^2$

$$\Rightarrow \quad v = \sqrt{\frac{2E}{m}}$$

And de Broglie wavelength (λ)

$$= \frac{h}{mv} = \frac{h}{\sqrt{2Em}}$$

Note : The above result can be used directly, whenever required.

In the given case, E = qV

$$\Rightarrow \quad \lambda = \frac{h}{\sqrt{2(qV)m}}$$

Illustration - 14 *Calculate the uncertainty in position assuming uncertainty in momentum within* 0.1 % *for* :

(*a*) *a tennis ball weighing* 0.2 *kg and moving with a velocity of* 10 *m/s.*

(*b*) *a electron moving in an atom with a velocity of* 2×10^6 *m/s.*

SOLUTION :

Using Uncertainty Principle,

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

(a) $p = mv = 0.2 \times 10 = 2.0$ Kg m/s

$\Delta p = 0.1\%$ of $p = 2 \times 10^{-3}$

$$\Rightarrow \quad \Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 2 \times 10^{-3}}$$

$$= 2.63 \times 10^{-32} \text{ m.}$$

(b) For an electron, $p = m\,v$

$$p = 9.1 \times 10^{-31} \times (2 \times 10^6)$$

$$= 1.82 \times 10^{-24} \text{ Kg m/s}$$

$\Delta p = 0.1\%$ of $p = 1.82 \times 10^{-27}$ Kg m/s

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 1.82 \times 10^{-27}}$$

$$\Rightarrow \quad \Delta x = 2.89 \times 10^{-8} \text{ m}$$

Note **:** This shows that for sub-atomic (microscopic) particles, Heisenberg's Principle is highly meaningful, as Δx is greater than their atomic radius.

CONCEPT OF QUANTUM NUMBERS

Introduction to Quantum Mechanics

Macroscopic Objects :

Motion of these objects *can be* described/calculated using classical mechanics (based on Newton's law of motion).

Microsopic Objects

Motion of these objects *can not be* described/calculated using classical mechanics (based on Newton's law of motion).

(i) Dual nature of matter is not considered in classical mechanics, so there is a need for Quantum Mechanics (takes into consideration the dual nature of matter).

(ii) Quatum mechanics can also be applied on macroscopic objects (we can ignore their wave like properties) and still get the same results as Classical Mechanics.

Equation of Quantum Mechanics :

It defines the laws of motion that microscopic objects must obey.

Schrödinger equation is the governing equation of Quantum Mechanics. It is a complex equation and difficult to understand and solve with the knowledge of mathematics in classes XI and XII.

Schrödinger equation is relatively easier to construct. For a H-atom, when this equation is solved, it gives the energy levels for the electrons and corresponding wave function (ψ) of the electron associated with each energy level.

What is a wave function (ψ) ?

- It is a mathematical function whose value depends upon the coordinates of the electron in the atom.
- It doesn't have any physical significance.
- It is characterized (represented) by set of three quantum numbers (n : Principal quantum number, ℓ : Azimuthal quantum number and m_ℓ : Magnetic quantum number).

Basically, it contains all the information about the electron.

Note :

- Schrödinger equation can not be solved exactly for multi-electron atom (but can be solved approximately).
- In case of single electron atom, energy of the orbital depends only on the principal quantum number (n) but in case of multi-electron atom, it depends on 'n' as well as ℓ.

Designation of An Electron in an Orbital

An orbital is basically designated by three quantum numbers n, ℓ and m_ℓ as defined below :

(i) Principal Quantum Number (n) :

It is a positive integer with values of n = 1, 2, 3, ... In other way, it can also be designated with letters as K (n = 1), L (n = 2), M (n = 3), ...

Significance :

(a) It determines the size and energy of the orbital.

Note : For H and H-like species, orbital size and energy depends only on 'n' but for multi electron species, orbital energy depends on both 'n' and 'ℓ'.

(b) It is also used to calculate the number of orbitals given by 'n^2'. Thus, the maximum number of electrons in a shell (i.e. energy level as designated with letters as K, L, M etc.) are given by '$2n^2$', since one orbital can at the maximum contains two electrons.

- As we have learnt in Bohr Model, increasing 'n' increases the energy of the electron, thus, energy of the orbital increases.
- Also, we have learnt that size of the energy shells increases with increasing 'n'. Thus, we can expect the orbital size to increase with 'n'.

(ii) **Azimuthal Quantum Number (ℓ) :** It is an integer having all values between 0 and n – 1. It is also also known as orbital angular momentum quantum number or subsidiary quantum number.

Significance :

(a) It is used to define the shape of an orbital.

(b) It is used to represent a subshell (Each shell has subshells equal to shell number). A subshell can be thought of as sub-energy level inside an energy level.

For example : n = 1 (K shell) has only one subshell ($\ell = 0$)
n = 2 (L shell) has two subshells ($\ell = 0, 1$)
And so on . . . . .

Each value of 'ℓ' can be designated with letters as s ($\ell = 0$), p ($\ell = 1$), d ($\ell = 2$), f ($\ell = 3$), g ($\ell = 4$) and so on . . . . .

We can create the following notation :

$n = 1,\ \ell = 0 \Rightarrow$ 1s
$n = 2,\ \ell = 0, 1 \Rightarrow$ 2s, 2p
$n = 3,\ \ell = 0, 1, 2 \Rightarrow$ 3s, 3p, 3d and so on . . . . .

(iii) Magnetic Quantum Number (m_ℓ) :

It is an integer having values between $-\ell$ to $+\ell$ including zero.

Significance :

(a) It gives information about the orientation of an orbital with respect to coordinate axis.

- ***For example* :** 's' orbital is spherical in shape. So, it can be oriented only in one way in space, hence only one orbital is possible.

***Note* :** Number of orbitals in a sub-shell ≡ Number of possible orientations of an orbital.

- 'p' orbital has lobes above and below the plane as shown :

  'p' subshell can be oriented in three ways (lobes can be along X, Y and Z axes).

Thus, three orbitals are possible in a p-subshell.
In general, number of orbitals in a sub-shell = $2\ell + 1$

Thus, 's' – subshell ($\ell = 0$) has $2(0) + 1 = 1$ orbital
'p' – subshell ($\ell = 1$) has $2(1) + 1 = 3$ orbital

Subshell	ℓ	**No. of orbitals**	**Max. e's per subshell**	**Possible values of m_ℓ**
s	0	1	2	0
p	1	3	6	–1, 0, 1
d	2	5	10	–2, –1, 0, 2
f	3	7	14	–3, –2, –1, 0, 1, 2, 3

Note the conventions :

's' – subshell

$m_\ell = 0$

'p' – subshell

Orbitals	m_ℓ
p_x	+1 or –1
p_y	+1 or –1
p_z	0

'd' – subshell

Orbitals	m_ℓ
d_{xy}	± 2
d_{yz}	± 1
d_{zx}	± 1
$d_{x^2-y^2}$	± 2
d_{z^2}	0

***Note* :** n, ℓ, m_ℓ are the solutions of Schrödinger equation. There is another quantum number known as spin quantum number (m_s) which has been obtained experimentally.

There is an orbital angular momentum associated with an electron in a subshell given by :

$$L=\sqrt{\ell(\ell+1)}\,\frac{h}{2\pi}\equiv\sqrt{\ell(\ell+1)}\,\hbar \qquad \left(\text{where } \hbar=\frac{h}{2\pi}=\text{reduced Planck's constant}\right)$$

Spin Quantum number (m_s) : This quantum number accounts for the spin of electron about its axis similar to earth's motion about the sun as well as about its own axis.

An orbital can have a maximum of two electrons spinning in opposite directions leading to a spin angular momentum (vector quantity).

Thus, for two electron in an orbital,

$$m_s=+\frac{1}{2}\ \text{(spin anticlockwise)}\equiv\uparrow\ ;$$

$$m_s=-\frac{1}{2}\ \text{(spin clockwise)}\equiv\downarrow$$

Magnitude of spin angular momentum is given by : $\sqrt{s(s+1)}\,\frac{h}{2\pi}$

$$\equiv\frac{\sqrt{3}}{2}\,\frac{h}{2\pi} \qquad \left(s=\frac{1}{2}\ \text{for an electron}\right)$$

$$\equiv\frac{\sqrt{3}}{2}\,\hbar \qquad \left(\hbar=\frac{h}{2\pi}=\text{reduced planck's constant}\right)$$

Note :

- $m_s=\frac{1}{2}$ for any electron. In an orbital, $m_s=\pm\frac{1}{2}$ has been taken so as to distinguish the two electrons in it.
- spin quantum number has no classical analogue.

Difference between Orbit and Orbital :

Orbit	Orbital
1. It is circular path around the nucleus in which an electron moves.	1. It is a quantum mechanical concept and refers to one electron wave.
2. It is characterized by n.	2. It is characterized by n, ℓ, m_ℓ.
3. It has no real meaning.	3. It represents the probability of finding an electron at any point (through $\lvert\psi\rvert^2$).

Hydrogen atom and the Schrodinger Equation:

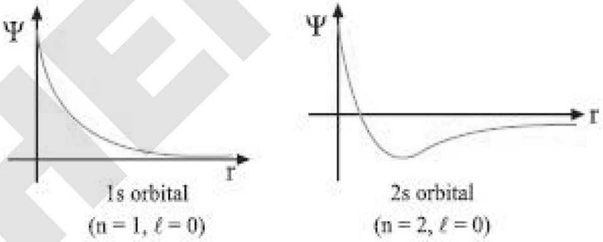
When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electrons can occupy function(s) (ψ) of the electron associated with each energy level. These quantized energy sates and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrodinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron system. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom specturm including of the hydrogen atom spectrum including sum phenomena that could not be explaoned by the Bohr model.

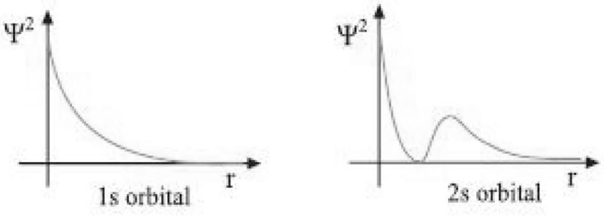
Application of Schrondinger equation of multi-electron atoms presents a difficulty: the Schrodinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals discussed above. The principal difference lies in the consecuence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen only on the quantum number n, the energies of the orbitals in multi-electron atoms depends on quantum numbers *n* and *l*.

Shapes of Atomic Orbitals :

Graph of ψ for various orbitals as a function of r (the distance from the nucleus is as shown :

ψ^2 at any point, gives the probability density of electron at that point.





As we see from the above graph, ψ^2 decreases and approaches to zero as r increases. Region where ψ^2 reduces to zero is called nodal surface (nodes). A node is a region of space where probability of finding the electron is zero. There also angular nodes (nodal plane) which represents plane passing through nucleus and having probability density function as zero.

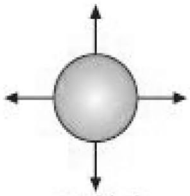
For a hydrogen like atom wave function, of principal quantum number n, there are
(i) $(n - \ell - 1)$ radial nodes (ii) ℓ angular nodes (iii) $(n - 1)$ total nodes.

Thus :

- 2s has one node. 3s has two nodes and so on.
- $1s$ ($n = 1$, $\ell = 0$) subshell is without any node.
- $2s$ ($n = 2$, $\ell = 0$) subshell will have only one radial node, while $2p$ ($n = 2$, $\ell = 1$) subshell will have only one angular node.
- $3s$ ($n = 3$, $\ell = 0$) subshell will have two radial nodes, $3p$ ($n = 3$, $\ell = 1$) subshell will have one radial and one angular node while $3d$ ($n = 3$, $\ell = 2$) will have two angular nodes.

Boundary surface diagram : It is surface (contour) which represents a constant $|\psi|^2$. In general, it is the region where the probability of finding the electron is 90%.

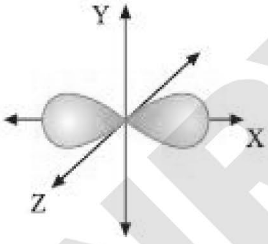
As mentioned earlier, the 's' orbitals are spherical in shape which means that the probability of finding the electron at a given distance is equal in all the direction.



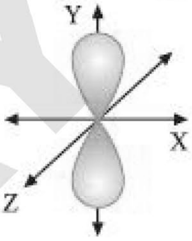
s-orbital

Also, the size of these orbitals increases as 'n' increases.

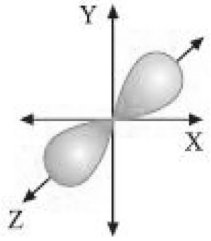
Boundary Surface Diagrams of p-orbitals are not spherical as shown :



p_x orbital



p_y orbital

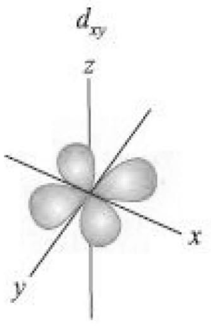


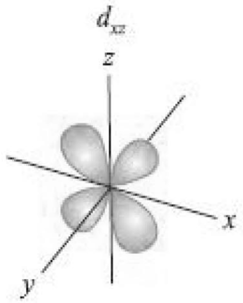
p_z orbital

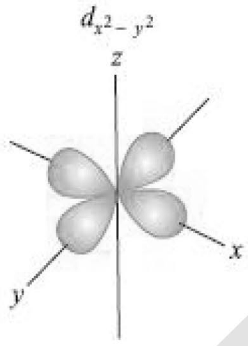
As we can see, there are two lobes on either side of the plane passing through the nucleus having probability of finding the electron as zero on it.

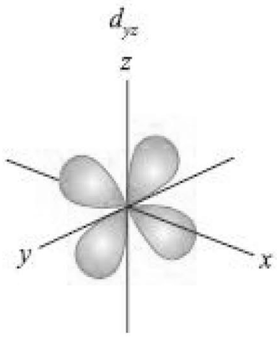
- All three orbital have same shapes and energy.
- Here also, energy of these orbitals increases with increasing 'n'.
- No. of radial nodes (for p-orbitals) are given by n – 2

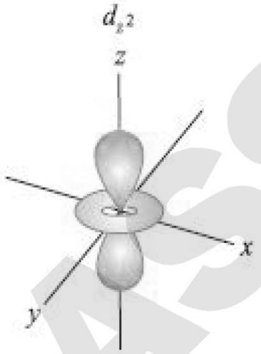
Boundary Surface Diagrams of d-orbitals are shown below. For d-subshells, there are 5 values of m_ℓ. Thus, d has 5 orbitals.











Energy of orbitals :

- For H-atom, energy of an orbital can be solely calculated by using ‘n’

  Thus, 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < ……

  Orbitals having same energy are called degenerate orbitals.
- For an atom containing multi electrons, energy of an electron depends on ‘n’ as well as ‘ℓ’.

In this case, each e^- is attracted by the nucleus but is repelled by every other electron. The electrons in the outer shell experiences less attractive force as there is a partial screening of positive change known as shielding of the outer shell electrons from the nucleus.

- ‘s’ orbitals are more tightly bound to nucleus than p orbitals, p orbitals are more tightly bound to nucleus than d orbitals and so no. Thus, energy of ‘s’ orbitals is more negative than p-orbitals.

Illustration - 15 *In all, how many nodal planes are there in the atomic orbitals for the principal quantum number n* = 3.

SOLUTION :

Shell with n = 3 has 1 ‘s’ (3s), 3 ‘p’ (p_x, p_y, p_z) and 5 ‘d’ (d_{xy}, d_{xz}, d_{yz}, $d_{(x^2-y^2)}$ and d_{z^2}) orbitals.

- ‘s’ has no nodal plane.
- Each of p_x, p_y, p_z has one nodal plane, which means a total of 3 nodal planes.
- $d_z{}^2$ has no nodal plane.

Each of d_{xy}, d_{xz}, d_{yz}, $d_{(x^2-y^2)}$ has 2 nodal planes, which means a total of 8 nodal planes.

Hence for n = 3, a total of 11 nodal planes are there.

ELECTRONIC CONFIGURATION OF ELEMENTS

Quantum numbers can now characterise the electrons in an atom. To describe the arrangements and distribution of electrons for different elements, following rules and selective principles are used. The distribution of electrons in an atom is known as *the electronic configuration of that element*.

Aufbau Principle

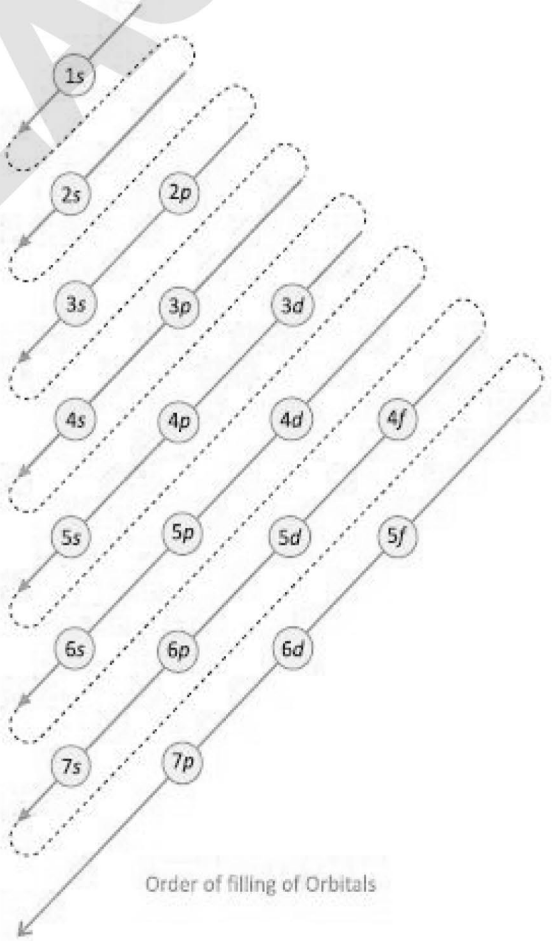
An atom in its lowest state of energy is said to be in *ground state*. The ground state is the most stable state in an atom. According to Aufbau principle:

> *" electrons are added progressively to the various orbitals in their order of increasing energy starting with the orbital of lowest energy."*

The order of increasing energy may be summed up as follows:

1s, 2s, 2p, 3s, 3p, **4s, 3d**, 4p, **5s, 4d**, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d,.....

As a working rule, a new electron enters an empty orbital for which the value of $(n + \ell)$ is minimum. If the value of $(n + \ell)$ is same for two or more orbitals, the new electron enters an orbital having lower value of n.



Order of filling of Orbitals

Pauli Exclusion Principle

According to this principle :

" no two electrons in an atom can have the same set of all the quantum numbers. or one can say that no two electrons can have the same quantised states."

Consider an electronic arrangement in Ist energy level $(n = 1)$. For $n = 1$, $\ell = 0$, and $m_\ell = 0$. Now m_s can have two values corresponding to each value of m_ℓ i.e. $m_s = +1/2, -1/2$. Hence the possible designation of an electron in a state with $n = 1$ is $(1, 0, 0, +1/2)$ and $(1, 0, 0, -1/2) \equiv (n, \ell, m_\ell, m_s)$ i.e., two quantised states. This implies that an orbital can accommodate (for $n = 1$, $m_\ell = 0$, i.e., one orbital) maximum of two electrons having opposite spins.

The maximum number of electrons in the different sub-shells are :

s sub-shell = 2, *p sub-shell* = 6, *d sub-shell* = 10 *and f sub-shell* = 14.

Hund's Rule Of Maximum Multiplicity

According to this rule : *" electrons never pair until no available empty degenerate orbitals are left to them."*

This means an electron always occupies a vacant orbital in the same sub-shell (degenerate orbital) and pairing starts only when all of the degenerate orbitals are filled up. This means that the pairing starts with 2nd electron in *s* sub-shell, 4th electron in *p* sub-shell, 6th electron in *d* sub-shell and 8th electron in *f* sub-shell.

By doing this, the electrons stay as far away from each other as possible. This is highly reasonable if we consider the *electron-electron repulsion*. Hence electrons obey Hund's rule as it results in lower energy state and hence more stability.

Extra Stability of Half And Fully Filled Orbitals

A particularly stable system is obtained when a set of equivalent orbitals (degenerate orbitals) is either fully filled or half filled, i.e., each containing one or a pair of electrons. This effect is more dominant in *d* and *f* sub-shells.

This means three or six electrons in *p* sub-shell, five or ten electrons in *d* sub-shell, and seven or fourteen electrons in *f* sub-shell forms a stable arrangement. Note this effect when filling of electrons takes place in *d* sub-shells (*for atomic numbers* $Z = 24$, 25 *and* 29, 30).

Electronic configuration of an element is represented by the notation $n\ell^x$:

n : principal quantum number ℓ : denotes the sub-shell x : number of electrons present in an orbital

Illustration - 16 *Write down the electronic configuration of following species. Also find the number of unpaired electrons in each.* (a) Fe, Fe^{2+}, Fe^{3+} (Z of Fe = 26) , (b) Br, Br^- (Z of Br = 35) , (c) V, V^{3+} (Z of Fe = 23)

SOLUTION :

Follow the order of increasing energy (Aufbau Rule) :
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d……..

(a) Fe(Z = 26): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
Note that 3d orbital are not fully filled.

$3d^6 \equiv$ 

Orbitals filled as per Hund's Rule.

Clearly the number of unpaired electrons is 4.

- Fe^{2+} : (Z = 26) [No. of electrons = 24]

While writing electronic configuration (e.c.) of cations, first write e.c of neutral atom and then "remove desired number of electrons from outermost orbital".

In Fe^{2+}, remove $2e^-$ from $4s^2$ since 4s orbital (through lower in energy then 3d) is the outermost. Hence e.c. of Fe^{2+} is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^0$

Note that number of unpaired electrons remains same as that in Fe, i.e. 4.

- Fe^{3+} $(Z = 26)$ [No. of electrons = 23]

Now remove $2e^-$ from $4s^2$ and $1e^-$ from $3d^6$ to get e.c. as : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^0$

Note that, now all 'd' orbits have an odd electron (i.e. are half filled).

1 1 1 1 1

Hence number of unpaired electrons in $Fe^{3+} = 5$.

(b) Br $(Z = 35)$ [No. of electrons = 35]

Following Aufbau rule, e.c. is : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

Clearly one of $4p^5$ orbitals contains unpaired electrons: $4p^5 \equiv$ ⥮ ⥮ 1

Orbitals filled as per Hund's Rule.

Hence Br has only one unpaired electron.

- Br^- $(Z = 35)$ [No. of electrons = 36]

Since anion(s) is(are) formed by adding electron(s), so simply write e.c. as per total number of electrons finally. For Z = 35, e.c. is : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

Clearly there are no unpaired electrons.

(c) Following on pattern in (a), we can write e.c. for V as follows.

$V(Z = 23)$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

$3d^3 \equiv$ 1 1 1 ○ ○

Orbitals filled as per Hund's Rule.

$\Rightarrow$ 3 unpaired electrons.

- V^{3+} $(Z = 23)$ [No. of electrons = 20]

Remove $3e^-$ from outermost orbitals successively i.e.,'$2e^-$' from $4s^2$ and $1e^-$ from $3d^3$. Hence e.c. of V^{3+} is :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^2$

$3d^2 \equiv$ 1 1 ○ ○ ○

Orbitals filled as per Hund's Rule.

$\Rightarrow$ 2 unpaired electrons.

Illustration - 17 *A compound of Vanadium has a magnetic moment of 1.73 B.M. Work out the electronic configuration of vanadium in the compound.*

SOLUTION :

The magnitude of magnetic moment (μ) of a compound/species/ion is given by :

$$\mu = \sqrt{n(n+2)}\, BM$$

(n = number of unpaired electrons ; BM : unit of magnetic moment in Bohr's Magneton)

$$\Rightarrow \qquad 1.73 = \sqrt{n(n+2)}$$

On solving for n, we get $n = 1$. This means that vanadium ion ($Z = 23$) in the compound has one unpaired electron.

3d : 

So its electronic configuration (e.c.) must be :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$

i.e., vanadium exists as V^{4+} ion in the compound since the ground state e.c. of $_{23}V$ is :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

3d :  4s : 

Note : In these kind of questions, keep on removing e^- from the outermost orbitals till the required number of unpaired e^- is achieved.