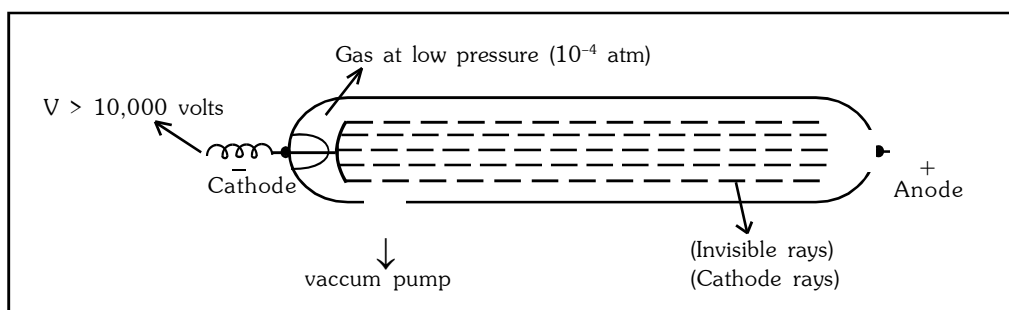


ATOMIC STRUCTURE

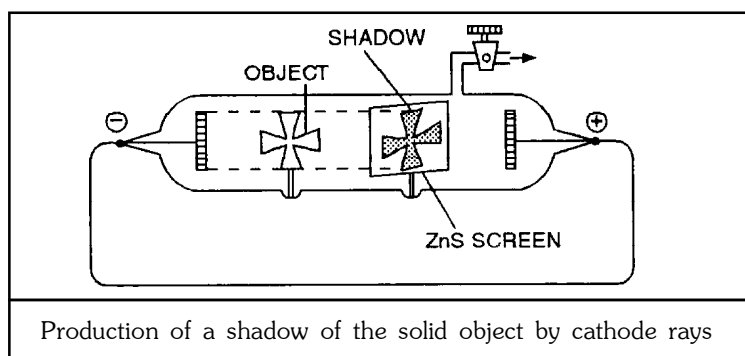
❑ CATHODE RAYS (Discovery of e^-)



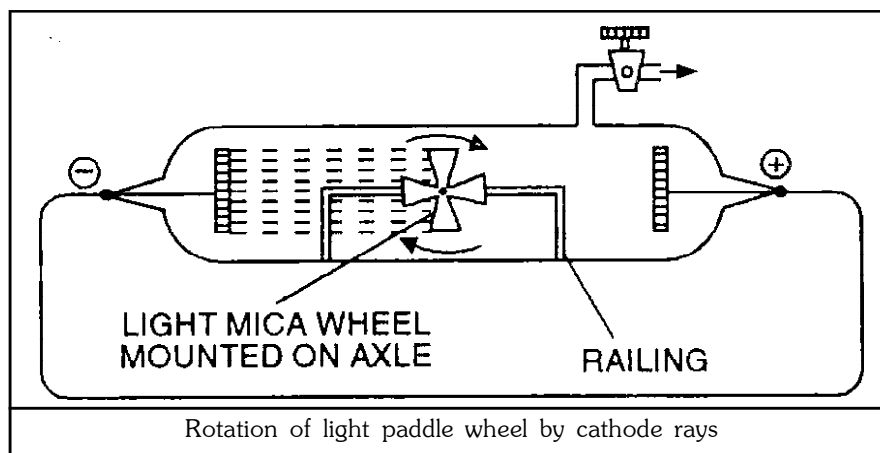
In 1859, **Julius plucker** started the study of conduction of electricity through gases at low pressure in a discharge tube. When a high voltage of the order 10, 000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the -ve electrode to the +ve electrode. Since the -ve electrode is referred to as cathode, these rays were called cathode rays.

◆ Properties of Cathode rays

- (1) They travel in straight lines away from cathode with very high velocity ranging from 10^7 to 10^9 m/sec.
- (2) A shadow of metallic object placed in the path is cast on the wall opposite to the cathode.

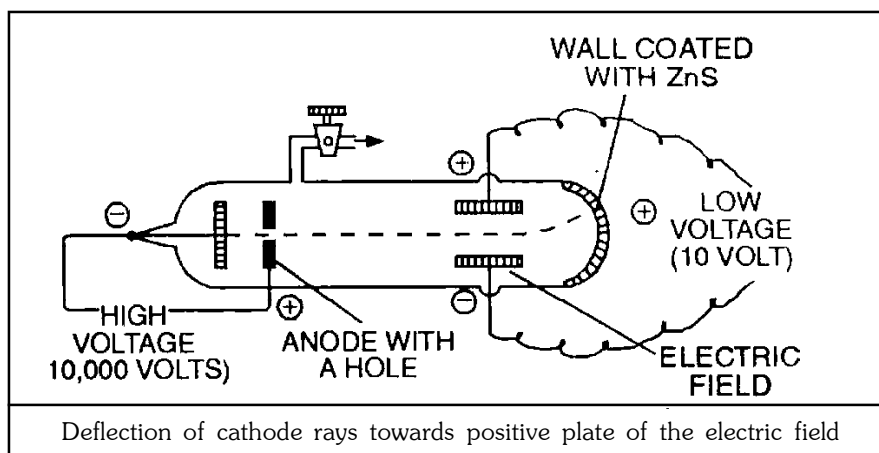


- (3) They produce a **green glow** when strike the glass wall matter. Light is emitted when they strike the zinc-sulphide screen.
- (4) When a small pin wheel 10.0 is placed in their path, the blades of the wheel are set in motion. Thus the cathode rays consist of material particles which have mass and velocity.



- (5) They are deflected by the electric and magnetic fields. When the rays are passed between two electrically charged plates, these are deflected towards the positively charged plate. It shows that cathode rays carry -ve charge. These particles carrying negative charge were called **negatrons** by **Thomson**.

The name negatron was changed to '**electron**' by **Stoney**



- (6) They produce heat energy when they collide with the matter. It shows that cathode rays possess **Kinetic energy** which is converted into heat energy when stopped by matter.
- (7) These rays affect the photographic plate.
- (8) Cathode rays can penetrate the thin foil of solid materials.
- (9) Cathode rays can ionize the gases through which they pass.
- (10) The nature of cathode rays is independent of
 - (a) The nature of cathode and
 - (b) The gas in discharge tube.

❑ MEASUREMENT OF e/m FOR ELECTRON :

In 1897, **J.J. Thomson** determined the **e/m value** (charge/mass) of the electron by studying the deflection of cathode rays in electric & magnetic fields.

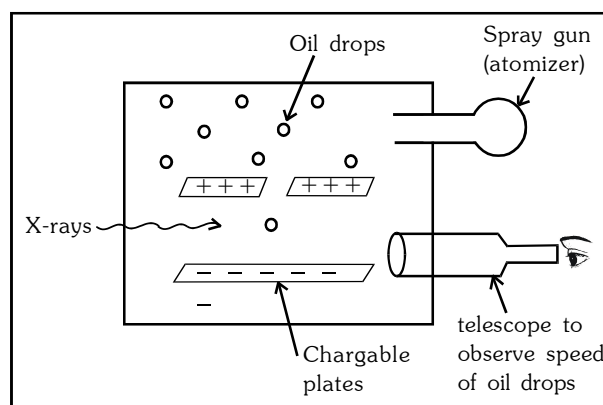
The value of e/m has been found to be -1.7588×10^8 coulomb/g.

- ◆ By performing a series of experiments, Thomson proved that whatever gas be taken in the discharge tube and whatever be the material of the electrodes the value of e/m is always the same.
- ◆ Electrons are thus common universal constituents of all atoms.

❑ DETERMINATION OF THE CHARGE ON AN ELECTRON :

The absolute value of the charge on an e^- was measured by **R.A. Milikan** in 1909 by the Milikan's oil drop experiment.

- ◆ The apparatus used by him is shown in fig.
- ◆ An oil droplet falls through a hole in the upper plate. The air between the plates is then exposed to X-rays which eject electrons from air molecules. Some of these e^- are captured by the oil droplet and it acquires a negative charge.



The metal plates were given an electric charge, and as the electric field between the plates was increased, it was possible to make some of the drops travel upwards at the same speed as they were previously falling.

By measuring the speed, and knowing things like the strength of the field and the density of the oil, radius of oil drops, Milikan was able to calculate the magnitude of the charge on the oil drops. He found that the smallest charge to be found on them was approximately $1.59 \times 10^{-19} \text{ C}$. This was recognised as the charge on an e^- . The modern value is $1.602 \times 10^{-19} \text{ C}$.

❑ MASS OF THE ELECTRON :

Mass of the e^- can be calculate from the value of e/m and the value of e

$$m = \frac{e}{e/m} = \frac{-1.602 \times 10^{-19}}{-1.7588 \times 10^8} = 9.1096 \times 10^{-28} \text{ g} \quad \text{or} \quad = 9.1096 \times 10^{-31} \text{ kg}$$

This is termed as the rest mass of the electron i.e. mass of the electron when moving with low speed. The mass of a moving e^- may be calculate by applying the following formula.

$$\text{Mass of moving } e^- = \frac{\text{rest mass of } e^-}{\sqrt{1 - (v/c)^2}}$$

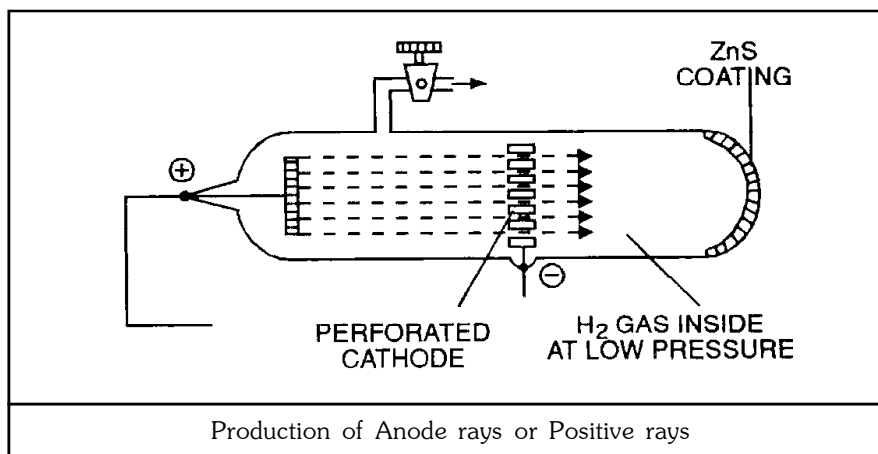
Where v is the velocity of the e^- and c is the velocity of light.

When $v = c \Rightarrow$ mass of $e^- = \infty$

$v > c \Rightarrow$ mass of $e^- = \text{imaginary}$

❑ POSITIVE RAYS - (DISCOVERY OF PROTON) :

- ◆ The first experiment that lead to the discovery of the +ve particle was conducted by 'Goldstein'.
- ◆ He used a **perforated cathode** in the modified cathode ray tube.



- ◆ It was observed that when a high potential difference was applied b/w the electrodes, not only cathode rays were produced but also a new type of rays were produced simultaneously from anode moving towards cathode and passed through the holes or canals of the cathode. These rays were termed canal rays since these passed through the canals of the cathode. These were also named anode rays as these originated from anode.
- ◆ When the properties of these rays were studied by **Thomson**, he observed that these rays consisted of positively charged particles and named them as positive rays.
- ◆ The following characteristics of the positive rays we recognised :
 - (i) The rays travel in straight lines and cast a shadow of the object placed in their path.
 - (ii) Like cathode rays, these rays also rotate the wheel placed in their path and also have heating effect. Thus, the rays possess K.E. i.e. mass particles are present.

- (iii) The rays are deflected by electric and magnetic fields towards the negatively charged plate showing thereby that these rays carry +ve charge.
- (iv) The rays produce flashes of light on ZnS screen
- (v) These rays can pass through thin metal foil.
- (vi) These rays can produce ionisation in gases.
- (vii) Positive particles in these rays have e/m value much smaller than that of e^- . For a small value of e/m , it is definite that positive particles possess high mass.
- (viii) e/m value is dependent on the nature of the gas taken in the discharge tube, i.e. +ve particles are different in different gases.

◆ Accurate measurements of the charge and the mass of the particles in the discharge tube containing hydrogen, the lightest of all gases, were made by **J.J. Thomson** in 1906. These particles were found to have the **e/m value** as **$+9.579 \times 10^4$ coulomb/g**. This was the **maximum** value of e/m observed for any +ve particle.

◆ It was thus assumed that the positive particle given by the hydrogen represents a fundamental particle of +ve charge. This particle was named **proton** by **Rutherford** in 1911. Its charge was found to be equal in magnitude but opposite in sign to that of electron.

Thus

$$\text{charge on proton} = + 1.602 \times 10^{-19} \text{ coulomb i.e. one unit +ve charge}$$

◆ The mass of the proton, thus can be calculated.

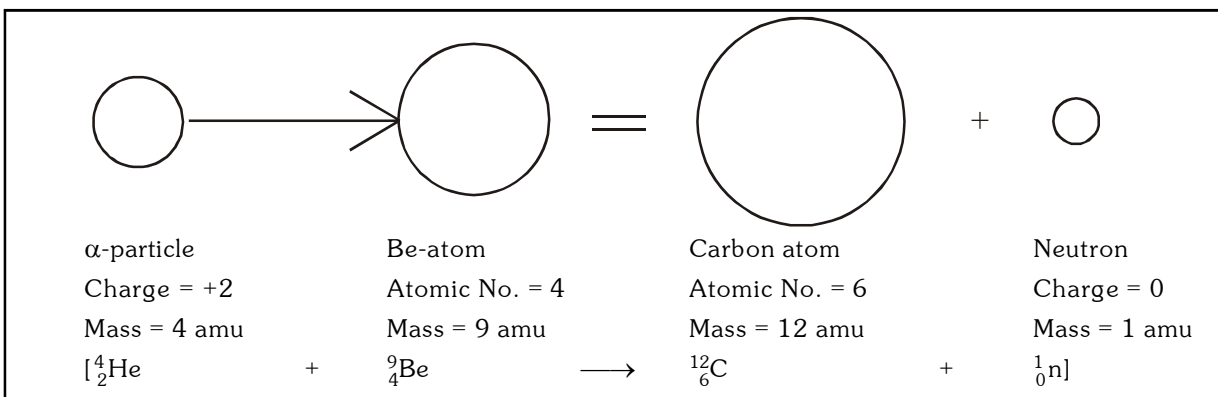
$$\text{Mass of the proton} = \frac{e}{e/m} = \frac{1.602 \times 10^{-19}}{9.579 \times 10^4} = 1.672 \times 10^{-24} \text{ g} = 1.672 \times 10^{-27} \text{ kg}$$

$$\text{Mass of proton in amu} = \frac{1.672 \times 10^{-24}}{1.66 \times 10^{-24}} = 1.00757 \text{ amu.}$$

□ NEUTRON

In 1920, **Rutherford** suggested that in an atom, there must be present at least a third type of fundamental particles which should be electrically neutral and possess mass nearly equal to that of proton. He proposed the name for such fundamental particles as neutron.

In 1932, **Chadwick** bombarded beryllium with a stream of α -particles. He observed that penetrating radiations were produced which were not affected by electric & magnetic fields. These radiations consisted of neutral particles, which were called **neutrons**. The nuclear reaction can be shown as



Thus a neutron is a sub atomic particle which has a mass **1.675×10^{-24} g** approximately 1amu, or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge.

◆ The e/m value of a **neutron** is zero.

❑ ATOMIC STRUCTURE :

Atom is actually made of 3 fundamental particles :

1. Electron
2. Proton
3. Neutron

Fundamental particle	Discovered By	Charge	Mass	$\left(\frac{\text{charge}}{\text{mass}}\right)$ (Specific Charge)
Electron (e^- or β)	J.J.Thomson	-1.6×10^{-19} coulomb -4.8×10^{-10} esu -1 Unit	9.1×10^{-31} kg 9.1×10^{-28} g 0.000548 amu	1.76×10^8 C/g
Proton (P) (Ionized H atom, H^+)	Goldstein	$+1.6 \times 10^{-19}$ coulomb $+4.8 \times 10^{-10}$ esu +1 Unit	1.672×10^{-27} kg 1.672×10^{-24} g 1.00757 amu	9.58×10^4 C/g
Neutron (${}_0n^1$)	James Chadwick	0	1.675×10^{-27} kg 1.675×10^{-24} g 1.00893 amu	0

❑ IMPORTANT POINT :

1. esu = electrostatic unit
(1 cb = 3×10^9 esu)
amu = atomic mass unit
 $1 \text{ amu} = 1.6 \times 10^{-24} \text{ g} = 1.6 \times 10^{-27} \text{ kg}$

2. Order of Mass

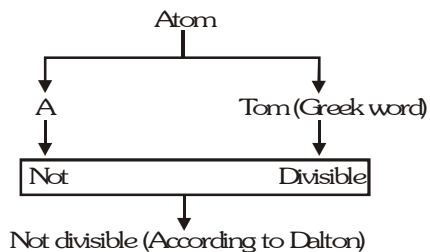
$$m_{e^-} < m_p < m_n$$

◆ Order of Specific Charge

$$\left(\frac{e}{m}\right)_n < (e/m)_p < (e/m)_{e^-}$$

$$\left(\frac{\text{mass of proton}}{\text{mass of electron}}\right) \frac{m_p}{m_{e^-}} = 1837$$

❑ INTRODUCTION :



◆ Atom is a Greek word

and its meaning **Indivisible** i.e. an ultimate particles which cannot be further subdivided.

John Dalton (1803 - 1808) considered that " all matter was composed of small particle called atom.

❑ **ACCORDING TO DALTON'S THEORY :**

- (1) Atom is the smallest indivisible part of matter which takes part in chemical reaction.
- (2) Atom is neither created nor destroyed.
- (3) Representation of atom : ${}_Z\text{X}^A$.

Where : A → Mass number, Z → Atomic number, X → Symbol of atom.

◆ **Mass Number :**

It is represented by capital A. The sum of number of neutrons and protons is called the mass number. of the element. It is also known as **number of nucleons** because neutron & proton are present in nucleus.

$$A = \text{number of protons} + \text{number of neutrons}$$

Note : It is always a whole number.

◆ **Atomic Number :**

It is represented by Z. The number of protons present in the Nucleus is called atomic number of an element. It is also known as **nuclear charge**.

For neutral atom : Number of proton = Number of electron

For charged atom : $\text{Number of } e^- = Z - (\text{charge on atom})$

Z = number of protons only

For Eg:



$$n = 18$$

$$p = 17$$

$$e = 17$$

Two different elements can not have the same Atomic Number

$$\begin{aligned} \text{Number of Neutrons} &= \text{Mass number} - \text{Atomic number} \\ &= A - Z \\ &= (p + n) - p \\ &= n \end{aligned}$$

◆ **Method for Analysis of atomic weight →**

eg.



$$p^+ \rightarrow 6$$

$$\text{Weight of Proton} = 6 \quad 1.00750$$

$$n^0 \rightarrow 6$$

$$\text{Weight of Neutron} = 6 \quad 1.00850$$

$$e^- \rightarrow 6$$

$$\text{Weight of Electron} = 6 \quad 0.000549$$

$$\text{Weight of C atom} = 12.011 \text{ a.m.u.}$$

Mass no. of C atom = 12 [P and n]

Note : Mass no. of atom is always a whole no. but atomic weight may be in decimal.

Q. If no. of protons in X^{-2} is 16. then no. of e^- in X^{+2} will be—

- (1) 14 (2) 16 (3) 18 (4) None

Sol. \therefore No. of proton in X^{-2} is = 16

\therefore No. of electron in X^{+2} is = 14

Q. In C^{12} atom if mass of e^- is doubled and mass of proton is halved, then calculate the percentage change in mass no. of C^{12} .

Sol.

$$\begin{array}{ccc}
 & {}_6C^{12} & \\
 & P^+ \rightarrow 3 & \\
 & e^- \rightarrow 12 & \\
 \hline
 e^- & P^+ & n \\
 6 & 6 & 6 \quad A \rightarrow 12 \\
 12 & 3 & 6 \quad A \rightarrow 9 \\
 \\
 \% \text{ change} = \frac{3}{12} \times 100 & & = 25\%
 \end{array}$$

Q. Assuming that atomic weight of C^{12} is 150 unit from atomic table, then according to this assumption, the weight of O^{16} will be :-

Sol. $\therefore 12 \text{ amu} = 150$

$$\therefore 1 \text{ amu} = \frac{150}{12}$$

$$\therefore 16 \text{ amu} = \frac{150}{12} \times 16 = 200 \text{ Unit}$$

◆ **Atomic Weight** : The atomic weight of an element is the average of weights of all the isotopes of that element.

◆ An element have three isotopes y_1 , y_2 and y_3 and their isotopic weights are w_1 , w_2 , w_3 and their percentage/possibility/probability/ratio of occurrence in nature are x_1 , x_2 , x_3 respectively then the average atomic weight of element is -

$$\text{ave. wt} = \frac{w_1x_1 + w_2x_2 + w_3x_3}{x_1 + x_2 + x_3}$$

Ex.	Cl^{35}	Cl^{37}
Probability ratio	75 %	25 %
	3	1
	:	
	$\frac{35 \times 3 + 37 \times 1}{3 + 1}$	$= \frac{142}{4} = 35.5$

Q. ${}_{35}Br^{79}$: ${}_{35}Br^{81}$
1 : 1

$$\frac{79 \times 1 + 81 \times 1}{1 + 1} = \frac{160}{2} = 80$$

Q. An element have three isotopes and their isotopic weight are 11, 12 , 13 unit and their percentage of occurrence in nature is 85, 10, 5 respectively then calculate the average atomic weight of element.

Sol. Average Atomic weight = $\frac{11 \times 85 + 12 \times 10 + 13 \times 5}{85 + 10 + 5}$
 $= \frac{935 + 120 + 65}{100}$
Average wt. = $\frac{1120}{100} = 11.2$

Q. Average atomic weight of an element M is 51.7. If two isotopes of M, M^{50} , M^{52} are present then calculate the percentage of occurrence of M^{50} in nature.

Sol.

$$\begin{array}{rcl}
 M^{50} & & M^{52} \\
 x_1 & + & x_2 = 100\% \\
 & & x_2 = (100 - x_1) \\
 \text{wt} = \frac{w_1x_1 + w_2x_2}{x_1 + x_2} \\
 51.7 = \frac{50 \times x_1 + 52 \times x_2}{x_1 + x_2} \\
 51.7 = \frac{50x_1 + 52(100 - x_1)}{x_1 + (100 - x_1)} \\
 5170 = 50x_1 + 5200 - 52x_1 \\
 5170 = -2x_1 + 5200 \\
 2x_1 = 30 \\
 x_1 = 15 \\
 M^{50} = 15\% \quad M^{52} = 85\%
 \end{array}$$

Q. Calculate the percentage of Deuterium in heavy water.

Sol.

$$\begin{array}{l}
 D_2O \\
 ({}_1H^2)_2 O^{16} \\
 4 + 16 = 20 \text{ (Molecular weight)} \\
 \frac{4}{20} \times 100 \\
 \text{Ans} = 20\%
 \end{array}$$

□ **Isotopes :** Given by **Soddy**

They are the atoms of a given element which have the same atomic number (Z) but different mass number (A) i.e. They have same Nuclear charge (Z) but different number of Neutrons (A-Z).

For Eg.1

${}_{17}Cl^{35}$	${}_{17}Cl^{37}$
n = 18	n = 20
e = 17	e = 17
p = 17	p = 17

◆ Isotopes have same chemical property but different physical property.

◆ Isotopes do not have the same value of $\frac{e}{m} \left(\frac{\text{Number of electron}}{\text{mass}} \right)$ because mass varies.
(No. of electron are same but mass varies).

For Eg.1

	(Protium)	Deuterium	Tritium)
	${}_1H^1$	${}_1H^2$	${}_1H^3$
e =	1	1	1
p =	1	1	1
n =	0	1	2
e/m	1/1	1/2	1/3

${}_1H^1$ is the only normal hydrogen which have n = 0 i.e. no neutrons

Deuterium is also called as heavy hydrogen. It represent by D

Eg. 2

${}_6C^{12}$	${}_6C^{13}$	${}_6C^{14}$
e = 6	e = 6	e = 6
p = 6	p = 6	p = 6
n = 6	n = 7	n = 8

❑ **Isobars** : Given by **Aston**

They are the atoms of different element which have the same mass number (A) but different Atomic number (Z)
i.e They have different number of Electron, Protons & Neutrons But sum of number of neutrons & Protons i.e. number of nucleons remains same.

For Eg.1

$$\begin{array}{l} {}_1\text{H}^3 \\ \left. \begin{array}{l} p = 1 \\ e = 1 \\ n = 2 \end{array} \right] \\ p + n = 3 \end{array} \qquad \begin{array}{l} {}_2\text{He}^3 \\ \left. \begin{array}{l} p = 2 \\ e = 2 \\ n = 1 \end{array} \right] \\ p + n = 3 \end{array}$$

◆ Isobars do not have the same chemical & physical property

◆ They do not have the same value of e/m

For Eg.2

$$\begin{array}{l} {}_{19}\text{K}^{40} \\ \left. \begin{array}{l} p = 19 \\ n = 21 \\ e = 19 \end{array} \right] \quad n + p = 40 \\ 19 + 21 = 40 \\ n + p = 40 \end{array} \qquad \begin{array}{l} {}_{20}\text{Ca}^{40} \\ \left. \begin{array}{l} p = 20 \\ n = 20 \\ e = 20 \end{array} \right] \quad n + p = 40 \\ 20 + 20 = 40 \end{array}$$

Number of Nucleons same

❑ **Isodiaphers** :

They are the atoms of different element which have the same difference of the number of Neutrons & protons.

For Eg1.

$$\begin{array}{l} {}_5\text{B}^{11} \\ \left. \begin{array}{l} p = 5 \\ n = 6 \\ e = 5 \end{array} \right] \quad n - p = 1 \end{array} \qquad \begin{array}{l} {}_6\text{C}^{13} \\ \left. \begin{array}{l} p = 6 \\ n = 7 \\ e = 6 \end{array} \right] \quad n - p = 1 \end{array}$$

For Eg 2.

$$\begin{array}{l} {}_7\text{N}^{15} \\ \left. \begin{array}{l} p = 7 \\ n = 8 \\ e = 7 \end{array} \right] \quad n - p = 1 \end{array} \qquad \begin{array}{l} {}_9\text{F}^{19} \\ \left. \begin{array}{l} p = 9 \\ n = 10 \\ e = 9 \end{array} \right] \quad n - p = 1 \end{array}$$

❑ **Isotones/ Isoneutronic species / Isotonic** :

They are the atoms of different element which have the same number of neutrons.

For Eg. 1.

$$\begin{array}{l} {}_1\text{H}^3 \\ p = 1 \\ n = 2 \\ e = 1 \end{array} \qquad \begin{array}{l} {}_2\text{He}^4 \\ p = 2 \\ n = 2 \\ e = 2 \end{array}$$

For Eg. 2.

$$\begin{array}{l} {}_{19}\text{K}^{39} \\ e = 19 \\ p = 19 \\ n = 20 \end{array} \qquad \begin{array}{l} {}_{20}\text{Ca}^{40} \\ e = 20 \\ p = 20 \\ n = 20 \end{array}$$

❑ **Isosters** :

They are the molecules which have the same number of atoms & electrons.

For Eg. 1

	CO_2		N_2O
Atoms	$= 1 + 2$	Atoms	$= 2 + 1$
	$= 3$		$= 3$
Electrons	$= 6 + 8 \times 2$	Electrons	$= 7 \times 2 + 8$
	$= 22 e^-$		$= 22 e^-$

For Eg. 2	CaO	KF
Atoms	2	2
Electrons	20 + 8	19 + 9
	28 e ⁻	28 e ⁻
For Eg. 3	OF ₂	HClO
Atoms	= 3	3
Electrons	= 8 + 18	1 + 17 + 8
	= 26 e ⁻	17 + 9
		26 e ⁻

❑ **Isoelectronic Species :**

They are the atoms, molecules or ions which have the same number of electrons.

For Eg. 1	Cl ⁻	Ar
Electron	18 e ⁻	18 e ⁻

For Eg. 2	H ₂ O	NH ₃
	e = 2 + 8	e = 7 + 3
	10 e ⁻	10 e ⁻

For Eg. 3	BF ₃	SO ₂
	e = 5 + 9 × 3	16 + 8 × 2
	5 + 27	16 + 16
	32 e ⁻	32 e ⁻

❑ **Nuclear Isomer :**

Nuclear isomers (isomeric nuclei) are the atoms with the same atomic number and same mass number but with different radioactive properties.

Example of nuclear isomers is

Uranium-X (half-life 1.4 min) and

Uranium-Z (half-life 6.7 hours)

The reason for nuclear isomerism is the different energy states of the two isomeric nuclei.

Other examples are

⁶⁹ ₃₀ Zn	⁶⁹ ₃₀ Zn	(T _{1/2} = 13.8 hr)	(T _{1/2} = 57 min)
⁸⁰ ₃₅ Br	⁸⁰ ₃₅ Br	(T _{1/2} = 4.4 hour)	(T _{1/2} = 18 min)

❑ **QUESTIONS BASED ON NUCLEAR STRUCTURE**

Ex. If the mass of neutrons is doubled & mass of electron is halved then find out the atomic mass of ⁶C¹² and the percent by which it is increased.

Sol. Step-1 ⁶C¹²
e = 6

$$\left. \begin{array}{l} p = 6 = 6 \text{ amu} \\ n = 6 = 6 \text{ amu} \end{array} \right\} = 12 \text{ amu}$$

If the mass of neutrons is doubled and mass of e⁻ is halved then.

$$\left. \begin{array}{l} n = 12 \text{ amu} \\ p = 6 \text{ amu} \end{array} \right\} = 18 \text{ amu}$$

Imp. Note : mass of e⁻ is negligible, so it is not considered in calculation of atomic mass.

Step-2

$$\begin{aligned} \% \text{ Increment} &= \frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 \\ &= \frac{18 - 12}{12} \times 100 \Rightarrow 50\% \end{aligned}$$

Ex. If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled then find out the change in At. wt of ${}_6\text{C}^{12}$

1. Remain same
2. Increased by 25%
3. Increased by 37.5%
4. None of them

Sol. **Step-1** ${}_6\text{C}^{12}$
 $e = 6$
 $\left. \begin{array}{l} p = 6 \\ n = 6 \end{array} \right\} = 12 \text{ amu}$

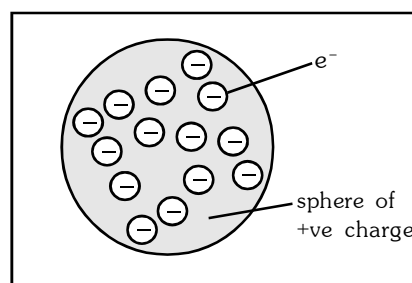
If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled, then new atomic mass will be :

$$\left. \begin{array}{l} n = 12 \text{ amu} \\ p = 3 \text{ amu} \end{array} \right\} = 15 \text{ amu}$$

Step-2 $\% \text{ Increment} = \frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 = \frac{15 - 12}{12} \times 100 \Rightarrow 25\%$

❑ THOMSON'S MODEL OF ATOM [1904]

- ◆ Thomson was the first to propose a detailed model of the atom.
- ◆ Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are present at some places.
- ◆ This model of atom is known as '**Plum-Pudding model**'.

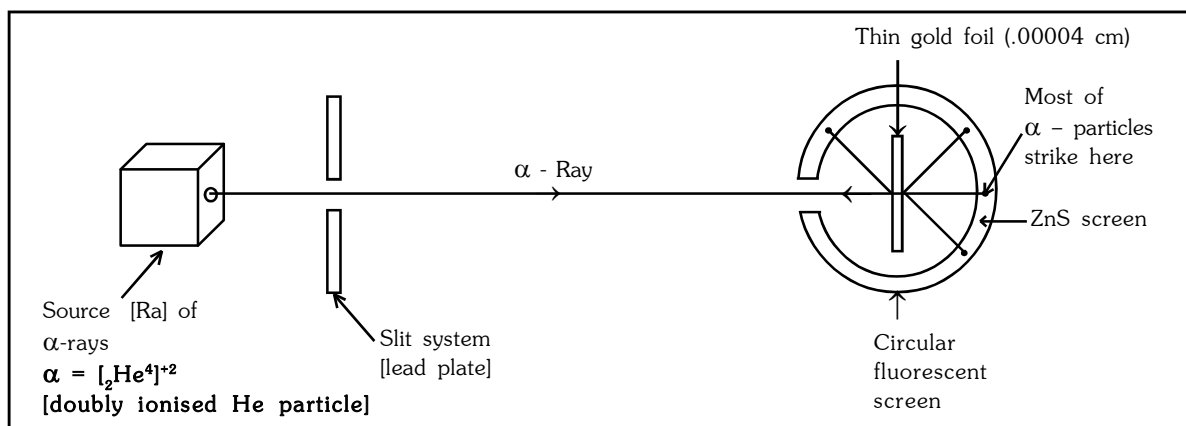


❑ DRAWBACKS :

- ◆ An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.
- ◆ It is a static model. It does not reflect the movement of electron.

❑ RUTHERFORD'S α - SCATTERING EXPERIMENT

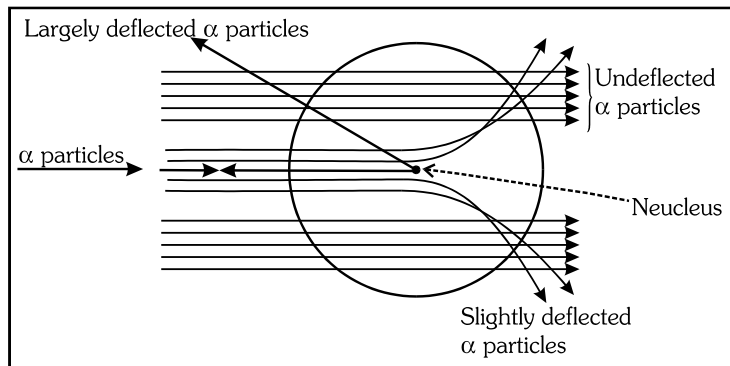
α -scattering experiment



❑ Rutherford observed that :

- (i) Most of the α -particles (nearly 99.9%) went straight without suffering any deflection.
- (ii) A few of them got deflected through small angles.

- (iii) A very few α -particles (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even come back in the direction from which they have come i.e. a deflection of 180° .



❑ **Following conclusions were drawn from the above observations :**

- (1) Since most of the α -particle went straight through the metal foil undeflected, it means that there must be very large empty space within the atom.
- (2) Since few of the α -particles were deflected from their original path through moderate angles; it was concluded that whole of the +ve charge is concentrated and the space occupied by this positive charge is very small in the atom.
- ◆ Whenever α -particles come closer to this point, they suffer a force of repulsion and deviate from their paths.
- ◆ The positively charged heavy mass which occupies only a small volume in an atom is called **nucleus**. It is supposed to be present at the centre of the atom.
- (3) A very few of the α -particles suffered strong deflections or even returned on their path indicating that the nucleus is rigid and α -particles recoil due to direct collision with the heavy positively charged mass.
- (4) The relation between number of deflected particles and deflection angle θ is

$$\mu = \frac{1}{\sin^4 \frac{\theta}{2}} \quad [\theta \text{ increases } \mu \text{ decreases}]$$

where μ = deflected particles

θ = deflection angle

- ◆ As atomic number increases, the number of protons increases which increases the repulsion and so deflection angle θ increases.

❑ **APPLICATIONS OF RUTHERFORD MODEL**

On the basis of scattering experiments, Rutherford proposed the model of an atom, which is known as nuclear atomic model. According to this model -

- (i) An atom consists of a heavy positively charged nucleus where all the protons are present.
- (ii) The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a radius of the order of 10^{-13} cm and the atom has a radius of the order of 10^{-8} cm

$$\frac{r_A}{r_N} = \frac{\text{radius of the atom}}{\text{radius of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5, \quad r_A = 10^5 r_N$$

Thus radius (size) of the atom is 10^5 times the radius of the nucleus.

- ◆ The radius of a nucleus is proportional to the cube root of the no. of nucleons within it.

$$R \propto A^{1/3} \Rightarrow R = R_0 A^{1/3} \text{ cm}$$

Where $R_0 = 1.33 \times 10^{-13}$ (a constant) and, A = mass number ($p + n$)

R = radius of the nucleus.

$$R = 1.33 \times 10^{-13} A^{1/3} \text{ cm}$$

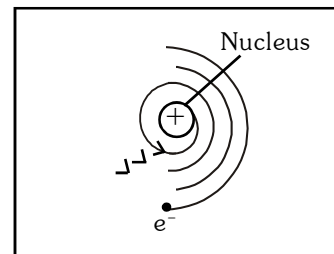
- (iii) There is an empty space around the nucleus called extra nuclear part. In this part electrons are present. The no. of electrons in an atom is always equal to no. of protons present in the nucleus. As the nuclear part of atom is responsible for the mass of the atom, the extra nuclear part is responsible for its volume. The volume of the atom is about 10^{15} times the volume of the nucleus.

$$\frac{\text{vol. of the atom}}{\text{vol. of the nucleus}} = \frac{\left(\frac{4}{3}\pi r_A^3\right)}{\left(\frac{4}{3}\pi r_N^3\right)} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

- (iv) Electrons revolve round the nucleus in closed orbits with high speeds.
- ◆ This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets.

❑ Drawbacks of Rutherford model :

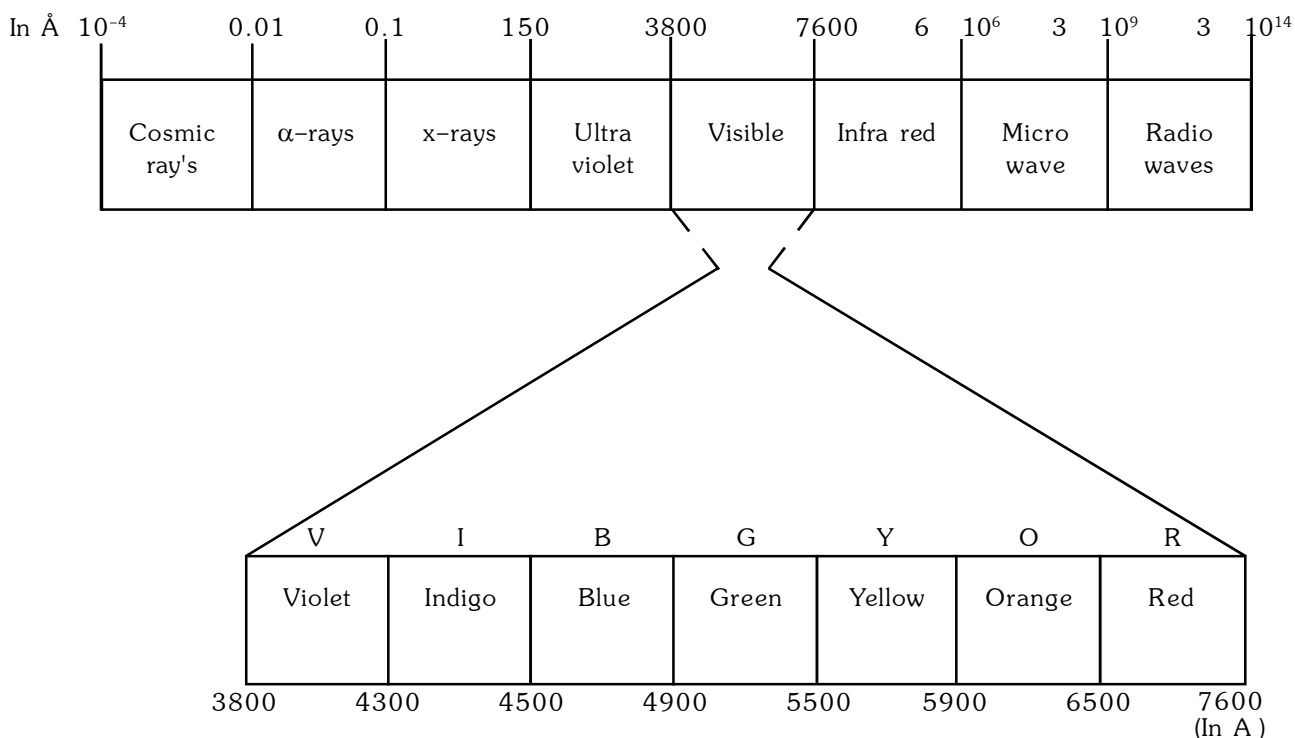
- (1) This theory could **not** explain the stability of an atom. According to Maxwell electron loses its energy continuously in the form of electromagnetic radiations. As a result of this, the e^- should lose energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable.
- (2) If the electrons lose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies (discontinuous). Hence, the loss of energy by electron is **not** continuous in an atom.



❑ Electromagnetic waves (EM waves) or Radiant Energy/Electromagnetic radiation :

- ◆ It is the energy transmitted from one body to another in the form of waves and these waves travel in the space with the same speed as light (3×10^8 m/s) and these waves are known as Electromagnetic waves or radiant energy.
- ◆ The radiant Energy does not need any medium for propagation.

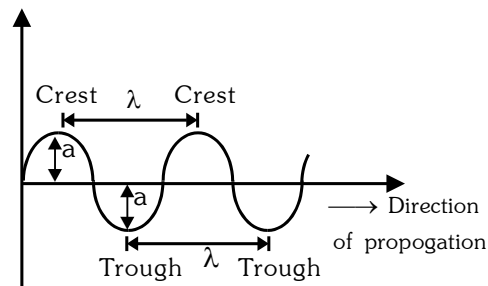
Ex : Radio waves, micro waves, Infra red rays, visible rays, ultraviolet rays, x-rays, gamma rays and cosmic rays.



A wave is characterized by following six characteristics.

The upper most point of the wave is called crest and the lower most point is called trough.

Some of the terms employed in dealing with the waves are described below.



1. **Wavelength λ (Lambda) :**

It is defined as the distance between two nearest crest or nearest trough.

It is measured in terms of \AA (Angstrom), pm (Picometre), nm (nanometer), cm (centimetre), m (metre)

$$1\text{\AA} = 10^{-10} \text{ m}, \quad 1 \text{ Pm} = 10^{-12} \text{ m}, \quad 1\text{nm} = 10^{-9} \text{ m}, \quad 1\text{cm} = 10^{-2}\text{m}$$

2. **Frequency (ν) (nu)→**

Frequency of a wave is defined as the number of waves which pass through a point in 1 sec.

◆ It is measured in terms of Hertz (Hz), sec^{-1} , or cycle per second (cps)

$$1 \text{ Hertz} = 1 \text{ sec}^{-1} = 1 \text{ cps.}$$

3. **Time period (T) :** Time taken by a wave to pass through one point.

$$T = \frac{1}{\nu} \text{ sec.}$$

4. **Velocity → (c)**

Velocity of a wave is defined as distance covered by a wave in 1 sec.

$$C = \lambda / T = \lambda \nu \quad \Rightarrow \quad \nu = C/\lambda$$

$$\text{Since } C \text{ is constants} \quad \nu \propto 1/\lambda$$

i.e. frequency is inversely proportional to λ

5. **Wave number → ($\bar{\nu}$) (nu bar) →** It is the reciprocal of the wave length that is number of waves present in 1cm

$$1 \text{ m} = 100 \text{ cm}$$

$$\bar{\nu} = \frac{1}{\lambda} \quad \frac{1}{\text{cm}} = \frac{100}{\text{m}}$$

$$(1\text{cm}^{-1} = 100 \text{ m}^{-1})$$

◆ It is measured in terms of cm^{-1} , m^{-1} etc,

6. **Amplitude → (a)**

The amplitude of a wave is defined as the height of crust or depth of trough.

$$\nu = \frac{C}{\lambda} = C\bar{\nu} \quad \left(\bar{\nu} = \frac{1}{\lambda} \right)$$

❑ **QUESTIONS BASED ON EM WAVES**

Ex. The vividh Bharti station of All India Radio broadcast on a frequency of 1368 Kilo Hertz. Calculate the wave length of the Electromagnetic waves emitted by the transmitter.

Sol. As we know velocity of light (C)

$$C = 3 \times 10^8 \text{ m/sec.}$$

Given ν (frequency)

$$= 1368 \text{ kHz}$$

$$= 1368 \times 10^3 \text{ Hz}$$

$$= 1368 \times 10^3 \text{ sec}^{-1}$$

$$\therefore \lambda = \frac{C}{\nu} \quad \therefore \lambda = \frac{3 \times 10^8 \text{ m sec}^{-1}}{1368 \times 10^3 \text{ sec}^{-1}} \Rightarrow \lambda = 219.3 \text{ m}$$

Ex. Calculate $\bar{\nu}$ in cm^{-1} and ν of yellow radiations have wavelength of 5800 \AA

Sol. As we known $\bar{\nu} = \frac{1}{\lambda}$

$$\bar{\nu} = \frac{1}{5800 \text{ \AA}}$$

$$\bar{\nu} = \frac{1}{5800 \times 10^{-8} \text{ cm}} \quad \{ \because 1 \text{ \AA} = 10^{-8} \text{ cm} \}$$

$$= \frac{10^8}{5800} \text{ cm}^{-1} = 17241.4 \text{ cm}^{-1}$$

$$\begin{aligned} \nu &= c\bar{\nu} \\ &= 3 \times 10^{10} \text{ cm sec}^{-1} \times 1.7 \times 10^4 \text{ cm}^{-1} \\ &= 3 \times 1.7 \times 10^{14} \\ &= 5.1 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

Ex. A particular radiostation broadcast at a frequency of 1120 Kilo Hertz another radio station broadcast at a frequency of 98.7 mega Hertz. What are the wave length of radiations from each station.

Sol. Station Ist

$$\lambda = \frac{C}{\nu} = \frac{3 \times 10^8 \text{ m sec}^{-1}}{1120 \times 10^3 \text{ sec}^{-1}} = 267.86 \text{ m}$$

Station IInd

$$\lambda = \frac{C}{\nu} = \frac{3 \times 10^8 \text{ m sec}^{-1}}{98.7 \times 10^6 \text{ sec}^{-1}}$$

$$= 3.0395 \text{ m}$$

Ex. How long would it take a radio wave of frequency $6 \times 10^3 \text{ sec}^{-1}$ to travel from mars to the earth, a distance of $8 \times 10^7 \text{ km}$?

Sol. Distance to be travelled from mars to earth

$$= 8 \times 10^7 \text{ km}$$

$$= 8 \times 10^{10} \text{ m}$$

\therefore Velocity of EM waves

$$= 3 \times 10^8 \text{ m/sec}$$

$$\therefore \text{Time} = \frac{\text{Distance}}{\text{Velocity}} = \frac{8 \times 10^{10} \text{ m}}{3 \times 10^8 \text{ m/sec}^{-1}}$$

$$= 2.66 \times 10^2 \text{ sec.}$$

Ex. What will be the frequency of photon of wavelength 2225 \AA traveling in vacuum ?

Sol. Velocity of light in vacuum = $3 \times 10^8 \text{ m sec}^{-1}$

Wavelength = $2225 \times 10^{-10} \text{ meter}$

$$\text{Frequency} = \frac{\text{Velocity}}{\text{Wavelength}} = \frac{3 \times 10^8 \text{ meter/sec}}{2225 \times 10^{-10} \text{ meter}} = \frac{3000}{2225} \times 10^5 \text{ sec}^{-1}$$

$$= 1.349 \times 10^{15} \text{ sec}^{-1}$$

❑ PLANCK'S QUANTUM THEORY

◆ According to planck's quantum theory :

1. The radiant energy emitted or absorbed by a body not continuously but discontinuously in the form of small discrete packets of energy and these packets are called quantum.
2. In case of light, the smallest packet of energy is called as '**photon**' but in general case the smallest packet of energy called as quantum.
3. The energy of each quantum is directly proportional to frequency of the radiation i.e.

$$E \propto \nu \Rightarrow E = h\nu \quad \text{or} \quad E = \frac{hc}{\lambda} \quad \left\{ \because \nu = \frac{c}{\lambda} \right\}$$

Proportionality constant or Plank's constant (h)

$$h = 6.626 \times 10^{-37} \text{ kJ sec.}$$

$$\text{or} \quad 6.626 \times 10^{-34} \text{ J sec} \quad (1 \text{ erg} = 10^{-7} \text{ J})$$

$$\text{or} \quad 6.626 \times 10^{-27} \text{ erg sec.}$$

4. Total amount of energy transmitted from one body to another will be some integral multiple of energy of a quantum.

$$E = nh\nu$$

Where n is an integer and n = number of quantum

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

Ex. Calculate the energy of a photon of sodium light of wave length $5.862 \times 10^{-16} \text{ m}$ in Joules.

Sol. $\lambda = 5.886 \times 10^{-16} \text{ m}$

$$c = 3 \times 10^8 \text{ m sec}^{-1}$$

$$E = nh\nu \quad \text{or} \quad \frac{nhc}{\lambda} \quad \{ \because n = 1 \}$$

$$\therefore E = \frac{hc}{\lambda}$$

$$E = \frac{1 \times 6.6 \times 10^{-34} \text{ Jules} \times 3 \times 10^8 \text{ m sec}^{-1}}{5.862 \times 10^{-16} \text{ m}}$$

$$= \frac{6.6 \times 3}{5.862} \times 10^{-10} \text{ Joules} = 3.38 \times 10^{-10} \text{ Joules.}$$

Ex. Calculate the frequency & energy of a photon of wave length 4000 \AA

Sol. (a) Calculation of frequency :

$$\lambda = 4000 \text{ \AA}$$

$$\lambda = 4000 \times 10^{-10} \text{ m}$$

$$\therefore \nu = \frac{C}{\lambda}$$

$$\therefore \nu = \frac{3 \times 10^8 \text{ m/sec}}{4 \times 10^{-7} \text{ m}}$$

$$= 0.75 \times 10^{15} \text{ sec}^{-1}$$

$$= 7.5 \times 10^{14} \text{ sec}^{-1}$$

(b) Calculation of energy :

$$E = h\nu$$

$$= 6.626 \times 10^{-34} \text{ Joule} \times 7.5 \times 10^{14} \text{ sec}^{-1}$$

$$= 4.96 \times 10^{-19} \text{ Joule}$$

Ex. Calculate the λ and frequency of a photon having an energy of 2 electron volt

Sol. $\therefore 1\text{ev} = 1.602 \times 10^{-19} \text{ J}$

$\therefore 2\text{ev} = 3.204 \times 10^{-19} \text{ J} = E$

(a) Calculation of wavelength (λ) :

$$\begin{aligned} E &= \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E} \\ &= \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ m sec}^{-1}}{3.204 \times 10^{-19} \text{ J}} \\ &= 6.204 \times 10^{-7} \text{ m} \end{aligned}$$

(b) Calculation of frequency (ν) :

$$\begin{aligned} \nu &= \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m sec}^{-1}}{6.204 \times 10^{-7} \text{ m}} \\ &= 0.48 \times 10^{15} \text{ sec}^{-1} \\ &= 4.8 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

Ex. Which has a higher energy ?

(a) A photon of violet light with wave length 4000 Å

or

(b) A photon of red light with wave length 7000 Å

Sol. (a) Violet light :

$$\begin{aligned} E_{\text{violet}} &= \frac{hc}{\lambda} \\ &= \frac{6.626 \times 10^{-34} \text{ J sec} \times 3 \times 10^8 \text{ m sec}^{-1}}{4000 \times 10^{-10} \text{ m}} \\ &= 4.97 \times 10^{-19} \text{ Joule} \end{aligned}$$

(b) Red light :

$$\begin{aligned} E_{\text{red}} &= \frac{hc}{\lambda} \\ &= \frac{6.626 \times 10^{-34} \text{ J sec} \times 3 \times 10^8 \text{ m sec}^{-1}}{7000 \times 10^{-10} \text{ m}} \\ &= 2.8 \times 10^{-19} \text{ Joule} \end{aligned}$$

So, $E_{\text{violet}} > E_{\text{red}}$

Ex. How many photons of lights having a wave length of 5000 Å are necessary to provide 1 Joule of energy.

Sol. $\therefore E = \frac{nhc}{\lambda}$

$\therefore n = \frac{E \times \lambda}{hc}$

$$\begin{aligned} &= \frac{1 \text{ Joule} \times 5000 \times 10^{-10} \text{ m}}{6.626 \times 10^{-34} \text{ Joule sec} \times 3 \times 10^8 \text{ m sec}^{-1}} \\ &= 2.5 \times 10^{18} \text{ photons} \end{aligned}$$

Ex. Calculate the energy associated with the photon passing through vacuum with wavelength 9900 Å.

Sol. For vacuum, velocity of photon = 3×10^8 m/sec

$$h = 6.6 \times 10^{-34} \text{ Joule sec}$$

$$\lambda = 9900 \times 10^{-10} \text{ meter}$$

$$E = h\nu = h \frac{c}{\lambda} = \frac{6.6 \times 10^{-34} \text{ J} \cdot \text{sec} \times 3 \times 10^8 \text{ m/sec}}{9900 \times 10^{-10} \text{ m}} = \frac{19.8 \times 10^{-16}}{9900} = 2 \times 10^{-19} \text{ Joule}$$

□ BOHR'S ATOMIC MODEL

Some Important formulae :

$$\text{Coulombic force} = \frac{kq_1q_2}{r^2}$$

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

$$\text{Angular momentum} = mvr$$

- ◆ It is a quantum mechanical model. This model was based on quantum theory of radiation and Classical law of physics.

- ◆ **The important postulates on which Bohr's Model is based are the following :**

1st Postulate :

- ◆ Atoms has a nucleus where all protons and neutrons are present.
- ◆ The size of nucleus is very small and it is present at the centre of the atom.

2nd Postulate :

- ◆ Negatively charged electron are revolving around the nucleus in the same way as the planets are revolving around the sun.
- ◆ The path of electron is circular.
- ◆ The attraction force (Coulombic or electrostatic force) between nucleus and electron is equal to the centrifugal force on electron.

i.e. Attraction force towards nucleus = centrifugal force away from nucleus.

3rd Postulate :

- ◆ Electrons can revolve only in those orbits whose angular momentum (mvr) is integral multiple of $\frac{h}{2\pi}$.

$$\text{i.e. } mvr = \frac{nh}{2\pi}$$

$$n = \text{Whole number}$$

Where h = Plank's constant,

$$\pi = \text{Constant}$$

- ◆ Angular momentum can have values such as $\frac{h}{2\pi}$, $2\frac{h}{2\pi}$, $3\frac{h}{2\pi}$, $4\frac{h}{2\pi}$, $5\frac{h}{2\pi}$ but can not have fractional values such as $1.5\frac{h}{2\pi}$, $1.2\frac{h}{2\pi}$, $.5\frac{h}{2\pi}$

4th Postulate :

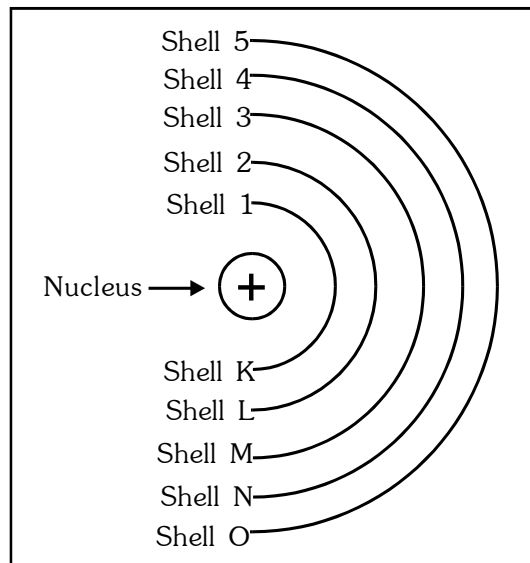
- ◆ The orbits in which electron can revolve are known as **stationary Orbits** because in these orbits energy of electron is always constant.

5th Postulate :

- ◆ Each stationary orbit is associated with definite amount of energy therefore these orbits are also called as energy levels and are numbered as 1, 2, 3, 4, 5, or K, L, M, N, O, from the nucleus outwards.

6th Postulate

- ◆ The emission or absorption of energy in the form of photon can only occur when electron jumps from one stationary state to another & it is $\Delta E = E_{\text{final state}} - E_{\text{initial state}}$
- ◆ Energy is absorbed when electron jumps from inner to outer orbit and is emitted when electron moves from outer to inner orbit.



◆ Radii of various orbits of hydrogen atom :

Consider, an electron of mass 'm' and charge 'e' revolving around a nucleus of charge Ze (where, Z = atomic number and e is the charge of the proton) with a tangential velocity v. r is the radius of the orbit in which electron is revolving.

By Coulomb's law, the electrostatic force of attraction between the moving electron and nucleus is Coulombic

$$\text{force} = \frac{KZe^2}{r^2}$$

$$K = \frac{1}{4\pi\epsilon_0} \quad (\text{where } \epsilon_0 \text{ is permittivity of free space})$$

$$K = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2}$$

In C.G.S. units, value of $K = 1 \text{ dyne cm}^2 (\text{esu})^{-2}$

The centrifugal force acting on the electron is $\frac{mv^2}{r}$

Since the electrostatic force balance the centrifugal force, for the stable electron orbit.

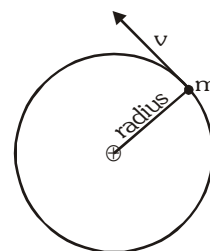
$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \quad \dots\dots(1)$$

$$(\text{or}) \quad v^2 = \frac{KZe^2}{mr} \quad \dots\dots(2)$$

According to Bohr's postulate of angular momentum quantization, we have

$$mvr = \frac{nh}{2\pi}$$

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



$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \quad \dots\dots(3)$$

Equating (2) and (3)

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

$$\text{Solving for } r \text{ we get } r = \frac{n^2 h^2}{4\pi^2 m KZe^2}$$

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

Hence, only certain orbits whose radii are given by the above equation are available for the electron. The greater the value of n , i.e., farther the energy level from the nucleus the greater is the radius.

The radius of the smallest orbit ($n = 1$) for hydrogen atom ($Z = 1$) is r_0 .

$$r_0 = \frac{n^2 h^2}{4\pi^2 m e^2 K} = \frac{1^2 \times (6.626 \times 10^{-34})^2}{4 \times (3.14)^2 \times 9 \times 10^{-31} \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9} = 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ \AA}$$

Radius of n^{th} orbit for an atom with atomic number Z is simply written as

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

□ CALCULATION OF ENERGY OF AN ELECTRON :

The total energy (E) of the electron is the sum of kinetic energy and potential energy.

Kinetic energy of the electron = $\frac{1}{2} mv^2$

$$\text{Potential energy} = \int \text{coulombic force} \cdot dr = \int \frac{KZe^2}{r^2} \cdot dr = \frac{-KZe^2}{r}$$

$$\text{Total energy} = \frac{1}{2} mv^2 - \frac{KZe^2}{r} \quad \dots\dots(4)$$

From equation (1) we know that

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

$$\therefore \frac{1}{2} mv^2 = \frac{KZe^2}{r^2}$$

Substituting this in equation (4)

$$\text{Total energy (E)} = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

Substituting for r , gives us

$$E = \frac{2\pi^2 m Z^2 e^4 K^2}{n^2 h^2} \quad \text{where } n = 1, 2, 3, \dots$$

This expression shows that only certain energies are allowed to the electron. Since this energy expression consist of so many fundamental constant, we are giving you the following simplified expressions.

$$E = -21.8 \times 10^{-12} \frac{Z^2}{n^2} \text{ erg per atom}$$

$$= -21.8 \times 10^{-19} \frac{Z^2}{n^2} \text{ J per atom} = -13.6 \frac{Z^2}{n^2} \text{ eV per atom}$$

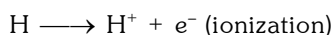
$$(1 \text{ eV} = 3.83 \times 10^{-23} \text{ Kcal})$$

$$1 \text{ eV} = 1.602 \times 10^{-12} \text{ erg}$$

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

$$[E = -313.6 \frac{Z^2}{n^2} \text{ Kcal/mole (1 cal} = 4.18 \text{ J)}]$$

The energies are negative since the energy of the electron in the atom is less than the energy of a free electron, i.e. the electron is at infinite distance from the nucleus which is taken as zero. The lowest energy level of the atom corresponds to $n = 1$, and as the quantum number increases, E becomes less negative. When $n = \infty$, $E = 0$, which corresponds to an ionized atom, i.e. the electron and nucleus are infinitely separated.



□ Calculation of velocity :

We know that

$$mvr = \frac{nh}{2\pi}; \quad v = \frac{hn}{2\pi mr}$$

By substituting for r we are getting

$$v = \frac{2\pi KZe^2}{nh}$$

where excepting n and Z all are constants

$$v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/sec.}$$

□ QUESTIONS BASED ON BOHR'S MODEL

Ex. Calculate the radius of 1st, 2nd, 3rd, 4th Bohr's Orbit of hydrogen.

Sol. Radius of Bohr's orbit

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

(a) Radius of 1st orbit :

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

(b) Radius of 2nd orbit :

$$\begin{aligned} r &= 0.529 \times \frac{2^2}{1} = 0.529 \times 4 \\ &= 2.116 \text{ \AA} \end{aligned}$$

(c) Radius of 3rd orbit :

$$\begin{aligned} r &= 0.529 \times \frac{3^2}{1} = 0.529 \times 9 \\ &= 4.761 \text{ \AA} \end{aligned}$$

(d) Radius of 4th orbit :

$$\begin{aligned} r &= 0.529 \times \frac{4^2}{1} = 0.529 \times 16 \\ &= 8.464 \text{ \AA} \end{aligned}$$

Ex. Calculate the radius ratio of 3rd & 5th orbit of He^+

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

At. Number of $\text{He} = 2$

Sol. $\therefore r_3 = 0.529 \times \frac{(3)^2}{2}$

$$= 0.529 \times \frac{9}{2}$$

$$r_5 = 0.529 \times \frac{(5)^2}{2}$$

$$= 0.529 \times \frac{25}{2}$$

$$\text{Therefore } \frac{r_3}{r_5} = \frac{0.529 \times \frac{(3)^2}{2}}{0.529 \times \frac{(5)^2}{2}}$$

$$\frac{r_3}{r_5} = \frac{9}{25} \quad r_3 : r_5 = 9 : 25$$

Ex. Calculate the radius ratio of 2nd orbit of hydrogen and 3rd orbit of Li⁺²

Sol. Atomic number of H = 1

Atomic number of Li = 3

2nd orbit radius of hydrogen

$$(r_2)_H = 0.529 \times \frac{2^2}{1}$$

3rd orbit radius of Li⁺²

$$(r_3)_{Li^{+2}} = 0.529 \times \frac{3^2}{3}$$

$$\therefore \frac{(r_2)_H}{(r_3)_{Li^{+2}}} = \frac{0.529 \times \frac{2^2}{1}}{0.529 \times \frac{3^2}{3}} = \frac{4}{3} \Rightarrow \therefore (r_2)_H : (r_3)_{Li^{+2}} = 4 : 3$$

Ex. The ratio of the radius of two Bohr's orbit of Li⁺² is 1:9. what Would be their nomenclature.

1. K & L

2. L & M

3. K & M

4. K & N

Sol.

$$\frac{r_x}{r_y} = \frac{1}{9} = \frac{0.529 \times \frac{n_x^2}{3}}{0.529 \times \frac{n_y^2}{3}} \Rightarrow \sqrt{\frac{n_x^2}{n_y^2}} \Rightarrow \sqrt{\frac{1}{9}}$$

$$\frac{n_x}{n_y} = \frac{1}{3} = \frac{\text{K Shell}}{\text{M Shell}}$$

Ex. Calculate the radius of 2nd excited state of Li⁺².

Sol. 2nd excited state, means e⁻ is present in 3rd shell so,

$$\begin{aligned} r_3 &= 0.529 \times \frac{3 \times 3}{3} \\ &= 0.529 \times 3 \text{ Å} \\ &= 1.587 \text{ Å} \end{aligned}$$

Ex. Calculate the radius ratio of 2nd excited state of H & 1st excited state of Li⁺².

Sol. 2nd excited state, means e⁻ is present in 3rd shell of hydrogen

$$r_3 = 0.529 \times \frac{(3)^2}{1} = 0.529 \times 9$$

1st excited state, means e⁻ exist in 2nd shell of Li⁺²

$$r_2 = 0.529 \times \frac{(2)^2}{3}$$

$$= 0.529 \times \frac{4}{3} \Rightarrow \frac{(r_3)_H}{(r_2)_{Li^{+2}}} = \frac{0.529 \times \frac{9}{1}}{0.529 \times \frac{4}{3}}$$

$$= \frac{\text{radius of 2nd excited state of hydrogen}}{\text{radius of 1st excited state of Li⁺²$$

Ex. Calculate the energy of Li^{+2} atom for 2nd excited state.

Sol. $E = -13.6 \times \frac{Z^2}{n^2}$
 $\therefore Z = 3$ and e^- exist in 2nd excited state, means e^- present in 3rd shell i.e. $n = 3$

$$\therefore E = -13.6 \times \frac{(3)^2}{(3)^2}$$

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

Ex. Calculate the ratio of energies of He^+ for 1st & 2nd excited state .

Sol. (He^+) 1st Excited state : $(\text{He}^+)_2$ 2nd Excited state
 i.e. $(\text{He}^+)2^{\text{nd}}$ shell : $(\text{He}^+)3^{\text{rd}}$ shell

$$-13.6 \times \frac{(2)^2}{(2)^2} : -13.6 \times \frac{(2)^2}{(3)^2}$$

$$\frac{4}{4} : \frac{4}{9}$$

$$\frac{1}{4} : \frac{1}{9}$$

$$9 : 4$$

Ex. If the P.E. of an electron is -6.8 eV in hydrogen atom then find out K.E., E of orbit where electron exist & radius of orbit.

Sol. 1. P.E. = -2K.E.

$$-6.8 = -2\text{K.E.}$$

$$\frac{6.8}{2} = \text{K.E.} \quad \text{K.E.} = 3.4 \text{ eV}$$

2. E. = - K.E.

$$= -3.4 \text{ eV}$$

3. Orbit = 2nd

$$\therefore E = -13.6 \times \frac{Z^2}{n^2}$$

$$\therefore 3.4 = -13.6 \times \frac{1^2}{n^2}$$

$$\Rightarrow n^2 = \frac{-13.6}{-3.4} = 4$$

$$\text{i.e. } n = 2$$

$$4. \quad r = 0.529 \times \frac{n^2}{Z} \text{ \AA}$$

$$r = 0.529 \times \frac{(2)^2}{1} \text{ \AA}$$

$$= 0.529 \times 4 \text{ \AA}$$

$$= 2.16 \text{ \AA}$$

Ex. The ionization energy for the hydrogen atom is 13.6 eV then calculate the required energy in eV to excite it from the ground state to 1st excited state.

Sol. Ionization energy = 13.6 eV

i.e. 1^{st} energy state = - 13.6 eV

Energy of 1^{st} excited state

i.e. 2^{nd} orbit = -3.4 eV

so, $E_2 - E_1 = -3.4 + 13.6 = 10.2 \text{ eV}$

Ex. If the total energy of an electron is -1.51 eV in hydrogen atom then find out K.E, P.E, orbit radius and velocity of the electron in that orbit.

Sol. Given $E = -1.51 \text{ eV}$

(i) $E = - \text{KE}$

$$\text{K.E} = -E \quad \{ \because Z = 1 \}$$

$$= 1.51 \text{ eV}$$

(ii) $\text{PE} = -2 \times 1.51$
 $= -3.02 \text{ eV}$

(iii) Orbit = 3^{rd}

$$\therefore E = -13.6 \times \frac{Z^2}{n^2} \text{ eV} \Rightarrow -1.51 = -13.6 \times \frac{1^2}{n^2}$$

$$n^2 = \frac{-13.6}{-1.51} = 9$$

$$\therefore n = 3$$

(iv) $r = 0.529 \times \frac{3 \times 3}{1}$
 $= 0.529 \times 9 = 4.761 \text{ \AA}$

$$v = 2.188 \times 10^8 \times \frac{1}{3} \text{ cm/sec}$$

$$= \frac{2.188 \times 10^8}{3} = 0.729 \times 10^8 \text{ cm / sec}$$

Ex. Calculate the velocity of an electron placed in the 3^{rd} orbit of the Li^{2+} ion. Also calculate the number of revolutions per second that it makes around the nucleus.

Sol. Radius of 2^{nd} orbit = $r_1 \times \frac{(n)^2}{Z}$

$$= 0.529 \times 10^{-8} \times \frac{(3)^2}{3} = 1.587 \times 10^{-8} \text{ cm}$$

Velocity of electron in 2^{nd} orbit,

$$v = 2.18 \times 10^8 \times \frac{Z}{n} \text{ cm/sec} = \frac{2.18 \times 10^8 \times 3}{3} = 2.18 \times 10^8 \text{ cm/sec}$$

$$\text{No. of revolutions/sec} = \frac{1}{2\pi r / v} = \frac{v}{2\pi r} = \frac{2.18 \times 10^8 \text{ cm/sec}}{2 \times 3.14 \times 1.587 \times 10^{-8} \text{ cm}} = 0.2187 \times 10^{16}$$

$$= 2.187 \times 10^{15} \text{ rev/sec}$$

❑ SPECTRUM

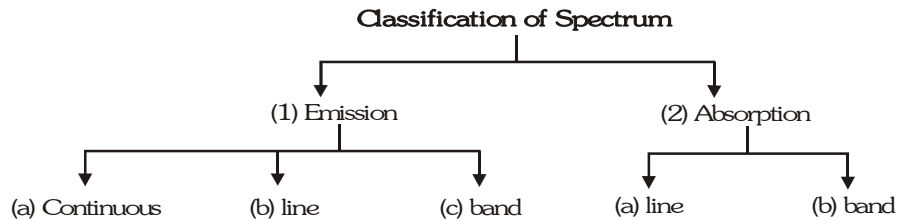
Electromagnetic spectrum or EM spectrum :

The arrangement obtained by arranging various types of EM waves in order of their increasing frequency or decreasing wave length is called as EM SPECTRUM

low ν low E longer λ	RW	MW	IR	Visible Rays	U.V	X-ray	γ	Cosmic	high ν high E Shorter λ
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◆ **Spectrum :**

When a radiation is passed through a spectroscope (Prism) for the dispersion of the radiation, the pattern (photograph) obtained on the screen (photographic plate) is called as spectrum of the given radiation

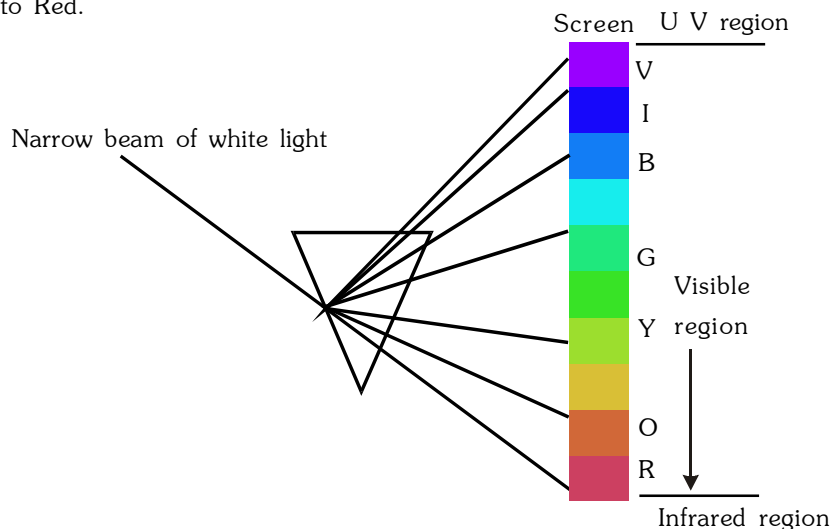


(1) Emissions spectrum :

When the radiation emitted from incandescence source (eg. from the candle, sun, tubelight, burner, bulb, or by passing electric discharge through a gas at low pressure, by heating some substance at high temp) is passed directly through the prism and then received on the screen then the obtained spectrum is called as emission spectrum.

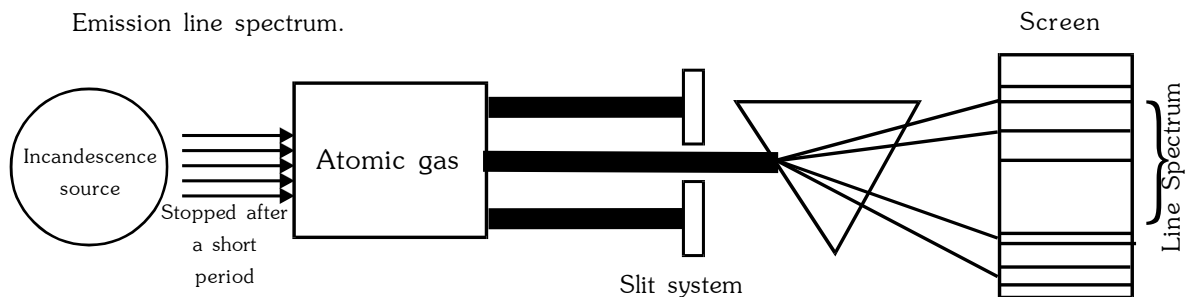
(a) Emission continuous spectrum or continuous spectrum :

When a narrow beam of white light is passed through a prism, it is dispersed into 7 colours from violet to Red.



(b) Emission line spectrum :

When an atomic gas is raised to incandescence source or subjected to electrical excitation, it first absorbs energy & then gives it out as radiation. On examining these radiation through a spectroscope a spectrum is obtained which have well defined lines, each corresponding to a definite wave length & these lines are separated from each other by dark space. This type of Emission spectrum is called as Emission line spectrum.



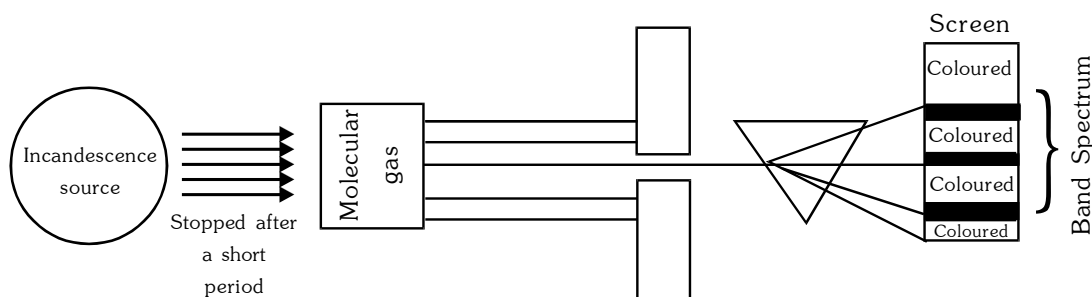
◆ **Special Note :**

1. No two elements will have identical line spectrum since no two elements have identical energy level therefore the line spectrum of the elements are described as finger prints differing from each other like the finger prints of the human beings.
2. Since line spectrum is obtained by the emission of energy through the atoms of the element therefore line spectrum is also called as atomic spectrum.

(c) **Emission band spectrum :**

If molecular form of the gas is used, it first absorbs energy for not only electron transition but for rotational, vibrational and translational then emits radiations.

On examining these radiations through a spectroscope a spectrum is obtained on the screen, which are group of closely packed lines called Bands, therefore this type of Emission spectrum is called as emission band spectrum. Bands are separated from each other by dark space.

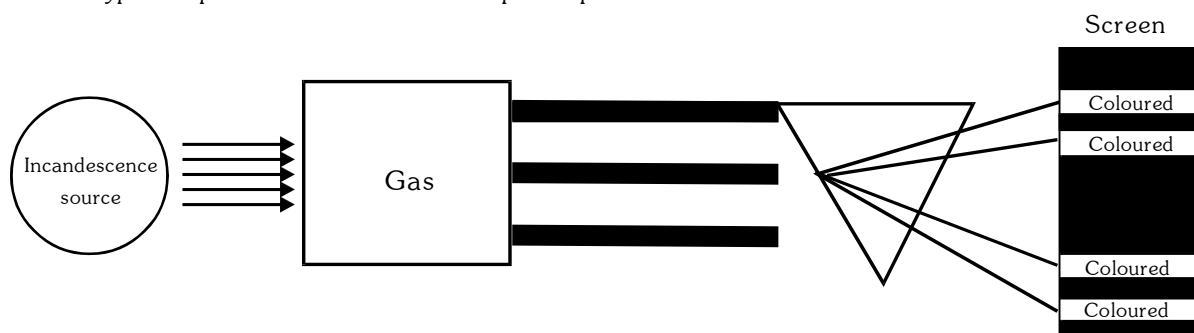


Note : Since band spectrum are caused by molecules therefore band spectrum are also called as molecular spectrum.

(2) **Absorption spectrum :**

When white light is first passed through a solution or vapours of chemical substance or gas and then analyzed by spectroscope, it is observed that some dark lines are obtained in otherwise continuous spectrum.

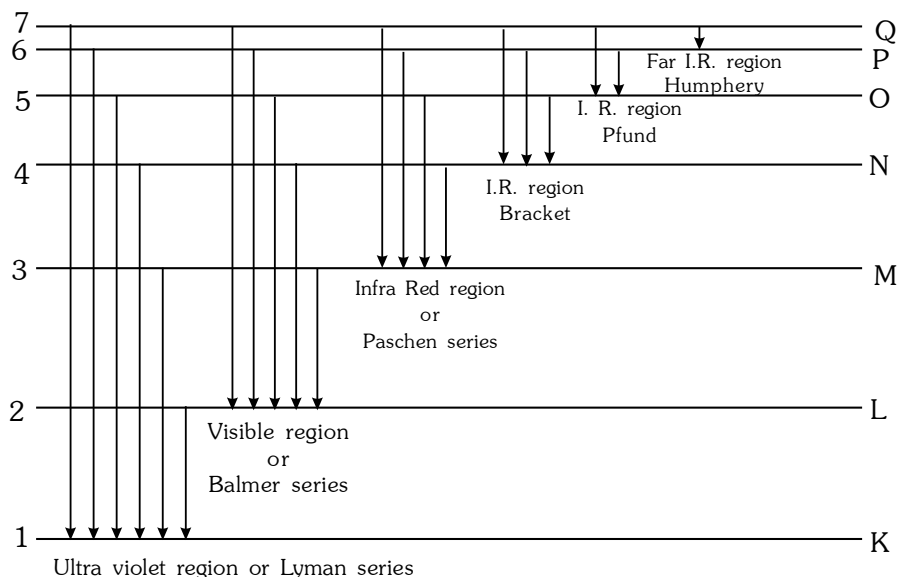
This type of spectrum is called as Absorption spectrum.



- ◆ If white light is passed through atomic gas then the obtained spectrum is called as Absorption line spectrum.
- ◆ If white light is passed through molecular gas then the obtained spectrum is called as Absorption band spectrum.

□ **Hydrogen line spectrum or Hydrogen spectrum :**

When an electric excitation is applied on atomic hydrogen gas at Low pressure, a bluish light is emitted. When a ray of this light is passed through a prism, a spectrum of several isolated sharp lines is obtained. The wavelength of various lines show that spectrum lines lie in Visible, Ultraviolet and Infra red region. These lines are grouped into different series.



Series	Discovered by	regions	$n_2 \rightarrow n_1$	Number of lines
lyman	lyman	U.V. region	$n_2 = 2, 3, 4 \dots / n_1 = 1$	$n_2 - 1$
Balmer	Balmer	Visible region	$n_2 = 3, 4, 5 \dots / n_1 = 2$	$n_2 - 2$
Paschen	Paschen	Infra red (I.R.)	$n_2 = 4, 5, 6 \dots / n_1 = 3$	$n_2 - 3$
Bracket	Bracket	I.R. region	$n_2 = 5, 6, 7 \dots / n_1 = 4$	$n_2 - 4$
Pfund	Pfund	I.R. region	$n_2 = 6, 7, 8 \dots / n_1 = 5$	$n_2 - 5$
Humphery	Humphery	far I.R. region	$n_2 = 7, 8, 9 \dots / n_1 = 6$	$n_2 - 6$

❑ QUESTIONS BASED ON SPECTRUM

Ex. In a hydrogen spectrum if electron moves from 7 to 1 orbit by transition in multi steps then find out the total number of lines in the spectrum.

Sol.

Lyman	=	$(n_1 - 1) = 7 - 1 = 6$
Balmer	=	$(n_2 - 2) = 7 - 2 = 5$
Paschen	=	$(n_2 - 3) = 7 - 3 = 4$
Bracket	=	$(n_2 - 4) = 7 - 4 = 3$
Pfund	=	$(n_2 - 5) = 7 - 5 = 2$
Humphrey	=	$(n_2 - 6) = 7 - 6 = 1$
Total	=	21

Total number of lines can be calculated as follows :

$$\text{Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(7 - 1)(6 + 1)}{2} = \frac{42}{2} = 21$$

Ex. In a hydrogen spectrum if electron moves from 6th to 2nd by transition in multi steps then find out the number of lines in spectrum

Sol.

Total number of line	=	$4 + 3 + 2 + 1 + 0$
	=	10

$$\text{Total number of lines} = \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 2)(4 + 1)}{2} \Rightarrow \frac{4 \times 5}{2} = 10$$

Ex. In a hydrogen spectrum if electron moves from 6th to 3rd orbit by transition in multi steps then find out the following steps :

- (a) Total number of lines in spectrum (b) Total number of lines in U.V. region
(c) Total number of lines in visible region (d) Total number of lines in IR region

Sol. (a) Calculation of total number of lines :

$$= \frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6 - 3)[(6 - 3) + 1]}{2} = \frac{3 \times 4}{2} = 6$$

(b) Calculation of number lines present in U.V. region.

e^- moves from 6th to 3rd orbit in multisteps.

For U.V. region, e^- should be comes into 1st shell. So the number of lines in U.V. region zero.

(c) Calculation of total number of lines in visible region.

For visible region, e^- should be comes into 2nd shell, so the number of lines in visible region zero.

(d) Calculation of total number of lines in I.R. region.

In I.R. region, Paschen, Bracket and Pfund series are present.

$$\begin{aligned} \text{Number of lines in Paschen series} &= n_2 - 3 \\ &= 6 - 3 \\ &= 3 \end{aligned}$$

$$\begin{aligned} \text{Number of lines in Bracket series} &= n_2 - 4 \\ &= 6 - 4 \\ &= 2 \end{aligned}$$

$$\begin{aligned} \text{Number of lines in Pfund series} &= n_2 - 5 \\ &= 6 - 5 \\ &= 1 \end{aligned}$$

$$\text{So total number of lines} = 3 + 2 + 1 = 6$$

Ex. In Balmer series of H atom/spectrum, which electronic transitions represents 3rd line ?

Sol. In Balmer series

$$\begin{aligned} 3^{\text{rd}} \text{ to } 2^{\text{nd}} &\rightarrow 1 \text{ line} \\ 4^{\text{th}} \text{ to } 2^{\text{nd}} &\rightarrow 2 \text{ line} \\ 5^{\text{th}} \text{ to } 2^{\text{nd}} &\rightarrow 3 \text{ line} \\ \text{Infinite to } 2^{\text{nd}} &\rightarrow \text{Last line or limiting line} \end{aligned}$$

$$\text{So, Ans is } 5^{\text{th}} \text{ to } 2^{\text{nd}} \text{ line } \rightarrow 3^{\text{rd}} \text{ line}$$

Ex. In H atom if e^- moves, from n^{th} orbit to 1st orbit by transition in multi steps, if there are total number of lines in spectrum are 10 then find out the value of n.

Sol. Total number of lines = $\frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2}$

$$\text{So, } 10 = \frac{(n_2 - n_1)(n_2)}{2}$$

$$n_2^2 - n_2 - 20 = 0$$

$$n_2^2 - 5n_2 + 4n_2 - 20 = 0$$

$$n_2(n_2 - 5) + 4(n_2 - 5) = 0$$

$$(n_2 + 4)(n_2 - 5) = 0$$

$$n_2 = 5$$

Ex. Calculate the wavelength of 1st line of Balmer series in Hydrogen spectrum.

Sol. For first line of Balmer series

$$n_1 = 2, n_2 = 3$$

$$\begin{aligned}\frac{1}{\lambda} &= R(1)^2 \left[\frac{1}{4} - \frac{1}{9} \right] \Rightarrow \frac{1}{\lambda} = R \left[\frac{9-4}{36} \right] \Rightarrow \frac{1}{\lambda} = R \left[\frac{5}{36} \right] \\ &= \lambda = \frac{36}{5R} \Rightarrow \lambda = \frac{36}{5} \times \frac{1}{R} = \frac{36}{5} \times 912 \text{ Å} \\ &= 6566.4 \text{ Å}\end{aligned}$$

Ex. Calculate the frequency of the last line of the lyman series in hydrogen spectrum.

Sol. For last line of Lyman series $n_1 = 1$, $n_2 = \infty$

$$\begin{aligned}\frac{1}{\lambda} &= RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ \frac{1}{\lambda} &= R \left(\frac{1}{1} - 0 \right) \\ \frac{1}{\lambda} &= R \\ \frac{1}{\lambda} &= 109700 \text{ cm}^{-1} \\ \nu &= \frac{C}{\lambda} \\ &= C \times \frac{1}{\lambda} \\ &= C \times R \\ &= 3 \times 10^8 \text{ m sec}^{-1} \times 109700 \text{ cm}^{-1} \\ &= 3 \times 10^{10} \text{ cm sec}^{-1} \times 109700 \text{ cm}^{-1} \\ &= 3.29 \times 10^{15} \text{ sec}^{-1}\end{aligned}$$

Ex. Calculate wavelength of 3rd line of Bracket series in hydrogen spectrum.

Sol. For 3rd line of Bracket series $n_1 = 4$, $n_2 = 7$

$$\begin{aligned}\frac{1}{\lambda} &= RZ^2 \left[\frac{1}{(4)^2} - \frac{1}{(7)^2} \right] \\ \frac{1}{\lambda} &= R \left[\frac{1}{16} - \frac{1}{49} \right] \\ \frac{1}{\lambda} &= R \left[\frac{49-16}{16 \times 49} \right] \\ \frac{1}{\lambda} &= R \frac{33}{784} \\ \frac{1}{\lambda} &= \frac{33R}{784}\end{aligned}$$

Therefore, $\lambda = \frac{784}{33R} \Rightarrow \frac{784}{33} \times 912 = 21666 \text{ Å}$

Ex. What will be the shortest and longest wavelength of absorption lines of hydrogen gas containing atoms in ground state ? Give $Z = 1$, $R = 109737.5$

Sol.
$$\frac{1}{\lambda} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

For shortest wavelength ΔE should be maximum for that $n_1 = 1$, $n_2 = \infty$

$$\frac{1}{\lambda} = 109737.5 \text{ cm}^{-1} \quad 1 \left[\frac{1}{1^2} - \frac{1}{\infty} \right] = 109737.5 \text{ cm}^{-1}$$

$$\lambda = 911 \quad 10^{-8} \text{ cm}$$

For largest wavelength ΔE should be minimum so $n_1 = 1$, $n_2 = 2$

$$\frac{1}{\lambda} = 109737.5 \text{ cm}^{-1} \quad \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$\lambda = 1215 \text{ \AA}$$

Ex. A series of lines in the spectrum of atomic hydrogen lies at wavelengths 656.46, 482.7, 434.17, 410.29 nm. What is the wavelength of next line in this series.

Sol. The give series of lines are in the visible region and thus appears to be Balmer series

Therefore, $n_1 = 2$ and $n_2 = ?$ for next line

If $\lambda = 410.29 \quad 10^{-7} \text{ cm}$ and $n_1 = 2$

n_2 may be calculated for the last line

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{410.29 \times 10^{-7}} = 109737 \left[\frac{1}{2^2} - \frac{1}{n_2^2} \right]$$

$$n_2 = 6$$

Thus next line will be obtained during the jump of electron from 7th to 2nd shell, i.e.

$$\frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{7^2} \right] = 109737 \left[\frac{1}{4} - \frac{1}{49} \right]$$

$$\lambda = 397.2 \quad 10^{-7} \text{ cm} = 397.2 \text{ nm}$$

Ex. The wave number of 1st line of Balmer series of hydrogen spectrum is 15200 cm^{-1} . The wave number of 1st line of Balmer series of Li^{+2} spectrum will be ?

Sol. Wave number of 1st line of Balmer series of hydrogen spectrum.

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

or
$$\bar{\nu} = Z^2 \times R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{for H, } Z = 1$$

$$\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 15200 \text{ cm}^{-1}$$

Wave number of 1st line of Balmer series of Li^{+2} ion is.

$$\bar{\nu} = Z^2 \times R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \{ \because Z = 3 \text{ for } \text{Li}^{+2} \}$$

$$\therefore \bar{\nu} = 3^2 \times 15200 = 9 \times 15200 = 136800 \text{ cm}^{-1}$$

Ex. Calculate the ratio of maximum λ of Lyman & Balmer series ?

Sol. $E \propto \nu \propto \frac{1}{\lambda}$

$$\frac{\text{Maximum } \lambda \text{ of Lyman series}}{\text{Maximum } \lambda \text{ of Balmer series}} = \frac{1^{\text{st}} \text{ line of Lyman series}}{1^{\text{st}} \text{ line of Balmer series}}$$

$$\frac{\text{Lyman}}{\text{Balmer}} = \frac{\frac{1}{\lambda_L}}{\frac{1}{\lambda_B}} \Rightarrow \frac{R \left[\frac{1}{1^2} - \frac{1}{2^2} \right]}{R \left[\frac{1}{2^2} - \frac{1}{3^2} \right]}$$

$$= \frac{R \left[\frac{1}{1} - \frac{1}{4} \right]}{R \left[\frac{1}{4} - \frac{1}{9} \right]} = \frac{R \left[\frac{3}{4} \right]}{R \left[\frac{5}{36} \right]}$$

$$\frac{\lambda_B}{\lambda_L} = \frac{27}{5} \Rightarrow \frac{\lambda_L}{\lambda_B} = \frac{5}{27}$$

Ex. A certain electronic transition from an excited state to ground state of the Hydrogen atom in one or more steps gives rise of 5 lines in the ultra violet region of the spectrum. How many lines does this transition produce in the infra red region of the spectrum?

Sol. (Lyman Series) ultra violet region : 5 Lines i.e. e^- is coming from 6th to 1st Orbit

$$n_2 - 1 = 5 \quad n_2 = 6$$

Infrared region line

(i) Paschen series = $(6 - 3) = 3$

(ii) Bracket = $(6 - 4) = 2$

(iii) Pfund = $(6 - 5) = 1$

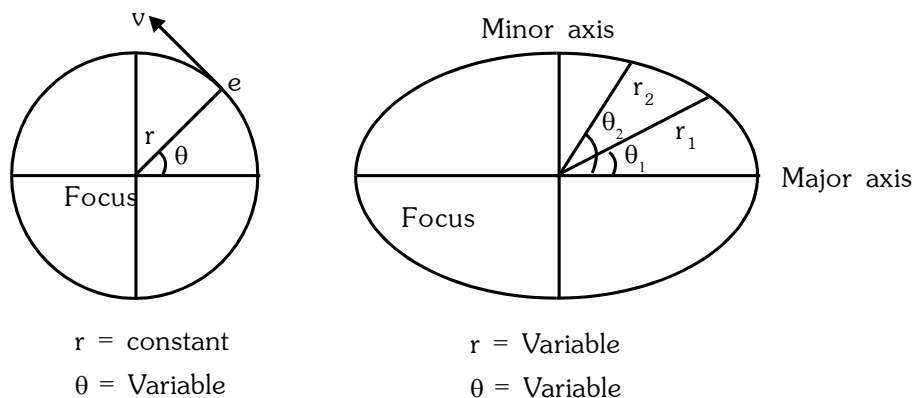
Total Number of lines are = 6

◆ **Limitation of the Bohr's model :**

- Bohr's theory does not explain the spectrum of multi electron atom.
- Why the Angular momentum of the revolving electron is equal to $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.
- Bohr interrelate quantum theory of radiation and classical law of physics with out any theoretical explanation. This was the biggest drawback of this model.
- Bohr's theory does not explain the fine structure of the spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by spectroscope of more resolution power.
- Bohr theory does not explain the splitting of spectral lines in the presence of magnetic field (**Zemman's effect**) or electric field (**Stark's effect**)

❑ SOMMERFELD EXTENSION OF THE BOHR'S MODEL

- ◆ According to sommerfeld electron revolve around the nucleus in the Elliptical Orbits.
- ◆ Circular orbit is a special case of elliptical orbit when the length of major axis becomes equal to the length of minor axis then the shape of orbit will be circular.



- ◆ If electrons revolve in elliptical orbit then its angular momentum shows two components

1. Radial component :

$$J_r = \frac{n_r h}{2\pi}$$

where n_r = radial quantum number.

$$[n_r = (n - 1) \dots \dots \dots 0]$$

n = Shell number

2. Azimuthal Components:

$$J_\phi = n_\phi \frac{h}{2\pi}$$

n_ϕ = Azimuthal quantum number

$$[n_\phi = 1, 2, 3, 4 \dots \dots \dots n]$$

n = Shell number

So total Angular momentum = J_n

$$J_n = J_r + J_\phi$$

$$\frac{nh}{2\pi} = \frac{n_r h}{2\pi} + n_\phi \frac{h}{2\pi}$$

$$n = n_r + n_\phi \text{ where } n = \text{principal quantum number}$$

Ex. Let $n = 4$

Then

$$n = n_r + n_\phi$$

$$4 = 3 + 1$$

$$4 = 2 + 2$$

$$4 = 1 + 3$$

$$4 = 0 + 4$$

- ◆ The length of major axis indicates by $n_r + n_\phi$ i.e. n and length of minor axis indicates by n_ϕ
- ◆ The path of electron

$$K = \frac{n_r + n_\phi}{n_\phi} = \frac{n}{n_\phi} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

- ◆ If $n = 4$ then $n_\phi = 1, 2, 3, 4$

$$K = \frac{4}{1}, \quad \frac{4}{2}, \quad \frac{4}{3}, \quad \frac{4}{4}$$

3 Elliptical path

circular path

◆ If $n = 5$ then $n_\phi = 1, 2, 3, 4, 5$

◆
$$K = \frac{5}{1}, \frac{5}{2}, \frac{5}{3}, \frac{5}{4}, \frac{5}{5}$$

4 Elliptical path Circular path

◆ If $n = 1$ Then Elliptical path = $(n - 1) = (1 - 1) = 0$
 Circular path = 1

In n^{th} orbit : Number of elliptical path = $(n - 1)$

Number of circular path = 1

In every atom, 1st orbit is always circular.

□ THE DUAL NATURE OF MATTER (THE WAVE NATURE OF ELECTRON)

1. In 1924, a French physicist, Louis De Broglie suggested that if the nature of light is both that of a particle and of a wave, then this dual behavior should be true for the matter also.
2. According to De Broglie, the wavelength λ of an electron is inversely proportional to its momentum p .

$$\lambda \propto \frac{1}{p} \quad \text{or} \quad \lambda \propto \frac{1}{mv}$$

$$\lambda = \frac{h}{p} \quad \text{Here } h = \text{Planck's constant}$$

p = momentum of electron

\therefore Momentum (p) = Mass (m) \times Velocity (v)

◆
$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m(\text{K.E.})}}$$

From the de-Broglie equation it follows that wavelength of a particle decrease with increase in velocity of the particle. Moreover, lighter particles would have longer wavelength than heavier particles, provided velocity is equal.

- ◆ If a charged particle Q is accelerated through potential difference V from rest then de-broglie wavelength is

$$\lambda = \frac{h}{\sqrt{2mQV}}$$

- ◆ de-Broglie concept is more significant for microscopic or sub-microscopic particles whose wavelength can be measured.
- ◆ The circumference of the n^{th} orbit is equal to n times the wavelength of the electron.

$$2\pi r_n = n\lambda$$

- ◆ Wavelength of electron is always calculated using De-broglie calculation.

Ex. Two particles X and Y are in motion. If the wavelength associated with particle X is $4 \times 10^{-8} \text{ m}$, calculate the wavelength associated with particle Y if its momentum is half of X.

Sol. According to de Broglie equation

$$\lambda_x = \frac{h}{p_x} \text{ and } \lambda_y = \frac{h}{p_y}$$

$$\frac{\lambda_x}{\lambda_y} = \frac{p_y}{p_x}$$

But $p_y = \frac{1}{2} p_x$ (given)

$$\frac{\lambda_x}{\lambda_y} = \frac{1/2 p_x}{p_x} = \frac{1}{2}$$

$$\lambda_B = 2\lambda_A = 2 \times 4 \times 10^{-8} \text{ m} = 8 \times 10^{-8} \text{ m}$$

Ex. Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of 30 ms⁻¹.

Sol. $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.1 \times 30}$

$$\lambda = 2.2 \times 10^{-34} \text{ m}$$

This is apparent that this wavelength is too small for ordinary observation.

Although the de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles.

Since, we come across macroscopic objects in our everyday life, de Broglie relationship has no significance in everyday life.

❑ HEISENBERG UNCERTAINTY PRINCIPLE

Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave is extending throughout a region of space.

In 1927, Werner Heisenberg presented a principle known as Heisenberg uncertainty principle which states as : "It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron."

The uncertainty of measurement of position, Δx , and the uncertainty of momentum Δp or $m\Delta v$, are related by Heisenberg's relationship as : ($p = mv$, $\Delta p = m\Delta v$)

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot m\Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

where h is Planck's constant.

$\Delta x \Delta v$ = uncertainty product

For an electron of mass m (9.10×10^{-28} g), the product of uncertainty is quite large.

$$\begin{aligned} \Delta x \cdot \Delta v &\geq \frac{6.624 \times 10^{-27}}{4\pi m} \\ &\geq \frac{6.624 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}} \\ &= 0.57 \text{ erg sec per gram approximately} \end{aligned}$$

When $\Delta x = 0$, $\Delta v = \infty$ and vice-versa.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, i.e., Δx is very small, Δv becomes large and vice-versa.

◆ In terms of uncertainty in energy ΔE , and uncertainty in time Δt , this principle is written as,

$$\boxed{\Delta E \cdot \Delta t \geq \frac{h}{4\pi}}$$

◆ Heisenberg replaced the concept of definite orbits by the concept of probability.

Ex. Why electron cannot exist inside the nucleus according to Heisenberg's uncertainty principle ?

Sol. Diameter of the atomic nucleus is of the order of 10^{-15} m

The maximum uncertainty in the position of electron is 10^{-15} m.

Mass of electron = 9.1×10^{-31} kg.

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

$$\Delta x \cdot (m \cdot \Delta v) = h/4\pi$$

$$\Delta v = \frac{h}{4\pi} \times \frac{1}{\Delta x.m} = \frac{6.63 \times 10^{-34}}{4 \times \frac{22}{7}} \times \frac{1}{10^{-15} \times 9.1 \times 10^{-31}}$$

$$\Delta v = 5.80 \times 10^{10} \text{ ms}^{-1}$$

This value is much higher than the velocity of light and hence not possible.

□ DE BROGLIE RELATIONSHIP & HEISENBERG'S UNCERTAINTY PRINCIPLE

Ex. The mass of a particle is 1 mg and its velocity is 4.5×10^5 cm per second. What should be the wavelength of this particle if $h = 6.652 \times 10^{-27}$ erg second.

(1) 1.4722×10^{-24} cm (2) 1.4722×10^{-29} cm (3) 1.4722×10^{-32} cm (4) 1.4722×10^{-34} cm

Sol. Given that

$$m = 1 \text{ mg} = 1 \times 10^{-3} \text{ g}$$

$$c = 4.5 \times 10^5 \text{ cm/sec.}$$

$$h = 6.652 \times 10^{-27} \text{ erg sec.}$$

$$\therefore \lambda = \frac{h}{mc} = \frac{6.652 \times 10^{-27}}{1 \times 10^{-3} \times 4.5 \times 10^5} = \frac{6.652 \times 10^{-29}}{4.5} \text{ cm} = 1.4722 \times 10^{-29} \text{ cm}$$

Ex. Which of the following should be the wavelength of an electron if its mass is 9.1×10^{-31} kg and its velocity is $1/10$ of that of light and the value of h is 6.6252×10^{-34} joule second?

(1) 2.446×10^{-7} metre (2) 2.246×10^{-9} metre (3) 2.246×10^{-11} metre (4) 2.246×10^{-13} metre

Sol. Given that

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$c = \frac{1}{10} \text{ of velocity of light}$$

$$\text{or } c = \frac{1}{10} \times 3 \times 10^8 \text{ metre/second i.e. } 3 \times 10^7 \text{ metre/second}$$

$$h = 6.6252 \times 10^{-34} \text{ joule second}$$

$$\lambda = \frac{h}{mc} = \frac{6.6252 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^7} = \frac{6.6252 \times 10^{-34}}{27.3 \times 10^{-24}}$$

$$\text{or } 0.2426 \times 10^{-10} \text{ metre}$$

$$\text{or } 2.426 \times 10^{-11} \text{ metre}$$

Ex. What should be the momentum (in gram cm per second) of a particle if its De Broglie wavelength is 1 \AA and the value of h is 6.6252×10^{-27} erg second ?

$$(1) 6.6252 \times 10^{-19}$$

$$(2) 6.6252 \times 10^{-21}$$

$$(3) 6.6252 \times 10^{-24}$$

$$(4) 6.6252 \times 10^{-27}$$

Sol. Given that

$$\lambda = 1 \text{ \AA} = 1 \times 10^{-8} \text{ cm}$$

$$h = 6.6252 \times 10^{-27} \text{ erg second}$$

$$\text{or } p = \frac{6.6252 \times 10^{-27}}{1 \times 10^{-8}} = 6.6252 \times 10^{-19} \text{ gram cm/sec.}$$

Ex. What should be the mass of the sodium photon if its wavelength is 5894\AA , the velocity of light is 3×10^8 metre/second and the value of h is $6.6252 \times 10^{-34} \text{ kg m}^2/\text{sec}.$

- (1) 3.746×10^{-26} (2) 3.746×10^{-30} (3) 3.746×10^{-34} (4) 3.746×10^{-36}

Sol. $\lambda = \frac{h}{m \times c} \Rightarrow m = \frac{h}{c\lambda}$
 $(\because \lambda = 5894\text{\AA} = 5894 \times 10^{-10} \text{ m})$

$$m = \frac{6.652 \times 10^{-34}}{3 \times 10^8 \times 5894 \times 10^{-10}} \text{ or } \frac{6.652}{17682} \times 10^{-32} = 0.0003746 \times 10^{-32}$$

$$\text{or } 3.746 \times 10^{-36} \text{ kg}$$

Ex. What should be the uncertainty in the velocity of an electron if the uncertainty in its position is 0.005 nm , the mass of electron is $9.109 \times 10^{-31} \text{ kg}$ and the value of h is $6.6252 \times 10^{-34} \text{ joule/second}.$

- (1) 2.316×10^5 (2) 1.158×10^7 (3) 2.316×10^9 (4) 2.316×10^{11}

Sol. Uncertainty in position $(\Delta x) = 0.005 \text{ nm} = 0.005 \times 10^{-9} \text{ m}$
 $= 5 \times 10^{-12} \text{ m}$

Mass of electron $(m) = 9.109 \times 10^{-31} \text{ kg}.$

$$\therefore \Delta v = \frac{h}{4\pi m \times \Delta x} = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 5 \times 10^{-12} \times 9.109 \times 10^{-31}} \text{ m/sec.}$$

$$\text{or } \Delta v = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 5 \times 9.109 \times 10^{-43}}$$

$$\therefore \Delta v = 1.15816 \times 10^7 \text{ m/sec.}$$

Ex. What should be the uncertainty in velocity of a particle of 1 kg mass if uncertainty in position is 1\AA and the value of h is $6.6252 \times 10^{-34} \text{ Joule sec}.$

- (1) 1.055×10^{-22} (2) 1.055×10^{22} (3) 5.25×10^{-25} (4) 1.055×10^{24}

Sol. Given that

$$\Delta x = 1\text{\AA} = 1 \times 10^{-10} \text{ m}$$

$$m = 1 \text{ kg}$$

$$h = 6.6252 \times 10^{-34} \text{ Joule sec.}$$

$$\Delta v = \frac{h}{4\pi \times m \times \Delta x} = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 1 \times 10^{-10}}$$

$$\text{or } \Delta v = \frac{6.6252 \times 10^{-34}}{12.56 \times 10^{-10}} \text{ m/sec.}$$

$$= 0.52525 \times 10^{-24} \text{ m/sec.}$$

$$= 5.25 \times 10^{-25} \text{ m/sec.}$$

Ex. What should be the uncertainty in position if uncertainty in momentum is $1 \times 10^{-2} \text{ g cm/sec.}$ and value of h is $6.6252 \times 10^{-34} \text{ Joule sec.}$?

- (1) $1.054 \times 10^{-22} \text{ m}$ (2) $1.054 \times 10^{-25} \text{ m}$
 (3) $0.525 \times 10^{-27} \text{ m}$ (4) $1.054 \times 10^{-32} \text{ m}$

Sol. Given that

$$\Delta p = 1 \times 10^{-2} \text{ g cm/sec.} = 1 \times 10^{-7} \text{ kg m/sec.}$$

$$h = 6.6252 \times 10^{-34} \text{ Joule sec.}$$

$$\Delta x \times \Delta p = \frac{h}{4\pi} \quad \therefore \Delta x = \frac{h}{4\pi \times \Delta p}$$

$$\text{or} \quad \Delta x = \frac{6.6252 \times 10^{-34}}{4 \times 3.14 \times 10^{-7}} = 0.525 \times 10^{-27} \text{ m}$$

Ex. A ball weighs 25 g moves with a velocity of 6.6×10^4 cm/sec then find out the De Broglie λ associated with it.

$$\begin{aligned} \text{Sol. } \lambda &= \frac{h}{mv} \\ &= \frac{6.6 \times 10^{-34} \times 10^7}{25 \times 6.6 \times 10^4 \text{ cm/sec}} \text{ erg sec} = 1 \times \frac{10^{-38}}{25} \\ &= 0.04 \times 10^{-38} \times 10^7 \\ &= 0.04 \times 10^{-31} \text{ cm} \\ &= 4 \times 10^{-33} \text{ cm} \end{aligned}$$

Ex. Which of the following has least De Broglie λ if they have same velocity.

1. e^- 2. p 3. CO_2 4. SO_2

$$\begin{aligned} \text{Sol. } \lambda &= \frac{h}{mv} \\ \therefore \text{mass of } \text{SO}_2 &\text{ is greater than the mass of } e^-, p, \text{CO}_2 \\ &= h \text{ constant} \\ &= v \text{ Same} \\ \therefore \text{least } \lambda &\text{ will be } \text{SO}_2 \\ \therefore \lambda &\propto \frac{1}{m} \end{aligned}$$

Ex. If uncertainty in position of an e^- is same as the Δx of He atom. If Δp of e^- is 32×10^5 then find Δp in He atom.

$$\text{Sol. } \Delta x \times \Delta p = \frac{h}{4\pi}$$

Since Δx is same for both.

therefore Δp will be same by

$$\frac{\Delta x_e \times \Delta p_e \geq \frac{h}{4\pi}}{\Delta x_{(\text{He})} \times \Delta P_{\text{He}} \geq \frac{h}{4\pi}} = \frac{\Delta P_e}{\Delta P_{\text{He}}} = 1$$

$$\therefore \Delta P_e = \Delta P_{\text{He}}$$

$$32 \times 10^5 = 32 \times 10^5$$

$$\Delta P_{\text{He}} = 32 \times 10^5$$

Ex. Calculate the uncertainty in the position of a particle when the uncertainty in momentum is
(a) $1 \times 10^{-3} \text{ g cm sec}^{-1}$ (b) Zero.

Sol. Given

$$\Delta p = 1 \times 10^{-3} \text{ g cm sec}^{-1}$$

$$h = 6.62 \times 10^{-27} \text{ erg sec.}$$

$$\pi = 3.142$$

According to uncertainty principle

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

So,

$$\Delta x \geq \frac{h}{4\pi} \cdot \frac{1}{\Delta p}$$

$$\geq \frac{6.62 \times 10^{-27}}{4 \times 3.142} \times \frac{1}{10^{-3}}$$

$$= 0.527 \times 10^{-24} \text{ cm}$$

(b) When the value of $\Delta p = 0$, the value of Δx will be infinity.

Ex. The uncertainty in position and velocity of a particle are 10^{-10} m and $5.27 \times 10^{-24} \text{ ms}^{-1}$ respectively. Calculate the mass of the particle ($h = 6.625 \times 10^{-34} \text{ Joule Sec.}$)

Sol. According to Heisenberg's uncertainty principle,

$$\Delta x \cdot m \Delta v = \frac{h}{4\pi} \quad \text{or} \quad m = \frac{h}{4\pi \Delta x \cdot \Delta v}$$

$$= \frac{6.625 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 5.27 \times 10^{-24}}$$

$$= 0.099 \text{ kg}$$

Ex. Calculate the uncertainty in velocity of a cricket ball of mass 150 g if the uncertainty in its position is of the order of 1 \AA ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$).

Sol. $\Delta x \cdot m \Delta v = \frac{h}{4\pi}$

$$\Delta v = \frac{h}{4\pi \Delta x \cdot m}$$

$$= \frac{6.6 \times 10^{-34}}{4 \times 3.143 \times 10^{-10} \times 0.150}$$

$$= 3.499 \times 10^{-24} \text{ ms}^{-1}$$



QUANTUM NUMBERS :

The set of four integers required to define an electron completely in an atom are called quantum numbers. The first three have been derived from Schrodinger wave equation.

(i) **Principle quantum number (n) :**

It describes the size of the electron wave and the total energy of the electron. It has integral values $1, 2, 3, 4, \dots$, etc, and is denoted by K, L, M, N, ..., etc.

The maximum number of electrons which can be present in a principal energy shell is equal to $2n^2$. No energy shell in the atoms of known elements possesses more than 32 electrons.

(ii) **Azimuthal quantum number (ℓ) :**

It describes the shape of electron cloud and the number of subshells in a shell. It can have values from 0 to $(n - 1)$, i.e., $\ell = 0$ (s-subshell), $\ell = 1$ (p-subshell), $\ell = 2$ (d-subshell), $\ell = 3$ (f-subshell).

(iii) **Magnetic quantum number (m) :**

It describes the orientations of the subshells. It can have values from $-\ell$ to $+\ell$ including zero, i.e., total $(2\ell + 1)$ values. Each value corresponds to an orbital. s-subshell has one orbital, p-subshell three orbitals (p_x , p_y and p_z), d-subshell five orbitals (d_{xy} , d_{yz} , d_{zx} , $d_{x^2 - y^2}$, d_{z^2}) and f-subshell has seven orbitals. The total number of orbitals present in a main energy level is ' n^2 '.

(iv) **Spin quantum number (s) :**

It describes the spin of the electron. It has values $+1/2$ and $-1/2$. (+) signifies clockwise spinning and (-) signifies anticlockwise spinning.

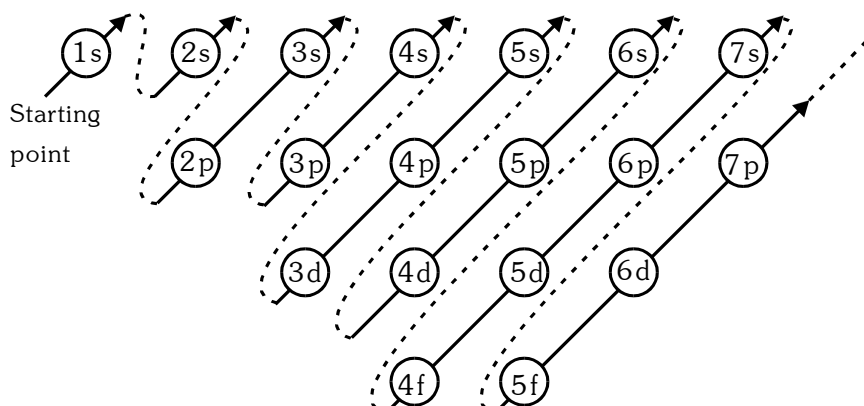
❑ **RULES FOR FILLING OF ORBITALS**

1. **Aufbau Principle :**

Aufbau is a German word and its meaning 'Building up'

Aufbau principle gives a sequence in which various subshell are filled up depending on the relative order of the Energies of various subshell.

- ◆ Principle : The subshell with minimum energy is filled up first and when this subshell obtained maximum quota of electrons then the next subshell of higher energy starts filling.
- ◆ The sequence in which various subshell are filled is the following.



$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, 7p^6$

2. **(n + ℓ) rule :**

According to it the sequence in which various subshell are filled up can also be determined with the help of (n + ℓ) value for a given subshell.

❑ **PRINCIPLE OF (n + ℓ) RULE :**

The subshell with lowest (n + ℓ) value is filled up first, when two or more subshell have same (n+ℓ) value then the subshell with lowest value of n is filled up first.

Sub Shell	n	ℓ	n + ℓ	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	(1)
3s	3	0	3	(2)
3p	3	1	4	(1)
4s	4	0	4	(2)
3d	3	2	5	(1)
4p	4	1	5	(2)
5s	5	0	5	(3)
4d	4	2	6	(1)
5p	5	1	6	(2)
6s	6	0	6	(3)

3. Pauli's Exclusion principle :

In 1925 Pauli stated that no two electron in an atom can have same values of all four quantum numbers.



- ◆ An orbital can accomodates maximum 2 electrons with opposite spin.

4. Hund's Maximum Multiplicity Rule :

(Multiplicity : Many of the same kind)

- ◆ According to Hund's rule electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electron with parallel spin. i.e. in a subshell pairing of electron will not start until and unless all the orbitals of that subshell will get one electron each with same spin.

□ SPIN MULTIPLICITY

It is given by $2S + 1$ where S is the total spin.



For (a), $S = +\frac{1}{2} - \frac{1}{2} = 0$

Spin multiplicity = $2S + 1 = 0 + 1 = 1$ (singlet)

For (b), $S = +\frac{1}{2} + \frac{1}{2} = 1$

Spin multiplicity = $2S + 1 = 2 \times 1 + 1 = 3$ (triplet)

Ex. Find out the angular momentum of an electron in

- (a) 4s orbital (b) 3p orbital (c) 4th orbital

Sol. Angular momentum in an orbital = $\frac{h}{2\pi} \sqrt{\ell(\ell+1)}$

- (a) $\ell = 0$ for 4s orbital, hence orbital angular momentum = 0

- (b) $\ell = 1$ for 3p orbital

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

- (c) Angular momentum in 4th orbit

$= \frac{nh}{2\pi} = \frac{4h}{2\pi} = \frac{2h}{\pi}$

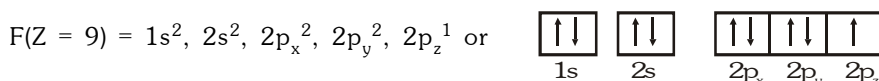
Ex. Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

- (i) $n = 4, \ell = 2, m = 0$ (ii) $n = 3, \ell = 1, m = \pm 1$
 (iii) $n = 4, \ell = 0, m = 0$ (iv) $n = 3, \ell = 2, m = \pm 2$

Sol. (i) 4dz² (ii) 3p_x or 3p_y
 (iii) 4s (iv) 3d_{x²-y²} or 3d_{xy}

□ ELECTRONIC CONFIGURATION OF ELEMENTS

Based on the rules, we can easily determine the electronic configurations of most element. We just need to know the atomic number of an element, the order in which orbitals are to be filled and the maximum number of electrons in a shell, sub-shell or orbital. The configurtion so obtained can be represented in two ways. As an illustration, let us consider fluorine (Z = 9) :



Importance of knowing the exact electronic configuration of an element lies in the fact that the chemical properties of an element are dependent on the behaviour and relative arrangement of its electrons.

Electronic configurations of heavier elements (beyond $Z = 56$) deviate a little from the order mentioned previously. These are listed below :

Lanthanides	La ($Z = 57$)	:	$[\text{Xe}]6s^25d^1$ (not $4f^1$)
	Ce ($Z = 58$)	:	$[\text{Xe}]6s^25d^14f^1$
	Pr ($Z = 59$)	:	$[\text{Xe}]6s^25d^14f^2$
Actinides	Ac ($Z = 89$)	:	$[\text{Rn}]7s^26d^1$ (not $5f^1$)
	Th ($Z = 90$)	:	$[\text{Rn}]7s^26d^15f^1$
	Pa ($Z = 91$)	:	$[\text{Rn}]7s^26d^15f^2$
Beyond $Z = 103$	$Z = 104$:	$[\text{Rn}]5f^{14}6d^27s^2$
	$Z = 105$:	$[\text{Rn}]5f^{14}6d^37s^2$
	$Z = 106$:	$[\text{Rn}]5f^{14}6d^47s^2$
	$Z = 112$:	$[\text{Rn}]5f^{14}6d^{10}7s^2$

❑ EXCEPTIONAL CONFIGURATIONS

Stability of Half Filled and Completely Filled Orbitals

Cu has 29 electrons. its expected electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^9$.

But a shift of one electron from lower energy 4s orbital to higher energy 3d orbital will make the distribution of electron symmetrical and hence will impart more stability.

Thus the electronic configuration of Cu is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, d^{10}$

Fully filled and half filled orbital are more stable.

Ex. We know that fully filled and half filled orbital are more stable. Can you write the electronic configuration of Cr($Z = 24$) ?

Sol. Cr ($Z = 24$)

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$.

Since half filled orbital is more stable, one 4s electron is shifted to 3d orbital.

Ex. A compound of vanadium has a magnetic moment of 1.73 BM work out the electronic configuration of the vanadium in the compound.

Sol. Magnetic moment = $\sqrt{n(n+2)}$

Where n is number of unpaired electrons

$$\therefore 1.73 = \sqrt{n(n+2)} \text{ or } (1.73)^2 = n^2 + 2n, n = 1$$

Vanadium atom must have the unpaired electron and thus its configuration is :

${}_{23}\text{V}^{4+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

❑ WAVE MECHANICAL MODEL OF ATOM

Schrodinger wave equation :

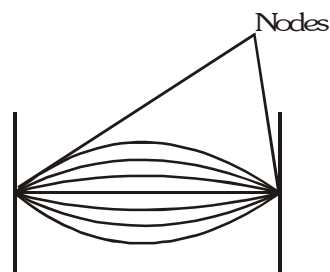
General wave equation

$$y = A \sin \omega t$$

where, y = displacement

A = amplitude

t = time



Developed by Schrodinger, this model is based on the particle and wave nature of electron is known as WAVE MECHANICAL MODEL of atom. The motion of electron around nucleus is round motion and may be considered to be analogous to the STANDING WAVES, the waves which are generated by plucking the stretched string. The amplitude of the standing wave is independent of time and is a function of the distance from one fixed end. The derived eq. by Schrodinger is

$$\text{Schrodinger wave equation} \Rightarrow \boxed{\frac{\delta^2 \psi}{\delta x^2} + \frac{\delta^2 \psi}{\delta y^2} + \frac{\delta^2 \psi}{\delta z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0}$$

where ψ = Amplitude of e^- wave (or wave function)

m = mass of e^-

E = Total energy

V = Potential energy

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

$$\text{where } \nabla^2 = \text{Laplacian operator} = \left(\frac{\delta}{\delta x^2} \right) + \left(\frac{\delta}{\delta y^2} \right) + \left(\frac{\delta}{\delta z^2} \right)$$

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

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

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

\therefore

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

Hemiltonion operator

❑ SCHRODINGER EQUATION IN CARTESIAN COORDINATE :

$$Z = r \cos \theta$$

$$y = r \sin \theta \sin \phi$$

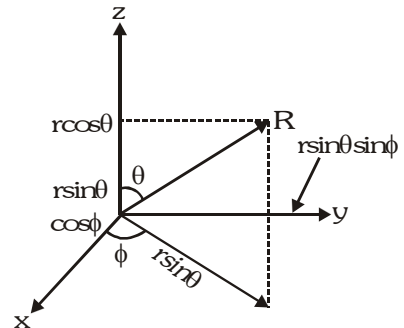
$$x = r \sin \theta \cos \phi$$

The Schrodinger equation can be written in terms of cartesian coordinates (x, y, z) or in terms of spherical polar coordinates (r, θ , ϕ). However for most calculations it is simpler to solve the wave equation in polar coordinates. When Schrodinger wave equation in polar coordinates is solved for hydrogen atom the solution obtained can be factorized into 2 separate parts, one being the function of r and other the function of θ and ϕ .

$$\psi(r, \theta, \phi) = R(r) f(\theta, \phi)$$

$R(r)$ = Radial function

$f(\theta, \phi)$ = Angular function



❑ **SIGNIFICANCE OF (ψ) :**

The wave function may be regarded as amplitude of electron wave expressed in terms of coordinates (x, y, z) or (r, θ , ϕ). The wave function may have +ve or -ve values depending on the values of coordinates. As such there is no physical significance of ψ .

❑ **SIGNIFICANCE OF (ψ)² :**

In classical theory of electromagnetic radiation, the square of amplitude is proportional to the intensity of light. A very similar concept was suggested by MAX BORN in QUANTUM MECHANICS according to which the square of function ψ at any point is proportional to the probability of finding an electron at that point ψ^2 is known as PROBABILITY DENSITY and is always +ve.

The region of space in which there is maximum probability of finding an electron (say 90%) is termed as an orbital.

❑ **QUANTUM NUMBERS :**

In an atom, a large no of orbitals are permissible. These orbitals are designated by a set of 3 numbers known as QUANTUM NUMBERS (principle, azimuthal, magnetic) which arise as a natural consequence in the solution of schrodinger wave equation. These quantum numbers describe energies of electron in an atom, information about shapes and orientation of orbitals. In order to designate the electron an additional quantum number called as SPIN QUANTUM NUMBER is needed to specify spin of the electron.

❑ **GRAPHICAL REPRESENTATION OF ψ :**

ψ = Amplitude of wave

ψ^2 = probability density \rightarrow It gives us probability of finding an electron at a point or per unit volume.

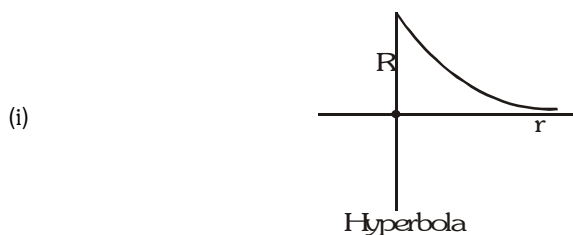
$$\boxed{\text{Probability} = \psi^2 \times dv}$$

$$\psi = \psi(x, y, z) = \psi(r, \theta, \phi)$$

$$\psi = R(r) \sim (\theta, \phi)$$

$$R^2 = \text{radial probability density, } r = \text{radius}$$

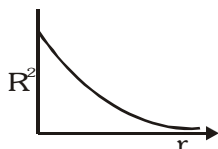
$$R^2 = \text{radial probability density of finding an electron at a distance } R \text{ from the nucleus in any direction.}$$



$$\boxed{R(r)_{1s} = 2 \left(\frac{1}{a_0} \right) e^{-\frac{\sigma}{2}}} \quad \text{where } \sigma = \frac{2r}{na_0}$$

$$a_0 = 0.529 \text{ \AA} \quad n = \text{principal quantum number}$$

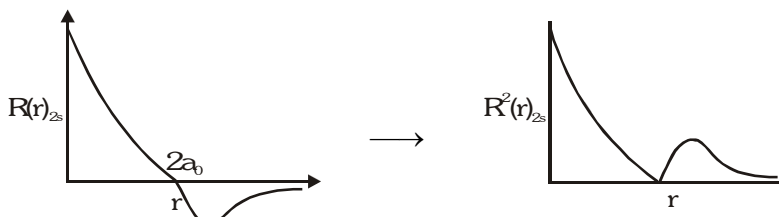
$$R(r)_{1s} = 2 \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$$



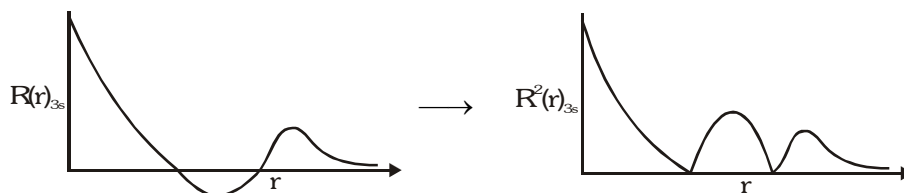
Graph between R^2 and r will be same hyperbolic.

(ii)
$$R(r)_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} (2 - \sigma) e^{-\frac{\sigma}{2}}$$

After reaching $2a_0$ now curve would start decreasing and again goes up to cut at ∞ .



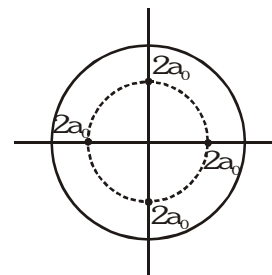
(iii) $R(r)_{3s}$ vs r



❑ **RADIAL NODES** : Points at which the probability of finding an electron is zero is known as radial nodes.

No. of radial nodes = $n - \ell - 1$

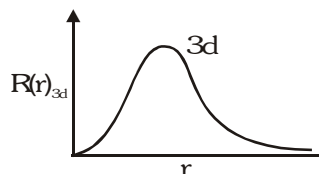
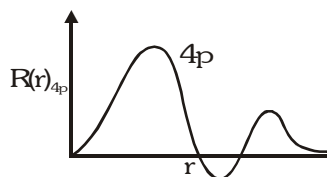
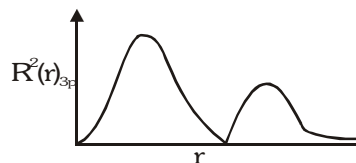
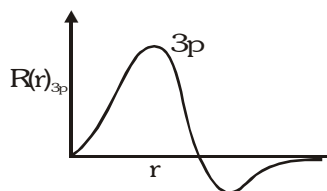
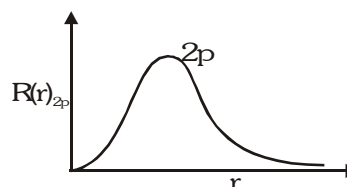
Electron cannot be present at $2a_0$ distance from nucleus. If we join all $2a_0$ points to form a sphere, we can say that electron cannot be present on surface of sphere, however it may be present inside or outside. At $2a_0$ distance probability of presence of electron is zero. Since a sphere is formed radial nodes are also called SPHERICAL NODES.



Radial nodes are spherical in shape also known as spherical nodes or nodal sphere.

❑ **GRAPHS FOR P-ORBITALS** :

$$R(r)_{2p} = \frac{1}{2\sqrt{6}} \left(\frac{1}{a_0} \right)^{\frac{3}{2}} \sigma e^{-\frac{\sigma}{2}}$$



❑ RADIAL PROBABILITY DISTRIBUTION FUNCTION :

dr is very very less

$$\text{volume} = \frac{4}{3} \pi ((r + dr)^3 - r^3) \text{ shell}$$

$$= \frac{4}{3} \pi (r^3 + 3r^2 dr + 3r dr^2 + dr^3 - r^3)$$

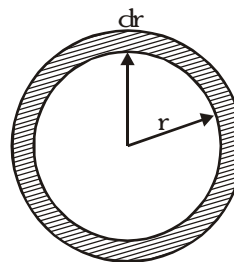
dr^2 and dr^3 are neglected

$$= \frac{4}{3} \pi (3r^2 dr) = 4\pi r^2 dr$$

Radial probability in given shell = $4\pi r^2 dR^2$

Radial probability function = $4\pi r^2 R^2$

The probability of finding an electron at a distance r from the nucleus in all the direction is called radial probability function (RPF).



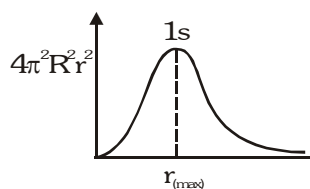
❑ GRAPHS BETWEEN RPF AND r :

$$R(r)_{1s} = C e^{-\frac{r}{a_0}}$$

$$4\pi r^2 R^2 = 4\pi r^2 C^2 e^{-\frac{2r}{a_0}}$$

$$= C' r^2 e^{-\frac{2r}{a_0}}$$

$$4\pi r^2 R^2 = C' r^2 e^{-\frac{2r}{a_0}}$$



For s-orbital, R and R^2 at nucleus is not zero but probability is almost equal to zero because of very small size.

$$R^2 dv \approx 0 \quad \text{as } dv \approx 0 \text{ for nucleus}$$

$r_{\text{max}} \rightarrow$ distance at which the probability of finding an electron is max.

$$\boxed{P = 4\pi R_{1s}^2 r^2} \quad \boxed{R_{1s} = 2 \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{r}{a_0}}}$$

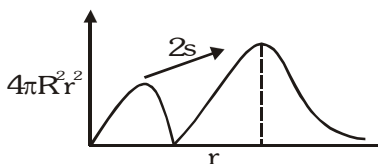
now differentiate eq. by putting value of R_{1s}

$$P = 4\pi r^2 \quad 4 \left(\frac{1}{a_0} \right)^3 e^{-\frac{2r}{a_0}}$$

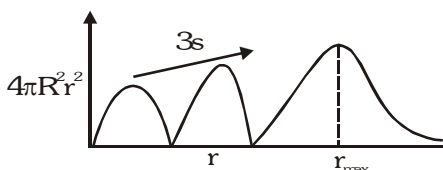
$$P = C r^2 e^{-\frac{2r}{a_0}} \quad \frac{dP}{dr} = C(2r e^{-\frac{2r}{a_0}} + r^2 e^{-\frac{2r}{a_0}})$$

$$\frac{dP}{dr} = C r e^{-\frac{2r}{a_0}} + \left(2 - \frac{2r}{a_0} \right) = 0$$

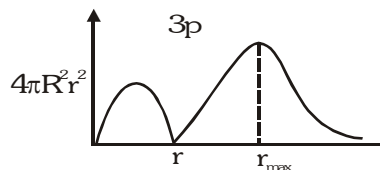
$$\therefore \boxed{r = a_0} \text{ Maxima}$$



Peaks of the curves are increasing



Here 1st peak is smaller than 2nd and 2nd smaller than 3rd.



ANTINODE POINT - Point at which probability of finding an electron is max.

❑ COMPARISON OF r_{\max} & r_{avg} FOR DIFFERENT ORBITALS :

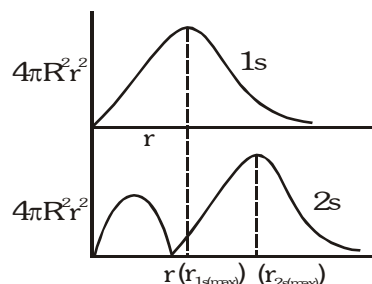
Note : r_{avg} is always greater than r_{\max}

Case I - when ℓ is same but n is different.

As value of n increases r_{\max} increases.

Peaks are numbered according to value of $(n - \ell)$.

As n increases r_{avg} increases if r_{avg} is more, electron will be more away from nucleus.



❑ PENETRATION POWER : Penetration power of orbital is a measure of its closeness to the nucleus.

$$1s > 2s > 3s$$

Case II - When ' n ' is same but ' ℓ ' different.

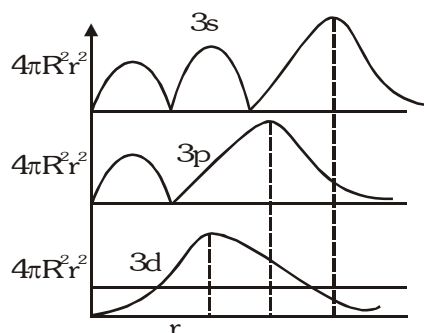
As value of ' ℓ ' increases, r_{avg} increases

As value of ' ℓ ' increases, r_{\max} decreases

$$\ell \uparrow \quad r_{\max} \downarrow$$

$$\ell \uparrow \quad r_{\text{avg}} \uparrow$$

Closeness to nucleus - $3s > 3p > 3d$



❑ ENERGY COMPARISON :

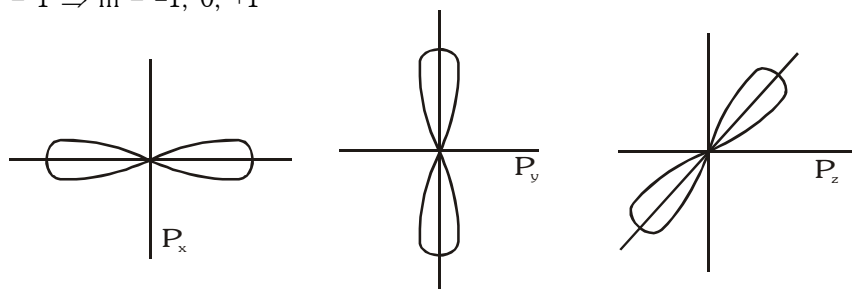
For energy comparison Aufbau rule should be used. But for hydrogen atom, subshell belonging to particular shell possess equal energy.

$$2p = 2s, 3s = 3p = 3d$$

❑ ANGULAR FUNCTION :

It gives us an idea about the shape, orientation of an orbital

eg. $\ell = 1 \Rightarrow m = -1, 0, +1$



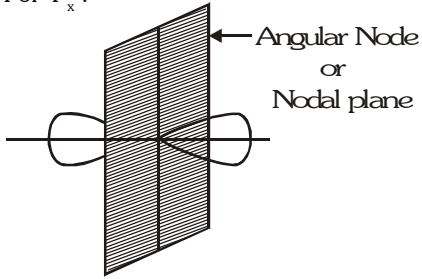
For s orbital, angular part is independent of θ and ϕ .

\therefore There would be zero angular nodes for s -orbital.

No. of angular nodes for any orbital = ℓ

❑ SHAPE OF ANGULAR NODE :

For P_x :



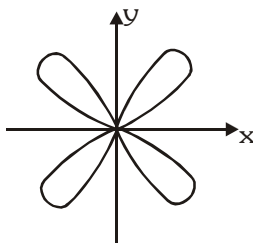
Angular node or nodal plane

∴ $P_x \rightarrow yz$ plane

$P_y \rightarrow xz$ plane

$P_z \rightarrow xy$ plane

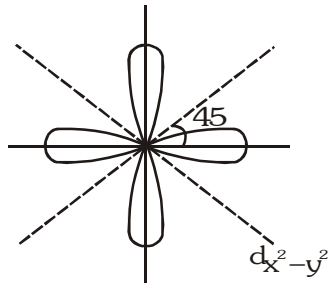
For d_{xy} :



∴ $d_{xy} \rightarrow xz$ and yz

$d_{yz} \rightarrow xz$ and xy

$d_{zx} \rightarrow xy$ and yz

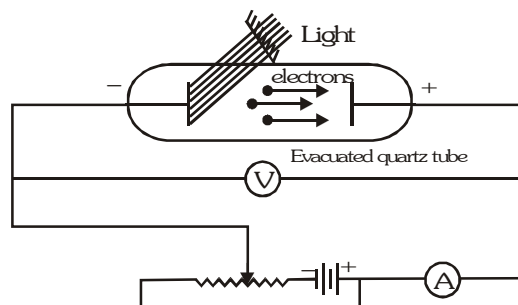


We cannot predict the designation of angular nodes but can be said that at an angle of 45° with axis.

❑ PHOTOELECTRIC EFFECT

Sir J.J. Thomson observed that when a light of certain frequency strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is known as photoelectric effect and the ejected electrons are called photoelectrons.

A few metals, which are having low ionisation energy like Cesium, show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light.

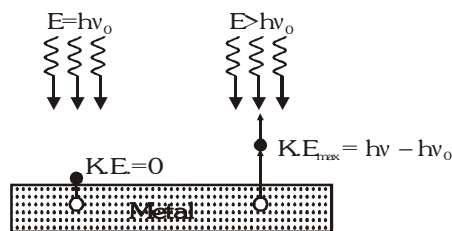


An evacuated tube contains two electrodes connected to a source of variable voltage, with the metal plate whose surface is irradiated as the anode. Some of the photoelectrons that emerge from this surface have enough energy to reach the cathode despite its negative polarity, and they constitute the measured current. The slower photoelectrons are repelled before they get to the cathode. When the voltage is increased to a certain value V_0 , of the order of several volts, no more photoelectrons arrive, as indicated by the current dropping to zero. This extinction voltage (or also referred as stopping potential) corresponds to the maximum photoelectron kinetic energy i.e. $eV_0 = \frac{1}{2} mv^2$

The experimental findings are summarized as below :

- ◆ Electrons come out as soon as the light (of sufficient energy) strikes the metal surface.
- ◆ The light of any frequency will not be able to cause ejection of electrons from a metal surface. There is a minimum frequency, called the threshold (or critical) frequency, which can just cause the ejection. This frequency varies with the nature of the metal. The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light.
- ◆ Photoelectric current is increased with increase intensity of light of same frequency, if emission is permitted, i.e. a bright light yields more photoelectrons than a dim one of the same frequency, but the electron energies remain the same.

Light must have stream of energy particles or quanta of energy ($h\nu$). Suppose, the threshold frequency of light required ejecting electrons from a metal is ν_0 , when a photon of light of this frequency strikes a metal it imparts its entire energy ($h\nu_0$) to the electron.



"This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus". Thus each photon can eject one electron. If the frequency of light is less than ν_0 there is no ejection of electron. If the frequency of light is higher than ν_0 (let it be ν), the photon of this light having higher energy ($h\nu$), will impart some energy to the electron that is needed to remove it away from the atom. The excess energy would give a certain velocity (i.e. kinetic energy) to the electron.

$$h\nu = h\nu_0 + K.E.$$

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

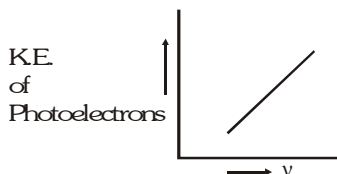
$$\frac{1}{2} mv^2 = h\nu - h\nu_0$$

where ν = frequency of the incident light

ν_0 = threshold frequency

$h\nu_0$ is the threshold energy (or) the work function denoted by $\phi = h\nu_0$ (minimum energy of the photon to liberate electron). It is constant for particular metal and is also equal to the ionization potential of gaseous atoms.

The kinetic energy of the photoelectrons increases linearly with the frequency of incident light. This, if the energy of the ejected electrons is plotted as a function of frequency, it result in a straight line whose slope is equal to Planck's constant 'h' and whose intercept is $h\nu_0$.



Ex. A photon of wavelength 3000 \AA strikes a metal surface, the work function of the metal being 2.20 eV . Calculate (i) the energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and (iii) the velocity of the photo electron.

Sol. (i) Energy of the photon

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{3 \times 10^{-7} \text{ m}} = 6.6 \times 10^{-19} \text{ J}$$

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$\text{Therefore } E = \frac{6.6 \times 10^{-19} \text{ J}}{1.6 \times 10^{-19} \text{ J/eV}} = 4.125 \text{ eV}$$

(ii) Kinetic energy of the emitted photo electron

$$\text{Work function} = 2.20 \text{ eV}$$

$$\text{Therefore, KE} = 4.125 - 2.20 = 1.925 \text{ eV} = 3.08 \times 10^{-19} \text{ J}$$

(iii) Velocity of the photo electron

$$\text{KE} = \frac{1}{2} mv^2 = 3.08 \times 10^{-19} \text{ J}$$

$$\text{Therefore, velocity (v)} = \sqrt{\frac{2 \times 3.08 \times 10^{-19}}{9.1 \times 10^{-31}}} = 8.22 \times 10^5 \text{ ms}^{-1}$$

Ex. Photoelectrons are liberated by ultra violet light of wavelength 2000 \AA from a metallic surface for which the photoelectric threshold is 4000 \AA . Calculate the de Broglie wavelength of electrons emitted with maximum kinetic energy.

Sol. K.E. = Quantum Energy – Threshold energy

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2000 \times 10^{-10}} - \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{10^{-10}} \left(\frac{1}{2000} - \frac{1}{4000} \right)$$

$$= 4.969 \times 10^{-19} \text{ Joule.}$$

$$\frac{1}{2} mv^2 = 4.969 \times 10^{-19} \Rightarrow m^2 v^2 = 2 \times 4.969 \times 10^{-19} \times 9.1 \times 10^{-31}$$

$$mv = 9.51 \times 10^{-25} \Rightarrow \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.51 \times 10^{-25}} = 0.696 \times 10^{-9} \text{ m}$$

MEMORY TIPS

1. Frequency, $\nu = \frac{c}{\lambda}$
2. Energy/photon, $E = h\nu = \frac{hc}{\lambda}$
Also, $E = \frac{12375}{\lambda} \text{ eV}$, if λ is in Å
3. Electronic energy change during transition, $\Delta E = E_{n_2} - E_{n_1}$
 $n_2 > n_1$, emission spectra if electron jumps from n_2 to n_1 shell and absorption spectra if electron excites from n_1 to n_2 shell.
4. Radius of n^{th} Bohr orbit of H atom, $r_n = \frac{n^2 h^2}{4\pi^2 m e^2 K}$ (where $K = 9 \times 10^9$)
 r_1 for H = 0.529 Å ; r_n for H like atom $r_n = 0.529 \frac{n^2}{Z} \text{ Å}$
5. Velocity of electron in n^{th} Bohr orbit of H atom, $v = \frac{2\pi K Z e^2}{nh}$
 $v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/sec}$.
6. Energy of electron in n^{th} Bohr orbit of H atom, $E = \frac{2\pi^2 m Z^2 e^4 K^2}{n^2 h^2}$
where $n = 1, 2, 3, \dots$
 $[E = -13.6 \frac{Z^2}{n^2} \text{ kcal/mole (1 cal = 4.18 J)}]$
 E_1 for H = $-21.72 \times 10^{-12} \text{ erg} = -13.6 \text{ eV}$, E_1 for H like atom = E_1 for H $\times Z^2$
7. Wavelength emitted during transition in H atom,
 $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = \frac{2\pi^2 m e^4}{ch^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ (in C.G.S.)
8. Photoelectric effect $h\nu = w + \frac{1}{2} m u^2$ or $h\nu = \text{I.E.} + \text{K.E.}$
9. Possible transitions for a jump from n_2 to $n_1 = \sum (n_2 - n_1)$
10. Angular momentum of electron in an orbit = $n \cdot (h/2\pi)$
11. Angular momentum of electron in an orbital = $(nh/2\pi) \sqrt{\ell(\ell+1)}$
12. Total spin = $\pm \left(\frac{1}{2} \times n \right)$; where n is no. of unpaired electrons.
13. Magnetic moment of an atom $\sqrt{n(n+2)} \text{ B.M.}$; where n is no. of unpaired electrons.
14. Nodal planes : Radial nodes = $n - \ell - 1$, Angular nodes = ℓ , Total nodes = $(n - \ell)$
15. de Broglie equation : $\lambda = \frac{h}{mu} = \sqrt{\frac{h^2}{2 \times \text{K.E.} \times m}}$
where λ is wavelength, m is mass and u is velocity of particle.
16. Heisenberg uncertainty principle :
 $\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$
 $\Delta u \cdot \Delta x \geq \frac{h}{4\pi m}$
where Δp , Δu and Δx are uncertainties in momentum, velocity and position respectively. Planck's constant is h and m is mass of subatomic particle.

SOLVED PROBLEMS (SUBJECTIVE)

Ex 1. Find the wavelengths of the first line of He^+ ion spectral series whose interval with extreme lines is

$$\frac{1}{\lambda_1} - \frac{1}{\lambda_2} = 2.7451 \times 10^4 \text{ cm}^{-1}$$

Sol. Extreme lines means first and last

$$\frac{1}{\lambda_1} - \frac{1}{\lambda_2} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{\infty^2} \right] - RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2} \right]$$

$$\text{or } \frac{1}{\lambda_1} - \frac{1}{\lambda_2} = \frac{RZ^2}{(n_1 + 1)^2}$$

$$2.7451 \times 10^4 = \frac{109677.76 \times 2^2}{(n_1 + 1)^2}$$

$$(n_1 + 1) = 4$$

$$n_1 = 3$$

Wavelength of first line,

$$\frac{1}{\lambda} = 109677.76 \times 2^2 \left[\frac{1}{3^2} - \frac{1}{4^2} \right]$$

$$\lambda = 4689 \times 10^{-8} \text{ cm} = 4689 \text{ Å}$$

Ex 2. Find the wavelength emitted during the transition of electron in between two levels of Li^{2+} ion whose sum is 5 and difference is 3.

Sol. Let the transition occurs between the level n_1 and n_2 and $n_2 > n_1$

$$\text{Given that } n_1 + n_2 = 5$$

$$n_2 - n_1 = 3$$

$$\therefore n_1 = 1 \text{ and } n_2 = 4$$

$$\text{Therefore, } \frac{1}{\lambda} = R_{\text{h}} Z^2 \left[\frac{1}{(1)^2} - \frac{1}{(4)^2} \right] = 109678 \times (3)^2 \left[\frac{15}{16} \right]$$

$$\therefore \lambda = 1.08 \times 10^{-6} \text{ cm}$$

Ex 3. The Lyman series of the hydrogen spectrum can be represented by the equation.

$$\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left[\frac{1}{(1)^2} - \frac{1}{(n)^2} \right]$$

(where $n = 2, 3, \dots$)

Calculate the maximum and minimum wavelength of lines in this series.

$$\text{Sol. } \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{3.2881 \times 10^{15}}{3 \times 10^8} \text{ m}^{-1} \left[\frac{1}{(1)^2} - \frac{1}{n^2} \right]$$

Wavelength is maximum ($\bar{\nu}_{\min}$) when n is minimum so that $\frac{1}{n^2}$ is maximum

$$\therefore \bar{\nu}_{\min} = \frac{1}{\lambda_{\max}} = \frac{3.2881 \times 10^{15}}{3 \times 10^8} \left[\frac{1}{(1)^2} - \frac{1}{(2)^2} \right]$$

$$\therefore \lambda_{\max} = \frac{3 \times 10^8}{3.2881 \times 10^{15}} \times \frac{4}{3}$$

$$= 1.2165 \times 10^{-7} \text{ m} = 121.67 \text{ nm}$$

Wavelength is minimum ($\bar{\nu}_{\max}$) when n is ∞

i.e. series converge

$$\therefore \nu_{\max} = \frac{1}{\lambda_{\min}} = \frac{3.2881 \times 10^{15}}{3 \times 10^8}$$

$$\therefore \lambda_{\min} = 0.9124 \times 10^{-7} \text{ m} = 91.24 \text{ nm}$$

Ex 4. When certain metal was irradiated with light frequency 0.4×10^{13} Hz the photo electrons emitted had twice the kinetic energy as did photo electrons emitted when the same metal was irradiated with light frequency 1.0×10^{13} Hz. Calculate threshold frequency (ν_0) for the metal.

Sol. $h\nu = h\nu_0 + \text{KE}$

$$\text{KE}_1 = h(\nu_1 - \nu_0)$$

$$\text{KE}_2 = h(\nu_2 - \nu_0) = \frac{\text{KE}_1}{2}$$

$$\therefore \frac{\nu_2 - \nu_0}{\nu_1 - \nu_0} = \frac{1}{2} \Rightarrow \frac{1.0 \times 10^{13} - \nu_0}{0.4 \times 10^{13} - \nu_0} = \frac{1}{2} \Rightarrow \nu_0 = 1.6 \times 10^{13} \text{ Hz}$$

Ex 5. Iodine molecule dissociates into atoms after absorbing light of 3000 \AA . If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of $\text{I}_2 = 240 \text{ kJ (mol)}$).

Sol. Energy given to iodine molecule

$$\frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{3000 \times 10^{-10}} = 6.62 \times 10^{-19} \text{ J}$$

Also energy used for breaking up

$$\text{I}_2 \text{ molecule} = \frac{240 \times 10^3}{6.023 \times 10^{23}} = 3.984 \times 10^{-19} \text{ J}$$

$$\therefore \text{Energy used in imparting kinetic to two atoms} = (6.62 - 3.984) \times 10^{-19} \text{ J}$$

$$\therefore \text{KE of iodine atom} = \frac{(6.62 - 3.984)}{2} \times 10^{-19} = 1.318 \times 10^{-19} \text{ J}$$

Ex 6. Two hydrogen atoms collide head on and end up with zero kinetic energy. Each atom then emits a photon of wavelength 121.6 nm . Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before collision?

Sol. Wavelength is emitted in UV region and thus $n_1 = 1$

$$\text{For H atom} = \frac{1}{\lambda} = R_H \left[\frac{1}{1^2} - \frac{1}{n^2} \right]$$

$$\therefore \frac{1}{121.6 \times 10^{-9}} = 1.097 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{n^2} \right]$$

$$\therefore n = 2$$

Also the energy released is due to collision and all the kinetic energy is released in form of photon.

$$\therefore \frac{1}{2}mv^2 = \frac{hc}{\lambda}$$

$$\therefore \frac{1}{2} \cdot 1.67 \cdot 10^{-27} \cdot v^2 = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{121.6 \times 10^{-9}}$$

$$\therefore v = 4.43 \cdot 10^4 \text{ m/sec}$$

Ex 7. Find the energy in kJ per mole of electronic charge accelerated by a potential of 2 volt.

Sol. Energy in joules = charge in coulombs potential difference in volt

$$= 1.6 \cdot 10^{-19} \cdot 6.02 \cdot 10^{23} \cdot 2 = 19.264 \cdot 10^4 \text{ J or } 192.264 \text{ kJ}$$

Ex 8. Which hydrogen like ionic species has wavelength difference between the first line of Balmer and first line of Lyman series equal to $59.3 \cdot 10^{-9} \text{ m}$? Neglect the reduced mass effect.

Sol. Wave number of first Balmer line of an species with atomic number Z is given by

$$\bar{\nu}' = RZ^2 \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = \frac{5RZ^2}{36}$$

Similarly wave number of $\bar{\nu}$ of first Lyman line is given by

$$\bar{\nu} = RZ^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3}{4}RZ^2 ; \bar{\nu} = \frac{1}{\lambda} \text{ and } \bar{\nu}' = \frac{1}{\lambda'}$$

$$\therefore \lambda' - \lambda = \frac{36}{5RZ^2} - \frac{4}{3RZ^2} = \frac{1}{RZ^2} \left[\frac{36}{5} - \frac{4}{3} \right] = \frac{88}{15RZ^2}$$

$$\therefore Z^2 = \frac{88}{59.3 \times 10^{-9} \times 15 \times 1.097 \times 10^7} = 9 \text{ or } Z = 3$$

\therefore Ionic species is Li^{2+}

Ex 9. (i) What is highest frequency photon that can be emitted from hydrogen atom ? What is wavelength of this photon ?

(ii) Find the longest wavelength transition in the Paschen series of Be^{3+} .

(iii) Find the ratio of the wavelength of first and the ultimate line of Balmer series of He^+ ?

Sol. (i) Highest frequency photon is emitted when electron comes from infinity to 1st energy level.

$$E = -\frac{13.6Z^2}{1^2} = -13.6 \text{ eV}$$

$$\text{or, } 13.6 \cdot 1.6 \cdot 10^{-19} \text{ Joule} = 2.176 \cdot 10^{-18} \text{ Joule}$$

$$E = h\nu$$

$$\therefore \nu = \frac{E}{h} = \frac{2.176 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 0.328 \cdot 10^{16} \text{ Hz}$$

$$\nu = \frac{c}{\lambda} \therefore \lambda = \frac{3 \times 10^8}{0.328 \times 10^{16}} = 9.146 \cdot 10^{-8} \text{ m}$$

$$(ii) \quad \bar{\nu} = R_H \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

For He ; $Z = 4$; For Paschen series $n_1 = 3$

For longest wavelength $n_2 = 4$

$$\frac{1}{\lambda} = 109678 \quad (4)^2 \left[\frac{1}{3^2} - \frac{1}{4^2} \right] = 109678 \quad 16 \left[\frac{1}{9} - \frac{1}{16} \right] = 109678 \quad 16 \quad \frac{7}{144}$$

$$\lambda = 1172.20 \text{ Å}$$

(iii) Wave number of first line of Balmer,

$$\bar{\nu}_1 = RZ^2 \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = \frac{5 \times 4R}{36} = \frac{5R}{9}$$

$$\therefore \text{Wavelength of first line of Balmer} = \frac{9}{5R}$$

$$\text{Wave number of ultimate line of Balmer, } \bar{\nu}_2 = RZ^2 \left[\frac{1}{2^2} - \frac{1}{\infty} \right] = \frac{4R}{4} = R$$

$$\therefore \text{Wavelength of ultimate line of Balmer} = \frac{1}{R}$$

$$\therefore \text{Ratio} = \frac{9}{5}$$

Ex 10. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.0 Å .

Sol. For an electron

$$\frac{1}{2}mv^2 = eV \quad \text{where } V \text{ is accelerating potential}$$

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

$$\therefore \frac{1}{2}m \left(\frac{h}{m\lambda} \right)^2 = eV$$

$$\therefore V = \frac{1}{2} \times \frac{h^2}{m\lambda^2 e} = \frac{1 \times (6.625 \times 10^{-34})^2}{2 \times 9.108 \times 10^{-31} \times (1.0 \times 10^{-10})^2 \times 1.602 \times 10^{-19}} = 150.40 \text{ volt}$$

Ex 11. The angular momentum of an electron in a Bohr's orbit of H-atom is $4.2178 \times 10^{-34} \text{ kgm}^2/\text{sec}$. Calculate the wavelength of the spectral line emitted when electrons falls from this level to next lower level.

$$\text{Sol. } mvr = \frac{nh}{2\pi}$$

$$\frac{nh}{2\pi} = 4.2178 \times 10^{-34}$$

$$n = \frac{4.2178 \times 10^{-34} \times 2 \times 3.14}{6.625 \times 10^{-34}} = 4$$

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

The wavelength for transition from $n = 4$ to $n = 3$

$$\frac{1}{\lambda} = 109678 \left[\frac{1}{3^2} - \frac{1}{4^2} \right]$$

$$\lambda = 1.8 \times 10^{-4} \text{ cm.}$$

Ex 12. The kinetic energy of an electron in H like atom is 6.04 eV. Find the area of the third Bohr orbit to which this electron belongs. Also report the atom.

Sol. K.E. = 6.04 in 3rd orbit

$$E_{\text{total}} = \text{K.E.} + \text{P.E.} = \text{K.E.} - 2 \text{ K.E.}$$

$$\Rightarrow -\text{K.E.} = -6.04 \text{ eV}$$

E_1 for H = -13.6 eV and not for any orbit $E = -6.04 \text{ eV}$ for H atom. Thus, atom for which K.E. is given is other than H.

$$E_n \text{ H like atom} = E_{\text{nH}} Z^2$$

$$\frac{E_1}{n^2} \times Z^2 \Rightarrow 6.04 = \frac{13.6}{3^2} \times Z^2$$

$$Z^2 = 3.99 \approx 4 \Rightarrow Z = 2$$

$$\therefore \text{The atom is He}^+ \Rightarrow r_n = 0.529 \frac{n^2}{Z} = 0.529 \frac{3^2}{2} = 2.3805 \text{ \AA}$$

$$\text{Area, } \pi r^2 = \frac{22}{7} \times (2.3805 \times 10^{-8})^2 = 17.8 \times 10^{-16} \text{ cm}^2$$

Ex 13. O_2 undergoes photochemical dissociation into one normal oxygen atom and one oxygen atom 1.967 eV more energetic than normal. The dissociation of O_2 into two normal atom of oxygen requires 498 kJmol^{-1} . What is the maximum wavelength effective for photo chemical dissociation of O_2 ?

Sol. We know



Energy required for simple dissociation of O_2 into two normal atoms = $498 \times 10^3 \text{ Jmol}^{-1}$

$$= \frac{498 \times 10^8}{6.023 \times 10^{23}} \text{ Jmol}^{-1}$$

If one atom in excited state has more energy, i.e., 1.967 eV

$$= 1.967 \times 1.602 \times 10^{-19} \text{ J}$$

The energy required for photochemical dissociation of O_2

$$= \frac{498 \times 10^3}{6.023 \times 10^{23}} + 1.967 \times 1.602 \times 10^{-19}$$

$$= 82.68 \times 10^{-20} + 31.51 \times 10^{-20} = 114.19 \times 10^{-20} \text{ Joule}$$

$$E = \frac{hc}{\lambda}$$

$$114.19 \times 10^{-20} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$\lambda = 1740.2 \times 10^{-10} \text{ m} = 1740.2 \text{ \AA}.$$

SOLVED PROBLEMS (OBJECTIVE)

Ex 1. The wave-mechanical model of atom is based upon :-

- (A) de Broglie concept of dual character of matter
- (B) Heisenberg's uncertainty principle
- (C) Schrodinger wave equation
- (D) All the above three

Sol. (D)

Ex 2. An orbital is correctly described by :-

- (A) Ψ^2
- (B) Ψ
- (C) $|\Psi^2| \Psi$
- (D) none

Sol. (A)

Ex 3. The orbital angular momentum of a d-electron is :-

- (A) $\sqrt{6}\hbar$
- (B) $\sqrt{2}\hbar$
- (C) \hbar
- (D) $2\hbar$

Sol. For d-electron, $\ell = 2$, orbital angular momentum $= \sqrt{\ell(\ell+1)}\hbar = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$

So, (A) is the correct answer

Ex 4. The following electron configuration of an atom in the ground state is not correct because :-



- (A) the energy of the atom is not minimum
- (B) Pauli's exclusion principle is violated
- (C) Hund's rule is violated
- (D) Aufbau principle is not followed

Sol. (C) is the correct answer.

Ex 5. In the first bohr orbit of H atom the energy of an electron is -13.6 eV. The possible energy value (s) of excited state (s) for electron in Bohr orbit of hydrogen is/are :-

- (A) -3.4 eV
- (B) -4.2 eV
- (C) 6.8 eV
- (D) $+6.8$ eV

Sol. $E_n = \frac{-13.6}{n^2} \text{ eV}$

For $n = 2$, $E_2 = \frac{-13.6}{4} = -3.4 \text{ eV}$

So, (A) is the correct answer.

Ex 6. The electronic configuration of an element is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$. This represents its :-

- (A) excited state
- (B) ground state
- (C) cationic form
- (D) anionic form

Sol. The given electronic configuration is ground state for chromium.

So, (B) is the correct answer

Ex 7. Which of the following sets of quantum number is/are incorrect ?

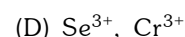
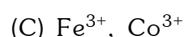
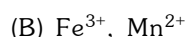
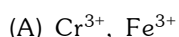
- (A) $n = 3, \ell = 3, m = 0, s = \frac{1}{2}$
- (B) $n = 3, \ell = 2, m = 2, s = -\frac{1}{2}$
- (C) $n = 3, \ell = 1, m = 2, s = -\frac{1}{2}$
- (D) $n = 3, \ell = 0, m = 0, s = +\frac{1}{2}$

Sol. When $n = 3$, ℓ cannot be 3, so (A) is incorrect when $\ell = 1$, m cannot be $= +2$.

So, (C) is incorrect

So, (A) and (C) is the correct answer.

Ex 8. Select the pairs of ions which have same electronic configuration ?



Sol. Fe^{3+} and Mn^{2+} have same electronic configuration

So **(B)** is the correct answer.

Ex 9. If an electron in H atom has an energy of -78.4 kcal/mol. The orbit in which the electron is present is :-

(A) 1st

(B) 2nd

(C) 3rd

(D) 4th

Sol. $E^n = \frac{-313.6}{n^2} \text{ kcal/mol} \Rightarrow -78.4 = \frac{-313.6}{n^2} \therefore n = 2$

Ex 10. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, $n = 4$ to $n = 2$ in the He^+ spectrum ?

(A) $n = 4$ to $n = 2$

(B) $n = 3$ to $n = 2$

(C) $n = 3$ to $n = 1$

(D) $n = 2$ to $n = 1$

Sol. $\bar{\nu} = \frac{1}{\lambda} = \left(\frac{1}{2^2} - \frac{1}{4^2} \right) RZ^2 = \frac{3}{4}R$

In H-spectrum for the same $\bar{\nu}$ or λ as $Z = 1$, $n = 1$, $n_2 = 2$

So, **(D)** is the correct answer.

Ex 11. Principal, azimuthal and magnetic quantum numbers are respectively related to :-

(A) size, orientation and shape

(B) size, shape and orientation

(C) shape, size and orientation

(D) none of these

Sol. Principal gives size, i.e. azimuthal gives shape and magnetic quantum number gives the orientation.

So, **(B)** is the correct answer.

Ex 12. If the radius of 2nd Bohr orbit of hydrogen atom is r_2 . The radius of third Bohr orbit will be :-

(A) $\frac{4}{9}r_2$

(B) $4r_2$

(C) $\frac{9}{4}r_2$

(D) $9r_2$

Sol. $r = \frac{n^2 h^2}{4\pi^2 mZe^2}$

$$\therefore \frac{r_2}{r_3} = \frac{2^2}{3^2} \quad \therefore r_3 = \frac{9}{4}r_2$$

So, **(C)** is the correct answer.

Ex 13. Difference between n^{th} and $(n + 1)^{\text{th}}$ Bohr's radius of H-atom is equal to its $(n - 1)^{\text{th}}$ Bohr's radius. The value of n is :-

(A) 1

(B) 2

(C) 3

(D) 4

Sol. $r_n \propto n^2$

$$\text{But } r_{n+1} - r_n = r_n - 1$$

$$(n+1)^2 - n^2 = (n-1)^2$$

$$n = 4$$

So **(D)** is the correct answer

Ex 14. The dissociation energy of H_2 is $430.53 \text{ kJ mol}^{-1}$. If H_2 is dissociated by illumination with radiation of wavelength 253.7 nm . The fraction of the radiant energy which will be converted into kinetic energy is given by :-

(A) 8.86%

(B) 2.33%

(C) 1.3%

(D) 90%

Sol. $\frac{hc}{\lambda} = \frac{430.53 \times 10^3}{6.023 \times 10^{23}} + \text{K.E.}$

$$\text{K.E.} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{253.7 \times 10^{-9}} - \frac{430.53 \times 10^3}{6.023 \times 10^{23}} = 6.9 \times 10^{-20}$$

$$\therefore \text{Fraction} = \frac{6.9 \times 10^{-20}}{7.83 \times 10^{-19}} = 0.088 = 8.86\%$$

Ex 15. No. of wave in third Bohr's orbit of hydrogen is :-

- (A) 3 (B) 6 (C) 9 (D) 12

Sol. Number of waves = $\frac{\text{Circumference}}{\text{Wavelength}}$

$$\frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} = \frac{2\pi}{h}(mvr) = \frac{2\pi}{h} \times \frac{nh}{2\pi}$$

$$\therefore n = 3$$

So, (A) is the correct answer.

Ex 16. In the hydrogen atoms, the electrons are excited to the 5th energy level. The number of the lines that may appear in the spectrum will be :-

- (A) 4 (B) 8 (C) 10 (D) 12

Sol. No. of lines produced for a jump from fifth orbit to 1st orbit is given by

$$= \frac{n(n-1)}{2} = \frac{5(5-1)}{2} = 10$$

So, (C) is the correct answer.

Ex 17. Light of wavelength λ shines on a metal surface with intensity x and the metal emits Y electrons per second of average energy, Z . What will happen to Y and Z if x is doubled ?

- (A) Y will be double and Z will become half (B) Y will remain same and Z will be doubled
(C) Both Y and Z will be doubled (D) Y will be doubled but Z will remain same

Sol. When intensity is doubled, number of electrons emitted per second is also doubled but average energy of photoelectrons emitted remains the same.

So, (D) is the correct answer.

Ex 18. Which of the following is the ground state electronic configuration of nitrogen :-

- (A) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\uparrow\uparrow}$ (B) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow\uparrow}$
(C) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow\downarrow}$ (D) $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\downarrow\downarrow\downarrow}$

Sol. In (A) and (D), the unpaired electrons have spin in the same direction.

So, (A) and (D) are the correct answer.

Ex 19. Select the wrong statement (s) from the following ?

- (A) If the value of $\ell = 0$, the electron distribution is spherical
(B) The shape of the orbital is given by magnetic quantum number
(C) Angular momentum of 1s, 2s, 3s electrons are equal
(D) In an atom, all electrons travel with the same velocity

Sol. (B) is wrong because shape is given by azimuthal quantum number and magnetic quantum number tells the orientation. (D) is wrong because electrons in different shells travel with different velocities.

So, (A) and (C) are the correct answer.

Ex 20. For the energy levels in an atom, which one of the following statement/s is/are correct ?

- (A) There are seven principal electron energy levels
- (B) The second principal energy level can have four sub-energy levels and contain a maximum of eight electrons
- (C) The M energy level can have a maximum of 32 electrons.
- (D) The 4s sub-energy level is at a lower energy than the 3d sub-energy level.

Sol. (A) and (D) are true. (B) is wrong because for $n = 2$, $\ell = 0, 1$ (two sub-energy levels). (C) is wrong because M shell means $n = 3$. Maximum electrons it can have $= 2n^2 = 2 \cdot 3^2 = 18$

So, **(A)** and **(D)** is the correct answer.

Ex 21. Which of the following statement (s) is (are) correct ?

- (A) The electronic configuration of Cr is $[\text{Ar}]3d^5, 4s^1$ (Atomic No. of Cr = 24)
- (B) The magnetic quantum number may have a negative value
- (C) In silver atom 23 electrons have spin of one type and 24 of the opposite type (Atomic No. of Ag = 47)
- (D) The oxidation state of nitrogen in HN_3 is -3

Sol. Only (D) is wrong because oxidation state of N in HN_3 is $-1/3$.

So, **(A)**, **(B)** and **(C)** are the correct answer.

Ex 22. Many elements have non-integral atomic masses because :-

- (A) they have isotopes
- (B) their isotopes have non-integral masses
- (C) their isotopes have different masses
- (D) the constituents, neutrons, protons and electrons combine to give rational masses

Sol. Non-integral atomic masses are due to isotopes which have different masses.

So, **(A)** and **(C)** are the correct answer.
