# Chapter 02

# Atomic Structure

## CONTENT

## 1. INTRODUCTION

**(a)** The word atom was first introduced by Dalton (1803 - 1807) in scientific world.

**(b)** According to him matter is ultimately made up of extremely small indivisible particles called atoms.

**(c)** It takes part in chemical reactions.

**(d)** Atom is neither created nor destroyed

## 2. FUNDAMENTAL PARTICLES

Atoms are made up of three fundamental particles. The charge and mass of these fundamental particles are as follows:

| | **Electron** | **Proton** | **Neutron** |
|---|---|---|---|
| **Symbol** | **e or $_{-1}e^0$ or $e^-$** | **p or $_1p^1$** | **n or $_0n^1$** |
| **Mass (in kg)** | $9.109534 \times 10^{-31}$ | $1.6726485 \times 10^{-27}$ | $1.6749543 \times 10^{-27}$ |
| Mass in amu | $5.4858026 \times 10^{-4}$ | 1.007276471 | 1.008665 012 |
| Relative mass | $\frac{1}{1837}$ | 1 | 1 |
| **Charge** (Actual (in C)) | $1.6021892 \times 10^{-19}$ | $1.6021892 \times 10^{-19}$ | 0 |
| Relative charge | -1 | +1 | 0 |
| Discovered by | J.J. Thomson | Goldstein | Chadwick |

One unit charge = $4.80298 \times 10^{-10}$ esu = $1.60210 \times 10^{-19}$ coulombs

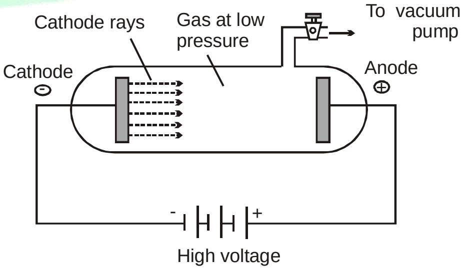
One amu = $\frac{1}{12} \times$ mass of $_6C^{12}$ atom

**DISCOVERY OF FUNDAMENTAL PARTICLES:**

➢ **Cathode rays**

**(a)** The electron was discovered as a result of the studies of the passage of electricity through gases at extremely low pressures known as discharge tube experiments.

**(b)** When a high voltage of the order of 10,000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrodes these rays are called as cathode rays



➢ **Properties of Cathode rays**

**(i)** Path of travelling is straight from the cathode with a very high velocity As it produces shadow of an object placed in its path

**(ii)** Cathode rays produce mechanical effects. If a small pedal wheel is placed between the electrodes, it rotates. This indicates that the cathode rays consist of material part.

**(iii)** When electric and magnetic fields are applied to the cathode rays in the discharge tube, the rays are deflected thus establishing that they consist of charged particles.

**(iv)** Cathode rays produce X-rays when they strike against hard metals like tungsten, copper etc.

**(v)** When the cathode rays are allowed to strike a thin metal foil, it gets heated up. Thus the cathode rays possess heating effect.

**(vi)** They produce glow On striking ZnS screen coated on the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.

**(vii)** Cathode rays penetrate through thin sheets of aluminium and other metals.

**(viii)** They affect the photographic plates

**(ix)** The ratio of charge to mass i.e. charge/mass is same for all the cathode rays irrespective of the gas used in the tube.

## SPOT LIGHT

**(a)** The mass of electron in motion is expressed as $m' = \dfrac{m}{\left(1-\dfrac{v^2}{c^2}\right)^{1/2}}$

where m' = mass of the electron in motion

m = rest mass, v = velocity of the electron, c = velocity of light

**(b)** In 1897, J.J. Thomson determined the e/m value (charge/mass) of the electron by studying the deflections of cathode rays in electric and magnetic fields. The value of e/m has been found to be $-1.7588 \times 10^{8}$ coulomb /g

**(c)** The first precise measurement of the charge on the electron was made by Robert A. Millikan. in 1909 by oil drop experiment. Its value was found to be $-1.6022 \times 10^{-19}$ coulomb.

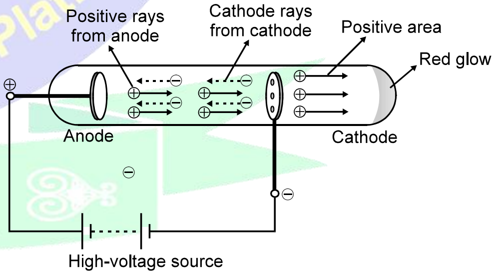
**(d)** The mass of electron can be calculated from the value of e/m and the value of e which is $9.1096 \times 10^{-31}$ Kg.

### Positive Rays-Discovery of Proton

**(a)** The existence of positively charged particles in an atom was shown by E. Goldstein in 1886

**(b)** He repeated the same discharge tube experiments by using a perforated cathode.

**(c)** It was observed that when a high potential difference was applied between 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 canal of the cathode. These were termed as canal ray or anode ray.



### Properties of Anode Rays

**(i)** These rays travel in straight lines and cast shadow of the object placed in their path.

**(ii)** The anode rays are deflected by the magnetic and electric fields like cathode rays but direction is different that mean these rays are positively charged.

**(iii)** These rays have kinetic energy and produces heating effect also.

**(iv)** The e/m ratio for these rays is smaller than that of electrons

**(v)** Unlike cathode rays, their e/m value is dependent upon the nature of the gas taken in the tube.

**(vi)** These rays produce flashes of light on ZnS screen

**(vii)** These rays can pass through thin metal foils

**(viii)** They are capable to produce ionisation in gases

**(ix)** They can produce physical and chemical changes.

## DISCOVERY OF NEUTRON

**(a)** Chadwick (1932), bombarded beryllium with a stream of α-particles and observed electrically and magnetically neutral radiations.

**(b)** There were neutral particles which were called neutron. Nuclear reaction is as follows

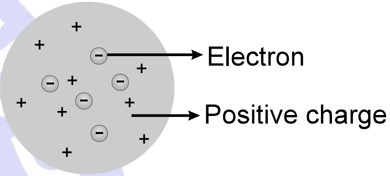
$${}_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$$

**(c)** A neutron is a subatomic particle which has a mass 1.675 x $10^{-24}$g, approximately 1 amu, or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge.

## 3. THOMSON'S ATOMIC MODEL

J.J. Thomson
(1856 –1940)

It states the arrangement of electrons and protons in an atom. After discovery of electron and proton attempts were made to find out their arrangement in an atom. The first simple model was proposed by J.J. Thomson known as Thomson's atomic model.



The main principles are

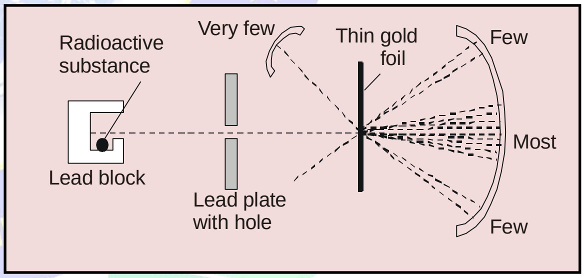
**(a)** He proposed that the positive charge is spread over a sphere of the size of the atom (i.e. $10^{-8}$ cm radius) in which electrons are embedded to make the atom as whole neutral.

**(b)** This model fails to explain stability of an atom.

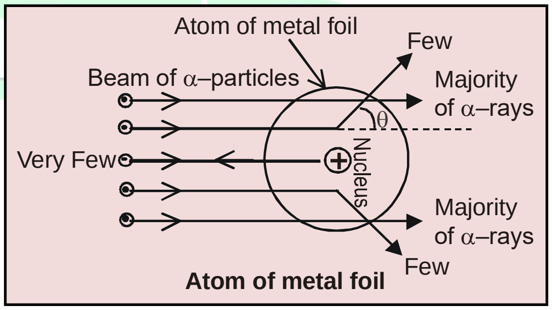
## 4. RUTHERFORD'S ATOMIC MODEL

**Ernest Rutherford**
**(1871-1937)**

**Rutherford's gold foil experiment:**
Rutherford carried out experiment on the bombardment of atoms by high speed positively charged α-particles emitted from radium and gave the following observations, which were based on his experiment.



- **Observation:**
  - **(a)** Most of the α - particles (nearly 99%) continued with their straight path.
  - **(b)** Some of the α - particles passed very close to the centre of the atom and deflected by small angles.
  - **(c)** Very few particles thrown back (180º) .

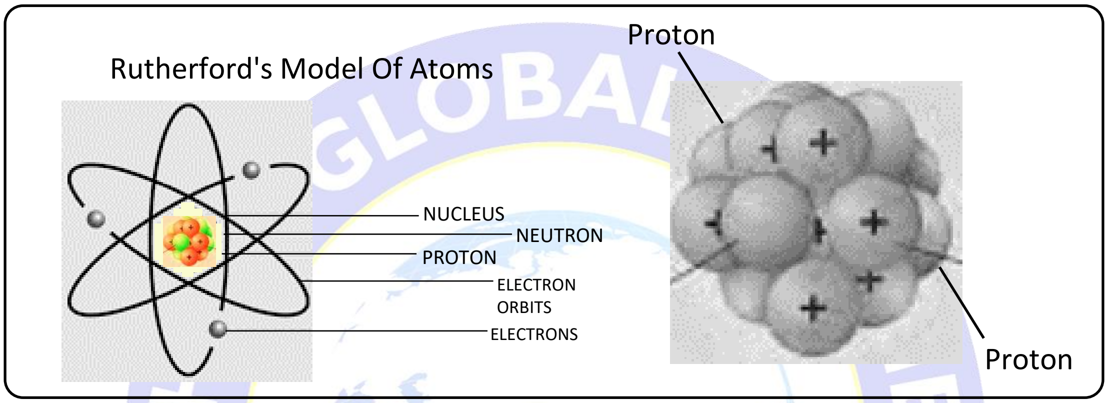


- **Atomic model:**
  - **(a)** Most of the α - particles were continued their straight path that means most of the space of the atom is empty.
  - **(b)** The centre of an atom has a positively charged body called **nucleus** which repel positively charged α - particles and thus explained the scattering phenomenon.

**(c)** Whole mass of an atom is concentrated in its nucleus and very few throw back means the size of the nucleus is very small $10^{-13}$ cm. It showed that the nucleus is $10^{-5}$ times small in size as compared to the total size of atom.

## ➢ APPLICATIONS OF RUTHERFORD MODEL

(i) An atom consists of a heavy positively charged nucleus where all the protons and neutrons are present. Protons & neutrons are collectively referred to as nucleons. Almost whole of the mass of the atom is contributed by these nucleons. The magnitude of the +ve charge on the nucleus is different for different atoms.



(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 diameter of the order of $10^{-12}$ to $10^{-13}$ cm and the atom has a diameter of the order of $10^{-8}$ cm

$$\frac{D_A}{D_N} = \frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5, \; D_A = 10^5 \, D_N$$

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

## RADIUS OF NUCLEUS

The radius of a nucleus is proportional to the cube root of the number of nucleons within it.

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

Where $R_0 = 1.33 \times 10^{-13}$(a constant) and A = mass number (p + n) and R = radius of the nucleus.

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

(iii) **ATOM TO NUCLEUS VOLUME RATIO**

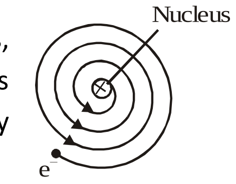
$$\frac{\text{volume of the atom}}{\text{volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

(iv) Electrons revolve around the nucleus in closed orbits with high speeds. The centrifugal force acting on the revolving $e^-$ is being counter balanced by the force of attraction between the electrons and the nucleus.

➢ 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 stability of atom. According to Maxwell electron loses it energy continuously in the form of electromagnetic radiations. As a result of this, the $e^-$ should loss 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 loose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well-defined lines of definite frequencies. Hence, the loss of energy by electron is **not** continuous in an atom.

**Some Important Definitions : -**

**Mass Number :** A = (number of protons + number of Neutrons)

**Atomic Number :** Z = Number of proton = Number of electron (for an atom).

For charged atom : Number of $e^-$ = Z – (charge on atom), Z= number of protons only

**Example.** $_{17}Cl^{35} \rightarrow$ n = 18, p = 17, e = 17

Two different elements cannot have the same Atomic Number

Number of Neutrons = Mass number – Atomic number

= A – Z = (p + n) – p = n

Representation of element $\rightarrow$ $_ZX^A$ (where X$\rightarrow$ symbol of element)

**Isotopes :** Given by Soddy, are the atoms of a given element which have the same atomic number but different mass number i.e. They have same Nuclear charge but different number of Neutrons.

| **Example :** | | **Example :** | | | **Example :** | | |
|---|---|---|---|---|---|---|---|
| | | | | | (Protium | Deuterium | Tritium) |
| $_{17}Cl^{35}$ | $_{17}Cl^{37}$ | $_6C^{12}$ | $_6C^{13}$ | $_6C^{14}$ | $_1H^1$ | $_1H^2$ | $_1H^3$ |
| n = 18 | n = 20 | e = 6 | e = 6 | e = 6 | e = 1 | e = 1 | e = 1 |
| e = 17 | e = 17 | p = 6 | p = 6 | p = 6 | p = 1 | p = 1 | p = 1 |
| p = 17 | p = 17 | n = 6 | n = 7 | n = 8 | n = 0 | n = 1 | n = 2 |

- Isotopes have same chemical property but different physical property.
- Isotopes do not have the same value of e/m.

**Isobars :**

- Given by Alfred Walter Stewart,
- Isobars are the atoms of different element which have the same mass number but Different Atomic number i.e. They have different number of Electron, Protons & Neutrons But sum of number of neutrons & Protons remains same.

| **Example :** | $_1H^3$ | $_2He^3$ | **Example :** | $_{19}K^{40}$ | $_{20}Ca^{40}$ |
|---|---|---|---|---|---|
| | p = 1 | p = 2 | | p = 19 | p = 20 |
| | e = 1 | e = 2 | | n = 21 | n = 20 |
| | n = 2 | n = 1 | | e = 19 | e = 20 |
| | p + n = 3 | p + n = 3 | | n + p = 40 | n + p = 40 |

- Isobars do not have the same chemical & physical property.

**Isodiapheres :**

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

| **Example :** | $_5B^{11}$ | $_6C^{13}$ | **Example :** | $_7N^{15}$ | $_9F^{19}$ |
|---|---|---|---|---|---|
| | p = 5 | p = 6 | | p = 7 | p = 9 |

| | | | |
|---|---|---|---|
| n = 6 | n = 7 | n = 8 | n = 10 |
| e = 5 | e = 6 | e = 7 | e = 9 |
| n – p =1 | n – p =1 | n – p =1 | n – p =1 |

**Isotones/ Isoneutronic species:**

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

| | | | | |
|---|---|---|---|---|
| **Example :** | $_1H^3$ | $_2He^4$ | **Example :** $_{19}K^{39}$ | $_{20}Ca^{40}$ |
| | p = 1 | p = 2 | e = 19 | e = 20 |
| | n = 2 | n = 2 | p = 19 | p = 20 |
| | e = 1 | e = 2 | n = 20 | n = 20 |

**Isosteres :**

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

| | | | | | |
|---|---|---|---|---|---|
| **Example :** | **$CO_2$** | **$N_2O$** | **Example :** | **CaO** | **KF** |
| Atoms | = 1 + 2 | = 2 + 1 | Atoms | 2 | 2 |
| | = 3 | = 3 | Electrons | 20 + 8 | 19 + 9 |
| Electrons | = 6 + 8 × 2 | = 7 × 2 + 8 | | $28\ e^-$ | $28\ e^-$ |
| | = $22\ e^-$ | = $22e^-$ | | | |

**Isoelectronic Species :**

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

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Example :** | $Cl^-$ | Ar | **Example :** | $H_2O$ | $NH_3$ | **Example :** | $BF_3$ | $SO_2$ |
| Electron | $18\ e^-$ | $18\ e^-$ | | e = 2 + 8 | e = 7 + 3 | | e = 5 +9 × 3 | 16 + 8 × 2 |
| | | | | $10\ e^-$ | $10\ e^-$ | | 5 + 27 | 16 + 16 |
| | | | | | | | $32\ e^-$ | $32\ e^-$ |

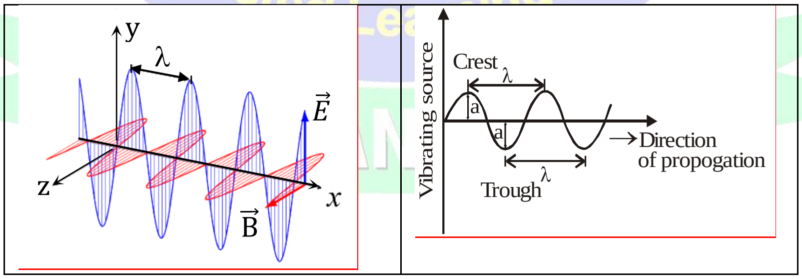
◆

## 5. ELECTROMAGNETIC WAVES (EM WAVES) THEORY OR RADIANT ENERGY

According to this theory 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 ($3 \times 10^8$ m/s) and these waves are known as Electro magnetic waves or radiant energy. The radiant Energy do not need any medium for propagation.

**Example:** Radio waves, micro waves, Infra red rays, visible rays, ultraviolet rays, x–rays, gamma rays.

- The radiant Energy have electric and magnetic fields and travel at right angle to these fields. The upper most point of the wave is called crest and the lower most portion is called trough. Some of the terms employed in dealing with the waves are described below.



| | |
|---|---|
| **Wavelength (λ) (Lambda) :** | It is defined as the distance between two nearest crest or trough. It is measured in terms of Å (Angstrom), pm (Picometre), nm (nanometer), cm(centimeter), m (meter) $1Å = 10^{-10}$ m, $1\ pm = 10^{-12}$ m, $1nm = 10^{-9}$ m, $1cm = 10^{-2}m$ |
| **Frequency (ν) (nu) :** | Frequency of a wave is defined as the number of waves which pass through a point in 1 second. It is measured in terms of Hertz (Hz ), $second^{-1}$ , or cycle per second (cps) (1 Hertz = 1 $second^{-1}$ ) |

| | |
|---|---|
| **Time period (T) :** | Time taken by a wave to pass through one point. $T = \frac{1}{\nu}$ second |
| **Velocity (c) :** | Velocity of a wave is defined as distance covered by a wave in 1 second<br>$c = \lambda / T = \lambda\nu$ or $\nu = c/\lambda$ or $c = \nu\ (s^{-1}) \times \lambda\ (m)$ or $c = \nu\lambda\ (m\ s^{-1})$<br>Since c is constant i.e. frequency is inversely proportional to $\lambda$ |
| **Wave number ( $\bar{\nu}$ ) (nu bar) :** | It is the reciprocal of the wave length that is number of waves present in 1cm $\bar{\nu} = \frac{1}{\lambda}$ It is measured in terms of $cm^{-1}$, $m^{-1}$ etc. |
| **Amplitude (a) :** | The amplitude of a wave is defined as the height of crust or depth of trough. |

**Important note :** $\boxed{\nu = \frac{c}{\lambda} = c\bar{\nu}}$ $\left(\bar{\nu} = \frac{1}{\lambda}\right)$

**Example :1** Calculate $\bar{\nu}$ in $cm^{-1}$ and $\nu$ of yellow radiation have wavelength of 5800 Å.

**Answer:** $5.1 \times 10^{14}\ sec^{-1}$

**Solution:** As we known $\bar{\nu} = \frac{1}{\lambda}$

$$\bar{\nu} = \frac{1}{5800\,\overset{o}{A}} = \frac{1}{5800\times10^{-8}\,cm} \left\{\because \overset{o}{A} = 10^{-8}\,cm\right\}$$

$= 17241.4\ cm^{-1}$

$\nu = c\bar{\nu}$

$= 3 \times 10^{10}\ cm\ sec^{-1} \times 1.7 \times 10^{4}\ cm^{-1}$

$= 3 \times 1.7 \times 10^{14} = 5.1 \times 10^{14}\ sec^{-1}$

**Example :2** How long would it take a radio wave of frequency $6 \times 10^{3}\ sec^{-1}$ to travel from mars to the earth, a distance of $8 \times 10^{7}$ km ?

**Answer:** **$2.66 \times 10^{2}$ sec.**

**Solution:** Distance to be travelled from mars to earth

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

$\because$ Velocity of EM waves

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

$\therefore$ Time $= \frac{\text{Distance}}{\text{Velocity}} = \frac{8\times10^{10}\,m}{3\times10^{8}\,m/sec^{-1}}$

$= 2.66 \times 10^{2}$

## ELECTROMAGNETIC SPECTRUM

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

(Å)

| S.No. | Name | Wavelength | Frequency(Hz) | Source |
|---|---|---|---|---|
| 1. | Radio wave | $3\times10^{7}-3\times10^{14}$ | $1\times10^{5}-1\times10^{9}$ | Alternating current of high frequency |
| 2. | Microwave | $6\times10^{6}-3\times10^{7}$ | $1\times10^{9}-5\times10^{11}$ | Klystron tube |
| 3. | Infrared (IR) | $7600-6\times10^{6}$ | $5\times10^{11}-3.95\times10^{16}$ | Incandescent objects |
| 4. | Visible | 3800 – 7600 | $3.95\times10^{16}-7.9\times10^{14}$ | Electric bulbs, sun rays |
| 5. | Ultraviolet(UV) | 150 – 3800 | $7.9\times10^{14}-2\times10^{16}$ | Sun rays, arc lamps with mercury vapours |
| 6. | X-Rays | 0.1– 150 | $2\times10^{16}-3\times10^{19}$ | Cathode rays striking metal plate |
| 7. | $\gamma$-Rays | 0.01 – 0.1 | $3\times10^{19}-3\times10^{20}$ | Secondary effect of radioactive decay |

**Order of wavelength in electromagnetic spectrum**

$\gamma$ – rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

## 6. PLANCK'S QUANTUM THEORY

Max Planck
(1858-1947)

**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. $E \propto \nu \Rightarrow E = h\nu$ or $E = \frac{hc}{\lambda}\left\{\because \nu = \frac{c}{\lambda}\right\}$ h is proportionality constant or Planck's constant

h = 6.626 × $10^{-31}$ kJ s or 6.626 × $10^{-34}$ J s or 6.626 × $10^{-27}$ erg s

**4.** Total amount of energy transmitted from one body to another will be some integral multiple of energy of a quantum. E = nhν Where n is an integer and n = number of quantum

$$\boxed{E = nh\nu = \frac{nhc}{\lambda} = nhc\bar{\nu}}$$

**Example :** 3 Calculate the energy of a photon of sodium light of wave length 5.862 × $10^{-16}$ m in Joules.

**Answer :** $3.37\times10^{-10}$ J

**Solution:** $\lambda = 5.862 \times 10^{-16}$ m

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

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

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

$$E = \frac{1 \times 6.6 \times 10^{-34}\ \text{joulesec.} \times 3 \times 10^{8}\ \text{msec}^{-1}}{5.862 \times 10^{-16}\ \text{m}} = \frac{6.6 \times 3}{5.862} \times 10^{-10} = 3.37 \times 10^{-10}\ \text{J}$$

**Example : 4** Calculate the wavelength and frequency of a photon having an energy of 2 eV.

**Answer :** $6.204 \times 10^{-7}$ m, $4.8 \times 10^{14}\ \text{sec}^{-1}$

**Solution :** $\because \quad 1\text{ev} = 1.602 \times 10^{-19}$ J

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

(a) Calculation of wavelength ( $\lambda$ ) :

$$E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3 \times 10^{8}\ \text{msec}^{-1}}{3.204 \times 10^{-19}\ \text{J}} = 6.204 \times 10^{-7}\ \text{m}$$

(b) Calculation of frequency ($\nu$) :

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

## 7. PHOTOELECTRIC EFFECT

When light of a suitable frequency is allowed to be incident on a metal, ejection of electrons take place. This phenomenon is known as photo electric effect.

Einstein theory of photo electric effect.

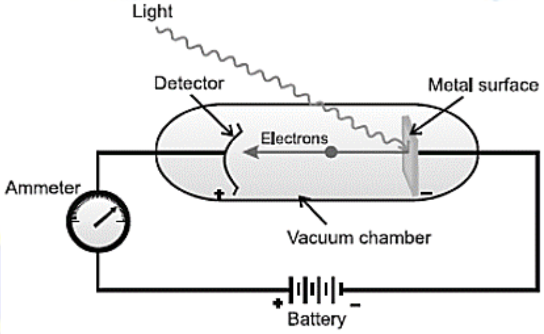


**Figure: Equipment for studying the photoelectric effect**

Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.

➢ **Main Point**

1. One photon of suitable frequency can eject one electron
2. Energy of the photon can be utilized in two ways:

(i) **Work function (w):** one part of incident photon is used to just eject the electron, this part is known as Work function can be calculated as

$W = h\nu_0$, where $\nu_0$ is threshold frequency

$W = \frac{hc}{\lambda_0}, \lambda_0 \rightarrow$ threshold wavelength

**Threshold frequency:** Minimum frequency that is required to just eject electron.

(ii) **Kinetic energy:** Remaining part of photon energy is used to provide kinetic energy.

So, Einstein equation is as given below

$$\underset{\substack{\text{Energy}\\ \text{of incidnet}\\ \text{photon}}}{h\nu} = \underset{\substack{\text{Work}\\ \text{Function}\\ \text{of metal}}}{h\nu_0} + \underset{\substack{\text{Kinetic energy}\\ \text{of emitted}\\ \text{electron}}}{KE}$$

3. **Intensity (I) :** Energy falling on metal surface of unit area of unit time

$$I=\frac{E}{At}=\frac{nh\nu}{At}$$

4. **Photo intensity ($I_P$) :** It is the number of photons falling per unit area unit time.

$$I_P=\frac{n}{At}$$

Relation between I and $I_P$ :

$$I=I_P h\nu$$

Photo intensity is independent of frequency while intensity depends on frequency.

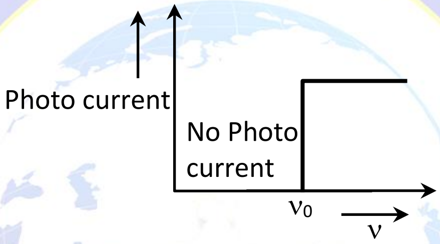
**Power :** Total energy radiated per unit time.

## EFFECT OF VARIATION FREQUENCY

### (a) Effect of Photo Emission :

$$I=I_p h\nu$$

If frequency of subject photon increase (intensity increases keeping photo intensity constant) then there is no change in no. of eject photo electrons as well as no change in photo current



### (b) Effect on kinetic Energy :

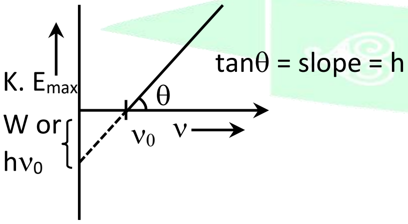
Kinetic Energy Increases with increases in frequency.

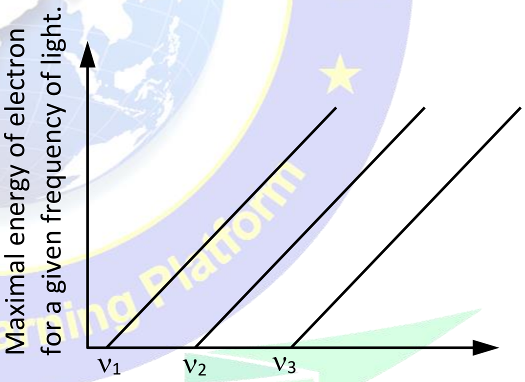
$h\nu - W = KE_{max.}$

$KE_{max} = h\nu - h\nu_0$ ; $y = mx + c$

$$KE_{max} = h\nu - \frac{hc}{\lambda_0}$$

$KE_{max} = h\nu - W$

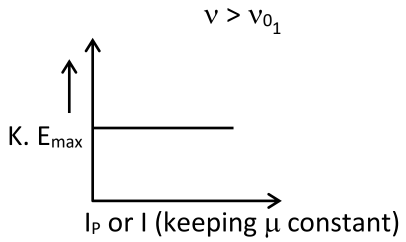




The diagram shown interdependence between light frequency and the maximal energy of electron emitted from metal. It show the interdependence for there different metals.
See that it clearly shows the limiting frequencies- different for different metals

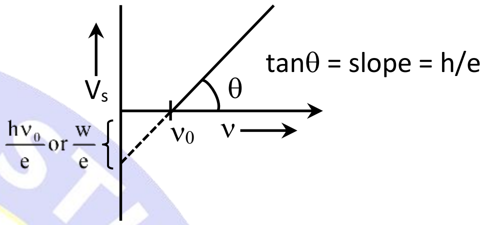
- **Intensity v/s Kinetic Energy**

  Average K.E. and $K.E_{max}$ remains constant with change in photo intensity



- **Stopping Potential or Retarding Potential ($V_s$)**

  It is the minimum potential require to stop the fastest moving electron completely or it is the minimum potential at which photo current becomes zero.



$\frac{1}{2}mv_2 = eV_S$, $V_S$ = Stopping potential

e = Charge on electron

$eV_S = h\nu - w$

$eV_S = h\nu - h\nu_0$

$\Rightarrow \quad V_S = \frac{h\nu}{e} - \frac{h\nu_0}{e}$

It can be commented that stopping potential increase with increase in frequency however if photo intensity is changed there is no effect on stopping potential.

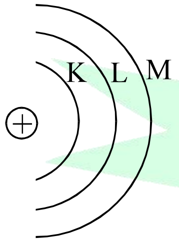
## 8. BOHR'S ATOMIC MODEL

- Bohr developed a model for hydrogen and hydrogen like atoms one-electron species (hydrogenic species). He applied quantum theory in considering the energy of an electron bond to the nucleus.

Niels Bohr
(1885-1962)

**Important postulates of Bohr's Model**

**(1) Electrons revolve around the nucleus along certain circular paths known as "ORBIT" or "SHELLS"**



K, L, M, ................. are shells

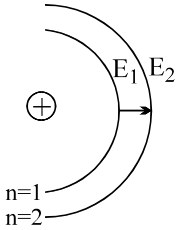
K → 1st orbit

L → 2nd orbit

M → 3rd orbit

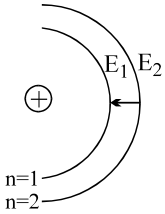
**(2)** Electron is associated with a fixed energy in a particular orbit. The change in electronic energy is possible only when; electron changes its orbit number.

(a) When an electron goes to higher orbit from lower orbit, then energy is absorbed.



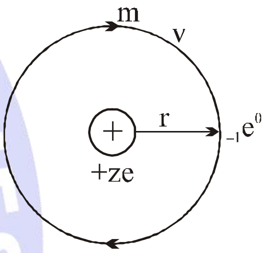
$E_2 - E_1 = \Delta E$ (Absorbed energy)

(b) If an electron jumps to lower orbit from higher orbit, then energy is radiated.



$E_2 - E_1 = \Delta E$ (Emission of energy)

**(3)** The electrostatic force of attraction acting between the electron and the nucleus is counterbalance by the centrifugal force

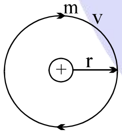


$$\frac{mv^2}{r} = K\frac{Ze^2}{r^2}$$

$$\text{or} \quad mv^2 = K\frac{Ze^2}{r} \qquad \text{..... (i)}$$

$$= \frac{1}{4\pi\in_0}.\frac{Ze^2}{r} \qquad \text{.....(ii)} \qquad [\in_0 = 8.8\times10^{-12}\ C^2N^{-1}\ m^{-2}]$$

**(4)** Electrons can revolve only in those orbits in which angular momentum is integral multiple of $\frac{h}{2\pi}$



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

where, h = Planck's constant = $6.62\times10^{-34}$ J $s^{-1}$ = $6.62\times10^{-27}$ erg. $sec^{-1}$

m = mass of electron

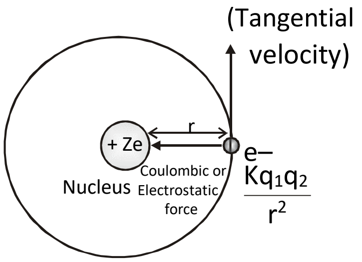
$v$ = Electronic velocity

n = orbit number

**SPOT LIGHT**

If the energy supplied to hydrogen atom is less than 13.6 eV, it will accept or absorb only those quanta which can take it to a certain higher energy level i.e., all those photons having energy less than or more than a particular energy level will not be absorbed by hydrogen atom. But if energy supplied to hydrogen atom is more than 13.6 eV then all photons are absorbed and excess energy appear as kinetic energy of emitted photo electron

## APPLICATION OF BOHR'S MODEL



### 1. Radius of various orbits (shell)

$$r = \frac{n^2h^2}{4\pi^2 mKZe^2}$$

**Derivation:**

Coulombic force $= \frac{Kq_1q_2}{r^2} = \frac{K.Ze.e}{r^2} = \frac{KZe^2}{r^2}$

(Where K is Constant) $K = 9 \times 10^9\ Nm^2/coulomb^2$

As we know that Coulombic force = Centrifugal force

$$\frac{KZe^2}{r^2} = \frac{mv^2}{r} \quad \text{or} \quad v^2 = \frac{KZe^2}{mr} \qquad ....(1)$$

As we know that $mvr = \frac{nh}{2\pi}$ or $v = \frac{nh}{2\pi mr}$ ....(2)

Now putting the value of v from eq$^n$.(2) to eq$^n$.(1)

$$\left(\frac{nh}{2\pi mr}\right)^2 = \frac{KZe^2}{mr} \quad \text{or} \quad \frac{n^2h^2}{4\pi^2m^2r^2} = \frac{KZe^2}{mr}$$

$$\boxed{r = \frac{n^2h^2}{4\pi^2 mKZe^2}} \qquad ....(3)$$

Putting the value of $\pi$, h, m, K, & e (Constants) in the above eq$^n$. (3)

$r = 0.529 \times 10^{-8} \times \frac{n^2}{Z}$ cm $\{1Å = 10^{-10}m = 10^{-8}\,cm\}$ $\boxed{r_n = 0.529 \times \frac{n^2}{Z}\ Å}$ $\boxed{r_n \propto \frac{n^2}{Z}}$

### 2. Velocity of an electron :

Since Coulombic force = Centrifugal force or $\frac{KZe^2}{r^2} = \frac{mv^2}{r}$ or $KZe^2 = (mvr)(v)$

now putting the value of Angular momentum $mvr = \frac{nh}{2\pi} \Rightarrow KZe^2 = \frac{nh}{2\pi}(v)$

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

now putting the value of $\pi$, k, e & h $\boxed{v = 2.188 \times 10^8 \times \frac{Z}{n}\ cm\,s^{-1}}$ $\boxed{v \propto \frac{Z}{n}}$

### 3. Energy of an electron

Let the total energy of an electron be E. It is the sum of kinetic and potential Energy.

i.e. E = K.E.+ P.E.

$$E = \left(\frac{1}{2}mv^2\right) + \left(\frac{Kq_1q_2}{r}\right) \qquad \left[P.E. = -\frac{Kze^2}{r}\right]$$

$$E = \frac{1}{2}mv^2 + \frac{K.Ze.(-e)}{r} = \frac{1}{2}mv^2 - \frac{KZe^2}{r}$$

now putting the value of $mv^2$ from eq. (1)

$$E = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

now putting the value of r from eq. (3)

$$E_n = -\frac{KZe^2 \times 4\pi^2 mKZe^2}{2n^2h^2} \quad \text{or} \quad \boxed{E_n = -\frac{2\pi^2 m \times K^2Z^2e^4}{n^2h^2}}$$

now putting the value of $\pi$, K, e, m, h, we get:

$$\boxed{E_n = -\frac{21.69 \times 10^{-19} \times Z^2}{n^2}\ \text{J/atom}} \quad \text{or} \quad \boxed{E_n = -13.6 \times \frac{Z^2}{n^2}\ \text{eV/atom}}$$

$$\boxed{E_n = -1312 \times \frac{Z^2}{n^2}\,\text{kJmol}^{-1}} \quad \text{or} \quad \boxed{E_n = -313.6 \times \frac{Z^2}{n^2}\,\text{kcalmol}^{-1}}$$

This formula is applicable for hydrogen atom & hydrogen like species i.e. single electron species.

Since n can have only integral values, it follows that total energy of the $e^-$ is quantised.

The –ve sign indicates that the $e^-$ is under attraction towards nucleus.

## DETECTIVE MIND

(i) $K.E = \frac{KZe^2}{2r}$ i.e. $K.E. \propto \frac{1}{r}$

On increasing radius, K.E. decreases.

(ii) $P.\ E. = -\frac{KZe^2}{r}$ i.e. $P.E. \propto -\frac{1}{r}$

On increasing radius, P.E. increases.

(iii) $E = -\frac{KZe^2}{2r}$ i.e. $E. \propto -\frac{1}{r}$

Results : On increasing radius, total energy increases.

$\boxed{PE = -2KE}$ $\boxed{KE = -E}$ $\boxed{P.E = 2E}$

This formula is only applicable for hydrogen and hydrogen like species i.e. species contains single electron.

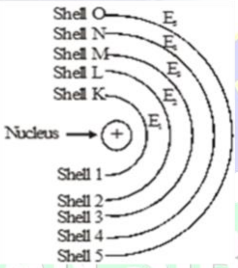
$KE = \frac{Kze^2}{2r}$ $PE = \frac{-Kze^2}{r}$ $TE = \frac{-Kze^2}{2r}$ $\boxed{\begin{array}{ccc} KE : & TE : & PE \\ 1 & -1 & -2 \end{array}}$

Energy difference between two energy levels : $E_{n_2} - E_{n_1} = -13.6 \times Z^2 \left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$

Energy level for H atom can be represented as follows :

| | | |
|---|---|---|
| n = 6 or P | $E_6 = -0.38$ eV | |
| n = 5 or O | $E_5 = -0.54$ eV | |
| n = 4 or N | $E_4 = -0.85$ eV | $E_5 - E_4 = 0.36$ eV |
| n = 3 or M | $E_3 = -1.51$ eV | $E_4 - E_3 = 0.66$ eV |
| n = 2 or L | $E_2 = -3.4$ eV | $E_3 - E_2 = 1.89$ eV |
| n = 1 or K | $E_1 = -13.6$ eV | $E_2 - E_1 = 10.2$ eV |

i.e. $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > (E_5 - E_4)$.....



**Example : 5** Calculate the radius of 1st, 2nd, 3rd, 4th Bohr's Orbit of hydrogen.

**Solution :** Radius of Bohr's orbit $r = 0.529 \times \frac{n^2}{Z}$

| | |
|---|---|
| (a) Radius of 1st orbit :<br>$r = 0.529 \times \frac{1^2}{1} = 0.529$ Å | (b) Radius of 2nd orbit :<br>$r = 0.529 \times \frac{2^2}{1} = 0.529 \times 4 = 2.116$ Å |
| (c) Radius of 3rd orbit :<br>$r = 0.529 \times \frac{3^2}{1} = 0.529 \times 9 = 4.761$ Å | (d) Radius of 4th orbit :<br>$r = 0.529 \times \frac{4^2}{1} = 0.529 \times 16 = 8.464$ Å |

**Example : 6** 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

**Answer :** (3)

**Solution :** $\frac{r_x}{r_y}=\frac{1}{9}=\frac{0.529\times\frac{n_x^2}{3}}{0.529\times\frac{n_y^2}{3}} \Rightarrow \sqrt{\frac{n_x^2}{n_y^2}}\Rightarrow\sqrt{\frac{1}{9}} \Rightarrow \frac{n_x}{n_y}=\frac{1}{3}=\frac{\text{K Shell}}{\text{M Shell}}$

**Example : 7** Calculate the energy for 2nd excited state of $Li^{+2}$ ion.

**Answer :** – 13.6 eV/atom

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

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

**Example : 8** If the potential energy of an electron in hydrogen atom is –6.8 eV, then find kinetic energy and total energy of electron in this orbit. Also find radius of this orbit.

**Answer :** (K.E. = 3.4 eV, T.E. = – 3.4 eV, r == 2.16 Å)

**Solution :**

1 P.E. = –2K.E. ⇒ –6.8 = –2K.E ⇒ K.E. = 3.4 eV

2. T.E. = – K.E. = – 3.4 eV

3. $\because E=-13.6\times\frac{Z^2}{n^2}$ $\therefore -3.4=-13.6\times\frac{1^2}{n^2}$

$\Rightarrow n^2=\frac{-13.6}{-3.4}=6$ i.e. n = 2

4. $r=0.529\times\frac{n^2}{Z}$ Å $\Rightarrow r=0.529\times\frac{(2)^2}{1}$ Å

$=0.529\times 4$Å $=2.16$ Å

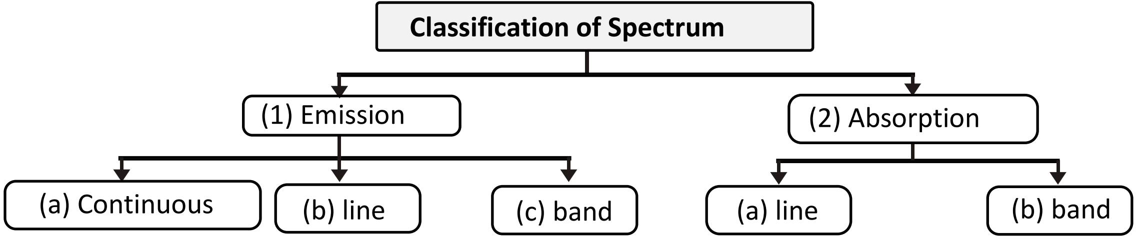
- **Energy Definitions**

| | | |
|---|---|---|
| **(a) Ground state (G. S.)**<br>**(Highest e⊖ occupied shell)**<br>The lowest energy state of an atom or ion or molecule<br>G. S. for H-atom n = 1<br>$He^+$ ion n = 1 | **(b) Excited state (E. S.)**<br>The energy states above the ground state are referred to as excited states<br>n = 2 1st E. S.<br>n = 3 2nd E. S.<br>n = 4 3rd E. S.<br>Total E. S. = (n – 1) | **(c) Excitation energy:** Energy required to excite an electron from its ground state to any excited state is called excitation energy.<br>$E_2 - E_1$ = first excitation energy<br>$E_3 - E_1$ = second excitation energy<br>$E_4 - E_1$ = third excitation energy<br>1st E. P. = $E_2 - E_1$<br>= –3.4 – (-13.6) = 10.2 eV<br>2nd E. P. $E_3 - E_1$<br>= –1.51 – (–13.6) = 12.09 eV |
| **(d) Ionization potential (I. P.)/Energy/Enthalpy**<br>Corresponding energy required to remove the electron from G.S. to the infinite excited state.<br>I. P. $= E_\infty - E_1$<br>= 0 – (–13.6)<br>= 13.6 eV | **(e) Separation Energy (S.E.) / BINDING ENERGY**<br>The amount of energy needed to remove to infinity the electron from the excited state.<br>e.g., S. E. = $E_\infty - E_2$ = 0 – (–3.4)<br>= 3.4 eV<br>also S. E. = $E_\infty - E_3$ = 0 – (–1.51)<br>= 1.51 eV | |

◆

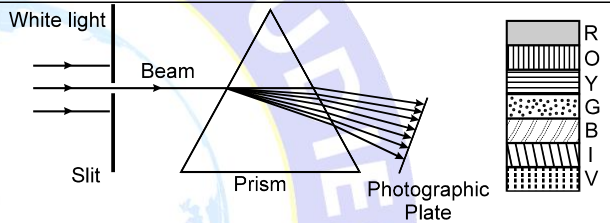
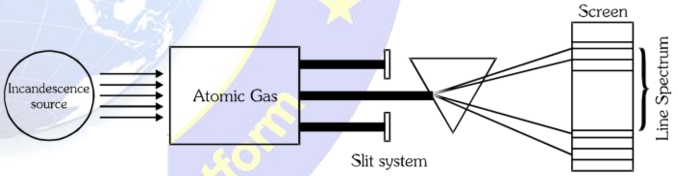
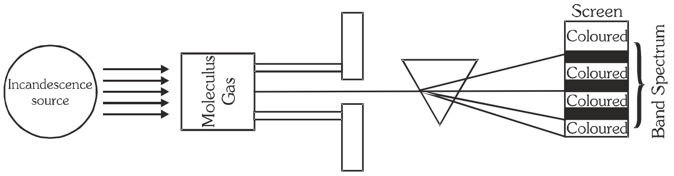
## 9. SPECTRUM

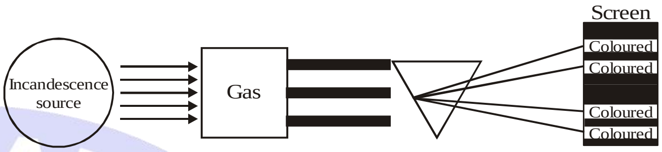
**Spectrum :** When a radiation is passed through a spectroscope (prism) for the dispersion of the radiation, the pattern (photograph) obtained on the screen (photographic plate) is called as spectrum of the given radiation



**Classification of Spectrum**

- (1) Emission
  - (a) Continuous
  - (b) line
  - (c) band
- (2) Absorption
  - (a) line
  - (b) band

| Spectrum | | |
|---|---|---|
| **(1)** | **Emissions spectrum :** When the radiation emitted from incandescence source (e.g. from the candle, sun, tube light, burner, bulb, or by-passing electric discharge through a gas at low pressure, by heating some substance at high temperature) is passed directly through the prism and the pattern obtained on the screen is known as emission spectrum | |
| **(a)** | **Emission continuous spectrum or continuous spectrum :**<br>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 radiations through a spectro scope, a spectrum is obtained which has 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. |  |
| **(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 electron translation then emits radiations.<br>On examining these radiations through a spectroscope a spectrum is obtained on the screen, which consists of groups of closely packed lines called Bands, therefore this type of Emission spectrum is called as emission band |  |

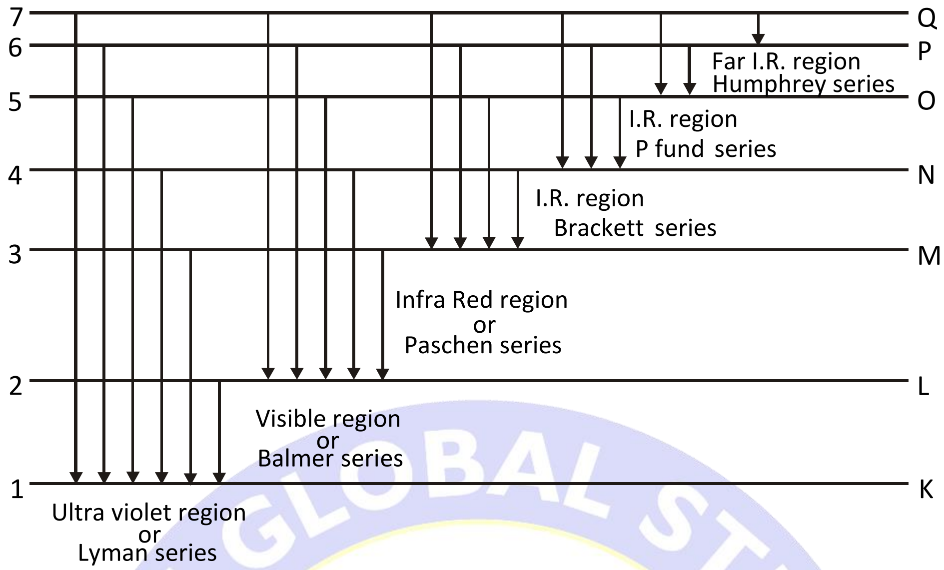
| | | |
|---|---|---|
| | spectrum. Bands are separated from each other by dark space. | |
| **(2)** | **Absorption spectrum :** When white light is first passed through a solution or vapours of a chemical substance or gas and then analyzed by spectroscope, it is observed that some dark lines are obtained in otherwise continuous spectrum. This type of spectrum is called as Absorption spectrum.<br>• If white light is passed through atomic gas then the obtained spectrum is called as Absorption line spectrum.<br>• If white light is passed through molecular gas then the obtained spectrum is called as Absorption band spectrum. |  |

## SPOT LIGHT

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.

## 10. HYDROGEN LINE SPECTRUM OR HYDROGEN SPECTRUM

When an electric excitation is applied on hydrogen atomic 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 Infrared region. These lines are grouped into different series.



| | Name of series | Wavelength | $n_1$ | $n_2$ | Region |
|---|---|---|---|---|---|
| 1. | Lyman | $\frac{1}{\lambda}=R_H\left[\frac{1}{1^2}-\frac{1}{n^2}\right]$ | 1 | n > 1 | UV |
| 2. | Balmer | $\frac{1}{\lambda}=R_H\left[\frac{1}{2^2}-\frac{1}{n^2}\right]$ | 2 | n > 2 | Visible |
| 3. | Paschen | $\frac{1}{\lambda}=R_H\left[\frac{1}{3^2}-\frac{1}{n^2}\right]$ | 3 | n > 3 | IR |
| 4. | Brackett | $\frac{1}{\lambda}=R_H\left[\frac{1}{4^2}-\frac{1}{n^2}\right]$ | 4 | n > 4 | IR |
| 5. | Pfund | $\frac{1}{\lambda}=R_H\left[\frac{1}{5^2}-\frac{1}{n^2}\right]$ | 5 | n > 5 | far IR |
| 6. | Humphrey | $\frac{1}{\lambda}=R_H\left[\frac{1}{6^2}-\frac{1}{n^2}\right]$ | 6 | n > 6 | far-far IR |

**Rydberg formula:** In 1890, Rydberg gave a very simplest theoretical Equation for the calculation of the wavelength of various lines of hydrogen like spectrum and the equation is

$$\bar{\nu}=\frac{1}{\lambda}=RZ^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$ where R = Rydberg constant = 109678 $cm^{-1} \simeq 109700\ cm^{-1}$

$$\frac{1}{R}=9.12\times10^{-6}\ cm = 912\ Å$$

## SPOT LIGHT

For any series

First line / initial line

$n_2 = n_1 + 1$

last line / marginal line / limiting line; $n_2 = \infty$

**Derivations of Rydberg formula :**

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = \frac{-2\pi^2 mK^2Z^2e^4}{n_2^2h^2} - \left[\frac{-2\pi^2 mK^2Z^2e^4}{n_1^2h^2}\right]$$

$$\Delta E = \frac{2\pi^2 mK^2Z^2e^4}{n_1^2h^2} - \frac{2\pi^2 mK^2Z^2e^4}{n_2^2h^2} \qquad \left(\because \Delta E = h\nu = \frac{hc}{\lambda}\right)$$

$$\frac{hc}{\lambda} = \frac{2\pi^2 mK^2Z^2e^4}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ or } \frac{1}{\lambda} = \frac{2\pi^2 mK^2e^4Z^2}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where $\frac{2\pi^2 mK^2e^4}{ch^3}$ is a constant which is equal to Rydberg constant (R).

$$\boxed{\frac{1}{\lambda} = \bar{\nu} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]}$$

- **Calculation of number of spectral lines**

(a) Total number of spectral lines = 1 + 2 + ..... $(n_2 - n_1)$ = $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

if $n_1$ = 1(ground state)

Total number of spectral lines = $\frac{(n_2 - 1)n_2}{2}$ = $\frac{n(n-1)}{2}$

(b) Number of spectral lines which falls in a particular series $(n_2 - n_1)$
where $n_2$ = higher energy series, $n_1$ = lower energy series

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

1. Bohr's theory does not explain the spectrum of multi electron atom.
2. Why the Angular momentum of the revolving electron is equal to $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.
3. Bohr interrelate quantum theory of radiation and classical law of physics without any theoretical explanation.
4. 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 higher resolution power.
5. Bohr theory does not explain the splitting of spectral lines in the presence of magnetic field (Zeman's effect) or electric field (Stark's effect)

**Example : 9** Calculate the wavelength of a photon emitted when an electron in H- atom make a transition from n = 2 to n = 1.

**Answer:** $\lambda = \frac{4}{3R}$

**Solution:** $\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$\therefore \frac{1}{\lambda} = R(1)\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$\therefore\ \frac{1}{\lambda} = \frac{3R}{4} \text{ or } \lambda = \frac{4}{3R}$$

**Example : 10** Calculate wavelength for 2nd line of Balmer series of $He^+$ ion

**Answer:** $\lambda = \frac{4}{3R}$

**Solution:**

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

$n_1 = 2 \quad n_2 = 4$

$$\frac{1}{\lambda} = R(2^2)\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

$$\frac{1}{\lambda} = \frac{3R}{4}\lambda = \frac{4}{3R}$$

**Example : 11** 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 IR region

**Answer:** **(a) 6** **(b) Zero** **(c) Zero** **(d) 6**

**Solution:**

**(a)** total number of lines:

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

**(b)** number lines present in U.V. region

e- moves from 6th to 3rd orbit in multi steps.

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

**(c)** 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 is zero.

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

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

Number of lines in Paschen series = $n_2 - 3$
= $6 - 3$
= $3$

Number of lines in Bracket series = $n_2 - 4$
= $6 - 4$
= $2$

Number of lines in P fund series = $n_2 - 5$
= $6 - 5$
= $1$

So total number of lines = $3 + 2 + 1 = 6$

## 11. WAVE MECHANICAL MODEL OF AN ATOM

This model consists three Basis.

1. de-Broglie concept (Dual nature of Matter)
2. Heisenberg's Uncertainty principle.
3. Schrodinger Equation.

### 1. The Dual nature of matter (The wave nature of electron)

(i) 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.

(ii) The wave nature of light rays and X-rays is proved on the basis of their interference and diffraction and many facts related to radiations can only be explained when the beam of light rays is regarded as composed of energy corpuscles or photons whose velocity is $3 \times 10^{10}$ cm/s.

(iii) According to de-Broglie, the wavelength $\lambda$ of an electron is inversely proportional to its momentum p.

$\lambda \propto \frac{1}{p}$ or $\lambda = \frac{h}{p}$ (Here h = Planck's constant, p = momentum of electron)

$\because$ Momentum (p) = Mass (m) × Velocity (v) $\therefore$ $\boxed{\lambda = \frac{h}{mv}}$

(iv) The above relation can be confined as follows by using Einstein's equation, Planck's quantum theory and wave theory of light.

Einstein's equation, $E = mc^2$ where E is energy, m is mass of a body and c is its velocity.

$\because$ $E = h\nu$ (According to Planck's quantum theory) and $c = \nu\lambda$ (According to wave theory of light)

$\therefore$ $\nu = \frac{c}{\lambda} \Rightarrow E = h \times \frac{c}{\lambda}$

But according to Einstein's equation $E = mc^2$

$E = mc^2 = h \times \frac{c}{\lambda}$ or $mc = \frac{h}{\lambda}$ or $p = \frac{h}{\lambda}$ or $\lambda = \frac{h}{p}$

(v) Relation between kinetic energy and wavelength

$$\text{K.E.} = \frac{1}{2}mv^2$$

$$m^2 v^2 = 2m\text{K.E.}$$

$$mv = \sqrt{2mKE}$$

$$\lambda = \frac{h}{\sqrt{2m\text{K.E.}}}$$

If charge Particle 'q' is accelerated by potential , the K.E. = qv $\Rightarrow$ $\lambda = \frac{h}{\sqrt{2mqV}}$ $\lambda_e = \frac{12.25A^\circ}{\sqrt{V}}$

(vi) It is clear from the above equation that the value of $\lambda$ decreases on increasing either m or v or both. The wavelength of many fast-moving objects like an aeroplane or a cricket ball, is very low because of their high mass.

- **Bohr's Theory and de-Broglie concept :**

(i) According to de-Broglie, the nature of an electron moving around the nucleus is like a wave that flows in circular orbits around the nucleus.

(ii) If an electron is regarded as a wave, the quantum condition as given by Bohr in his theory is readily fulfilled.

(iii) If the radius of a circular orbit is r, then its circumference will be $2\pi r$.

(iv) We know that according to Bohr theory, $mvr = \frac{nh}{2\pi}$

or $2\pi r = \frac{nh}{mv}$ ($\because$ mv = p momentum) or $2\pi r = \frac{nh}{p}$ $\left(\because \frac{h}{p} = \lambda \text{ de-Broglie equation}\right)$

$\therefore$ $2\pi r = n\lambda$ (where n = total number of waves 1, 2, 3, 4, 5, .....$\infty$ and $\lambda$ = Wavelength

(v) $\because$ $2\pi r = \frac{nh}{mv}$ or $mvr = \frac{nh}{2\pi}$

$\because$ mvr = Angular momentum

Thus mvr = Angular momentum, which is a integral multiple of $\frac{h}{2\pi}$.

(vi) It is clear from the above description that according to de-Broglie there is similarity between wave theory and Bohr theory.

number of waves made by electron in one complete revolution

$= \frac{2\pi r}{\lambda}$ = n (orbit number)

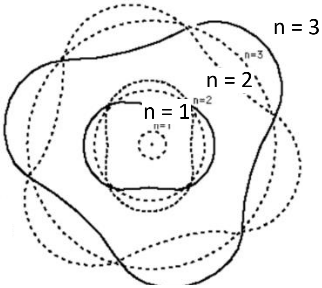
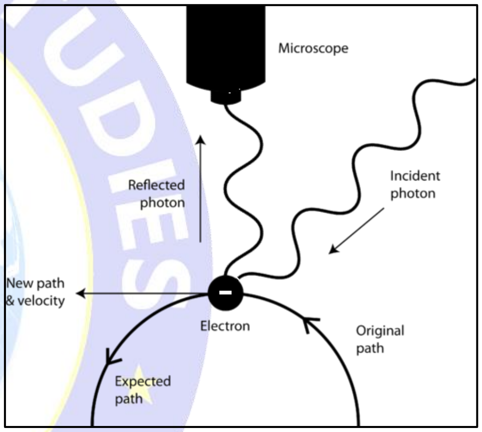


**Figure:** Similarity between de-Broglie waves and Bohr's orbit

## 2. Heisenberg uncertainty principle

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 ($\Delta x$) and the uncertainty of momentum ($\Delta p$) or $\Delta(mv)$, are related by Heisenberg's relationship as :



$$\Delta x \, . \, \Delta p \geq \frac{h}{4\pi} \quad \text{or } \Delta x \, . \, \Delta\, (mv) \geq \frac{h}{4\pi}$$

(where h is Planck's constant.)

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

$$\Delta x \, . \, \Delta v \geq \frac{h}{4\pi m} \qquad \Delta x . \, \Delta v \geq \frac{6.624 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}} = 0.57 \text{ erg second per gram approximately}$$

$\Delta x \, \Delta v$ is called uncertainty product

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., $\Delta x$ is very small, $\Delta v$ becomes large and vice-versa.

$$\Delta E \, \Delta t \geq \frac{h}{4\pi} \quad \text{(for energy and time)}$$

On the basis of this principle, therefore, Bohr's picture of an electron in an atom, which gives a fixed position in a fixed orbit best we can think of in terms of probability of locating an electron with a probable velocity in a given region of space at a given time. The space or a three-dimensional region round the nucleus where there is maximum probability of finding an electron of a specific energy is called an atomic orbital.

**Example : 12** Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of 30 $ms^{-1}$

**Answer:** $2.2 \times 10^{-34}$ m

**Solution:** $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.1 \times 30} = 2.2 \times 10^{-34}$ 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 only macroscopic objects in our everyday life, de Broglie relationship has no significance in everyday life.

**Example : 13** A golf ball has a mass of 40 g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

**Solution:** The uncertainty in the speed is 2%, i.e., $45 \times \frac{2}{100} = 0.9\ \text{m s}^{-1}$

Using the equation, $\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626\times10^{-34}}{4\times3.14\times40\times10^{-3}\left(0.9\text{ms}^{-1}\right)} = 1.46 \times 10^{-33}\ \text{m}$

This is nearly ~$10^{18}$ times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

**Example : 14** What should be the uncertainty in position if uncertainty in momentum is $1 \times 10^{-2}$ g cm/sec. and value of h is $6.6252 \times 10^{-34}$ Joule sec.?

(A) $1.054 \times 10^{-22}$ m (B) $1.054 \times 10^{-25}$ m (C) $0.525 \times 10^{-27}$ m (D) $1.054 \times 10^{-32}$ m

**Solution:** Given that

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

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

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

or $\Delta x = \frac{6.6252\times10^{-34}}{4\times3.14\times10^{-7}} = 0.525 \times 10^{-27}$ m

## 3. Schrodinger Equation

The nature of electron in atom can be discussed in terms of the solution of Schrodinger wave equation

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

$\psi$ - wave function

$\psi^2$ - probability of finding electron

E - total energy

U - potential energy

The wave function of an electron ($\psi$) in the field of nucleus of atom is called atomic orbital. It is a three dimensional amplitude.

$\psi^2\delta v$ is the probability of finding the electron in a volume element $\delta v$ surrounding the nucleus of an atom.

Solution of Schrodinger equation provide set of three quantum number (n, *l*, m)

## Practice Section-03

## 12. QUANTUM NUMBER

As we know to search a particular person in this world 4 things are needed:-

- Country to which the person belongs.
- The city in that country where the person is residing
- The area in that city
- House number

Similarly to locate the position of an electron in the atom 4 identification number are required and these identification numbers are called as quantum numbers.

1. Principal quantum number (n) → Shell (Orbit)
2. Azimuthal quantum number (l) → Sub shell

3. Magnetic quantum number (m) → Orbital
4. Spin quantum number (S) → Spin of $e^-$

1. **Principal quantum number :** Given By → Bohr's

It represents the name, size and energy of the shell to which $e^-$ belongs

- The value of n lies between 1 to ∞

i.e. n = 1, 2, 3, 4............. ∞ corresponding name of shells are K, L, M, N, O, .............

- Greater the value of n, greater is the distance from the nucleus.

$$r = 0.529 \times \frac{n^2}{z} \text{ Å}$$

$r_1 < r_2 < r_3 < r_4 < r_5$ .............

- Greater the value of n, greater is the energy of shell

$$E = -13.6 \times \frac{z^2}{n^2} \text{ eV/atom}$$

$E_1 < E_2 < E_3 < E_4$ .............

- The angular momentum of a revolving electron is $mvr = \frac{nh}{2\pi}$

Where n = Principal quantum number.

- Number of Sub – shell = n
- Number of orbitals = $n^2$
- The number of electrons in a particular shell is equal to $2n^2$

2. **Azimuthal quantum number / Angular quantum number / Secondary quantum number /Subsidiary quantum number :**

Represented by '$\ell$' (Given by – Sommerfeld)

- It represents the shape of the subshell and orbital angular momentum
- Value of $\ell$ between 0 to (n – 1)

i.e. $\ell$ = 0, 1, 2 – – – – – – – – – – (n–1)

$\ell$ = 0(s Subshell)

$\ell$ = 1(p Subshell)

$\ell$ = 2(d Subshell)

$\ell$ = 3(f Subshell)

**Example:** If n = 1 then $\ell = 0 \Rightarrow$ 1s i.e. in n =1 shell, only one subshell 's' is present.

If n = 2 then $\ell = 0, 1 \Rightarrow$ 2s, 2p i.e. in n =2 shell, two subshell 's' & 'p' are present.

If n = 3 then $\ell = 0, 1, 2 \Rightarrow$ 3s, 3p, 3d i.e. in n =3 shell, three subshell's', 'p' & 'd' are present.

If n = 4 then $\ell = 0, 1, 2, 3 \Rightarrow$ 4s,4p, 4d, 4f i.e. in n =4 shell, four subshell 's' , 'p' , 'd' & 'f' are present.

- The orbital angular momentum = $\sqrt{\ell(\ell+1)}\,\frac{h}{2\pi}$ or $\sqrt{\ell(\ell+1)}\,\hbar$ $\left\{\because \hbar = \frac{h}{2\pi}\right\}$ { $\hbar$ is called as 'hash' }

Orbital angular momentum : For s subshell = 0 For p Subshell = $\sqrt{2}\,\frac{h}{2\pi}$ or $\sqrt{2}\,\hbar$

- Number of orbitals in a subshell = $2\ell + 1$
- The number of electron in a particular subshell is equal to $2(2\ell + 1)$

for s subshell number of electrons = 2 $e^-$ for p subshell number of electrons = 6 $e^-$

for d subshell number of electrons = 10 $e^-$ for f subshell number of electrons = 14 $e^-$

- Shape of the subshell :

s → spherical

p → dumb bell shape

d → double dumb bell shape

f → complex shape

**3. Magnetic quantum number /Orientation quantum number (m) :** given by → Linde

It represents the shape of different orbitals and the orientation of electron cloud (orbital)

- Under the influence of magnetic field each subshell is further subdivided into orbitals (The electron cloud is known as orbital)

  Magnetic quantum number describe these different distribution of electron cloud.
- Value of m = all integral value from $-\ell$ to $+\ell$ including zero.

  i.e. Value of m = $-\ell, \ldots -1, 0, 1, \ldots + \ell$

**Case-I** If $\ell$ = 0 then m = 0 it implies that s subshell has only one orbital called as s orbital.

**4. Spin Quantum number (s) :** (Given by → Gold schmidt)

It represents the direction of electron Spin around its own axis

- for clock wise spin/spin up(↑) electron → $\pm\frac{1}{2}$
- for anti-clock wise spin/spin down(↓) electron → $\mp\frac{1}{2}$

Spin angular momentum of an $e^-$ = $\sqrt{s(s+1)}.\frac{h}{2\pi}$ or $\sqrt{s(s+1)}\hbar$

- Each orbital can accommodate 2 electrons with opposite spin or spin paired.

  Correct $\boxed{\uparrow\downarrow}$ Spin paired $e^-$ Wrong $\boxed{\uparrow\uparrow}$ Spin parallel $e^-$

| Principal Q.No. 'n' | Azimuthal Q.No. 'l' | Magnetic Q.No. 'm' | Spin Q.No. 's' | No. of electrons in a subshell | No. of electrons in a main shell |
|---|---|---|---|---|---|
| 1 | 0 (s) | 0 | +1/2, –1/2 | 2 | 2 |
| 2 | 0 (s) | 0 | +1/2, –1/2 | 2 | 8 |
|  | 1 (p) | –1 | +1/2, –1/2 | 6 |  |
|  |  | 0 | +1/2, –1/2 |  |  |
|  |  | +1 | +1/2, –1/2 |  |  |
| 3 | 0 (s) | 0 | +1/2, –1/2 | 2 | 18 |
|  | 1 (p) | –1 | +1/2, –1/2 | 6 |  |
|  |  | 0 | +1/2, –1/2 |  |  |
|  |  | +1 | +1/2, –1/2 |  |  |
|  | 2 (d) | –2 | +1/2, –1/2 | 10 |  |
|  |  | –1 | +1/2, –1/2 |  |  |
|  |  | 0 | +1/2, –1/2 |  |  |
|  |  | +1 | +1/2, –1/2 |  |  |
|  |  | +2 | +1/2, –1/2 |  |  |
| 4 | 0 (s) | 0 | +1/2, –1/2 | 2 | 32 |
|  | 1 (p) |  |  | 6 |  |
|  | 2 (d) |  |  | 10 |  |
|  | 3 (f) | –3 | +1/2, –1/2 | 14 |  |
|  |  | –2 | +1/2, –1/2 |  |  |
|  |  | –1 | +1/2, –1/2 |  |  |
|  |  | 0 | +1/2, –1/2 |  |  |
|  |  | +1 | +1/2, –1/2 |  |  |
|  |  | +2 | +1/2, –1/2 |  |  |
|  |  | +3 | +1/2, –1/2 |  |  |

**Example: 15** Calculate the value of n, $\ell$ and m for 3s orbital ?

**Solution:** n = 3, $\ell$ = 0, m = 0

**Example: 16** Which of the following set of quantum numbers is not possible ?

(a) n = 2, $\ell$ = 0, m – 1, s = $-\frac{1}{2}$ (b) n = 3, $\ell$ = 2, m = 0, s = $\pm\frac{1}{2}$

(c) n = 2, $\ell$ = 3, m = –2, s = $\pm\frac{1}{2}$

**Solution:** (a) not possible (b) possible (c) not possible

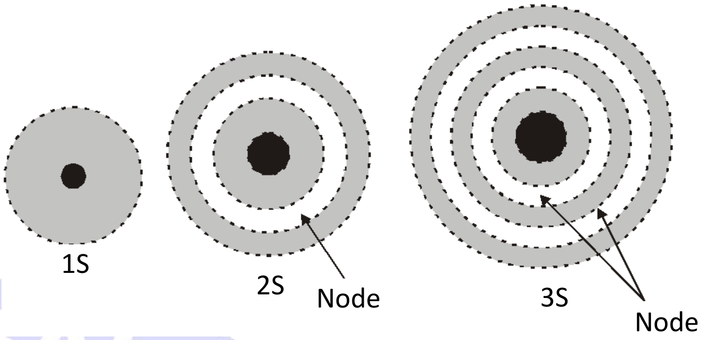
**Example:17** Calculate the value of n, $\ell$ and m for $3p_z$ orbital?

**Solution:** $n = 3, \ell = 1, m = 0$

## 13. SHAPE OF ATOMIC ORBITALS

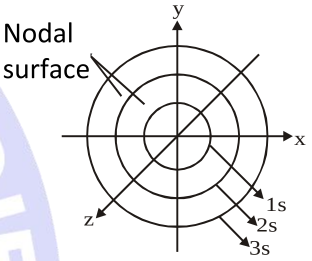
➢ **Shapes of s-orbitals :**

The s-orbitals are spherically symmetrical about the nucleus, i.e., the probability of finding s electron is same in all directions from the nucleus. The size of the orbital depends on the value of principal quantum number, there is one spherically symmetrical orbital. The 1s orbital is smaller than 2s-orbital and 2s-orbital is smaller than 3s, but all are spherical in shape as shown in figure.



Although the s-orbitals belonging to different shells are spherically symmetrical, yet they differ in certain respects as explained below :

- The probability of 1s electron is found to be maximum near the nucleus and decreases as the distance from the nucleus increases. In case of 2s electrons, the probability is again maximum near the nucleus and then decreases to zero and increases again and then decreases as the distance from the nucleus from the nucleus increases. The intermediate region (a spherical shell) where the probability is zero is called a nodal surface or simply node. Thus, 2s-orbital differs from 1s-orbital in having one node within it. Similarly, 3s has two nodes. in general, any ns orbital has (n -1) nodes.



- The size and energy of the s-orbital increases as the principal quantum number increases, i.e., the size and energy of s-orbital increases in the order 1s < 2s < 3s ....

The s orbital of higher energy levels are also symmetrically spherical and can be represented as follows :s

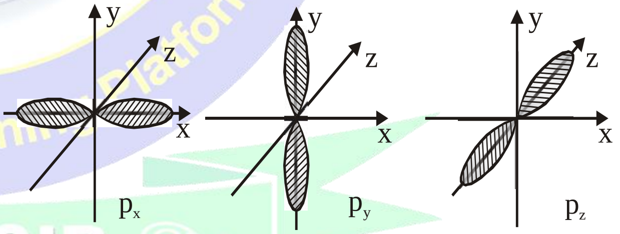
**Case-II** If $\ell = 1$ (p - subshell) then $m = \begin{array}{c|c|c} -1 & 0 & +1 \\ \hline p_x & p_z & p_y \end{array}$

It implies that, p subshell have three orbitals called as $p_x$, $p_y$ and $p_z$.

**Shape of p-orbitals:**

There are three p-orbitals, commonly referred to as $p_x$, $p_y$ and $p_z$. These three p-orbitals, possess equivalent energy and therefore, have same relation with the nucleus. They, however, differ in their direction & distribution of the charge.

These three p-orbitals are situated at right angle to one another and are directed along x, y and z axes (figure)



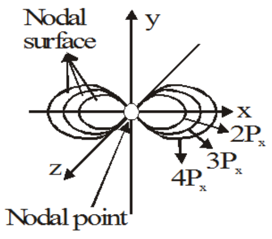
- Each p orbital has dumb bell shape (2 lobes which are separated from each other by a point of zero probability called nodal point or node or nucleus).
- The two lobes of each orbital are separated by a plane of zero electron density called nodal plane.
- Each p orbital of higher energy level are also dumb bell shape but they have nodal surface.

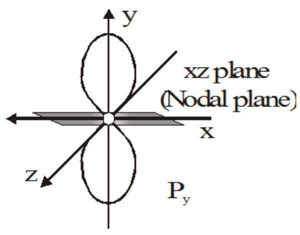
**Nodal surface :**

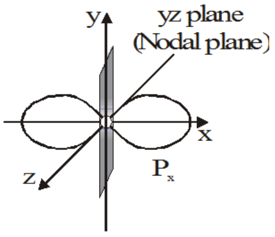
| Orbital | Nodal surface |
|---|---|
| 2 $p_x$ | 0 |
| 3 $p_x$ | 1 |
| 4 $p_x$ | 2 |
| $np_x$ | (n – 2) |

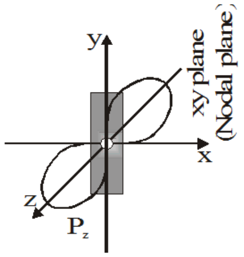
**Nodal Plane :**

| Orbital | Nodal plane |
|---|---|
| $p_x$ | yz plane |
| $p_y$ | xz plane |
| $p_z$ | xy plane |







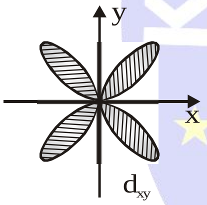


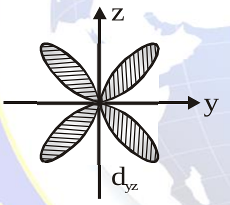
**Case III** When $\ell$ = 2, 'm' has five values – 2, –1, 0, +1, +2. It implies that d subshell of any energy shell has five orbitals. All the five orbitals are not identical in shape. Four of the d orbitals $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_{x^2-y^2}$ contain four lobes while fifth orbital $d_{z^2}$ consists of only two lobes. The lobes $d_{xy}$ orbital lie between x and y axis. Similar is the case for $d_{yz}$ and $d_{xz}$. Four lobes of $d_{x^2-y^2}$ orbital are lying along x and y axes while the two lobes of $d_{z^2}$ orbital are lying along z axis and contain a ring of negative charge surrounding the nucleus in xy plane. Geometry of d orbital is Double Dumb bell.

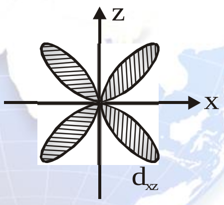
$$m=\left|\begin{array}{c|c|c|c|c} -2 & -1 & 0 & +1 & +2 \\ d_{xy} & d_{yz} & d_{z^2} & d_{zx} & d_{x^2-y^2} \end{array}\right|$$

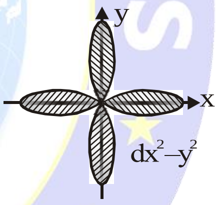
**Shape of d–orbitals :**

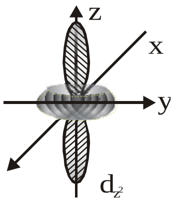
- It implies that d subshell has 5 orbitals i.e. five electron cloud and can be represented as follows.









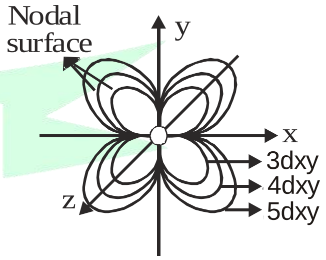


**In d orbital:**

Number of nodal surface = n–$\ell$ –1

number of nodal plane = $\ell$

total node = n – $\ell$ – 1 + $\ell$ = (n - 1)



- **Nodal plane:** $d_{xy} \rightarrow$ xz & yz nodal plane :

$d_{xz} \rightarrow$ xy & zy nodal plane :

$d_{zy} \rightarrow$ zx & yx nodal plane :

$d_{x^2-y^2} \rightarrow$ 2, nodal plane :

$d_{z^2} \rightarrow$ 0, nodal plane :

**Note:** Orbitals of d subshell are Equivalent in energy.

**f subshell** : When $\ell$ = 3 (f subshell)

Then $$\left|\begin{array}{c|c|c|c|c|c|c} m=-3 & -2 & -1 & 0 & +1 & +2 & +3 \\ f_{x^3} & f_{y^3} & f_{xyz} & f_{z^3} & f_{x(y^2-z^2)} & f_{y(z^2-x^2)} & f_{z(x^2-y^2)} \end{array}\right|$$

- The structure of f-orbital is very complex
- The number of values of f-orbitals in f subshell show that f subshell has 7 orbitals which are equivalent in Energy.

**Representation of the orbitals :**

s subshell → $\overset{s}{\boxed{s}}$ p subshell → $\overset{p}{\boxed{p_x}\boxed{p_y}\boxed{p_z}}$

d subshell → $\overset{d}{\boxed{d_{xy}}\boxed{d_{yz}}\boxed{d_{z^2}}\boxed{d_{xz}}\boxed{d_{x^2-y^2}}}$ f subshell → $\overset{f}{\boxed{f_{x^3}}\boxed{f_{y^3}}\boxed{f_{z^3}}\boxed{f_{xyz}}\boxed{f_{x(y^2-z^2)}}\boxed{f_{y(z^2-x^2)}}\boxed{f_{z(x^2-y^2)}}}$

## 14. ELECTRONIC CONFIGURATION

Filling of electron in different energy subshell is electronic configuration.

**Rules for filling Subshell** :

1. Aufbau Principle 2. (n +ℓ) rule

3. Hund's rule of maximum multiplicity 4. Pauli's exclusion principle

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 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 are as follows.

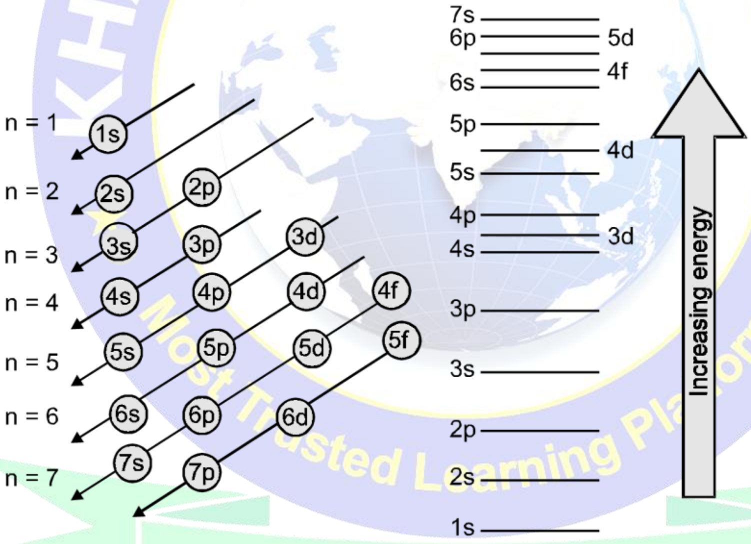


Fig. Sequence of filling of electrons in orbitals belonging to different energy levels

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

**For Example:**

$_1H$ → $1s^1$

$_2He$ → $1s^2$

$_3Li$ → $1s^2, 2s^1$

$_4Be$ → $1s^2, 2s^2$

$_5B$ → $1s^2, 2s^2, 2p^1$

$_6C$ → $1s^2, 2s^2, 2p^2$

$_7N$ → $1s^2, 2s^2, 2p^3$

$_8O$ → $1s^2, 2s^2, 2p^4$

$_{9}$F → $1s^2, 2s^2, 2p^5$

$_{10}$Ne → $1s^2, 2s^2, 2p^6$

$_{11}$Na → $1s^2, 2s^2, 2p^6, 3s^1$

$_{12}$Mg → $1s^2, 2s^2, 2p^6, 3s^2$

$_{13}$Aℓ → $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

$_{14}$Si → $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$

$_{15}$P → $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

$_{16}$S → $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

$_{17}$Cl → $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

$_{18}$Ar → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

$_{19}$K → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

$_{20}$Ca → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$

$_{21}$Sc → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$

$_{22}$Ti → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$

$_{23}$V → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$

$_{24}$Cr → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$ [Exception]

$_{25}$Mn → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$

$_{26}$Fe → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

$_{27}$Co → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$

$_{28}$Ni → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

$_{29}$Cu → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$ [Exception]

$_{30}$Zn → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

**Electronic configuration can be written by following different methods :**

- $_{26}$Fe → (1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
  (2) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$
  (3) $1s^2, 2s^2p^6, 3s^2p^6d^6, 4s^2$
  (4) [Ar] $4s^2\ 3d^6$
- $_{26}$Fe → $1s^2\ \underbrace{2s^2 2p^6}_{(n-2)}\ \underbrace{3s^2 3p^6 3d^6}_{(n-1)}\ \underbrace{4s^2}_{n}$

  n → Outer most Shell or Ultimate Shell or Valence Shell

  In this Shell e$^-$ are called as Valance electron or this is called core charge

  (n–1) → Penultimate Shell or core or pre valence Shell

  (n–2) → Pre Penultimate Shell
- If we remove the last n Shell (ultimate Shell) then the remaining shell collectively be called as Kernel.

  **Example:** $_{26}$Fe → $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6 3d^6}_{\text{Kernel}}\ 4s^2$

**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.

**In case of H-atom :** Energy only depends on principle quantum number

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f <$ ..................

| 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) |

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

**3.** **Hund's rule of Maximum Multiplicity:** (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.
- Thus the Orbital available in the subshell are first filled singly with parallel spin electron before they begin to pair this means that pairing of electrons occurs with the introduction of second electron in 's' subshell, fourth electron in 'p' subshell, 6th electron in 'd' Subshell & 8th $e^-$ in 'f' subshell.

**Example :** $_5B \rightarrow$ $1s^2$ $2s^2$ $2p^1$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\phantom{\uparrow}}\boxed{\phantom{\uparrow}}$

$_6C \rightarrow$ $1s^2$ $2s^2$ $2p^2$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\phantom{\uparrow}}$

$_7N \rightarrow$ $1s^2$ $2s^2$ $2p^3$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

$_8O \rightarrow$ $1s^2$ $2s^2$ $2p^4$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

$_9F \rightarrow$ $1s^2$ $2s^2$ $2p^5$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

$_{10}Ne \rightarrow$ $1s^2$ $2s^2$ $2p^6$

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

**4.** **Pauli's Exclusion principle :** In 1925 Pauli stated that no two electron in an atom can have same values of all four quantum numbers. i.e. An orbital can accommodates maximum 2 electrons with opposite spin.

**Example :** $_6C^{12}$ → $1s^2$ $2s^2$ $2p^2$

| | | | |
|---|---|---|---|
| | ↑↓ | ↑↓ | ↑ ↑ ☐ |
| | | | $p_x$ $p_z$ $p_y$ |
| n | 1 | 2 | 2 |
| ℓ | 0 | 0 | 1 |
| m | 0 | 0 | + 1, – 1, 0 |
| s | +½ , −½ | +½ , −½ | +½ , −½ , |

**Example :** $_{17}$Cl →

| | $1s^2$ | $2s^2$ | $2p^6$ | $3s^2$ | $3P^5$ |
|---|---|---|---|---|---|
| | ↑↓ | ↑↓ | ↑↓ ↑↓ ↑↓ | ↑↓ | ↑↓ ↑↓ ↑ |
| n = | 1 | 2 | 2 | 3 | 3 |
| ℓ = | 0 | 0 | 1 | 0 | 1 |
| m = | 0 | 0 | +1, –1, 0 | 0 | + 1, –1, 0 |
| s = | $+\frac{1}{2},-\frac{1}{2}$ | $+\frac{1}{2},-\frac{1}{2}$ | $+\frac{1}{2},-\frac{1}{2}$ $+\frac{1}{2},-\frac{1}{2}$ $+\frac{1}{2},-\frac{1}{2}$ | $+\frac{1}{2},-\frac{1}{2}$ | $+\frac{1}{2},-\frac{1}{2}$ $+\frac{1}{2},-\frac{1}{2}$ $+\frac{1}{2}$ |

**Exception of Aufbau principle :** In some cases it is seen that the electronic configuration is slightly different from the arrangement given by Aufbau principle. A simple reason behind this is that half filled & full filled subshell have got extra stability.

| | Actual | Expected |
|---|---|---|
| Cr | [Ar] $3d^5$ $4s^1$ | [Ar] $3d^4$ $4s^2$ |
| Cu | [Ar] $3d^{10}$ $4s^1$ | [Ar] $3d^9$ $4s^2$ |
| Nb | [Kr] $4d^4$ $5s^1$ | [Kr] $4d^3$ $5s^2$ |
| Mo | [Kr] $4d^5$ $5s^1$ | [Kr] $4d^4$ $5s^2$ |
| Ru | [Kr] $4d^7$ $5s^1$ | [Kr] $4d^6$ $5s^2$ |
| Rh | [Kr] $4d^8$ $5s^1$ | [Kr] $4d^7$ $5s^2$ |
| Pd | [Kr] $4d^{10}$ $5s^0$ | [Kr] $4d^8$ $5s^2$ |
| Ag | [Kr] $4d^{10}$ $5s^1$ | [Kr] $4d^9$ $5s^2$ |
| Pt | [Xe] $4f^{14}$ $5d^9$ $6s^1$ | [Xe] $4f^{14}$ $5d^8$ $6s^2$ |
| Au | [Xe] $4f^{14}$ $5d^{10}$ $6s^1$ | [Xe] $4f^{14}$ $5d^9$ $6s^2$ |

**Example:18** Calculate the number of unpaired electrons in Cr

**Solution:** $_{24}$Cr → $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^1$ $3d^5$

In 24Cr, 6 electrons are unpaired.

**Example: 19** Calculate the number of unpaired electrons in $Cr^{+3}$

**Solution:** $Cr^{+3}$ → $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^0$ $3d^3$

In $Cr^{+3}$, 3 electrons are unpaired

## 15. EXTRA STABILITY OF HALF FILLED AND COMPLETELY FILLED ORBITALS

Half-filled and completely filled sub-shells have extra stability due to the following reasons.

**Symmetry of orbitals :**

**(a)** It is a well known fact that symmetry leads to stability.

**(b)** Thus, if the shift of an electron from one orbital to another orbital differing slightly in energy results in the symmetrical electronic configuration. it becomes more stable

**(c)** For example $p^3$, $d^5$, $f^7$ configurations are more stable than their near ones

- **Exchange Energy**

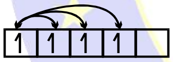
**(a)** The $e^-$ in various subshells can exchange their positions, since $e^-$ in the same subshell have equal energies.

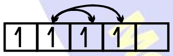
**(b)** The energy is released during the exchange process with in the same subshell.

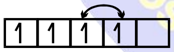
**(c)** In case of half filled and completely filled orbitals, the exchange energy is maximum and is greater then the loss of orbital energy due to the transfer of electron from a higher to a lower sublevel e.g. from 4s to 3d orbitals in case of Cu and Cr

**(d)** The greater the number of possible exchanges between the electrons of parallel spins present in the degenerate orbitals, the higher would be the amount of energy released and more will be the stability

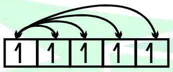
**(e)** Let us count the number of exchange that are possible in $d^4$ and $d^5$ configuration among electrons with parallel spins :

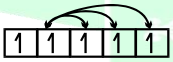
$d^4$ (A)  3 exchanges by 1st $e^-$

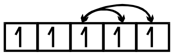
(B)  2 exchanges by 2nd $e^-$

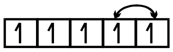
(C)  only 1 exchange by 3rd $e^-$

Total number of possible exchanges = 3 + 2 + 1 = 6

$d^5$ (A)  4 exchanges by 1st $e^-$

(B)  3 exchanges by 2nd $e^-$

(C)  2 exchanges by 3rd $e^-$

(D)  1 exchange by 4th $e^-$

Total number of possible exchanges = 4 + 3 + 2 + 1 = 10

## 16. PROBABILITY DISTRIBUTION CURVE

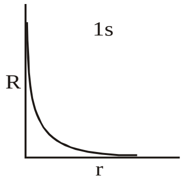
The orbital wave function $\psi$ does not have any physical significance but the square of ($\psi$) provides the information regarding the probability of electron at a point in an atom.

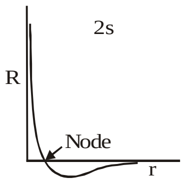
To draw the representation of variation of $\psi^2$ in space we required following functions:

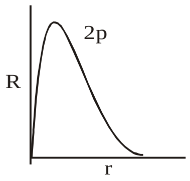
(a) Radial wave function (b) Radial probability density ($R^2$) (c) Radial probability function ($4\pi r^2R^2$)

**(a) Radial wave functions (R) :** By drawing these curve we can find the node in 2s, radial function. At node as figure indicates the value of radial function changes from positive to negative.

By drawing these we can get the information that how the radial wave function changes with distance r.

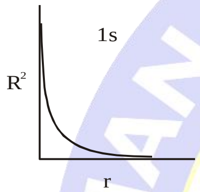


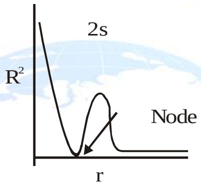


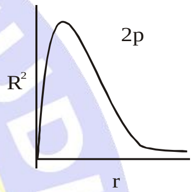


**(b) Radial probability density ($R^2$) :** The square of radial wave function $R^2$ for an orbital give the radial density & this radial density give the probability density of finding the electron.

By drawing the curve we can obtain the useful information about probability density or relative electron density at a point as a function of radius.

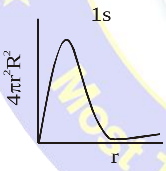


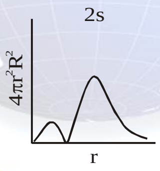


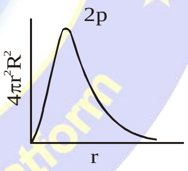


**(c) Radial probability function ($4\pi r^2R^2$) :** The shape of an atom is assumed to be spherical so it better to discuss the probability of finding the electron in a spherical shell between the radius (r + dr) and r. This probability which is independent of direction is called radial probability & equal to ($4\pi$ $r^2$ dr, $R^2$)

By drawing the curve we can obtain the information regarding the variation of radial probability a function ($4\pi$ $r^2$, $R^2$) with distance r.







## QUICK FOLLOW UP

### (1) sub atomic particles, atomic model.

Charge is quantised Q = ne

Potential energy of particle = $\frac{1}{4\pi\in_0}\frac{q_1q_2}{r^2}$

Distance of closest approach = $r_{(min)} = \frac{2Kq_1q_2}{mv^2}$

### (2) Quantum theory of light

Energy of a photon E= hν, n photon E= nhν

$E_0 = h\nu$ , $\nu = \frac{c}{\lambda}$ , $E_0 = \frac{hc}{\lambda}$ ,

### (3) Photo electric effect and black body radiation (spectrum)

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

### (4) Bohr model

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

Force balancing of moving $e^-$ in a orbit

$$\frac{mv^2}{r} = \frac{kq_1q_2}{r^2}$$

Radius of orbit $r_a = \frac{n^2h^2}{4\pi^2mkZe^2} = 0.529 \times \frac{n^2}{Z}$ Å

Velocity $v_n = \frac{2\pi Zek}{nh} = 2.18 \times 10^6 \times \frac{Z}{n}$ m/sec

$T = \frac{2\pi r}{v}$ , $f = \frac{v}{2\pi r}$ ,

Total energy $E_n = -\frac{2\pi^2me^4K^2}{h^2}\left(\frac{Z^2}{n^2}\right)$

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

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

$T.E = \frac{1}{2}P.E$ , TE = –KE

### (5) Hydrogen spectrum

$\frac{1}{\lambda} = \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ R= Rydberg constant= $1.0678 \times 10^7$ $m^{-1}$

Number of lines produce = $\frac{\Delta n(\Delta n + 1)}{2}$

Where Δn = $n_2 - n_1$ ,$n_2$ & $n_1$ are higher and lower energy orbit.

Maximum number of spectral line for single isolated atom = (n–1)

### (6) De-broglie concept & Heisenberg Uncertainty principle or wave nature of electron

Wave length of particle

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2emv}} = \frac{12.3}{\sqrt{v}}\text{Å}$$

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

Schrodinger wave equation

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

### (7) Quantum numbers, nodes and electronic configuration

number of subshells in $n^{th}$ shell = n

number of orbitals in $n^{th}$ shell = $n^2$

Maximum number of $e^-$s in principal energy shell = $2n^2$

Angular momentum of any orbit = $\frac{nh}{2\pi}$

No. of orbitals in a sub-shell = (2l + 1)

No. of $e^-$s in a sub shell = 2(2l + 1)

Orbital angular momentum L =

$$\frac{h}{2\pi}\sqrt{(l+1)l} = \sqrt{l(l+1)}\hbar \quad \left(\hbar = \frac{h}{2\pi}\right)$$

spin angular momentum = $\frac{h}{2\pi}\sqrt{s(s+1)}$

Maximum spin of atom = $\frac{1}{2}$ × No. of unpaired electrons