ATOMIC STRUCTURE

Contents

1. ATOMIC STRUCTURE

1.1 INTRODUCTION

The word **"Atom"** is a Greek word which means indivisible, i.e., an ultimate particle which cannot be further subdivided. The idea that all matter ultimately consists of extremely small particles was conceived by ancient Indian and Greek philosophers. Around 500 BC, an Indian philosopher **Maharishi Kanad** postulate that if we go on dividing matter (padarth), we shall get smaller and smaller particles. Ultimately a time will come when we shall come across the smallest particle beyond which further division will not possible. He named these particles **Parmanu** (or **Kan** after his name Kanad).

Around the same era, ancient Greek philosopher **Democritus** suggested that if we go on dividing matter, a stage will come when particles obtained will not be divided further. Democritus called these indivisible particles **atoms**. All these were based on philosophical considerations and not much experimental work was done.

The old concept was put on firm footing by **John Dalton** in the form of **Atomic Theory**, which he developed in the years 1803–1808. This theory was a landmark in the history of chemistry. According to this theory, atom is the smallest indivisible part of matter, which takes part in chemical reactions. Atom is neither created nor destroyed. Atoms of the same element are similar in size, mass and characteristics; however, atoms of different elements have different size, mass and characteristics.

In 1833, Michael Faraday showed that there is a relationship between matter and electricity. This was the first major break-through to suggest that atom was not a simple indivisible particle of all matter but was made up of small particles. Discovery of electrons, protons and neutrons discarded the indivisible nature of the atom proposed by John Dalton.

The complexity of the atom was further revealed when the following discoveries were made in subsequent years.

(i) Discovery of Cathode Rays
(ii) Discovery of Anode Rays.
(iii) Discovery of X-Rays
(iv) Discovery of Radio-activity.
(v) Discovery of Isotopes and Isobars
(vi) Discovery of the new Atomic Model.

During the past 100 years, scientists have made contributions, which helped in the development of modern theory of atomic structure. The works of **J.J. Thomson** and **Ernst Rutherford** actually laid the foundation of the modern picture of the atom. It is now believed that the atom consists of several particles called **sub-atomic particles** like electron, proton, neutron, positron, neutrino, meson, etc. Out of these particles, the electron, the proton and the neutron are called **fundamental particles** and are the building blocks of the atoms.

Some sub-atomic particles are-

Neutrino: It was discovered by Pauling.
It has zero charge and mass is less than electron.

Positron: It was discovered by C.D. Anderson.
It has +1 charge and mass is very less than electron.

Meason: It was discovered by Yukawa it may have +1, 0 ,-1 charge and mass is 200 times greater than electron .

Antiproton: It was discovered by Segre it has –1 charge and mass is equal to proton.

1.2 DISCOVERY OF FUNDAMENTAL PARTICLES

1.2.1 Discovery of Electron (Cathode rays)

The nature and existence of electron was established by experiments on conduction of electricity through gases. In 1859, Julius Plucker started the study of conduction of electricity through gases at low pressure in a discharge tube. Air was almost completely removed from the discharge tube (pressure about 10^{-4} atmosphere). 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 electrode. Since the negative electrode is referred to as cathode, these rays were called **cathode rays.** Further investigations were made by W. Crookes, J. Perrin, J.J. Thomson and others. (Fig 1)
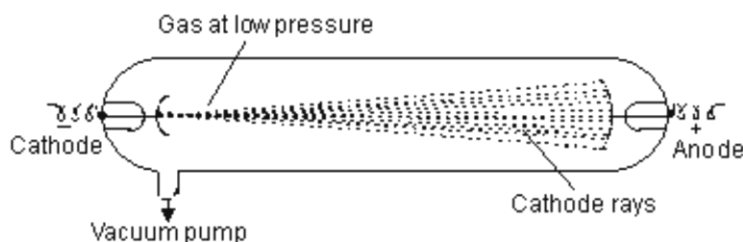

Fig. Production of cathode rays

Cathode rays possess the following properties:
1. They travel in straight lines away from the cathode with very high velocities ranging from 10^9 - 10^{11} cm per second. A shadow of metallic object placed in the path is cast on the wall opposite to the cathode.
2. They produce a green glow when strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.
3. 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.
4. 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. They discharge a positively charged gold leaf electroscope. It shows that **cathode rays carry negative charge.**
5. They possess kinetic energy. It is shown by the experiment that when a small pinwheel 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.** These particles carrying negative charge were called **negatrons** by Thomson.
   The name `negatron' was changed to 'electron' by **Stoney.**
6. Cathode rays produce X-rays. When Cathode rays fall on material having high atomic mass, new type of penetrating rays of very small wavelength are emitted called X-rays.
7. These rays affect the photographic plate.
8. These rays can penetrate through thin foils of solid materials and cause ionization in gases through which they pass.
9. The nature of the cathode rays is independent of:
   1. The nature of the cathode and
   2. The gas in the discharge tube.

Further experiments were carried out to determine the exact charge and mass of the electrons:

(a) Charge/mass ratio of an electron

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 × 10⁸ coulomb/g.**

(b) Charge of an electron

The first precise measurement of the charge on the electron was made by **Robert A. Millikan** in 1917 by oil drop experiment. The charge on the electron was found to be -1.6022×10^{-19} Coulomb. **Since an electron has the smallest charge known, it was, thus,** designated as unit negative charge.

(c) Mass of the electron

The mass of the electron can be calculated from the value of e/m and the value of *e*.

$$m = \frac{e}{e/m} = \frac{-1.6022 \times 10^{-19}}{-1.7588 \times 10^{8}}$$

$$= 9.1096 \times 10^{-28} \text{ g or } 9.1096 \times 10^{-31} \text{ kg}$$

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 electron may be calculated by applying the following formula:

Mass of a moving electron, $m_e = \dfrac{m_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}$

Where

m_0 is the rest mass of an electron $= 9.1096 \times 10^{-28}$ g or 9.1096×10^{-31} kg

v is the velocity of the moving electron.

c is the speed of light$=3\times10^{8}$m/sec

When v becomes equal to c, mass of the moving electron becomes infinity and when the velocity of the electron becomes greater than c then mass of the electron becomes imaginary.

Mass of the electron relative to that of hydrogen atom:

Mass of hydrogen atom = 1.008 amu

$= 1.008 \times 1.66 \times 10^{-24}$ g (since 1 amu $= 1.66 \times 10^{-24}$ g)

$= 1.673 \times 10^{-24}$ g

$$\frac{\text{Mass of hydrogen atom}}{\text{Mass of the electron}} = \frac{1.673 \times 10^{-24}}{9.1096 \times 10^{-28}} = 1837$$

$$\text{Thus, Mass of an electron} = \frac{1}{1837} \times \text{mass of hydrogen atom}$$

$$= \frac{1.008}{1837} = 0.000549 \text{ amu}$$

Thus, Mass of an electron $= \frac{1}{1837}$ th $\times$ mass of hydrogen atom

Note:

The device which is used **by J.J. Thomson** to do the first of all mass- separating experiments was **Mass-spectrometry**. Mass-spectrometry is an analytical technique to generate ions from either inorganic or organic compounds and to measure their **mass-to-charge ratio**, by any suitable method i.e. thermally, by electric fields or by impacting energetic electrons, ions or photons.

1.2.2 Discovery of Proton (Positive Rays)

The first experiment that led to the discovery of the positive particle was conducted by **Goldstein** in 1886. He used a perforated cathode in the modified cathode ray tube. 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 luminous rays were produced simultaneously passing through the holes or perforations of the cathode and moving in a direction opposite to the cathode rays. Thus, these rays consisted of positively charged particles moving away from the anode and were named as **positive rays** or **anode rays** or as **canal rays**.

Anode rays are not emitted from the anode but from a space between anode and cathode.

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.**
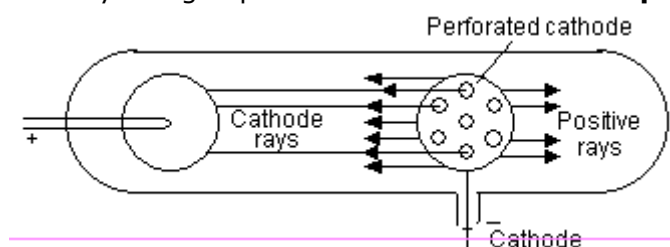

Fig - Production of Anode rays

The following characteristics of the positive rays were recognized:

1. The rays travel in straight lines and cast a shadow of the object placed in their path.
2. Like cathode rays, these rays also rotate the wheel placed in their path and also have heating effect. Thus, the rays possess kinetic energy, *i.e.*, mass particles are present.
3. The rays produce flashes of light on zinc sulphide screen.
4. The rays are deflected by electric and magnetic fields in a direction opposite to that of cathode rays. These rays are attracted towards the negatively charged plate showing thereby that **these rays carry positive charge.**
5. These rays can pass through thin metal foils.
6. These rays can produce ionization in gases.
7. These rays are capable of producing physical and chemical changes.
8. Positive particles in these rays have e/m values much smaller than that of electron. This means either *m* is high or the value of charge is small in comparison to electron. Since positive particle is formed by the loss of electron or electrons, the charge on the positive particle must be an integral multiple of the charge present on the electron. Hence, for a smaller value of e/m, it is definite that positive particles possess high mass.
9. The e/m value is dependent on the nature of the gas taken in the discharge tube, *i.e.*, positive particles are different in different gases.

Accurate measurements of the charge and the mass of the particles obtained 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 positive particle. It was thus assumed that the positive particle given by hydrogen represents a fundamental particle of positive 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, proton carries a charge $+ 1.602 \times 10^{-19}$ Coulomb, i**.**e**.,** one unit positive charge.

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

Mass of the proton:

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

$$= 1.672 \times 10^{-24} g$$

$$= 1.672 \times 10^{-27} g$$

$$\text{Mass of the proton in amu} = \frac{1.672 \times 10^{-24}}{1.66 \times 10^{-24}} = 1.0072 \text{ amu}$$

**Hence, a proton is defined as a sub-atomic particle, which has a mass nearly 1 amu, and a charge of +1 unit (+1.602 × 10⁻¹⁹ coulomb).**

Protons are produced in a number of nuclear reactions. On the basis of such reactions, proton has been recognized as a fundamental building unit of the atom.

Radioactivity

After the discovery of electron and proton, it was well established that atom is divisible and is made up of charged particles. This was further confirmed by the phenomenon of radioactivity, discovered by Becquerel in 1896.

Radioactivity is the phenomenon of spontaneous emission of radiations by certain elements like uranium, radium etc. The elements emitting such radiations are called radioactive elements.

Effect of electric field on the
radiations emitted from a
radioactive element.
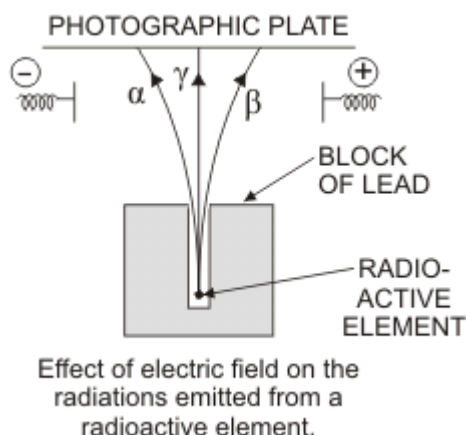
The phenomenon can be observed by placing the radioactive element in a cavity made in a block of lead and applying electric or magnetic field on the radiations being emitted and then allowing them to fall on the photographic plate.

Three types of radiations are emitted as explained below:

(i) Those, which are deflected slightly towards the negative plate and hence carry positive charge, are called α-rays. The particles present in them are called α-particles. Each α-particle has charge = + 2 units and mass = 4 u. Hence, they are same as helium nuclei and are represented as $_{2}^{4}He$.

(ii) Those, which are deflected towards the positive plate to a larger extent and hence carry negative charge, are called β-rays. The particles present in them are called β-particles. Each β-particle has same charge and mass as that of electron. Hence, it is represented as $_{-1}^{0}e$.

(iii) Those that remain undeflected are called γ-rays. They are simple electromagnetic radiations.

(iv) The penetrating power of β-rays is nearly 100 times more than that of α–rays, while that of the γ–rays is about 1000 times more than that of the β-rays. In other words, the α–rays have the least penetrating power while the γ–rays have the maximum magnitude.

1.2.3 Discovery of Neutron

The discovery of neutron was actually made about 20 years after the structure of atom was elucidated by Rutherford.

Moseley, in 1913, performed experiments to determine the exact quantity of charge present on the nucleus.

1.2.3.1 Moseley Experiment–Atomic Number

Roentgen, in 1895, discovered that when high energy electrons in a discharge tube collide with the anode, penetrating radiations is produced called X-rays.

X-rays are electromagnetic radiations of very small wave-lengths (0.1–20 Å). X-rays are diffracted by diffraction gratings like ordinary light rays and X-ray spectra are, thus, produced. Each such spectrum is a characteristic property of the element used as anode.
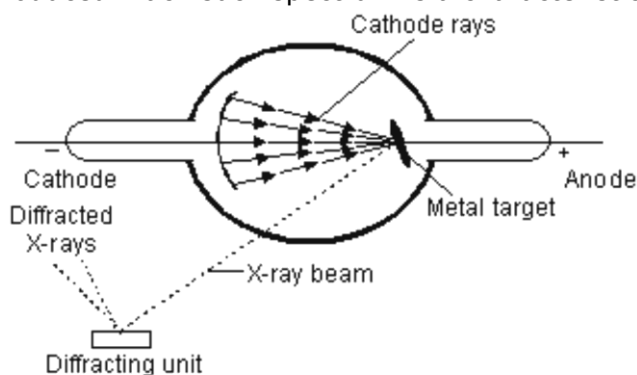

Fig - Moseley Experiment

Moseley (1912–13), investigated the X-ray spectra of 38 different elements, starting from aluminium and ending in gold. He measured the frequency of principal lines of a particular series of the spectra. It was observed that the frequency of a particular spectral line gradually increased with the increase of atomic mass of the element. But, it was soon realized that the frequency of the particular spectral line was more precisely related with the serial number of the element in the periodic table, which he termed as atomic number (Z). He presented the following relationship.

$$\sqrt{v} = a\,(Z-b)$$

Where v= frequency of X-rays,
Z = atomic number,
a ,b are constants.

When the values of square root of the frequency were plotted against atomic numbers of the elements producing X-rays, a straight line was obtained.
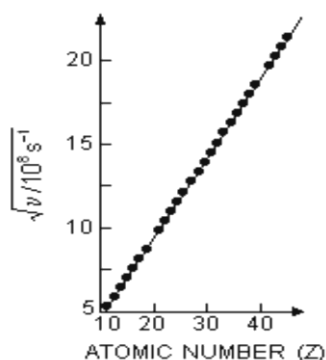
Van den Broek (1913) pointed out that the atomic number of an element is equal to the total positive charge contained in the nucleus of its atom. Rutherford was also having the same opinion that the atomic number of an element represents the number of protons in the nucleus of its atom. Thus, The number of units of positive charge present on the nucleus was called the **atomic number** of the element.

Atomic number of the element

= Serial number of the element in periodic table

= Charge on the nucleus of the atom of the element

= Number of protons present in the nucleus of the atom of the element

= Number of extra nuclear electrons present in the atom of the element

Since each unit of positive charge corresponds to one proton, therefore, atomic number was equal to the number of protons present in the nucleus. Further, since each proton has one unit mass on the atomic mass scale, therefore, the mass of the atom was calculated from the number of protons present in the nucleus (remembering that electrons have negligible mass). However, for any element (except hydrogen), this mass was found to be much less than the actual mass of the atom. This led to the idea that there must be some other particles present in the nucleus and that these particles should be neutral but should have considerable mass.

Atomic masses of different atoms could not be explained if it was accepted that atoms consisted only of protons and electrons. Thus, it was 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 particle 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 and magnetic fields. These radiations consisted of neutral particles, which were called neutrons. The nuclear reaction can be shown as:

$$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1$$
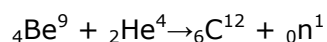
The mass of the neutron was determined. It was 1.675×10^{-24} g, i.e., nearly equal to the mass of proton.

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

1.3 ATOMIC MODELS

1.3.1 Thomson Model of Atom

J.J. Thomson, in 1904, proposed that an atom was a sphere of approximately radius 10^{-8} cm carrying positively charged particles in which number of electrons were embedded, sufficient to neutralize the positive charge. The stability of the atom was explained as a result of the balance between the repulsive forces between the electrons and their attraction towards the center of the positive sphere. This model is compared with a watermelon in which seeds are embedded or with a cake or pudding in which raisins (dried grapes/kishmish) are embedded. That is why this model is sometimes called raising pudding model or watermelon model.

Thomson model of atom.
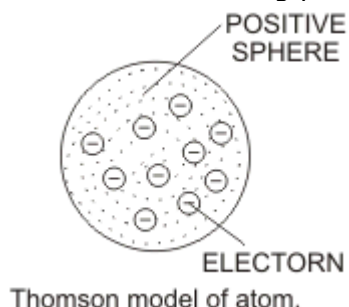
Limitation of Thomson's model
Though this model was able to explain the overall neutrality of the atom, it could not satisfactorily explain the results of scattering experiments, carried out by Rutherford in 1911 and was rejected.

1.3.2 Rutherford Model of Atom – Discovery of Nucleus

(Rutherford's alpha-ray scattering Experiment)

In 1911, Ernst Rutherford and his co-workers carried out a series of experiments called α-ray scattering experiment. A beam of α-particles was directed against a thin foil of about 0.0004 cm thickness of gold, platinum, silver or copper respectively. The source of α-particles was radium, a radioactive substance, placed in a block of lead. The foil was surrounded by circular fluorescent zinc sulphide screen. Whenever an α-particle struck the screen, it produced a flash of light.
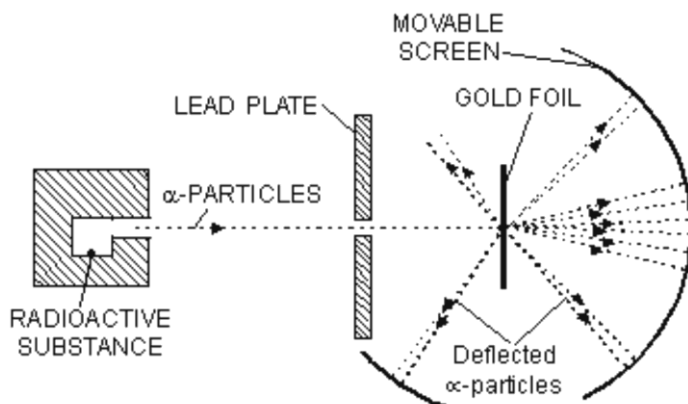

Fig. Rutherford's alpha-ray scattering Experiment

The following observations were made:

1. Most of the α-particles (nearly 99%) went straight without suffering any deflection.
2. A few of α-particle got deflected through small angles.
3. A very few (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even came back in more or less the direction from which they have come, i.e., a deflection of 180°.
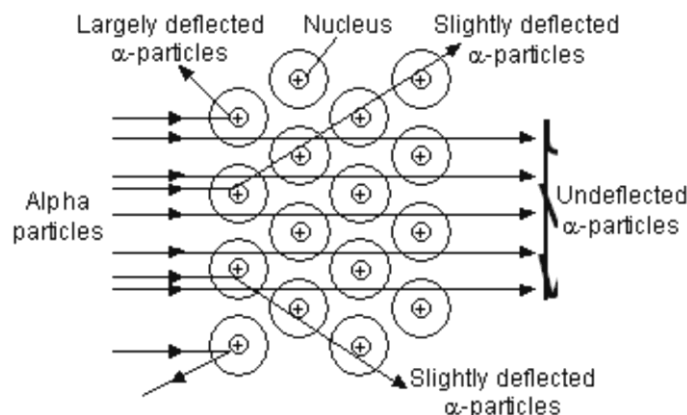

Fig - Discovery of Nucleus

Following conclusions were drawn from the above observations:

1. Since most of the α-particles went straight through the metal foil undeflected, it means that there must be very large empty space within the atom or the atom is extra-ordinarily hollow.
2. A few of the α-particles were deflected from their original paths through moderate angles; it was concluded that whole of the positive charge is concentrated in the center and the space occupied by this positive charge is very small in the atom. When α-particles comes 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.

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.

On the basis of scattering experiments, Rutherford proposed a model of the atom, which is known as **Nuclear Atomic Model**. According to this model:

1. An atom consists of a heavy positively charged nucleus located where all the protons and neutrons are present. The magnitude of the positive charge on the nucleus is different for different atoms.
2. There is an empty space around the nucleus called extra nuclear part. In this part electrons are present. The number of electrons in an atom is always equal to number of protons present in the nucleus.
3. As the nucleus part of the atom is responsible for the mass of the atom, the extra nuclear part is responsible for its volume. 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. Hence the volume of the atom is about 10^{15} times the volume of the nucleus.

4. The radius of a nucleus is proportional to the cube root of the number of nucleons within it. $R = R_0 A^{1/3}$ cm
   where $R_0 = 1.33 \times 10^{-13}$; A = mass number; R = Radius of the nucleus

5. Electrons revolve round the nucleus in closed orbits with high speeds. The centrifugal force acting on the revolving electrons is being counter balanced by the force of attraction between the electron and the nucleus.
   This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets. The electrons are, therefore, generally referred to as planetary electrons.

Drawbacks of Rutherford model

(i) According to classical electromagnetic theory, a small charged particle moving around an oppositely charged center continuously loses its energy". If an electron does so, it should also continuously lose its energy and should set up spiral motion ultimately falling into the nucleus. Since the atom is quite stable, it means the electrons do not fall into the nucleus, thereby this model does not explain the stability of the atom.
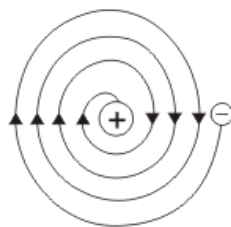
Continuous loss of energy by revolving electron.

(ii) It could not explain the line spectra of H – atom and discontinuous spectrum nature.

(iii) He was unable to explain how the electrons are distributed around the nucleus and what were their energies.

1.3.3 Bohr's model of Atom

In 1913, Neil Bohr proposed a model of an atom based on the Planck's quantum theory of radiation. The basic postulates of Bohr's theory are:

- An atom consists of a small, heavily positively charged nucleus around which electrons revolve in definite circular paths called orbits.

- These orbits are associated with definite energies called energy shells/energy levels. They are designated as K, L, M, N ... shells or numbered as 1, 2, 3, 4… from the nucleus.

- As long as the electron remains in a particular orbit /energy shell, its energy remains constant. This accounts for the stability of an atom.

- Only those orbits are permitted in which angular momentum of the electron is a whole number multiple of $\dfrac{h}{2\pi}$. i.e., $mvr = n\,\dfrac{h}{2\pi}$ Where m= mass of the electron, v=velocity of the electron, r=radius of the orbit, n=number of orbit.

This postulate introduces the concept of quantization of angular momentum.

- Electrons can either lose or absorb energy abruptly, when they jump from one energy level to another. For instance when an electron moves from the 'normal or ground state E_1' of an atom i.e., the state of lowest energy as required by its 'n' and 'l' values, to a higher level, it causes the atom to be in its 'excited state - E_2' i.e., where electrons in an

atom occupy energy levels higher than those permitted by its 'n' and '*l*' values. The reverse is also true and the change in energy is ΔE,

$$\Delta E = E_2 - E_1 = h\nu$$

Where v is the frequency absorbed or emitted when transition occurs between two stationary states.

$$\therefore \quad \nu = \frac{\Delta E}{h} = \frac{E2 - E1}{h}$$

The above equation is most commonly known as Bohr's frequency rule.

Explanation for Bohr's model

Bohr's atomic model successfully explained:

- Bohr postulated that as long an electron remains in a particular orbit it does not emit radiation i.e. lose energy. Hence atom is stable.
- Bohr also explained the atomic spectra of hydrogen on the basis of his atomic model. The line spectra of hydrogen lies in three regions of electromagnetic spectrum viz. infra red, visible and UV region. The set of lines in the visible region is known as **Balmer series**, that in ultra violet region as **Lyman series** and there are three sets of lines in infra red region namely **Paschen, Brackett and Pfund series**.

Hydrogen atom contains only one electron but its spectrum consists of several lines. Why?

A sample of hydrogen contains a very large number of atoms. When energy is supplied, the electrons present in different atoms may be excited to different energy levels and when they fall back to various lower levels emit radiations of different frequencies and wavelengths.

Wave number ($\bar{v}$) is defined as reciprocal of the wavelength i.e. $\bar{v} = \frac{1}{\lambda}$

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

Where R=Rydberg constant
For Lyman series $n_1=1$ and $n_2=2, 3, 4$.
For Balmer series $n_1=2$ and $n_2=3, 4, 5$.
For Paschen series $n_1=3$ and $n_2=4, 5, 6$.
For Brackett series $n_1=4$ and $n_2= 5, 6,7$
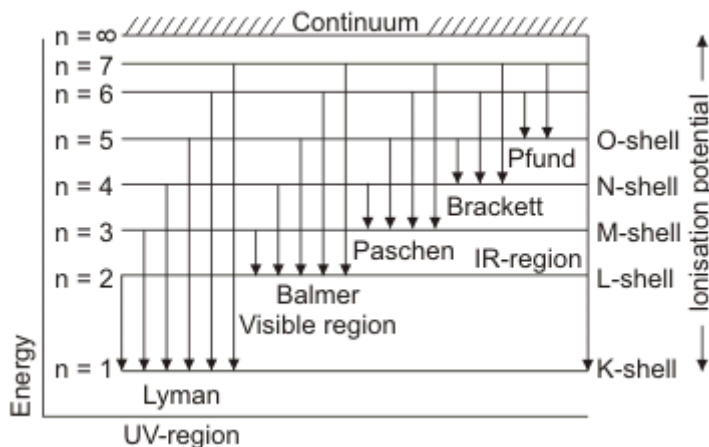For Pfund series $n_1=5$ and $n_2= 6,7,8$……....

Figure - Electronic transition producing different series in the hydrogen spectrum

- The radius of the electron in a particular orbit of hydrogen atom could be calculated by Bohr's theory. In a hydrogen atom, the electron revolves around the nucleus in a circular orbit. For the system to be stable, the columbic attraction between the electron and the nucleus must be the source of the necessary centripetal force for circular motion. i,e. coulombic force of attraction = centripetal force

$$\frac{K \times (Ze) \times e}{r^2} = \frac{mv^2}{r}$$

Where,

e = magnitude of charge on an electron (or a proton).

Z = atomic number (e.g. for H-atom, Z = 1)

r = radius of the orbit

m = mass of the electron

v = velocity of the electron

K = coulomb's law constant $= \dfrac{1}{4\pi\varepsilon_0}$

$= 9 \times 10^9 \ \text{Nm}^2 C^{-2}$ in SI system and = 1 in CGS units.

The above equation becomes,

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

The angular momentum of a body moving in a circular orbit is mvr and as per the Bohr's theory,

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

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

Substituting in equation (i)

$$\frac{Kze^2}{r} = m\left(\frac{nh}{2\pi mr}\right)^2 \qquad \text{........(ii)}$$

Solving for r, we get

$$r = \frac{n^2 h^2}{4\pi^2 KZme^2} \qquad \text{..........(iii)}$$

This is the equation for the radius of the orbit of the electron. For hydrogen atom in the ground state, n = 1 and substituting the values of the constants in equation (iii), we get

$r_1 = 0.529 \times 10^{-10}$ m = 0.529 Å

The radius of any other orbit in H atoms will be,

$r_n = 0.529 \ n^2$ Å

- Using these postulates, Bohr calculated the energy of the electron in an orbit. The total energy of electron will be the sum of potential and kinetic energy,i.e.

Total energy, E = PE + KE

The potential energy is the energy due to coulombic attraction and so

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

Kinetic energy can be calculated from the velocity of the electron.

$$KE = \tfrac{1}{2} mv^2$$

Total energy, $\quad E = \dfrac{-KZe^2}{r} + \tfrac{1}{2} mv^2 \quad$ ....(iv)

Substituting the value of mv^2 from the equation (i),

$$E = \dfrac{-KZe^2}{r} + \dfrac{KZe^2}{2r} \qquad\qquad ....(v)$$

$$E = \dfrac{-KZe^2}{2r} \qquad\qquad ....(vi)$$

Substituting (iii) in (vi), we get

$$E = \dfrac{-2\pi^2 K^2 Z^2 me^4}{n^2 h^2} \qquad\qquad ....(vii)$$

From equation (v), it is found that the magnitude of the potential energy is twice that of kinetic energy.

The negative sign in the equation (vii) represents that the energy is released when the electron moves from ∞ to any orbit. Thus the energy of the electron in an atom is lower than the energy of a free electron (which is zero). As 'r' increases, the energy becomes less negative which means that energy increases.

We can calculate the energy of the ground state of the electron in hydrogen atom.

$$E = \dfrac{-2\times(3\cdot14)^2\times(9\times10^9)\times1^2\times9.1\times10^{-31}\times(1.6\times10^{-19})^4}{1^2\times6.626\times10^{-34}}$$

E = -2.179 × 10^{-18} J per atom

E = - 13.6 eV per atom ($\therefore$ 1eV =96.368 J/mole)

E = - 1312 kJ/mole

From this ground state energy of hydrogen atom, we can find the energy in any other atom.

$$E_n = E_H \times \dfrac{Z^2}{n^2}$$

n can have only positive integral values and so the total energy of the electron is quantized.

Suppose an electron jumps from n_2 to n_1 level in a hydrogen atom ($n_2 > n_1$)

$$E_{n_1} = \dfrac{-2\pi^2 K^2 me^4}{n_1^2 h^2} \text{ (in C.G.S units)}$$

$$E_{n_2} = \dfrac{-2\pi^2 K^2 me^4}{n_2^2 h^2}$$

The difference in energy emitted is

$$hv = \dfrac{-2\pi^2 K^2 me^4}{h^2}\left[\dfrac{1}{n_2^2} - \dfrac{1}{n_1^2}\right]$$

$$v = \dfrac{2\pi^2 K^2 me^4}{h^3}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$$

$$\bar{v} = \dfrac{v}{c} = \dfrac{2\pi^2 K^2 me^4}{h^3 c}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$$

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

$$R = \frac{2\pi^2 K^2 m e^4}{h^3 c} = 109677 cm^{-1}$$

This empirical value of R deduced from Balmer, Lyman and other series agreed excellently with the experimental results. The energy of the electron of hydrogen atom in the nth orbit as

$$E_n = \frac{-21.76 \times 10^{-19} J}{n^2}$$

$$E_n = \frac{-13.6}{n^2} eV$$

it can be assumed that the electron and the nucleus revolve around their common center of mass. Therefore, instead of the mass of the electron, the reduced mass of the system was introduced and the equation becomes

$$\bar{v} = \frac{2\pi^2 K^2 \mu e^4}{h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where μ is the reduced mass $= \frac{Mm}{M+m}$, whose M is the mass of the nucleus and m is the mass of the electron.

Limitations of Bohr model:

1. It could not explain the line spectrum of multi electron atoms.
2. It could not explain Zeeman and stark effect (i.e., splitting of spectral lines under the influence of magnetic and electric field respectively)
3. The shapes of molecules arising out of directional bonding could not be explained.
4. The dual nature of electrons (both as wave and particle) and the path of motion of the electron in well-defined orbits were not correct.

Example: Calculate the wavelength of the radiation emitted when an electron in a hydrogen atom undergoes a transition from 4th energy level to the 2nd energy level. In which part of the electromagnetic spectrum does this line lie?

Solution: For hydrogen atom

$$En = -\frac{21.8 \times 10^{-19}}{n^2} \text{ J atom}^{-1}$$

Energy emitted when the electron jumps from b = 4 to n = 2 will be given by

$$\Delta E = E_4 - E_2 = 21.8 \times 10^{-19}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$= 21.8 \times 10^{-19} \times \frac{3}{16} = 4.0875 \times 10^{-19} J$$

The wavelength corresponding to this energy can be calculated using the expression

$$E = h\nu = h.\frac{c}{\lambda} \quad (\because c = \nu\lambda)$$

so that $\lambda = \frac{hc}{E}$

$$= \frac{(6.626 \times 10^{-34} Js)(3 \times 10^8 ms^{-1})}{(4.0875 \times 10^{-19} J)}$$

$$= 4.863 \times 10^{-7} m = 4863 Å \qquad \text{(or 486.3 nm)}$$

It lies in the visible region.

Example: Calculate the velocity of electron in the first Bohr orbit of hydrogen atom. Given that Boh'r radius = 0.529 Å, Planck's constant, h = 6.626 $\times$ 10^{-34} J s, mass of electron = 9.11 $\times$ 10^{-31} kg and 1 J = 1kg m^2s^{-2}.

Solution:

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

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

$$= \frac{(1)(6.626\times10^{-34}Js)}{2\times3.14\times(9.11\times10^{-31}kg)\times(0.529\times10^{-10}m)}$$

$$= 2.189\times10^6 Jskg^{-1}m^{-1}$$

But $1J = 1kgm^2s^{-2}$

Hence, $v = 2.189\times10^6 ms^{-1}$

1.3.4 Sommerfeld Extension to Bohr's Model

The observed fine structure of the spectrum of atomic hydrogen was against Bohr's concept of fixed energy levels for the electrons. If, according to Bohr, an electron undergoes transition from one definite energy level to another, the difference of energy should come out as radiation of a particular frequency-giving rise to a single line of spectrum. The fine structure suggests that these frequencies may vary slightly for each pair of Bohr energy levels; this indicates the presence of energy sublevels (which we shall call as azimuthal quantum number later on) corresponding to each Bohr orbit.

In 1915, Sommerfeld proposed that corresponding to each principal quantum number (n), several orbits of varying ellipicity were possible, the nucleus was now situated at a focus of the ellipse describing the electron's orbit.

The motion of an electron along an elliptical orbit was described by two quantum numbers:
(i) Radial quantum number n_r and
(ii) an azimuthal quantum number k

$$n = n_r + k$$

and $\quad \dfrac{n}{k} = \dfrac{\text{length of semi-major axis (a)}}{\text{length of semi-minor axis (b)}}$

The ellipicity of the orbits was thus determined by the relative values of n and k. For a given values of n, k = 1, 2, …. n.

Accordingly, there exists various elliptical orbits in addition to one circular orbit ($n = k$). For $n =$ 3, following orbits could be possible:

a	k	$\dfrac{a}{b}$	Orbit
3	3	1 : 1	circular
3	2	1.5 : 1	elliptical
3	1	3 : 1	elliptical

The velocity is greater when the electron is closest to the nucleus; it decreases gradually as the electron moves farther. According to the theory of relativity, the mass of the electron also changes accordingly as given

$$m = \frac{m_0}{\sqrt{1-\dfrac{v^2}{c^2}}}$$
$\quad$ (m_0 = mass of the electron at rest)

Sommerfeld showed that this variation of the electron's mass with change in velocity is significant and causes slight differences in energy of the electron in orbits of varying ellipicity. At the same time, the electron can no longer describe a closed path; each time the semimajor axis of the ellipse undergoes a gradual shift and thus the resulting path is as traced in Fig.
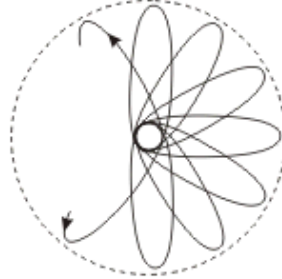

Fig. Elliptical paths traced as mass changes

The fine structure of the spectra was now explained by assuming transition between orbits of different *n* and *k*. However, only those transitions were possible for which *k* changes by one unit only $\Delta k = \pm 1$. The azimuthal quantum number *k* has been replaced by the symbol *l* [*l* = 0, 1, 2, …., (*n* – 1)]
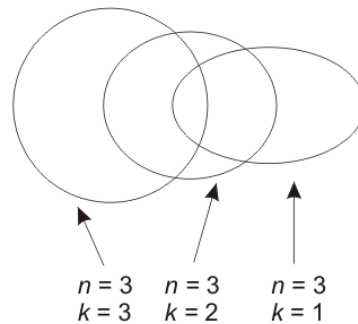

Fig- The possible orbits for n = 3

From Bohr's theory $E_n = \dfrac{-2\pi^2 m Z^2 e^4 k^2}{n^2 h^2}$

Introducing (*n* = n_r + *k*) from Sommerfeld's treatment, we have

$$E_n = -\frac{2\pi^2 m Z^2 e^4 k^2}{(n_r + k)^2 h^2}$$

Fig. The motion of an electron along an elliptical orbit
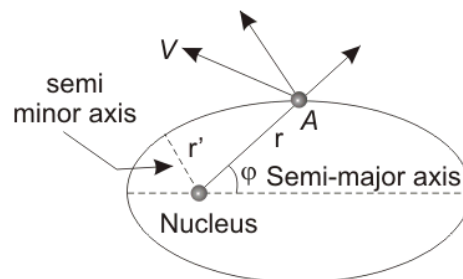
as the expression for the energy of an electron moving in an elliptical orbit with principal quantum number *n.* This implies that the energy of an electron would be same in all the elliptical orbits belonging o given *n*, irrespective of the value of *k*. But a close analysis of the elliptical motion enabled Sommerfeld to establish a dependence of the energy on the

eccentricity of the ellipse. To maintain balance with the varying electrostatic force at different distances, an electron moving along an elliptical orbit has to change its velocity continuously.

Example: *If velocity of the electron in first orbit of* H-*atom is* 2.182 x 10^6 *m s^{-1}, what is its value in third orbit?*

Solution: Velocity of the electron in *n*th orbit is

$$v_n = \frac{2.182 x 10^6}{n}$$

$$\frac{v_3}{v_1} = \frac{1}{3}$$

$$v_3 = \frac{v_1}{3} = \frac{2.182 x 10^6}{3}$$

$$= 7.273 \text{ x } 10^5 \text{ m s}^{-1}$$

1.3.5 Quantum mechanical model of an atom.

A new atomic model, was needed to explain

- Wave nature (dual character) of atoms.
- The idea of uncertainty in the position of electrons in an atom.
- Concept of fixed energy states.

Hence, a new branch of science, which takes dual nature of matter into consideration has, been put forward. This is known as 'Quantum mechanics.'

Schrodinger Wave Equation:

Erwin Schrodinger developed Quantum mechanics in 1926, he put the wave model or quantum mechanical model of atom forward. The behavior of an electron is defined by the mathematical representation:

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

Where,

Ψ = (psi) is a wave function of space coordinates 'x', 'y', 'z' and represents the amplitude of the electron wave.

m = mass of the electron

E = the total permissible energy level, which the electron can have.

V = potential energy of the electron given by ze^2/r.

h = Planck's constant having the value 6.626 x 10^{-34} J s.

∂ = (delta) stands for infinitesimal change.

The wavelength function Ψ (psi) describes a number of possible states of an electron in an atom. Since a large number of solutions are possible, four quantum numbers were introduced, which describe meaningful permissible values of energy and location with respect to its nucleus.

Note: For hydrogen atom, the solution of the Schrodinger wave equation gives the value of energy (E), which the electron can have.

The values of energy are called Eigen values and the corresponding values of wave function (ψ) are called Eigen functions.

Important features of Quantum mechanical model:

- The quantum mechanical model of an atom is essentially based on Schrodinger wave equation. Its main features are: The energy of the electron is quantized and can be obtained through Schrodinger wave equation.

- The wave function ψ is also found by solving, the Schrodinger wave equation. Though the function ψ doesn't have any physical significance as such but the square of the function (ψ^2) represents the probability density of the electron at that point. At the same time, the energy of a wave at a particular point is proportional to the ψ^2.

- By estimating the value of the wave function ψ at different points around the nucleus, a region can be defined where the probability of presence of electron is maximum. This region is called atomic orbital. So, the wave function is also called orbital wave function or simply atomic orbital.

- An electron can have multiple values of wave function which means an atom can have multiple atomic orbitals.

- The distribution of an electron in an orbital can be described in terms of the **electron density** in various regions of the orbital. The electron density is high in those regions of the orbital where the probability of finding an electron is relatively high, and it is low in those regions where that probability is low. Although the electron might be located anywhere within an orbital at any instant in time, it spends more of its time in certain high-probability regions. For example, in an isolated hydrogen atom in its ground state, the electron is almost always found within a sphere that has a radius of about 1 Å and is centered about the nucleus. Within this spherical orbital the electron has the greatest probability of being approximately 0.529 Å. For the nucleus we can determine the probability of finding the electron at a given point at a distance r from the nucleus if we calculate the value of Ψ^2 at that point. The radial probability density $4\pi r^2 \Psi^2$ indicates probability of finding the electron within the volume of a very thin spherical shell at a distance r from the nucleus.

- Fig. given below illustrates radial probability density in the occupied orbital of a hydrogen atom in the ground state. The probability of finding the electron in a thin shell very close to the nucleus is practically zero; the probability increases rapidly just beyond the nucleus and becomes highest in a thin shell at a distance of 0.529 Å. The probability then decreases rapidly and becomes exceedingly small at any distance greater than about 1 Å. Thus, most of the time, but not always, the electron is located within a sphere with a radius of 1 Å.

Cross-section of the electron density for an H atom in its ground electron

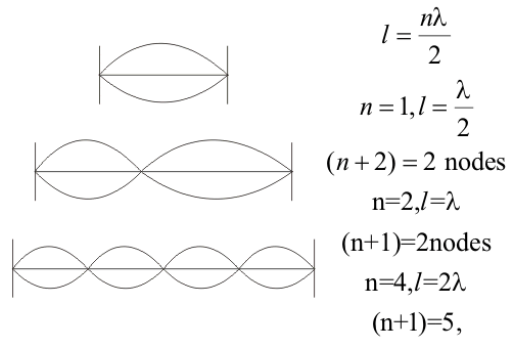The radial probability distribution for the electron
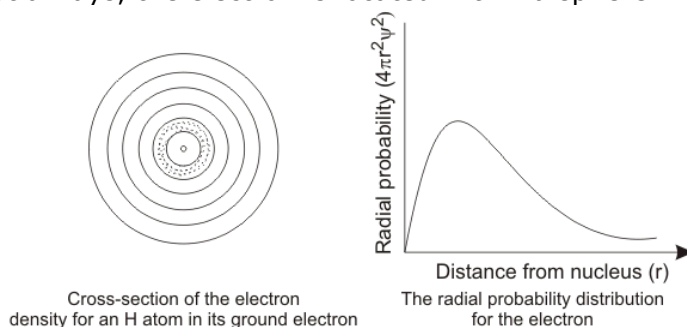
- Fig. given below represents the electron charge distribution in an orbital of the type 2*s*. A new feature seen in this orbital (as compared to 1 *s* electron in H-atom) is a spherical shell in which the electron probability or electron charge density is zero. This is called a **spherical node**.
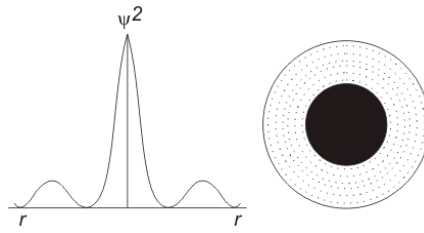
(A)   (B)

- From Fig. (a), it is clear that the electron charge density is highest in the vicinity of the nucleus. It drops to zero at a particular distance from the nucleus (a condition called a spherical node), rises to a second highest value at a somewhat greater distance, and again gradually decreases, approaching zero at large distance from the nucleus.
- Fig. (b) contains two regions will a high density of dots, corresponding to the two regions of high values of Ψ^2 in Fig.(a).
- If there are $(n + 1)$ nodes (where $n = 1,2, …$) in a string of length l, then it is related to wavelength λ by relation.

$$l = \frac{n\lambda}{2}$$

$$n = 1, l = \frac{\lambda}{2}$$

$(n+2) = 2$ nodes

n=2, l=λ

(n+1)=2nodes

n=4, l=2λ

(n+1)=5,

1.4 DUAL NATURE OF RADIATION AND MATTER

1.4.1 Wave Nature of Electromagnetic Radiation

According to Newton, light was regarded as a stream of particles also known as corpuscles of light, the particle nature could explain certain phenomena such as reflection and refraction associated with light. But at the same time, it failed to explain two other important phenomena called interference and diffraction. The corpuscles theory of light was, therefore, replaced by wave theory.

1.4.1.1 Electromagnetic Wave Theory

This theory was put forward by James Clark Maxwell in 1864. The main points of this theory are:

1. The energy is emitted from any source (like the heated rod or the filament of a bulb through which electric current is passed) continuously in the form of radiations (or waves) and is called the radiant energy.
2. The radiations consist of electric and magnetic fields oscillating perpendicular to each other and both perpendicular to the direction of propagation of the radiation.
3. The radiations possess wave character and travel with the velocity of light (i.e. nearly 3 $\times 10^8$ m/sec).
   Because of the above characteristics, the radiations are called **Electromagnetic radiations** or **Electromagnetic waves.**
4. These waves do not require any material medium for propagation. For example, rays from the sun reach us through space, which is a non-material medium.

Important characteristics of a wave:

The main characteristics of a wave are its wavelength (λ), frequency (n) and velocity (*c*). These are defined as follows:

Wavelength *of a wave is defined as the distance between any two consecutive crests or troughs*. It is represented by λ and is expressed in Å or m or cm or nm (nanometer) or pm (picometer).

1 Å = 10^{-8} cm = 10^{-10} m

1 nm = 10^{-9} m, 1 pm = 10^{-12} m

Frequency *of a wave is defined as the number of waves passing through a point in one second*. It is represented by ν (nu) and is expressed in Hertz (Hz) or cycles/sec or simply sec^{-1} or s^{-1}.

$$1 \text{ Hz} = 1 \text{ cycle/sec}$$

Velocity *of a wave is defined as the linear distance travelled by the wave in one second*. It is represented by *c* and is expressed in cm/sec or m/sec (ms^{-1}).

Amplitude *of a wave is the height of the crest or the depth of the trough*. It is represented by `*a*' and is expressed in the units of length.

Wave number *is defined as the number of waves present in 1 cm length. Evidently, it will be equal to the reciprocal of the wavelength*. It is represented by $\bar{\nu}$ (read us nu bar).

$$\overline{\nu} = \frac{1}{\lambda}$$

If λ is expressed in cm, $\bar{\nu}$ unit is cm^{-1}.

Relationship between velocity, wavelength and frequency of a wave

As frequency is the number of waves passing through a point per second and λ is the length of each wave, hence their product will give the velocity of the wave.

Thus $c = n \times \lambda$.

Electromagnetic spectrum: The different types of electromagnetic radiations differ only in their wavelength and hence frequencies. Their wavelengths increase in the following order:

Cosmic rays < γ-rays < X-rays < Ultra-violet rays < Visible < Infrared < Micro waves < Radio waves

When these electromagnetic radiations are arranged in order of their increasing wavelengths or decreasing frequencies, the complete spectrum obtained is called **electromagnetic spectrum.**

Limitations of Electromagnetic Wave Theory: Electromagnetic wave theory was successful in explaining the properties of light such as interference; diffraction etc. but it could not explain the phenomena of 'Black body radiation', and 'Photoelectric effect'.

1.4.1.2 Atomic Spectra

Figure. Continuous spectrum of white light.
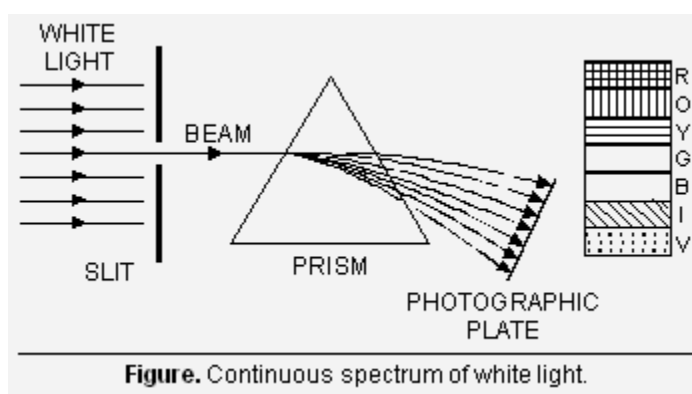
Electromagnetic spectrum consists of radiations of different wavelengths and frequencies. A spectrum is an assembly of energy levels in the form of radiations emitted by an atom in its excited state. An instrument used to separate the radiations of different wavelengths (or frequencies) is called spectroscope or a spectrograph *and the* photograph (or the pattern) of the emergent radiation recorded on the film is called a spectrogram or simply a spectrum of the given radiation*.

Every atom gives discontinuous line spectra. Each line in the spectra corresponds to a specific wavelength and it is unique to a given element. No two elements give same pattern of lines in their spectra.

Depending upon the source of radiation, the spectra are broadly classified into

(i) Emission spectra

(ii) Absorption spectra

These are briefly explained below:

1) **Emission spectra:** When the radiation emitted from some source e.g. from the sun or by passing electric discharge through a gas at low pressure or by heating some substance to high temperature etc. is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called 'Emission spectrum'. In emission spectrum bright lines are observed.

   The emission spectra are mainly of two types:

   (i) Continuous spectra: When white light from any source such as sun, a bulb or any hot glowing body is analyzed by passing through a prism, it is observed that it splits up into seven different wide bands of colours from violet to red, (like rainbow). These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum.

(ii) Line spectra (Atomic emission spectra): When some volatile salt (e.g., sodium chloride) is placed in the Bunsen flame or an electric discharge is passed through a gas at low pressure (as shown in below fig.), light is emitted. If this light is resolved in a spectroscope, it is found that no continuous spectrum is obtained but some isolated coloured lines are obtained on the photographic plate separated from each other by dark spaces. This spectrum is called *'Line spectrum'*.
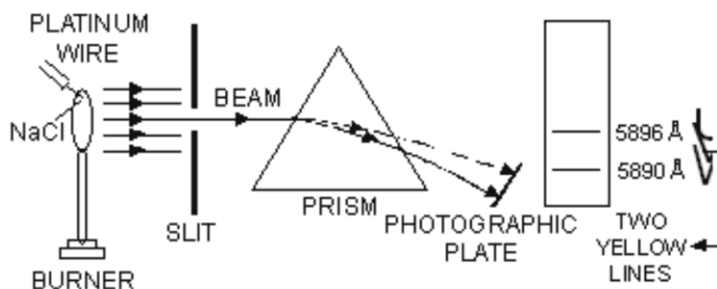

Figure   Line spectrum produced from a volatile salt placed in a flame.

Each line in the spectrum corresponds to a particular wavelength. Each element gives its own characteristic spectrum, differing from those of all other elements. For example, sodium always gives two yellow lines (corresponding to wavelengths 5890 and 5896 Å).

The line spectra are also obtained as a result of absorption and subsequent emission of energy by the electrons in the individual atoms of the element. Hence the line spectrum is also called **atomic spectrum**.
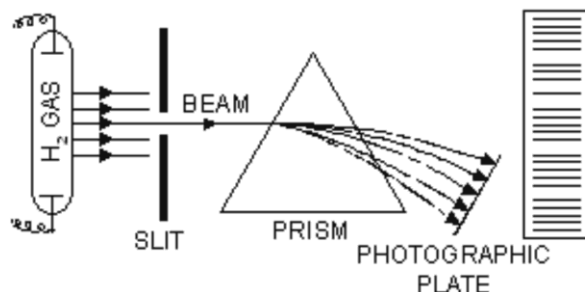

Figure   Line spectrum produced from light emitted by discharge tube.

When a substance is heated to a high temperature, the atoms in the vapours get energized. These energized atoms then return to the ground state by emitting electromagnetic radiations of certain definite wavelength. A series of bright lines separated from each other by dark spaces is obtained and this is called atomic emission spectra.

2) Absorption spectra:

When the atomic vapours from a sample are placed in the path of white light from an arc lamp, it absorbs the light of certain characteristic wavelengths and the light of other wavelengths get transmitted. In such conditions a series of **dark lines** on a white background are formed. This is called an absorption spectrum.

Atomic spectra of hydrogen atom:

Hydrogen being the simplest element with its atom having only one electron, the atomic spectrum of hydrogen has played a significant role in the development of atomic structure.

In the emission spectrum of hydrogen, when an electric discharge is passed through hydrogen gas, the molecules of hydrogen break into atoms. The hydrogen atoms get energized and go into an excited state. The excited atoms then return to the ground state by emitting light. Hydrogen atoms emit bluish light. On passing this light through a prism, a discontinuous line spectrum consisting of several sharp lines is obtained. This is the line spectrum of hydrogen.

Four sharp coloured lines were observed in the visible region of this spectrum by Balmer, in the ultra violet region by Lyman, in the infrared region by Paschen, Brackett and Pfund. These series of lines are named after the scientists who discovered them.
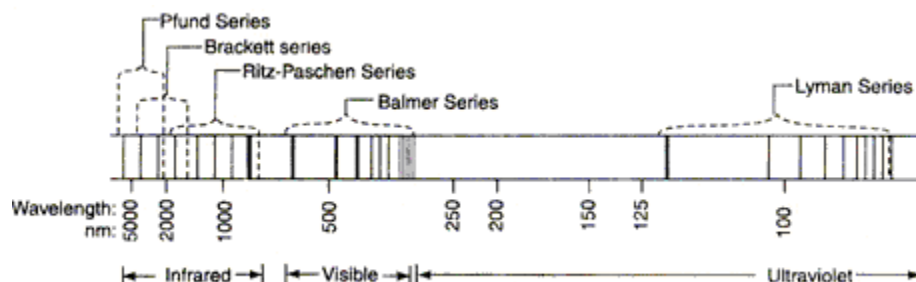
Fig: - Line spectrum of hydrogen atom

Balmer expressed these lines in terms of inverse of their wavelength by a mathematical relation, which was later modified by Rydberg.

$$\text{Wave number },\ \bar{v}(cm^{-1}) = \frac{1}{\lambda(cm)} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where 'R_H' is the Rydberg's constant for Hydrogen$=109{,}677 cm^{-1}$

'n_1', 'n_2' are integers ($n_2 > n_1$, $n_1 > 0$)

λ is the wavelength.

Example: The Lyman series of the hydrogen spectrum can be represented by the equation

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

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

Solution: Frequency is maximum when n = ∞

$$v_{max} = 3.2881 \times 10^{15} s^{-1}$$

Frequency is minimum when n = 2 that is $\frac{1}{n^2}$ maximum

$$\therefore\ v_{max} = 3.2881 \times 10^{15} \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$= 2.4661 \times 10^{15} s^{-1}$$

1.4.2 Particle nature of Electromagnetic Radiation

1.4.2.1 Black Body Radiation and Photoelectric Effect

Electromagnetic Wave Theory was successful in explaining the properties of light such as interference, diffraction etc. But it could not explain the following:

(a) Black body Radiation

If any substance with high melting point (e.g., an iron bar) is heated, it first becomes red, then yellow and finally begins to glow with white light.

If the substance beings heated is a black body (which is a perfect absorber and perfect radiator of energy) the radiation emitted is called black body radiation.

According to electromagnetic wave theory, the energy is emitted or absorbed continuously.

Hence, the energy of any electromagnetic radiation is proportional to its intensity i.e. a square of amplitude and is independent of its frequency or wavelength. Thus, according to the wave theory, the radiation emitted by the body being heated should have the same colour, although its intensity may vary as the heating is continued.

(b) Photoelectric Effect

When radiations with certain minimum frequency (v_0) strike the surface of a metal, the electrons are ejected from the surface of the metal (Figure). This phenomenon is called photoelectric effect. The electrons emitted are called photo-electrons.
However, the following three important facts are observed about the photoelectric effect:

Figure. Photo-electric effect.
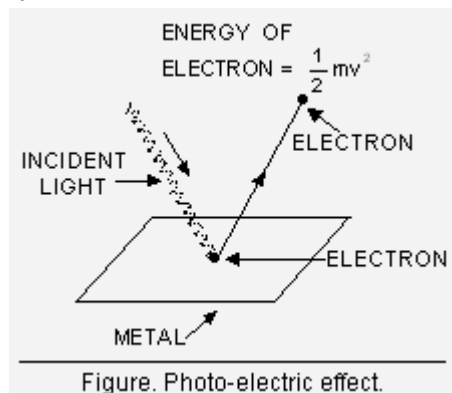
(i) The electrons are ejected only if the radiation striking the surface of the metal has at least a minimum frequency (v_0). If the frequency is less than, v_0 ,electrons are not ejected. This value (v_0) is called Threshold Frequency.

(ii) The velocity (and hence the kinetic energy) of the electron ejected depends upon the frequency of the incident radiation and is independent of its intensity.

Work function (W_0) = required minimum energy for the radiation

$$W_0 = h\, v_0$$

$$W_0 = \frac{hc}{\lambda_{max}}$$

Threshold frequency (v_0) = minimum frequency of the radiation

$$E = KE + W_0$$
$$E = hv$$
$$\therefore \frac{1}{2} mv^2 = h(v - v_0)$$

(iii) The number of photoelectrons ejected is proportional to the intensity of incident radiation.

The above observations cannot be explained by the Electromagnetic wave theory. According to this theory, since radiations are continuous, therefore it should be possible to accumulate energy on the surface of the metal, irrespective of its frequency and thus radiations of all frequencies should be able to eject electrons.
Similarly, according to this theory, the energy of the electrons ejected should depend upon the intensity of the incident radiation.

(c) The line spectra of atoms with special reference to hydrogen.

1.4.2.2 Planck's Quantum Theory

To explain the phenomena of 'Black body radiation' and 'Photoelectric effect', Max Planck in 1900 put forward a theory known after his name as Planck's quantum theory. This theory was further extended by Einstein in 1905. The main points of this theory are:

(i) The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy, each such packet of energy is called a 'quantum'. In case of light, the quantum of energy is called a **'photon'.**

(ii) The energy of each quantum is directly proportional to the frequency of the radiation, i.e.,

$$E \propto v$$

$$E = hv$$

Where, h is proportionality constant, called Planck's constant.

Its value is approximate 6.62×10^{-34} Joules sec.

(iii) The total amount of energy emitted or absorbed by a body will be some whole number quanta.

$$\therefore E_T = nhv, \text{ where n is any integer.}$$

Example: A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution: Power of the bulb = 100 watt

$$= 100 \text{ J s}^{-1}$$

Energy of one photon, $E = hv = \dfrac{hc}{\lambda}$

$$= \dfrac{(6.626 \times 10^{-34} Js) \times (3 \times 10^8 ms^{-1})}{400 \times 10^{-9} m}$$

$$= 4.969 \times 10^{-19} J$$

$$= \dfrac{100 Js^{-1}}{4.969 \times 10^{-19} J} = 2.012 \times 10^{20} s^{-1}$$

1.4.3 Dual Nature of Matter

In case of light, some phenomena like interference; diffraction etc. can be explained if the light is supposed to have wave character. However, certain other phenomena such as black body radiation and photoelectric effect can be explained only if it is believed to be a stream of photons i.e., has particle character (or is corpuscular in nature). Thus, light is said to have a dual character. Such studies on light were made by Einstein in 1905.

Louis de Broglie, a French physicist, in 1924, advanced the idea that like photons, all material particles such as *electron, proton, atom, molecule, a piece of chalk, a piece of stone or an iron ball (i.e. microscopic as well as macroscopic objects) possessed both wave character as well as particle character.*

The wave associated with a particle is called a matter wave.

1.4.3.1 The De Broglie Relationship

De-Broglie explains the dual nature of electron (i.e., wave nature as well as particle nature).

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

Where, λ = wavelength

v = velocity of particle

m = mass of particle

h is Planck's constant

The significance of de Broglie equation lies in the fact that it relates the particle character with the wave character of matter.

Characteristics of Matter waves and Electromagnetic waves

Matter waves differ from electromagnetic waves in the various respects given in table.

Table Difference between electromagnetic waves and matter waves

Electromagnetic Waves	Matter Waves
1. The electromagnetic waves are associated with electric and magnetic fields, perpendicular to each other and to the direction of propagation.	1. Matter waves are not associated with electric and magnetic fields.
2. They do not require any medium for propagation i.e. they can pass through vacuum.	2. They require medium for their propagation i.e. they cannot pass through vacuum.
3. They travel with the same speed as that of light.	3. The speed of these waves is not the same as that of light. Moreover it is not constant for all matter waves.
4. They leave the source.	4. They do not leave the moving objects.
5. Their wavelength is given by $\lambda = c/v$	5. Their wavelength is given by $l = h/mv$

Derivation of Bohr's postulate of angular momentum from de Broglie equation:

According to Bohr's model, the electron revolves around the nucleus in circular orbits. According to de Broglie concept, the electron is not only a particle but has a wave character. Thus in order that the wave may be completely in phase, the circumference of the orbit must be equal to an integral multiple of wavelength (λ) i.e.

$$2\pi r = n\lambda$$
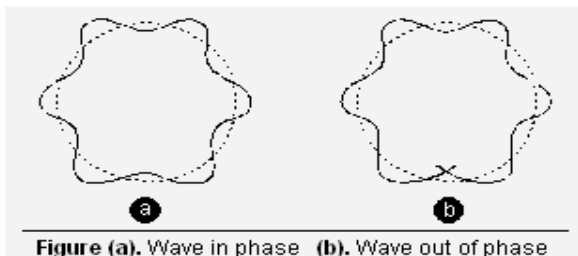
But $\lambda = \dfrac{h}{mv}$ (deBroglie equation)

$$\therefore 2\pi r = \dfrac{nh}{mv}$$

or $\qquad mvr = n\dfrac{h}{2\pi}$

Which is Bohr's postulate of angular momentum.

$2\pi r = n\lambda$

where r is the radius of the orbit and n is an integer.

Figure (a). Wave in phase (b). Wave out of phase

de-Broglie's equation explains only systems in which energy of particle is described only in terms of speed. In the case of electrons where energy is partly due to speed and partly due to position the de-Broglie's theorem is used as an approximation.

Note: de-Broglie's equation explains only systems in which energy of particle is described only in terms of speed. In the case of electrons where energy is partly due to speed and partly due to position the de-Broglie's theorem is used as an approximation.

Example: Calculate the wavelength associated with an electron (mass 9.1×10^{-31}) kg m^2 sec^{-1}.

Solution: Here, we are given,

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

$V = 10^3$ m sec^{-1}

$h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34} kgm^2 s^{-1}}{(9.1 \times 10^{-31} kg) \times (10^3 ms^{-1})}$$

$$= 7.25 \times 10^{-7} m$$

1.4.3.2 Heisenberg's Uncertainty Principle:

It states that it is impossible to specify at any given instant, both the momentum and the position of subatomic particles like electron.

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

Where, Δx = uncertainity in position

Δp = uncertainty in momentum

Why electron cannot exist in the nucleus?

On the basis of Heisenberg's uncertainty principle, it can be shown why electrons cannot exist within the atomic nucleus. This is because the diameter of the atomic nucleus is of the order of 10^{-14} m. Hence, if the electron were to exist within the nucleus, the maximum uncertainty in its position would have been 10^{-14} m. Taking the mass of electron as 9.1×10^{-31} kg, the minimum uncertainty in velocity can be calculated by applying uncertainty principle as follows:–

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

$$\text{or} \quad \Delta x. (m \times \Delta v) = \frac{h}{4\pi}$$

$$\text{or} \quad \Delta v = \frac{h}{4\pi} \cdot \frac{1}{\Delta x \times m}$$

$$= \frac{6.6 \times 10^{-34}}{4 \times \frac{22}{7}} \times \frac{1}{10^{-14} \times 9.1 \times 10^{-31}}$$

$$\approx 6 \times 10^9 \, ms^{-1}$$

This value is much higher than the velocity of light (viz 3×10^8 ms^{-1}) and hence is not possible.

Significance of Heisenberg's uncertainty principle

Like de Broglie equation, although Heisenberg's uncertainty principle holds good for all objects but it is of significance only for microscopic particles. The reason for this is quite obvious. The energy of the photon is insufficient to change the position and velocity of bigger bodies when it collides with them. For example, the light from a torch falling on a running rat in a dark room neither changes the speed of the rat nor its direction i.e. position. Since in everyday life, we come across big objects only, the position and velocity of which can be measured accurately, *Heisenberg's uncertainty principle has no significance in everyday life.*

Example: Calculate the uncertainty in the velocity of a wagon of mass 3000 kg whose

Position is known to an accuracy of $\pm$ 10 pm (Planck's constant = 6.63 $\times 10^{-34}$ J s)

Solution: Here, we are given m = 3000 kg

$$\Delta x = 10pm = 10 \times 10^{-12}m = 10^{-11}m$$

$\therefore$ By uncertainty principle, $\Delta u = \dfrac{h}{4\pi \times m \times \Delta x}$

$$= \dfrac{6.63 \times 10^{-34}kgm^2s^{-1}}{4 \times \frac{22}{7} \times 3000kg \times 10^{-11}m}$$

$$= 1.76 \times 10^{-27}ms^{-1}$$

1.5. QUANTUM NUMBERS

An atom contains a large number of orbitals. These are distinguished from each other on the basis of their *size, shape and orientation (direction) in space*. Definite energies and angular movements characterize atomic orbitals. The state of an electron in any atom is defined by certain permissible values of energy and angular momentum, which describe its location with respect to its nucleus and its energy level. These permissible states are called orbitals and these parameters of an orbital are expressed in terms of three numbers, called **Principal *'n'*, Azimuthal *'l'* and Magnetic quantum numbers, 'm'.** Further to represent the spin (rotation) of the electron about its own axis, a fourth quantum number, called **Spin quantum number's'** is introduced. These numbers serve as the signature of the electrons, uniquely describing its position in the atom. The 'n', 'l' and 'm' indicate the spatial distribution while 's' indicates the spin orientation of the electrons.

Thus, Quantum numbers may be defined as a set of four numbers which give complete information about the electron in an atom i.e., energy, orbital occupied, size, shape and orientation of that orbital and the direction of electron spin.

Brief explanations about Quantum numbers are given below:

1.5.1 Principal Quantum Number:

- This quantum number determines the main energy shell or energy level in which the electron is present.
- It is denoted by the letter 'n' that can take whole number values starting from 1, 2, 3, 4…. The shell with n = 1 is called first shell or 'K' shell. The shell with n = 2 is the 'L' shell and so on. The first shell is closest to the nucleus. The number of electrons in a shell is given by **$2n^2$**.
- This quantum number determines the energy of the shell. For e.g., for hydrogen atom the energy is given by $E_n = -\dfrac{2\pi^2 me^4 Z^2}{n^2 h^2} = -\dfrac{1.312 \times 10^6 Z^2}{n^2}$ J per mol .

  Where n is the principal quantum number.
- Principal quantum number gives the average distance of an electron from the nucleus and specifies the energy of that electron. As the value of 'n' increases, the distance from the nucleus as well as the energy of the electrons increases.
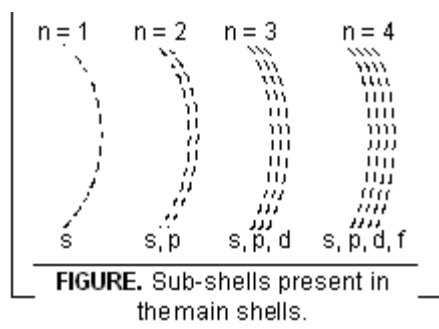
1.5.2 Azimuthal Quantum Number

(Subsidiary or Orbital angular momentum):

- This number is represented by '*l* '. It defines the three dimensional shape of the orbital. This quantum number denotes the sub-level or sub-shell in a given principal energy shell to which an electron belongs. This is also called secondary quantum number. It is denoted by l and corresponding to each value of n, there are n possible values of l ranging from zero to one less than n for that state i.e., l = 0, 1, 2...(n - 1).
- Each value of l represents a particular sub-shell or sub-level. For a given value of n, l can have values from 0 to n – 1.The number of sub shells in a principal shell is equal to the value of n.
- The various sub-levels or sub-shells are also designated by letters **s, p, d, f** (derived from the first letter of the words sharp, principal, diffused and fundamental lines of the spectra) depending upon the values of l as shown below:

Shell	Sub-shells present
1st (K)	1s
2nd (L)	2s, 2p
3rd (M)	3s, 3p, 3d
4th (N)	4s, 4p, 4d, 4f

- The energies of the different sub-shells present within the same main shell are found to be in the order s < p < d < f

FIGURE. Sub-shells present in the main shells.

- This quantum number gives the energy of an electron due to the angular momentum of the electron. The relation between angular momentum of the electron and Azimuthal number 'l' is

$$\text{orbital angular momentum} = \sqrt{l(l+1)} . \frac{h}{2\pi}$$

Thus, angular quantum number determines the sub-level in a given principal energy level. Different values of 'l' correspond to different orbital angular momentums. As a result the azimuthal quantum 'l' determines the shape of orbitals.

1.5.3 Magnetic Quantum Number:

- The fact that when the source giving the line spectrum is placed in a magnetic field, each spectral line splits into a number of lines (Zeeman Effect) is explained by this number. This was obviously due to the fact that each sub shell contains a number of orbitals which take up different orientations under the influence of the external magnetic field.

- The magnetic quantum number tells the number of orientations, which the orbitals present within the same sub-shell, can take up. In other words, it tells the number of orbitals present within the same sub-shell (as each orientation represents an orbital).

- In the absence of external magnetic field electrons, orbitals having same values of 'n' and 'l' but different values on 'm' have the same energies. They are called degenerate orbitals. However, in the presence of an external magnetic field the orbitals vary in their energies slightly. This is because the preferred orientation of the orbital in space is a result of interaction of its own magnetic field with that of the external magnetic field.

- It is denoted by the letter 'm' the value of which depends on 'l'. This quantum number can have all integral values from '$-l$' to '$+l$' including 0. Thus for given 'l' value there are ($2l + 1$) values of 'm'. Two orbitals in the same shell can have identical 'n' and 'l' values but they must have different fixed values of 'm'.

- The number of orbitals in each sub shell is given below:

- l = 0, s sub shell, m = 0 only one orientation and one orbital.
- l = 1, p sub shell, m = +1, 0, -1 three orientations and three orbitals.
- l = 2, d sub shell m = +2, +1, 0,-1,-2 five orientations and five orbitals.

1.5.4 Spin Quantum Number:

- It is represented by '*s'*. This was introduced for the fact that the electron in an atom not only moves around the nucleus but also spins about its own axis (like the earth which not only revolves around the sun but also spins around its own axis).

- The spin of the electron produces a small magnetic field as a result of which the electron behaves as a 'tiny magnet'. This quantum number describes the spin orientation of the electron.

- Since the electron can spin only in two ways: clockwise and anti-clockwise and, therefore, the spin quantum number can take only two values: **+ ½ or - ½.**

FIGURE. Spinning of electrons.
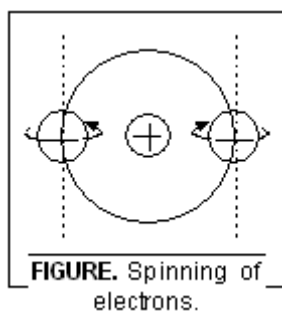
- This quantum number has a value independent of the value of the other three quantum numbers. Instead of giving + ½ and - ½, the two orientations are usually designated by arrows pointing up ↑ and down ↓ respectively.

- This quantum number helps to explain the magnetic properties of the substances. A spinning electron behaves like a micro magnet with a definite magnetic moment. If an orbital contains two electrons, the two magnetic moments oppose and cancel each other.
Spin angular momentum = $\sqrt{S(S+1)}\ \frac{1}{2\pi}$ where S = $\frac{1}{2}$

If all the orbitals are fully filled, net magnetic moment is zero and the sub-stance is *diamagnetic* (i.e. repelled by the external magnetic field). However, if some half-filled orbitals are present, the substance has a net *magnetic* moment and is *paramagnetic* (i.e. attracted by the external magnetic field).

The four quantum numbers describe position of an electron in an atom by specifying its main energy level (n), sub-level (*l*) the orientation of the orbital (m) and the direction of its spin (s). The various permitted values of the quantum numbers are summarized below:

Quantum number	Designation	Values
Principal	n	1,2,3,4 any integer
Angular	*l*	0,1,2,3....(n - 1)
Magnetic	m	- 1.... 0.... +1
Spin	s	+ ½ or - ½

Example: Write down the quantum numbers n, l and m for the following orbitals:

(i) $3d_{x2-y2}$
(ii) $4d_z{}^2$
(iii) $3d_{xy}$
(iv) $4d_{xz}$
(v) $2P_z$
(vi) $2P_x$

Solution: (i)   m = 3, l = 2, m = + 2
(ii)   n = 4, l = 2, m = 0
(iii)   n = 3, l = 2, m = - 2
(iv)   n = 4, l = 2, m = +1
(v)   n = 2, l = 1, m = 0
(vi)   n = 3, l = 1, m = + 1

1.6 ATOMIC ORBITALS

1.6.1 Shapes of Atomic orbitals

An atomic orbital is the space around the nucleus in which the probability of finding the electron is maximum. These most probable regions can be diagrammatically represented by cloud density (dot) diagrams. The density of dots (or lack of them) in any region of the cloud diagram indicates the degree of probability of finding the electron in that region. It is not always convenient to draw dot diagrams of orbitals, since the probability of finding an electron decreases with distance (but does not become zero), thus not giving it any definite shape. Drawing boundary surfaces, which enclose 95-99% of the probability of locating an electron, is the method generally used, to show the shape of an orbital.

As definite energies and angular movements characterize atomic orbitals, the permissible values of these parameters are expressed in terms of quantum numbers. As different values of 'l' correspond to different orbital angular momentums, the azimuthal quantum 'l' determines the shape of orbitals.

Spherical nodes and nodal planes:

(a) Spherical node or Radial Node: The spherical surface where the probability of finding an electron is zero is called a spherical node.

In general, number of spherical nodes in an orbital = n – l – 1.

Where n is the principal quantum number and l is the azimuthal quantum number. For example,

(i) For 1s, n = 1 and l = 0
∴ No. of spherical nodes = 1 – 0 – 1 = 0

(ii) For 2s, n = 2 and l = 0
∴ No. of spherical nodes = 2 – 0 – 1 = 1

(iii) For 2p, n = 2 and l = 1
∴ No. of spherical nodes = 2 – 1 – 1 = 0

(iv) For 3s, n = 3 and l = 0
∴ No. of spherical nodes = 3 – 0 – 1 = 2

(v) For 3p, n = 3 and l = 1
∴ No. of spherical nodes = 3 – 1 – 1 = 1

(b) Nodal planes: The plane in which the probability of finding an electron is zero is called a nodal plane. Number of nodal planes for an orbital = l. For example,

(i) s-orbital (l = 0) has no nodal plane
(ii) p-orbital (l = 1) has one nodal plane
(iii) d-orbital (l = 2) has two nodal planes
(iv) f-orbital (l = 3) has three nodal planes.

Shapes of atomic orbitals:

Shape of 's' orbital:

- When l = 0, m = 0, i.e., one value implies that 's' sub-shell has only one space orientation and hence, it can be arranged in space only in one way along x, y or z axes. Thus, 's' orbital has a symmetrical spherical shape and is represented as

1s orbital   2s orbital
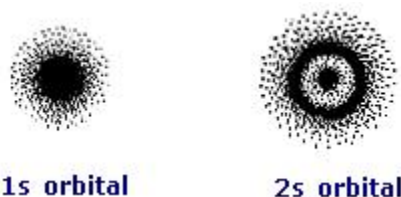
- The electron cloud is maximum at the nucleus and decreases with the distance. The electron density at a particular distance is uniform in all directions. The region of maximum electron density is called **antinode**.

- The total number of concentric spheres at any given main energy level in an 's' orbital is equal to the principal quantum number of that level. Thus for example '1s' orbital consists of only one sphere while a '3s' orbital consists of three concentric spheres.

- Secondly, as the value of the principal quantum number 'n' increases, the 's' orbital becomes larger and the energy of the's' orbital increases, while retaining the spherical symmetry. The energies of the various 's' orbitals follow the order 1s < 2s < 3s < 4s.

Shape of 'p' orbital:

- For 'p' orbitals 'l' = 1. So,

Angular momentum of an electron in '2p' orbital = $\sqrt{l(l+1)} \cdot \dfrac{h}{2\pi} = \sqrt{2}\,\dfrac{h}{2\pi}$

Thus the distribution around the nucleus is not spherical. The 'p' orbital probability diagram is dumb-bell shaped i.e., it consists of distorted spheres of high probability, one on each side of the nucleus, concentrated along a particular direction.

- The probability of finding the electron in a particular 'p' orbital is equal in both the lobes.

- Since 'l' = 1, irrespective of the value of n, three values of magnetic quantum number 'm' exists i.e., +1, 0 and 1. Thus three 'p' orbitals exist in each 'p' sub-shell. These are oriented symmetrically around the three axes 'x', 'y' and 'z'.
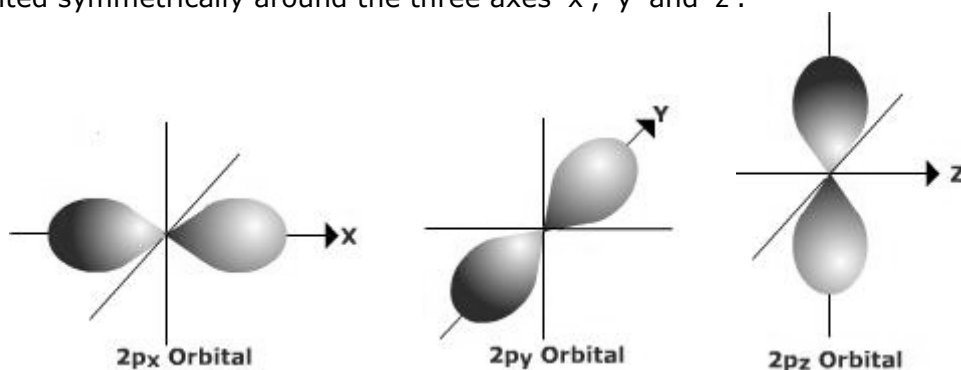

2px Orbital   2py Orbital   2pz Orbital

Fig: - Shapes of $2p_x$, $2p_y$ and $2p_z$ orbitals

Shape of 'd' orbital:

- For 'l' = 2, five values of 'm', the magnetic quantum number, exists i.e., -2, -1, 0, +1, and +1 and the minimum value of principal quantum number (n) has to be three.

- Accordingly there are five space orientations for 'd' orbitals, which are not identical in shape. These are designated as: d_{xy}, $d_{x^2-y^2}$, d_{yz}, d_{zx}, d_{z^2}

- The lobes of d_{xy} orbital lie between x and y-axes. Similar is the case for d_{yz} and d_{zx}. 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-axes and contains a ring of negative charge surrounding the nucleus in x-y plane.
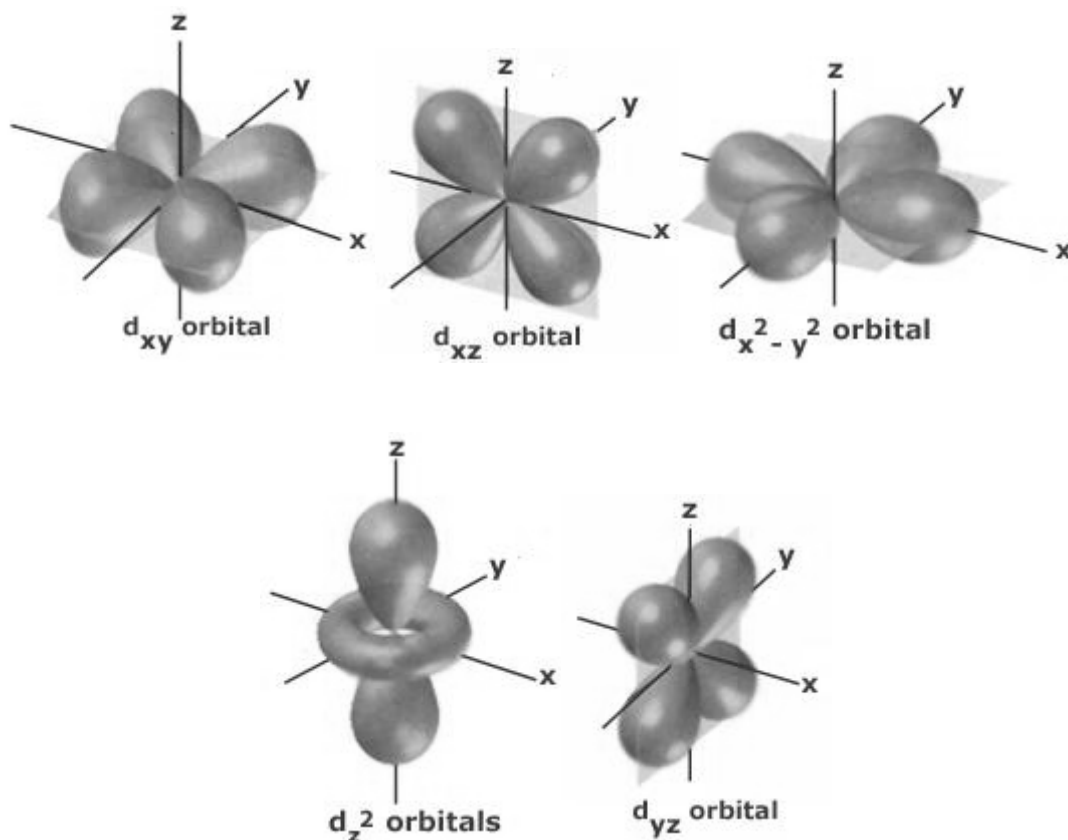
Fig: - Shapes of five 'd' orbitals

The shape of rest higher orbitals is complex in structure.

1.6.2 Energies of Atomic Orbitals

Single electron atoms:

The relative energies of various orbitals of single electrons depend on the value of the principal quantum number 'n' and is independent of the value of ' l '. This can be shown by an arrangement known as energy level diagram. The diagram given below illustrates the relative energy of various energy levels for hydrogen and hydrogen like atoms.
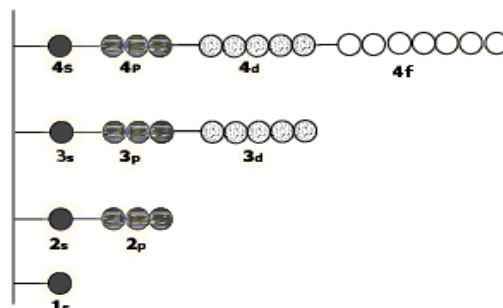
Multi-electron atoms:

In these atoms the energy of orbitals have the same values of 'n' but different values of ' l '. Thus both values of 'n' and ' l ' determine the energy of an orbital. The following hold good for multi-electron atoms.

- Different orbitals having the same principle quantum number 'n' (sub shell) may have different energies.
- For a particular main energy level, the orbital having higher value of the azimuthal quantum number ' l ' has higher energy. In general, energies of orbitals belonging to the same main energy level follow the order, 's' < 'p'<'d'< 'f'.
- When 'n' ≥ 3 some orbitals belonging to a lower main energy level may have higher energy than some orbitals belonging to the higher main energy levels. For examples the energy of '3d' orbitals >'4s' orbitals.
- The (n + l) rule states as follows: Lower the value of (n + l) for an orbital, the lower is its energy. Hence orbitals are filled in order of increasing (n + l) values. If two orbitals have the same (n + l) value, the orbital with lower value of n has lower energy and hence is filled first. For example,

  4p orbital, n + l = 4 + 1 = 5; 3d orbital, n + l = 3 + 2 = 5.

  So according to (n + l) rule, 3d orbital has lower energy since the value of n is less than the 4p orbital.

1.6.3 Filling of Orbitals Atoms:

The filling of electrons into the orbitals of different atoms takes place according to the following three rules:

(1) Aufbau Principle:

It states that **in the ground state of the atoms, the orbitals are filled in order of their increasing energies**. In other words, electrons first occupy the lowest-energy orbital available to them and enter into higher energy orbitals only when the lower energy orbitals are filled.
The order in which the energies of the orbitals increase and hence the order in which the orbitals are filled is as follows:
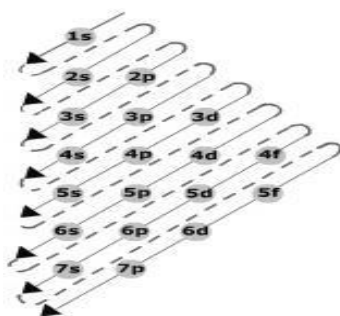Starting from the top, the direction of the arrows gives the order of filling of orbitals.

Figure: Order of filling of orbitals

(2) Pauli Exclusion Principle:

- It states that **no two electrons in an atom can have same values for all the four quantum numbers.** Electrons having the same value of n, l and m are said to belong to the same orbital.

- For instance, consider K shell, i.e. n =1. The electron will have only one value of (l) which is l = 0 and one value of m, which is m = 0 but it can have two values of s, either + ½ or - ½. This means that although n, l and m are the same for the two electrons but their spin quantum numbers are different. Thus, an orbital can have maximum of two electrons.

- If an orbital has two electrons, they must be of opposite spin. For one s = + ½ and for other s = - ½. Thus, the Pauli's exclusion principle may also be stated as "Only two electrons may exist in same orbital and these electrons must have opposite spin".

	n	l	m	m_s
1st electron	1	0	0	$+\dfrac{1}{2}$
2nd electron	1	0	0	$-\dfrac{1}{2}$

- The maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.

- If an orbital is represented by a circle and it contains two electrons, it is represented as:

$$(\uparrow\downarrow) \quad \text{or} \quad (\downarrow\uparrow)$$
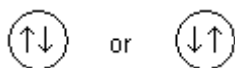
i.e. the two arrows must point in the opposite direction. The electrons are said to be paired or the orbitals is said to be fully filled.

If orbitals contain only one electron, it is represented as

$$(\downarrow) \quad \text{or} \quad (\uparrow)$$
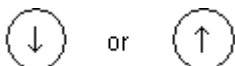
and is said to be half-filled. The electron is said to be in an unpaired state.

(3) Hund's Rule of Maximum Multiplicity:

- This rule deals with the filling of electrons into the orbitals belonging to the same sub-shell (i.e. orbitals of equal energy, called *degenerate* orbitals).

- It states that the pairing of electrons in the orbitals belonging to the same sub-shell (p, d or f) does not take place until each orbital belonging to that sub-shell has got one electron each i.e. is singly occupied.
- Since there are three p, five d and seven f orbitals, therefore the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron respectively.

For Example, the element nitrogen, which contains 7 electrons, the following configurations can be written:
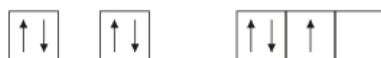
1s   2s $2p_x$ $2p_y$ $2p_z$

(a) Total spin of unpaired electrons

$$= \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1\frac{1}{2}$$

(b) Total spin of unpaired electrons

$$= +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} = \frac{1}{2}$$

(c)   Total spin $= \frac{1}{2}$

In accordance with the Hund's rule, the configuration (a) in which the three unpaired electrons occupying 2px, 2py, and 2pz orbitals have parallel spins is correct while configuration (b) and (c) are not consistant with the Hund's rule of maximum multiplicity.

1.**7 ELECTRONIC CONFIGURATION OF ATOMS**

The distribution of electrons into different levels, sublevels and orbitals of an atom is called its electronic configuration.

Usually the electronic configuration of the atom of any element is simply represented by the notation:
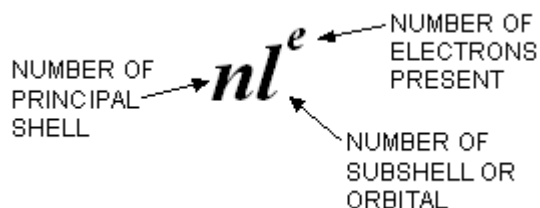
e.g. $1s^2$ means 2 electrons are present in the s-sub-shell of the 1st main shell.

To get the complete configuration of an atom, a number of such notations are written one after the other in order of increasing energies of the orbitals, starting always with the orbital of lowest energy i.e. 1s.

The electronic configurations of the various elements are:

Lithium   Li   3 $1s^2 2s^1$

Carbon   C   6 $1s^2 2s^2 2p_x^1 2p_y^1$

Nitrogen   N   7 $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

Oxygen   O   8 $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

Neon   Ne   10 $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

While writing the electronic configurations, the following points may also be noted:

(i) To avoid the writing of electronic configurations in a lengthy way, usually the symbols [He] [2], [Ne] [10], [Ar] [18] etc. are used as the first part of the configuration. Such a symbol stands for the electronic configuration of that inert gas and is usually called the core of the inert gas.

(ii) While writing down the electronic configuration of ion (cation or anion), first write configuration of basic atom and then add or remove the electron from the system otherwise always there is a chance of error. For example
Electronic configuration of Cr^{+3}:
Electronic configuration of Cr is [Ar] [18] $3d^5 4s^1$
Hence the Electronic configuration of Cr^{+3} is [Ar] [18] $3d^3$
For elements with very high atomic numbers, some deviations are observed other than on account of half-filled and fully filled sub-shells.

Some exceptional electronic configurations:

Some elements such as chromium (At. No. 24), copper (At. No. 29) etc. possess electronic configurations different from those expected from the aufbau order. This is because of the tendency of the sub-shells to be exactly half-filled or completely filled.

We explain this with an example:

Consider Molybdenum (Atomic number=42)

Expected configuration: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^4\,5s^2$

Actual configuration: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^5\,5s^1$

In general only one electron jumps from lower energy orbital to higher energy orbital i.e. from 5s to 4d. The reason for the tendency of the sub-shells to be completely filled or exactly half-filled is that it leads to greater stability**.**

The greater stability of exactly half-filled and completely filled configurations is due to the following two reasons:

(i) Symmetrical distribution of electrons:

The configurations in which all the orbitals of the same sub-shell are half-filled or completely filled involve symmetrical distribution of electrons. Symmetry of electronic distribution leads to extra stability.

(ii) Exchange energy:

The electrons present in the different orbitals of the same sub-shell can exchange their positions. Each such exchange leads to a greater stability which can be explained in terms of exchange energy. As the number of exchanges that can take place is maximum in the exactly half-filled and completely filled arrangements (i.e. more in d^5 than in d^4 and more in d^{10} than in d^9), therefore exchange energy is maximum and hence the stability is maximum.

1.**8 ATOMIC TERMS**

1.8.1 Atomic Number (Z)

The atomic number of an element is the number of protons contained in the nucleus of the atom of that element.

1.8.2 Nucleons

Protons and neutrons are present in a nucleus, so these fundamental particles are collectively known as nucleons.

1.8.3 Mass Number (A)

The total number of protons and neutrons i.e., the number of nucleons present in the nucleus is called the mass number of the element.

1.8.4 Atomic mass unit

It is exactly equal to 1/12 of the mass of $_6C^{12}$ atom.
1amu = 1.66 x 10^{-27} Kg. = 931.5 MeV

IUPAC notation of an atom (nuclide)

Let X be the symbol of the element, its atomic number be Z and mass number be A. Then the element can be represented as $_ZX^A$.

1.8.5 Atomic Species:

1. Isotopes

Atoms of the element with same atomic number but different mass number.

Example: $_1H^1$ and $_1H^2$ are isotopes.

2. Isobars

Atoms having the same mass number but different atomic numbers.

Example: $_{15}P^{32}$ and $_{16}S^{32}$ called isobars.

3. Isotones

Atoms having the same number of neutrons but different number of protons or mass number.

Example: $_6C^{14}$, $_8O^{16,}$ $_7N^{15}$ are called isotones.

4. Isoelectronic

Atoms, molecules or ions having same number of electrons are isoelectronic.

Example: (a) N_2 , CO, CN^- (b) N_2O, CO_2.

5. 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:

Uranium-X (half life 1.4 min) and Uranium-Z (half life 6.7 hours)

6. Isosters

Molecules having same number of atoms and also same number of electrons are called isosters.

Example: N_2 and CO

7. Isodiaphers

Species with same isotopic number are called isodiaphers.

Example: $_{19}K^{39}$, $_9F^{19}$.

Isotopic number = mass number - 2 × atomic number.

Or the species which have same n-p value, called isodiaphers.

Where n = no. of neturons

P = no. of protons

Example: Calculate the number of protons, neutrons and electrons in $^{80}_{35}Br$.

Solution: Here, Z = 35, A = 80

∴ No. of protons = Atomic No. = 35

No. of neutrons = A-Z = 80-35 = 45.

As the atom is neutral, No. of electrons = N. of protons = 35.