2

ATOMIC STRUCTURE

After completing this lesson, you will be able to:

This is 10 days lesson (period including homework)

- Define proton as a unit of radiation energy.
- Use the Bohr's model for calculating the radii of orbits.
- Explain production, properties, types and uses of X-rays.
- Describe the concept of orbitals.
- Distinguish among principal energy levels, energy sub levels, and atomic orbitals.
- Describe the general shapes of s, p and d orbitals.
- Describe the hydrogen atom using the Quantum Theory.
- Describe the orbitals of hydrogen atom in order of increasing energy. Summarize the Bohr's atomic theory
- Use the Bohr's model for calculating energy of electron in a given orbit of hydrogen atom.
- Relate energy equation (for electron) to frequency, wave length and wave number of radiation emitted or absorbed by electron.
- Explain the significance of quantized energies of electrons.
- Relate the discrete-line spectrum of hydrogen to energy levels of electrons in the hydrogen atom.
- Use the Aufbau Principle, the Pauli Exclusion Principle, and Hund's Rule to write the electronic configuration of the elements. Explain the sequence of filling of electrons in many electron atoms.
- Write electron configuration of atoms.

INTRODUCTION

A series of discoveries beginning during the later part of 19^{th} century have modified the Daltonian concept of the atom by demonstrating that an atom is a complex unit made up of similar discrete parts. Atoms are not simple, compact bodies as supposed by Dalton but are complex systems composed of several fundamental particles of matter. The modern theories have proved that an atom is made up of about 100 particles out of which electrons, protons and neutrons are whole time existing and important particles.

We need to understand atomic structure in order to understand chemical bonds that hold atoms together and chemical reactions.

The atoms are made up of sub-atomic particles, electron, proton and neutron. These three particles are called elementary or fundamental particles as they are building blocks of all atoms. Many of the characteristics of an atom are dependent upon these three particles. The only atom which do not contain neutron is protium (hydrogen). Many other particles such as neutrino, antineutrino, positron, pions and muons have also been discovered. Many of them are unstable and exist for a fraction of second only.

2.1 DISCHARGE TUBE EXPERIMENTS

A gas discharge tube is fitted with two metallic electrodes, as cathode and anode. The tube is filled with a gas, air or vapour of a substance at any desired pressure. The electrodes are connected to a source of high voltage battery. The tube is attached to the vacuum pump as shown in the diagram (2.1). In the beginning an electric current was passed through the gas in the discharge tube at ordinary pressure. The gas in the tube was not affected even at high potential of 5000 volts. However, the gas was discharged from tube up to a low pressure of 0.01 torr, and was connected to high voltage of 5000-10,000 volts. It was observed that at very low pressure of 0.1 torr and high potential, the gas becomes conductor, current starts to flow through the gas and gas starts to emit light (modern example of such a discharge tube is "a neon sign"). When the pressure is reduced even further upto 0.01 torr, emission of light by the gas ceased, certain rays were given out from cathode and travel towards anode. Such rays were called cathode rays because they originate from cathode. J.J. Thomson first identified the electrons in cathode ray tube (electric discharge tube) in 1887. Many other scientists like Faraday & Crookes studied the effects of passing electric current through a gas. As a result a sub-atomic particle with a negative charge was discovered.

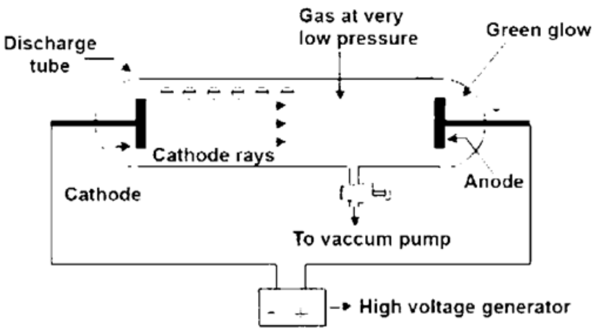

Fig. 2.1: A discharge tube

Through different discharge tube experiments electrons were discovered by J. J. Thomson in 1887 (but the name electrons was given by Stoney in 1886).

Properties of Cathode Rays

Some systematic studies were made by certain scientists in order to investigate the properties of cathode rays. These properties are mentioned below.

Cathode rays are negatively charged particles. J-Perrin (1895) showed that cathode rays are deflected in a magnetic field. J.J. Thomson (1897) proved that these rays can be deflected towards anode showing that they are negatively charged. They produce a greenish fluorescence on striking the walls of the glass tube.

Hittorf (1869) proved that cathode rays cast a sharp shadow when an opaque object is placed in their path. This proves that they travel in straight line perpendicular to the surface of cathode.

They can drive a small paddle wheel placed in their path. This verifies that they are material particles and have certain momentum also.

They can produce X-rays when they strike on an anode, particularly with large atomic mass. They produce

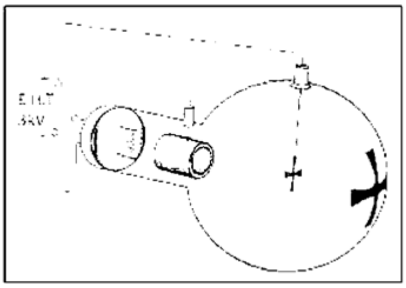
Fig. 2.2: Cathode rays casting shadow of an opaque object

heat when they fall on a platinum foil and foil begins to glow. They can ionize gases. They can cause a chemical change in a material on which they fall. They are capable of penetration in metallic sheets like of Aluminium or Gold.

J.J. Thomson determined charge to mass ratio (e/m) of an electron. He concluded that all atoms contain electrons. The value of e/m is 1.7588×10^{11} Coulombs kg^{-1}. Whatever the gases and the vapour in the discharge tube, the cathode rays and the electrons are always the same. This proves that electrons are present in all atoms.

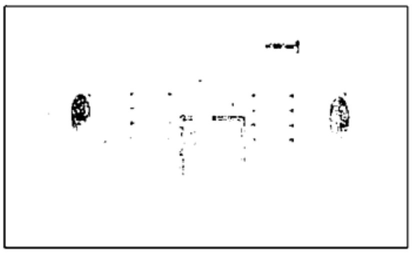

Fig. 2.3: Cathode rays moving a small paddle wheel

Measurement of charge to mass ratio (e/m) and charge of an electron:

(J. J. Thomson's cathode rays experiment 1897)

J. J. Thomson subjected a beam of cathode rays (electron particles) to see the effects of electric and magnetic fields as shown in figure 2.4.

In the beginning, in absence of any electric or magnetic field, the electrons from cathode rays struck the fluorescent screen at B. Then under the effect of electric field, they strike at point A. Similarly they strike at point C under the influence of magnetic field only. Now electric and magnetic fields were adjusted in such a way that the electron again strike at point B.

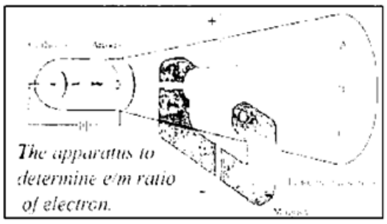

Fig. 2.4 Cathode rays in electric and magnetic rays

In this way by comparing the strength of the two fields, he determined the e/m value of an electron which is 1.7588×10^{11} Coulombs kg^{-1}. This means that 1 kg of electrons have 1.7588×10^{11} Coulombs of charge.

Measurement of charge on Electron (Millikan's oil drop experiment 1909)

R.A. Millikan Succeeded in measusring the charge of electron with great precision in 1909. Millikan constructed a box which consisted of two chambers. The upper chamber was filled with air whose pressure was adjusted by a vacuum pump. There were installed two electrodes A and A′. The electrodes were attached with electricity to generate an electric field in the space between the electrodes. The upper electrode had a hole in it as shown in the diagram. A fine spray of oil droplets was created

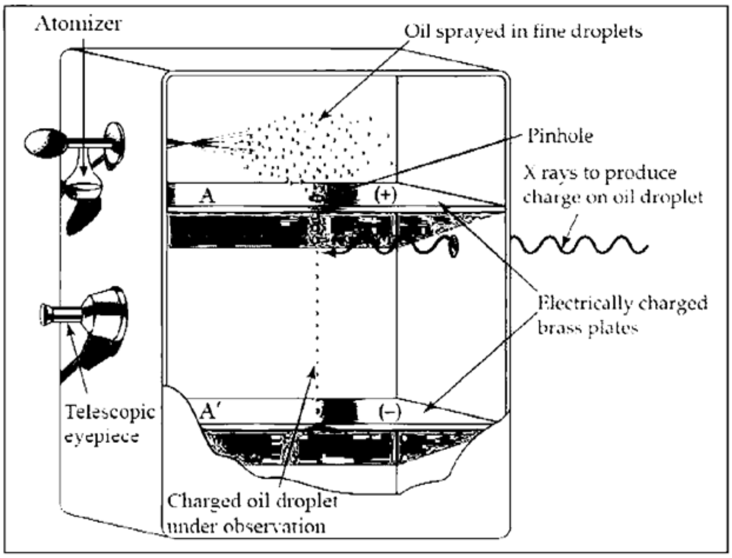

Fig. 2.5: Millikan's oil drop experiment

by an atomizer. Few droplets entered the hole. Then the hole was closed. An arc lamp was used to illuminate the space between the electrodes. The droplet fell under the force of gravity. The velocity (V_1) of the droplet was determined depending upon its weight.

$$V_1 \propto m \times g \qquad \text{------ (1)}$$

Where m is mass of particle and g is acceleration due to gravity.

After that the air between the electrodes was ionized by X-rays. The droplet under observation took up an electron and got charged. Then A and A′ were connected to a battery which generated an electric field having a strength E. The droplet moved upwards against gravitational force with a velocity V_2.

i.e. $$V_2 \ \alpha \ E \times e - m \times g \qquad \text{-----(2)}$$

Where E is strength of electric field and e is charge on electron.

Dividing Eq. (2) by Eq. (1)

$$\frac{V_1}{V_2} = \frac{mg}{Ee - mg}$$

If V_1, V_2, g and E are known, mass of an electron can be determined by varying the electric field in such a way that the droplet is suspended in the chamber. Hence "e" can be calculated which is 1.6022×10^{-19} coulombs.

Determination of Mass of an Electron

We know that $$\frac{e}{m} = 1.7588\times10^{11}\text{Coulomb kg}^{-1}$$

but $$e = 1.6022\times10^{-19}\text{Coulomb}$$

$$\therefore \quad \frac{1.60\times10^{-19}\text{C}}{m} = \frac{1.7588\times10^{11}\text{Ckg}^{-1}}{1}$$

or $$m\times1.7588\times10^{11}\text{C kg}^{-1} = 1.60\times10^{-19}\text{C}$$

$$m = \frac{1.60\times10^{-19}\text{C}}{1.7588\times10^{11}\text{Ckg}^{-1}}$$

$$\mathbf{m = 9.1095\times10^{-31}kg}$$

Example 2.1 How much heavier is the H-atom as compared to an electron?

Solution: as we know that

Mass of H atom = 1.6736×10^{-27} kg

Mass of electron = 9.1095×10^{-31} kg

$$\frac{\text{Mass of H}-\text{atom}}{\text{Mass of electron}} = \frac{1.6736\times10^{-27}\text{kg / H atom}}{9.1095\times10^{-31}\text{kg / electron}} = \frac{1837}{1}$$

Hence Hydrogen atom is 1837 times heavier than an electron.

In 1886 Goldstein, a German Physicist discovered proton in cathode ray tube.

In a discharge tube, atoms or molecules lose electrons forming positive ions. Typical example is of ionization of Neon gas.

$$Ne \rightarrow Ne^{+1} + e^{-}$$

It is observed that the positive ions move towards cathode in a discharge tube.

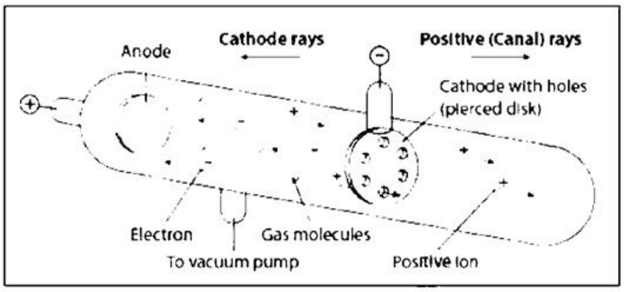

Fig. 2.6 Positive particles moving towards cathode in a discharge tube.

Construction and Working

About one metre long tube was taken which was provided with a perforated cathode as shown in the diagram. The electrodes were connected to a high voltage battery.

Atom being electrically neutral must contain equal number of positive and negative particles. When electric current was passed through the gas under reduced pressure, some rays are produced from cathode which traveled away from cathode. Such rays ionize the gas in the middle of the discharge tube. They knocked out electron from the gas molecules. As a result positive ions were produced, which start moving towards the perforated cathode.

$$M \rightarrow M^{+1} + e^{-}$$

$$He \rightarrow He^{+1} + e^{-}$$

Since these rays passed through the canals (small holes) of cathode so they were also called as "Canal rays". Later on they were called Positive rays because they carried positive charge.

Properties of Positive Rays

Positive rays have the following properties:

1) They travel in straight line perpendicular to the anode surface.
2) They can be deflected by electric field.
3) Their deflection is towards cathode showing that they are positively charged.
4) They produce flashes on ZnS plate.
5) Their $\frac{e}{m}$ ratio is smaller than that of an electron.
6) The $\frac{e}{m}$ ratio depends upon the nature of the gas. The highest $\frac{e}{m}$ is obtained if Hydrogen gas is present in the tube.
7) The mass of a +ive particle is never less than that of a proton.
8) The positive particle obtained from H_2 gas is the lightest among all the positive particles.
9) A particle obtained from positive rays is called proton, a name suggested by Rutherford.
10) The mass of a proton is 1837 times more than that of an electron.

As proton is present in all the atoms therefore proton is a common constituent of all matter.

2.2 DISCOVERY OF NEUTRONS

James Chadwick

After the discovery of electrons and protons in an atom, nothing extra was known about it until 1932. Rutherford in 1920 predicted that some neutral particles must also be present in it because he noticed that atomic mass of atoms could not be explained if it were supposed that atoms had only electrons and protons.

James Chadwick in 1932 performed an experiment and proved that certain neutral particles also exist in nucleus of an atom and he was awarded Nobel Prize in Physics in 1935 for this discovery.

Experiment by James Chadwick

A stream of α-particles produced from Polonium (Po) was directed at target metal foil ${}_4Be^9$.

It was noticed that some penetrating radiations were produced. These radiations were called neutrons, because the charge detector showed them to be neutral.

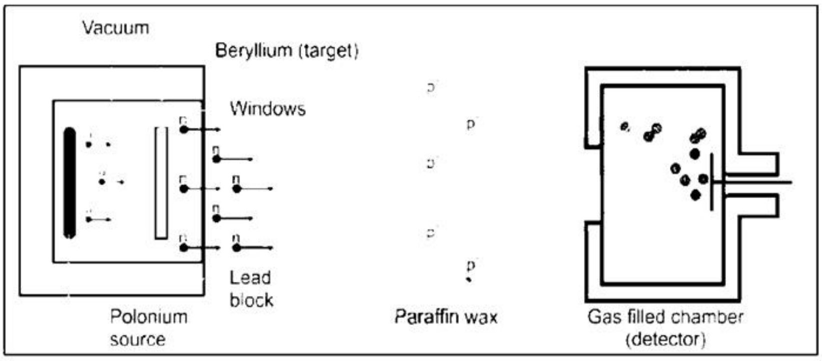

Fig. 2.7: α – rays bombarded on Beryllium sheet

The nuclear reaction is as follows:

${}_4Be^9 + {}_2He^4$ (α-particles) $\longrightarrow$ ${}_6C^{12} + {}_0n^1$ (neutron).

Properties of neutrons

Neutrons have the following properties,

1. Free neutron decays into a proton with the emission of electron and neutrino.
   ${}_0n^{1+} \longrightarrow {}_1p^1 + {}_{-1}e^0 + {}_0n^0$ (neutrino, particle of a small mass).
2. They cannot ionize gases.
3. They are highly penetrating particles.
4. When neutrons travel with energy 1.2 MeV or more, they are called **Fast Neutrons**. And when have energy below 1 e.V., they are called **slow neutrons**.
5. They are not deflected in electric and magnetic fields. Hence they are neutral in nature.
6. They can knockout high speed protons from paraffins, water, paper and cellulose.
7. Slow neutrons are more effective than the fast ones for the fission purposes.
8. When neutrons are used as projectile, they can carry out the nuclear reactions.
   e.g. ${}_7N^{14} + {}_0n^1 \longrightarrow {}_5B^{11} + {}_2He^4$

When slow moving neutrons hit the Cu metal, β – radiations are emitted.

$$ {}_{29}Cu^{65} + {}_0n^1 \longrightarrow {}_{30}Zn^{66} + {}_{-1}e^{\circ}(\beta - \text{ray}) $$

Because of their intense biological effects, they are used in the treatment of cancer.

2.3 THE DISCOVERY OF NUCLEUS (RUTHERFORD'S EXPERIMENT, 1910 – 11)

After the discovery of electron, proton and neutron in an atom, the next problem was to locate their positions. Rutherford in 1910 performed an experiment by bombarding α– particles ($_2He^4$) from a radioactive element (Ra or Po) on a thin metallic foil (0.00004 cm thick) as shown by Fig 2.8. He observed that most of the α - particles passed un-deflected. A few were deflected through various angles and a very few of them were deflected in backward direction as shown by Fig 2.8.

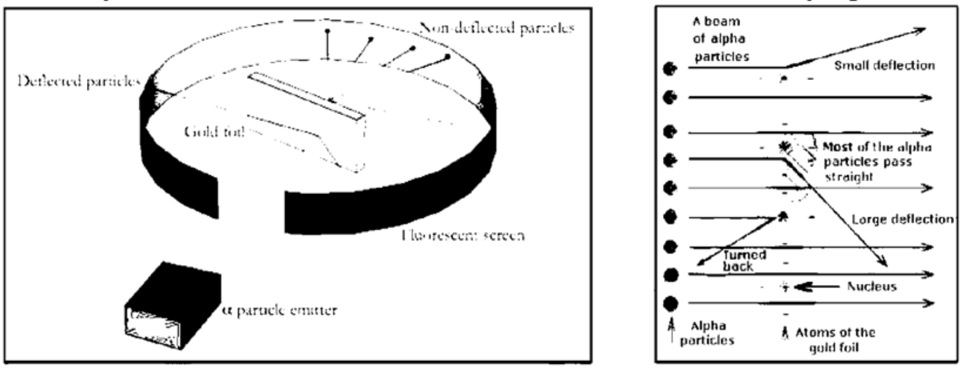

Fig. 2.8: α-rays bombarded on gold foil

Rutherford's Conclusions (Rutherford's Atomic Model)

1. An atom consists of a small heavy positively charged portion called Nucleus.
2. There is a negatively charged portion which surround the nucleus containing electrons called extra – nuclear portion or planetary.
3. The number of protons in the nucleus are equal to the number of electrons in the planetary.
4. The electrons revolve around the nucleus.
5. The centripetal force is equal to the electrostatic force.
6. Only a very small volume is occupied by the nucleus.

Defects of Rutherford Atomic Model

The defects of Rutherford Atomic Model are:

1. Rutherford Atomic Model is based upon laws of motion and gravitation which are applicable to neutral bodies but not to the charge bodies like electron and proton.
2. According to Maxwell's theory any charge particle moving in a circular path must radiate energy continuously and ultimately the electron must be spiral into the nucleus and the atom will collapse.
3. If electron emits energy continuously, it should form continuous spectrum. But actually, a line spectrum is obtained.

Particle	Charge/ Coulomb	Relative charge	Mass/Kg	Mass(a.m.u)	Where found
Proton	$+1.6022\times10^{-19}$	+ 1	1.6727×10^{-27}	1.0073	In the nucleus
Neutron	O	O	1.6750×10^{-27}	1.0087	In the nucleus
Electron	-1.6022×10^{-19}	-1	9.1095×10^{-31}	5.4858×10^{-4}	Outside nucleus

2.4 BOHR'S ATOMIC MODEL AND ITS APPLICATIONS

In order to remove the defects of Rutherford atomic model and the investigate the internal structure of an atom, Neil Bohr, an English scientist (1913) proposed another possible structure of an atom called Bohr's atomic model. According to this model;

1. Electrons revolve around the nucleus in definite energy levels called orbits or shells.
2. As long as an electron remain in a shell it never gains or losses energy.
3. The gain or loss of energy occurs within orbits only due to jumping of electrons from one energy level to another energy level.

   $\Delta E = E_2 - E_1$
4. Angular momentum (mvr) of an electron is equal to $nh/2\pi$.

   The angular momentum of an orbit depends upon its quantum number and it is an integral multiple of the factor $h/2\pi$

   i.e. $mvr = nh/2\pi$ Where n = 1, 2, 3, ...

Bohr derived expressions for the calculations of radius of nth orbit of an atom of hydrogen or ions like He^{+1}, Li^{+2} etc.

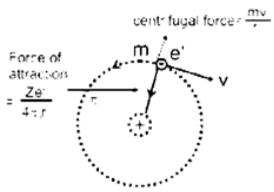

Figure 2.9 Electron revolving in an atom

Let us consider an atom having an electron (e^-) moving around the nucleus having charge $Z e^+$, where Z is the atomic number. Let m be the mass of electron, r the radius of the orbit and v is the velocity of the revolving electron.

According to coulomb's law, the electrostatic force or

Coulomb's force of attraction = $\dfrac{Ze^+ \times e^-}{4\pi\epsilon_o r^2} = \dfrac{Ze^2}{4\pi\epsilon_o r^2}$

Where ϵ_o (the vacuum permittivity constant) = $8.84 \times 10^{-12}\ C^2\ J^{-1}\ m^{-1}$.

Centrifugal force acting on the moving electron $= \dfrac{mv^2}{r}$

These two forces are equal and opposite and balance each other. So,

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_o r^2} \qquad \text{.........................} (1)$$

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_o r}$$

$$r = \frac{Ze^2}{4\pi\epsilon_o mv^2} \qquad \text{.........................} (2)$$

Thus we conclude that the radius of a moving electron is inversely proportional to the square of its velocity.

Now we consider angular momentum. According to Neil Bohr,

$$mvr = \frac{nh}{2\pi} \qquad \text{.........................} (3)$$

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

Taking square on both sides,

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

Putting this value of v^2 in (2),

$$r = \frac{Ze^2}{4\pi \in_o m} \frac{4\pi^2m^2r^2}{n^2h^2}$$

$$\frac{1}{r} = \frac{Ze^2\pi m}{\in_o h^2 n^2}$$

or $\quad Ze^2\pi\, mr = \in_o n^2h^2$

$$r = \in_o n^2h^2 / Ze^2m\pi \qquad \text{.........................} (5)$$

For hydrogen, $Z = 1$

So, $\quad r = \dfrac{\in_o n^2h^2}{\pi me^2} \qquad \text{.........................} (6)$

or $\quad r = n^2 a_o$

where $a_o = \dfrac{\in_o h^2}{\pi me^2}$, a constant quantity having a value of

$$0.529 \times 10^{-10} m = 0.529 \text{ Å} \quad (\text{where } 1 \text{ Å} = 10^{-10} \text{ m})$$

So $\quad r = n^2 \times 0.529$ Å

Therefore radius of orbits having $n = 1, 2,$------ are as follows.

When $n = 1$, $r = 1^2 \times 0.529$ Å $= 0.529$ Å

When $n = 2$, $r = 2^2 \times 0.529$ Å $= 4 \times 0.529$ Å $= 2.116$ Å

The energy of an electron in an orbit is the sum of its potential energy and kinetic energy.

$$\therefore \quad E_{Total} = K.E + P.E.$$

$$= (\frac{1}{2}mv^2) + (-\frac{Ze^2}{4\pi \in_o r}) \qquad \text{.........................} (7)$$

$$E_{Total} = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi \in_o r}$$

This potential energy is governed by the coulomb's Law of Electrostatic force.

Putting the value of mv^2 from eq. (1) into eq. (7)

$$E_{Total} = E_n = \frac{1}{2}\left(\frac{Ze^2}{4\pi\epsilon_o r}\right) - \frac{Ze^2}{4\pi\epsilon_o r}$$

$$= \frac{Ze^2}{4\pi\epsilon_o r}\left(\frac{1}{2} - \frac{1}{1}\right) = \frac{Ze^2}{4\pi\epsilon_o r}\left(-\frac{1}{2}\right)$$

$$= -\frac{Ze^2}{8\pi\epsilon_o r} \qquad \text{.......................... (8)}$$

Now putting the value of r from eq. (5) in to eq. (8)

$$E_n = -\frac{Ze^2}{8\pi\epsilon_o} \times \left[\frac{\pi m Ze^2}{\epsilon_o n^2 h^2}\right]$$

$$= -\frac{mZ^2e^4}{8\epsilon_o^2 n^2 h^2} \qquad \text{.......................... (9)}$$

For Hydrogen atom; Z = 1

$$\therefore \quad E_n = -\frac{me^4}{8\epsilon_o^2 n^2 h^2}$$

$$= -\frac{me^4}{8\epsilon_o^2 h^2}\left[\frac{1}{n^2}\right]$$

But $\frac{me^4}{8\epsilon_o^2 h^2} = 2.18 \times 10^{-18}$ J

This value is obtained by putting the values of constants.

$$\therefore \quad E_n = -2.18 \times 10^{-18}\left[\frac{1}{n^2}\right] \text{J} \qquad \text{.......................... (10)}$$

$$= -\frac{k}{n^2} \qquad \text{where } k = 2.18 \times 10^{-18} \text{ J}$$

The negative sign indicates decrease in energy of the electron.

The value of energy obtained is in Joules/atom. If this quantity is multiplied by Avogadro's No. and divided by 1000, the value of E_n becomes.

$$E_n = -\frac{1313.35}{n^2} \text{ kJ / mole.}$$

This energy is associated with 1.008 gram-atoms of hydrogen.

If n = 1, 2, 3 4, 5……

then

$$E_1 = -\frac{1313.35}{1^2} = -1313.35 \text{kJ mole}^{-1}$$

$$E_2 = -\frac{1313.35}{2^2} = -328.32 \text{ kJ mole}^{-1}$$

$$E_3 = -\frac{1313.35}{3^2} = -145.92 \text{ kJ mole}^{-1}$$

$$E_4 = -\frac{1313.35}{4^2} = -82.08 \text{ kJ mole}^{-1}$$

$$E_5 = -\frac{1313.35}{5^2} = -52.53 \text{ kJ mole}^{-1}$$

The first energy level when n = 1 is known as the ground state of the hydrogen atom. All other energy levels are known as excited states.

[illegible]

According to Eq. (9) $E = -\dfrac{mZ^2e^4}{8\epsilon_o^2 n^2h^2}$

Let E_1 be the energy of the lower energy orbit n_1 and E_2 that of higher energy orbit n_2,

Then

$$\begin{aligned}
\Delta E &= E_2 - E_1 \\
&= \left(-\frac{mZ^2e^4}{8\epsilon_o^2 n_2^2h^2}\right) - \left(-\frac{mZ^2e^4}{8\epsilon_o^2 n_1^2h^2}\right) \\
&= -\frac{mZ^2e^4}{8\epsilon_o^2 n_2^2h^2} + \frac{mZ^2e^4}{8\epsilon_o^2 n_1^2h^2} \\
&= \frac{mZ^2e^4}{8\epsilon_o^2 n_1^2h^2} - \frac{mZ^2e^4}{8\epsilon_o^2 n_2^2h^2} \\
&= \frac{mZ^2e^4}{8\epsilon_o^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]
\end{aligned}$$

For Hydrogen, Z = 1

$$\therefore \Delta E = \frac{me^4}{8\epsilon_0^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{.............. (11)}$$

Here, $\dfrac{me^4}{8\epsilon_0^2 h^2} = 2.18 \times 10^{-18}$ J.

$$\therefore \quad \Delta E = 2.18 \times 10^{-18}\ \text{J}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{.............. (12)}$$

[illegible]

According to Plank's Quantum theory,

$$\Delta E = h\nu$$

$$\therefore \quad h\nu = 2.18 \times 10^{-18}\ \text{J} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right].$$

again $h\nu$ $= \dfrac{me^4}{8\epsilon_0^2 h^2}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

or ν $= \dfrac{me^4}{8\epsilon_0^2 h^3}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$ Hz or cycles sec^{-1} .... (13)

[illegible] $\bar{\upsilon}$

The relationship between frequency (ν) and wave number ($\bar{\upsilon}$) is

$$\nu = \bar{\upsilon} c \qquad \text{.......................... (14)}$$

Where c is the velocity of light.

Putting the value of ν from eq. (13) in eq. (14)

$$\bar{\upsilon}c = \frac{Z^2me^4}{8\epsilon_o^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or $$\bar{\upsilon} = \frac{Z^2me^4}{8\epsilon_o^2 h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{.......................... (15)}$$

Putting values of constants, $\frac{me^4}{8\epsilon_o^2 h^3 c}$ = R = 1.09678 × 10^7 m^{-1},

R called Rydberg's constant?

$$\bar{\upsilon} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{...................... (16)}$$

$$\therefore \bar{\upsilon} = 1.09678 \times 10^7\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] m^{-1}$$

Example 2.2

Calculate the value of a_o of H – atom.

Solution

We know that $a_o = \frac{\epsilon_o h^2}{\pi m e^2}$

The values of the constant are:

ϵ_o = 8.854 × 10^{-12} C^2 J^{-1} m^{-1} h = 6.626 × 10^{-34} J s

π = 3.142 m = 9.11 × 10^{-31} kg

e = 1.60 × 10^{-19} C.

Putting these values in equation, $a_o = \frac{\epsilon_o n^2 h^2}{\pi m e^2}$

$$a_o = \frac{8.854 \times 10^{-12} \times (6.626 \times 10^{-34})^2}{3.142 \times 9.11 \times 10^{-31} \times (1.60 \times 10^{-19})^2}$$

$$= 5.29 \times 10^{-11} m = 0.529 \mathring{A}$$

Example 2.3

Calculate the radius of 3^{rd} orbit of electron in H-atom.

Solution

$r_n = a_o n^2$

As a_o = 5.29 × 10^{-11} m. and n = 3

$\therefore$ $r^3 = (3)^2 \times 5.29 \times 10^{-11}$m

$= 9 \times 5.29 \times 10^{-11}$m

$= 47.61 \times 10^{-11}$m $= 4.761 \mathring{A}$

Example 2.4

Calculate energies of n_1 for (i) $_2He^+$ (ii) $_3Li^{+2}$

Solution:

$E_n = -\frac{k Z^2}{n^2}$ where $k = \frac{e^4 m}{8\epsilon_o^2 h^2 n^2}$

(i) $Z = 2$ for $_2He^+$,

Then $E_{He^+} = -\frac{(2)^2 k}{1^2}$

or $E_{He^+} = -\frac{4 \times 2.18 \times 10^{-18}}{1} = -8.72 \times 10^{-18} J.$

(ii) $Z = 3$ for $_3Li^{+2}$

$E_{Li^{+2}} = -\frac{(3)^2 k}{1^2}$ $\quad E_{Li^{+2}} = -\frac{9 \times 2.18 \times 10^{-18} J}{1}$

$= -1.962 \times 10^{-17}$ J.

Example 2.5

How much energy is required to make electron of H-atom to jump from n = 2 to n = 4.

Solution:

$$\Delta E = E_{Final} - E_{initial}$$

Here $n_1 = 2$, & $n_2 = 4$
(lower energy orbit) (higher energy orbit)

So $$\Delta E = = k\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= k\left[\frac{1}{4} - \frac{1}{16}\right]$$

$$= k\left[\frac{4-1}{16}\right]$$

But $k = 2.18 \times 10^{-18} J.$

$\therefore$ $\Delta E = 2.18 \times 10^{-18} \times \frac{3}{16} J$

$= 4.08 \times 10^{-19} J$

Self Check Exercise 2.1

1. Calculate how much energy is required in order to remove electron of hydrogen atom. (**Ans**:2.18×10^{-18}J)

(Hint consider $n_1 = 1$, $n_2 = \infty$)

2. Convert this energy into ν and $\bar{\nu}$ (**Ans:** 3.288×10^{15} s^{-1} , 1.096×10^{7} m^{-1}

1. Bohr's atomic model is applicable to one electron system and cannot explain the origin of the spectrum of multi-electrons or polyelectronic systems like He, Li, Be etc.
2. When a spectrum of Hydrogen gas is seen through a powerful spectrometer, the origin of spectral lines are replaced by several very fine lines. i.e., original lines are divided into other fine lines. Bohr's theory cannot explain this fine structure.
3. Bohr suggested circular orbits of electrons around the nucleus of H-atom. But it is proved that the motion of electron is not in a single plane, but takes place in three-dimensional space.
4. Bohr's theory cannot explain the effect of magnetic field (Zeeman Effect) and electric field (Stark Effect) on the spectra of atoms.

Zeeman's Effect:

"The splitting of spectral lines of H-spectrum under the influence of magnetic field."

Stark's Effect:

"The splitting of spectral lines of H-spectrum under the influence of electric field."

Bohr's picture of an atom is not satisfactory. In Bohr's atom, the electrons are moving in orbits with specific velocities in specific radii. But according to **Heisenberg's uncertainty principle, both the exact position and velocity of electron cannot be measured simultaneously.** In order to solve this difficulty, Schrodinger gave a wave equation for hydrogen atom. According to him, although the position and velocity of an electron cannot be found exactly, the probability of finding an electron can be ascertained. The maximum probability is at a distance of 0.0529 nm.

The visual display or dispersion of the components of visible light, when it is passed through a prism is called spectrum. These are two types of spectrum:

(a) Continuous Spectrum:

When the boundary lines between the colors cannot be marked it is called continuous spectrum.

(b) Line Spectrum:

When the boundary lines between the colors are separately isolated and marked it is called line spectrum.

When Hydrogen is enclosed in a container and heated, it emits radiation. These radiation are actually emitted due to excitation and de-excitation of electron of hydrogen.

According to equation 16.

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

With this equation, Bohr was able to predict the wave number in the hydrogen emission spectrum and the electron transition (changes of energy levels) that occur in hydrogen atom.

The wave number of different spectral lines can be calculated corresponding to the values of n_1 and n_2. In the hydrogen spectrum, different series of lines have been identified for n_1 and n_2 values. These series are,

Lyman series	n_1	=	1	n_2 = 2,3,4,5 ...
Balmer series	n_1	=	2	n_2 = 3,4,5,6 ...
Paschen series	n_1	=	3	n_2 = 4,5,6,7 ...
Brackett series	n_1	=	4	n_2 = 5,6,7,8 ...
Pfund series	n_1	=	5	n_2 = 6,7,8,9 ...

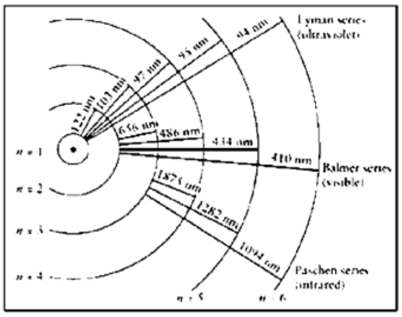

Fig. 2.10: Spectrum of hydrogen atom showing electronic transition to give different series

Only the Balmer series was observed in the visible part of the spectrum. Lyman series lie in the ultraviolet region while the Paschen, Brackett and Pfund series have been observed in the infrared region.

Origin of Hydrogen Spectrum on the Basis of Bohr's Model.

The first spectral lines were discovered in 1887 by Lyman and Balmer. No satisfactory reason became available till 1913. Neil Bohr presented his explanation of line spectra in 1913.

According to Bohr when current is passed through the hydrogen gas in the discharge tube at low pressure, the molecules of hydrogen break in to atoms. These atoms absorb energy from the electric spark. The electrons of hydrogen atoms are excited to high energy levels. The higher energy orbits to which the electron migrate depend upon the amount of energy absorbed by the electron. Above diagram shows the possibilities of movement of electron from lower to higher levels.

These excited electrons being unstable come back to one of the lower energy levels. The electrons may come to the lowest energy levels. In this way they emit energy, they had absorbed. Lyman series is produced when the electrons jump from n=2,3,4,5,6...etc to n=1.In Balmer series the electrons from n=3,4,5,6....come back to n=2.

Let us calculate the various lines of Lyman series, Balmer series, Paschen series, Brackett series and Pfund series from Bohr's equation of wave number.

$$\bar{\nu} = 1.09678\times10^7[\frac{1}{n_1^2} - \frac{1}{n_2^2}]m^{-1}$$

Lyman Series

The various lines in Lyman series got their explanation by considering that the electronos of hydrogen atom fall back to **n=1** from higher levels. The higher levels occupied by the electrons due to the electric spark.

First line: $n_1 = 1$ $n_2 = 2$

$$\bar{\nu} = 1.09678\times10^7 (\frac{1}{1^2} - \frac{1}{2^2})m^{-1} = 82.26\times10^5\, m^{-1}$$

Second line: $n_1 = 1$ $n_2 = 3$

$$\bar{\nu} = 1.09678\times10^7(\frac{1}{1^2} - \frac{1}{3^2})m^{-1} = 97.60\times10^5\, m^{-1}$$

Third line: $n_1 = 1$ $n_2 = 4$

$$\bar{\nu} = 1.09678\times10^7 (\frac{1}{1^2} - \frac{1}{4^2})m^{-1} = 102.70\times10^5\, m^{-1}$$

Limiting line: $n_1 = 1$ $n_2 = \infty$

$$\bar{\nu} = 1.09678\times10^7 (\frac{1}{1^2} - \frac{1}{\infty^2})m^{-1} = 109.678\times10^5\, m^{-1}$$

This limiting line shows that the energy difference between the first level and the infinite level is the ionization energy of the hydrogen atom. All these lines of Lyman series have close values. They appear in the form of a group. These values of wave numbers lie in the UV region of the spectrum.

Balmer series:

In this series the electrons fall back to **n=2**.

First line (Hα line): $n_1 = 2$ $n_2 = 3$

$\bar{\upsilon} = 1.09678\times10^7 (\frac{1}{2^2} - \frac{1}{3^2})m^{-1} = 15.234\times10^5 m^{-1}$

Second line (Hβ line): $n_1 = 2$ $n_2 = 4$

$\bar{\upsilon} = 1.09678\times10^7 (\frac{1}{2^2} - \frac{1}{4^2})m^{-1} = 20.566\times10^5 m^{-1}$

Third line (Hγ line): $n_1 = 2$ $n_2 = 5$

$\bar{\upsilon} = 1.09678\times10^7 (\frac{1}{2^2} - \frac{1}{5^2})m^{-1} = 23.05\times10^5 m^{-1}$

Limiting line: $n_1 = 2$ $n_2 = \infty$

$\bar{\upsilon} = 1.09678\times10^7 (\frac{1}{2^2} - \frac{1}{\infty^2})m^{-1} = 27.421\times10^5 m^{-1}$

All these lines of Balmer series are very close to each other and appear in the form of group of lines. These lines lie in the visible region of the spectrum.

Paschen Series:

The electrons from higher levels fall back to **n=3**.

First line: $n_1 = 3$ $n_2 = 4$

$\bar{\upsilon} = 1.09678\times10^7 (\frac{1}{3^2} - \frac{1}{4^2})m^{-1} = 5.3310\times10^5 m^{-1}$

Second line: $n_1 = 3$ $n_2 = 5$

$\bar{\upsilon} = 1.09678\times10^7 (\frac{1}{3^2} - \frac{1}{5^2})m^{-1} = 7.799\times10^5 m^{-1}$

Limiting line: $n_1 = 3$ $n_2 = \infty$

$\bar{\upsilon} = 1.09678\times10^7 (\frac{1}{3^2} - \frac{1}{\infty^2})m^{-1} = 12.187\times10^5 m^{-1}$

These are again the groups of lines close to each other and appear in IR region.

Brackett series:

The electrons from higher levels fall back to **n=4**.

First line: $n_1 = 4$ $n_2 = 5$ $\bar{\upsilon} = 2.45\times10^5 m^{-1}$

Second line: $n_1 = 4$ $n_2 = 6$ $\bar{\upsilon} = 3.808\times10^5 m^{-1}$

Limiting line: $n_1 = 4$ $n_2 = \infty$ $\bar{\upsilon} = 6.855\times10^5 m^{-1}$

Pfund series:

The electrons from higher energy levels fall back to **n=5**.

First line: $n_1 = 5$ $n_2 = 6$ $\bar{\upsilon} = 1.340\times10^5 m^{-1}$

Second line: $n_1 = 5$ $n_2 = 7$ $\bar{\upsilon} = 2.148\times10^5 m^{-1}$

Limiting line: $n_1 = 5$ $n_2 = \infty$ $\bar{\upsilon} = 4.387\times10^5 m^{-1}$

2.5 PLANK'S QUANTUM THEORY

Max Plank (1900) proposed a theory about nature of light. According to this theory,

(a) Energy is not emitted or absorbed continuously. It is emited or absorbed in the form of wave packets or quanta. In case of light the quantum of energy is often called photon.

(b) The amount of energy associated with quantum of radiation is directly proportional to the frequency (υ) of radiation. i.e.

$E \propto \upsilon$ or $E = h\,\upsilon$ .... (1)

where h = Plank's constant and has a value of 6.625×10^{-34} Joules sec.

(c) A body can emit or absorb energy only in terms of integral multiple of a quantum.

$E = nh\upsilon$ where n = 1, 2, 3

Now $\upsilon \propto 1/\lambda$

or $\upsilon = c/\lambda$

Where "λ" is wave length and "c" is the velocity of light, a constant quantity.

Putting the value of ν in eq. (1), we get

$$E = hc/\lambda \qquad \text{.................. (2)}$$

Thus greater the value of λ, smaller will be the energy.

Now $\bar{\upsilon} = 1/\lambda$ .... (3)

Where $\bar{\upsilon}$ = wave number.

Putting the value of $1/\lambda$ in eq. (2), we get,

$$E = hc\bar{\upsilon}$$

Thus energy of radiation is directly proportional to the frequency.

So, it can be concluded that the energy of photon is related to frequency, wavelength and wave number. **The number of waves passing through a point per second is called Frequency. The distance between two adjacent crests or troughs is called wavelength.** It is expressed in Å (Where Å is an angstrom and one Angstrom = 10^{-10}m) or in nanometers (1 nanometre = 10^{-9} m).

Example 2.6

A photon of light with energy 10^{-19} J is emitted by a source of light.

a) Convert this light in to the wave length, frequency and wave number of the photon in terms of meters, Hertz and m^{-1}, respectively.
b) Convert this energy of photon into ergs and calculate the wavelength in cm, frequency in Hz and wave number in cm^{-1}.

Solution: (a)

Data: Energy of photon $= 10^{-19}$ J

Wavelength $= \lambda = ?$

Frequency $= \upsilon = ?$

Wave number $= \bar{\upsilon} = ?$

First of all we calculate υ

Formula applied:

$$E = h\upsilon$$

and $$\upsilon = \frac{E}{h}$$

$$h = 6.625\times10^{-34}\text{Js}$$

Putting the values of E and h

$$\upsilon = \frac{10^{-19}\text{J}}{6.625\times10^{-34}\text{Js}}$$

$$= 0.151\times10^{15}\text{s}^{-1}$$

$$= 1.51\times10^{14}\text{s}^{-1}$$

From υ we can calculate wavelength λ

Formula applied:

$$\upsilon = \frac{c}{\lambda}$$

$$\text{So, wavelength } \lambda = \frac{c}{\upsilon}$$

$$= \frac{3\times10^{8}ms^{-1}}{1.51\times10^{14}s^{-1}}$$

$$\lambda = 1.98\times10^{-6}m$$

From λ we can calculate wave number

Formula applied:

$$\text{Wave number } \bar{\upsilon} = \frac{1}{\lambda}$$

$$\bar{\upsilon} = \frac{1}{1.98\times10^{-6}m}$$

$$\bar{\upsilon} = 0.50\times10^{6}m^{-1}$$

$$= 5\times10^{5}\,m^{-1}$$

(b) Now we convert energy of the photon from joules into ergs;

$$1J = 10^{7}erg$$

So $$E = 10^{-19}\times10^{7}erg = 10^{-12}ergs$$

$$h = 6.625\times10^{-27}erg\times s \text{ or } erg.s$$

Now calculate frequency in Hz

Formula applied:

$$\upsilon = \frac{E}{h}$$

Putting the values

$$\upsilon = \frac{10^{-12}ergs}{6.625\times10^{-27}erg.s}$$

$$\upsilon = 0.151\times10^{15}s^{-1}$$

$$= 1.51\times10^{14}s^{-1}$$

Now we can calculate wavelength in cm

Formula applied:

$$\lambda = \frac{c}{\nu}$$

Putting the values

$$\lambda = \frac{3\times10^{10}cms^{-1}}{1.51\times10^{14}s^{-1}}$$

$$= 1.98\times10^{-4}cm$$

Now calculate wave number in cm^{-1}

Formula applied:

$$\bar{\upsilon} = \frac{1}{\lambda}$$

$$\bar{\upsilon} = \frac{1}{1.98\times10^{-4}}$$

$$= 5\times10^{3}cm^{-1}$$

2.6 X-RAYS

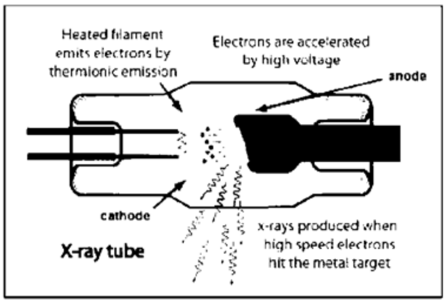

Figure 2.11: Cathode rays pointed at heavy metal (W, Cu etc.)

Wilhelm Roentgen (1895) accidentally discovered that if cathode rays are pointed to fall on a heavy metal target, there are produced some penetrating short wave length rays. He called them the X-rays. The X-rays are electromagnetic radiations of very high frequency depending upon the nature of anode. Oftenly a tungsten filament is used for this purpose.

X-rays are emitted from the target in all directions. A small portion of them is used for useful purpose through the windows. The wavelength of X-rays produced depends upon the nature of target metal. Every metal has its own characteristic X-rays.

Moseley undertook a systematic and comprehensive study of X-rays in 1913. His researches covered a range of wavelengths 0.04 – 0.08 Å.

Moseley proved that the frequencies of X-rays increase in a regular manner from one element to the other in the Periodic Table. He further suggested that the frequencies of these rays are directly proportional to the no of protons in the nucleus. The no of protons in the nucleus is called "Atomic Number".

Moreover Moseley drew the following conclusions from the detailed analysis of spectral lines which he obtained from 38 different elements. (from Al to Au) as targets in X-rays tube.

(a) The spectral lines could be classified into two distinct groups. One, which belongs to shorter wavelength, called K-series and the other with longer wavelength called as L-series.

(b) If the target element is of higher atomic number the wave-length of X-rays becomes shorter.

(c) A relationship between frequency (υ) and atomic number (Z) of the elements is given as

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

This is called **Moseley Law**. Where a and b are called constant quantities. **This law states that the frequency of a spectral line in X-ray spectrum varies as the square of atomic number of an element emitting it.**

In 1913 Henry G. J. Moseley, a student of Rutherford, used the technique of X-rays spectroscopy (just discovered by Max von Laue) to determine the atomic numbers of the elements, X-rays are produced in a cathode-ray tube when the electron beam (cathode ray) falls on a metal target. The explanation for the production of X-rays is as follows: When an electron in the cathode ray hits a metal atom in the target, it can (if it has sufficient energy) knock out an electron from an inner shell of the atom. This produces a metal ion with an electron missing from an inner orbital. The electronic configuration is unstable, and an electron from an orbital of higher energy drops in to the half-filled orbital and a photon is emitted. The photon corresponds to electromagnetic radiations in the x-ray region.

1. X-rays have different penetrating powers for different types of matter. X-rays cannot pass through metals, but they can pass through plastic, leather etc. easily. That' s why they can be used for security purposes to photograph interior of objects.
2. They are used in medical radiography to locate fracture in the bones.
3. In England, in 1913 William Bragg and Lawrence Bragg used X-ray diffraction (XRD) technique to study the crystal structure.
4. X-rays can be used to ionize gases.

2.7 THE QUANTUM NUMBERS AND ORBITALS

Schrodinger in 1926 gave an equation in which electrons are treated as moving with wave like motion in the three dimensional space around the nucleus. It differs from Bohr's atomic model in the sense that the electrons move in orbits. It also specifies the distance between the electron and the nucleus.

The solution of Schrodinger's wave equation gives certain mathematical integers. **These sets of numerical values, which give the acceptable picture of an atom, are called Quantum Numbers.** There are four quantum numbers which can describe the electron completely.

1. Principal Quantum No. (n)

It determines the size of the orbit and the distance from the nucleus. Greater the distance from the nucleus, larger will be the size of the orbit. The shells are named as,

If n = 1 — K shell.
n = 2 — L shell.
n = 3 — M shell.
n = 4 — N shell.

The number of electrons accommodated in an orbit is given by **$2n^2$**.

The no of electrons accommodated in various orbits are as follows,

K = 2, L = 8, M = 18, N = 32.

The higher the value of n, the higher will be the energy of the electron and space around the nucleus.

2. The Azimuthal Quantum No. (l)

It describes the shape of an orbital. Its value is always one less than that of value of n. The various energy sub-levels (l) are s, p, d, f having at the most 2, 6, 10 and 14 electrons in them respectively. They are designated as s for sharp, p for principal, d for diffused and f for fundamental. The values of l are:

l = 0……… (n –1)

The maximum number of electrons in a subshell is given by a formula: **$2(2l+1)$**

If,	n = 1 (K),	l = 0 (s),	and e = 2
	n = 2 (L),	l = 0 (s) and 1 (p),	and e = 2, 6
	n = 3 (M),	l = 0 (s), 1(p), and 2(d)	and e = 2, 6, 10
	n = 4 (N),	l = 0 (s), 1(p), 2 (d) and 3 (f) and	e = 2, 6, 10, 14

From here we conclude that the number of orbit gives the no of orbitals.

i.e.	n = 1 (K)	orbital	= 1 s
	n = 2 (L)	orbitals	= 2s, 2p
	n = 3 (M)	orbitals	= 3s, 3 p, 3 d
	n = 4 (N)	orbitals	= 4s, 4p, 4d, 4f.

The shapes of orbitals described by Azimuthal Quantum number are s = spherical, p = dumbbell, d = sausage and f = complicated.

3. Magnetic Quantum No. (m)

It explains the effect of an orbital in the magnetic field. It is related with Azimuthal Quantum number as follows:

$$m = +\ell \longrightarrow 0 \longrightarrow -\ell$$

If ℓ = o (s), m = o. It means that an s-orbital is spherical in shape because it is not deflected in any particular direction on placing in a magnetic field.

If ℓ = 1 (p), m = + 1, 0, –1. It means that a p–orbital can be deflected in three directions on placing in a magnetic field. i.e. a p-orbital splits in to three degenerate orbitals in a magnetic field.

If ℓ = 2 (d), then m = +2, + 1, 0, –1, –2. It means that a d–orbital can be deflected in 5–directions on placing in a magnetic field.

If ℓ = 3 (f), then, m = + 3, + 2, +1, 0, –1, –2, –3. i.e. an f–orbital can be deflected in 7–direction in a magnetic field.

The whole discussion shows that magnetic quantum number determines the orientation of orbital.

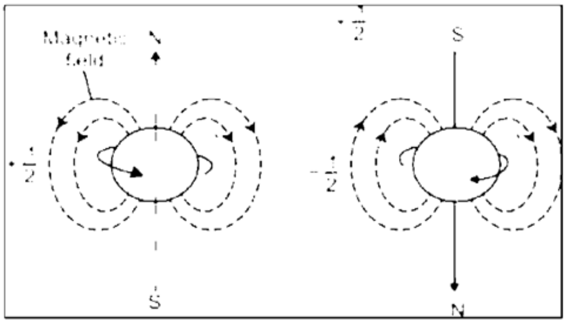

Figure 2.12: Two different spins of electrons and their magnetic fields

4. Spin Quantum Number (s)

It describes the direction of spin of an electron. In 1925 Goudsmit suggested that an electron while moving in an orbital around the nucleus also rotates or spins about its own axis either in a clockwise or anti-clockwise direction. It may be 50% clockwise $\left(-\frac{1}{2}\right)$ (↑) and 50% anti-clockwise $\left(+\frac{1}{2}\right)$(↓).

This is also called self-rotation. This spinning of electron is associated with a magnetic field and hence a magnetic moment.

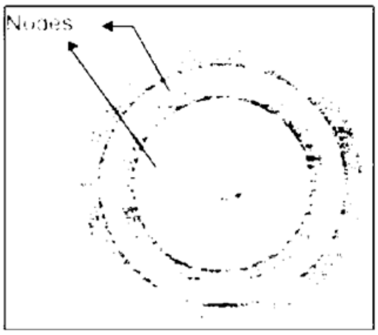

Figure 2.13: Shapes of orbits or shells

The circular path of an electron around the nucleus is called an orbit. The orbits or shells are denoted by K, L, M, N etc. The orbits of an atom can be shown as in figure 2.13.

A cloud showing the probability of finding the electron in terms of charged cloud around the nucleus is called Electron Cloud.

The circular paths in which electrons revolve around the nucleus are called orbits or shells. An orbit or a shell consists of the orbitals or sub-shells.

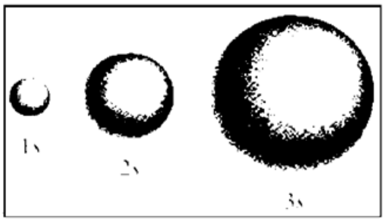

Figure 2.14: Shapes of s orbitals

Shapes of orbitals

s-orbital:

An s-orbital is spherical and symmetrical in shape.

With the increase of value of n, the size of s-orbital increases e.g. 2s orbital is larger in size than 1s – orbital. The probability of finding the electron is zero between two orbitals. This plane is called nodal plane or nodal surface.

p-orbitals:

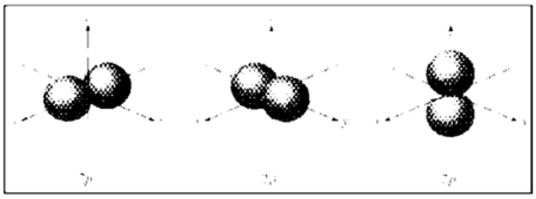

Figure 2.15: Shapes of p orbitals

A p-orbital is dumbbell in shape and has three directions in space. Such orbitals which have different directions but equal energy are called “Degenerate Orbitals”.

d – orbitals:

These orbitals have dumbbell like structures and can move in the 5-directions. They are d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}.

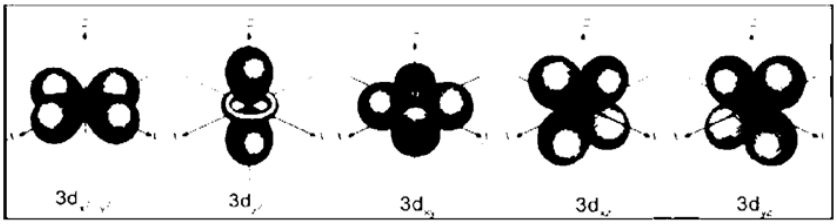

Figure 2.16: Shapes of d orbitals

In the absence of magnetic field all the five d-orbitals are degenerate.

f-orbitals:

It has seven directions in space on placing in a magnetic field, which are very complicated to draw.

Example 2.7

Describe the allowed combinations of the n, ℓ and m quantum numbers when n = 4.

Solution:

The allowed combinations are

n	ℓ	m
4	0	0
	1	–1, 0, +1
	2	–2, –1, 0, +1, + 2
	3	–3, –2, –1, 0, +1, +2, +3

2.8 ELECTRONIC CONFIGURATIONS

The representation of filling of electrons in different orbitals of an atom is called its electronic configuration.

The relative energies depend upon the size of the orbitals and therefore, according to the *Principal Quantum Number (n),* an s – orbital has the lowest energy and increases as follows.

$$s < p < d < f$$

The relative energies are arranged in the figure 2.17.

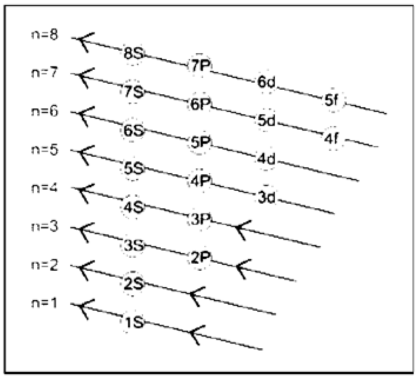

Figure 2.17: Energy sequence of different orbitals of an atom

The following facts must be observed before writing the electronic configuration of an atom.

(a) An orbital like s, p_x, p_y, p_z, d_{xy} etc. can have maximum two electrons.

(b) The energy order of an orbital is governed by "n + l" rule, (where l -value is the value of Azimuthal Quantum number). This states that

(i) An added electron will always enter in an orbit having lower n + l value.

For example	2s,	n = 2,	l = 0,	n + l = 2
	3d,	n = 3,	l = 2,	n + l = 5

So, 2s-orbital is filled first because it has lower value of n + l than that for 3d orbital.

(ii) If n + l values of two orbitals are same, then the orbital with lower n value has lower energy and electron will be added to that orbital first. For example

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

But here 3d orbital is filled first because the value of n for 3d is smaller than that of 4p therefore an added electron would enter in 3d orbital first than that of 4p.

Auf-Bau Principle:

The electrons are placed in energy sub-levels in the order of increasing energy values of sub-levels.

Pauli's Exclusion Principle:

According to it "No two electrons in the same orbital can have the same set of four Quantum numbers.

Let us take the example of an orbital having two electrons.

For first electron:	n = 1,	l = 0,	m = 0,	$s = +\frac{1}{2}$ (↑)
For second electron:	n = 1,	l = 0,	m = 0,	$s = -\frac{1}{2}$ (↓)

So this orbital will have a maximum no. of two electrons with opposite spin i.e. (↑↓). Such an orbital is said to be completely filled and may contain a single electron in it, called as un-paired electron.

Hund's Rule:

If degenerate orbitals are available for electrons, then electron would like to live in separate orbitals and have rather parallel spin. It means that the arrangement ⊙⊙ will be more stable than the arrangement ⊙○, provided the two circles represent the orbitals of equal energies. The Hund's rule can be applied to predict the valency of an element because the numbers of unpaired electrons give the valency of that element. The rule is equally applicable in case of hybridized orbitals and molecular orbitals which are degenerate

e.g.	O = 8	$(\overset{\downarrow\uparrow}{1s}, \overset{\downarrow\uparrow}{2s}, \overset{\downarrow\uparrow}{2px}, \overset{\uparrow}{2py}, \overset{\uparrow}{2pz})$	Divalent
	N = 7	$(\overset{\downarrow\uparrow}{1s}, \overset{\downarrow\uparrow}{2s}, \overset{\uparrow}{2px}, \overset{\uparrow}{2py}, \overset{\uparrow}{2pz})$	Trivalent
	Ne = 10	$(\overset{\downarrow\uparrow}{1s}, \overset{\downarrow\uparrow}{2s}, \overset{\downarrow\uparrow}{2px}, \overset{\downarrow\uparrow}{2py}, \overset{\downarrow\uparrow}{2pz})$	No valency or zero valency.

But in case of carbon

$C = 6 \qquad (1s^{\downarrow\uparrow}, 2s^{\downarrow\uparrow}, 2p_x^{\uparrow}, 2p_y^{\uparrow}, 2p_z)$

It looks divalent but actually it is tetravalent.

Example 2.8

Pick the orbital with the lower energy from each of the given pairs.

(a) 3d, 4s, (b) 2p, 3s,

Solution:

We apply $n + l$ rule here,

(a) For 3d, $n = 3$, $l = 2$, $n + l = 5$

For 4s $n = 4$, $l = 0$, $n + l = 4$

So, 4s–orbital will be filled first because it has lower energy than that of 3d.

(b) For 2p, $n = 2$, $l = 1$, $n + l = 3$

3s, $n = 3$, $l = 0$, $n + l = 3$

As the values of $n + l$ are equal in both the cases, therefore, 2p will be filled first than 3s.

Example 2.9

Write the electronic configuration of $_{21}Sc$, $_{25}Mn$, $_{30}Zn$.

Solution

$_{21}Sc$	$= 1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6\ 4s^2\ 3d^1$	or	$[Ar]\ 4s^2\ 3d^1$
$_{25}Mn$	$= 1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^5$	or	$[Ar]\ 4s^2 3d^5$
$_{30}Zn$	$= 1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^{10}$	or	$[Ar]\ 4s^2 3d^{10}$

Self Check Exercise 2.2

Write the electronic configuration of following elements:

(i) $_{20}Ca^{40}$ (ii) $_{17}Cl^{35}$ (iii) $_{13}Al^{27}$

References for additional information

- Philip Mathews, Advanced Chemistry.
- Martin S. Silberger, Chemistry, The molecular Nature of matter and change.
- John C. Kotz, Paul M. Treichel and Gabriela C. Weaver, Chemistry and chemical reactivity.
- E. N. Ramesden, A – Level chemistry.

1 **Choose the correct answer (MCQs).**

i. For which species Bohr's theory does not apply;

(a) H (b) He^+ (c) Li^{2+} (d) Be

ii. From the discharge tube experiment, it is concluded that;

(a) Mass of a proton is in fraction. (b) Matter contained electrons.

(c) Nucleus contains positive charge. (d) Positive rays are heavier than protons.

iii. When an electron of charge 'e' and mass 'm' moves with velocity 'v' about the nuclear change Ze in the circular orbit of radius 'r', the P.E of electron is given by;
(a) Ze^2/r (b) $-Ze^2/r$ (c) Ze^2/r^2 (d) mv^2/r

iv. Which of following tell about shells of an atom?
(a) Principal quantum number, n (b) Azimuthal quantum number, l
(c) Magnetic quantum number, m (d) Spin quantum number, s

v. Electronic configuration of species M^{2+} is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6$ and its atomic weight is 56 number of neutrons in the nucleus of species M is
(a) 20 (b) 26 (c) 28 (d) 30

vi. The energy of an electromagnetic radiation is 3×10^{-12} ergs. What is its wave-length in nano meters?
(a) 400 (b) 228.3 (c) 3000 (d) 662.5

vii. Which of the following configuration is not correct according to Hund's rule?
(a) [↑↓] [↑↓ | ↑ | ↑] (b) [↑↓] [↑ | ↑ |]
(c) [↑↓] [↑↓ | ↑ |] (d) [↑↓] [↑ | ↑ | ↑]

viii. Which one of the following statement is not correct?
(a) Rydberg's constant and wave number have same unit.
(b) Lyman series of hydrogen spectrum occurs in the ultraviolet region.
(c) The angular movement of the electron in the ground state of hydrogen atom is equal to $h/2\pi$.
(d) The radius of first Bohr orbit of hydrogen atom is 2.116×10^{-8} cm.

ix. Which one of the following is not isoelectronic pair?
(a) Mg^{2-}, Be^{2+} (b) N^{3-}, O^{2-} (c) N^{-3}, F^{-} (d) Na^{+1}, Al^{3-}

x. The third line in Balmer series corresponds to an electronic transfer between which Bohr's orbit in hydrogen.
(a) $5 \to 3$ (b) $5 \to 2$ (c) $4 \to 3$ (d) $4 \to 2$.

2 **Short questions and answers:**

i. How mass of electron can be calculated from e/m ratio and charge?
ii. How does Mosley's Law help in the production of X-rays?
iii. Which quantum number is also called sub-shell quantum number?
iv. What is the difference between orbit and orbital?
v. What is the relationship between?
(a) energy and wavelength
(b) frequency and wavelength
vi. Which species are formed by the decay of neutron?
vii. Hydrogen atom and He^+ are mono electronic system, but the size of He^+ is much smaller than H, why?
viii. Why is 4s orbital lower in energy than 3d orbital?
ix. Write electronic configuration of $_{25}Mn$, $_{30}Zn$, and $_{13}Al$.
x. What is (n+l) rule?

xi. Point out the defects of Bohr's Model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle.

xii. Calculate the energy of electron of a hydrogen atom in the orbit for which the value of n = 3. **Ans.** $E_3 = -145.92$ kJ mole^{-1}

xiii. Bohr's equation for the radius of nth orbit of electron in the hydrogen atom is

$$r_n = \frac{\varepsilon_o h^2 n^2}{\pi e^2 m}$$

(a) When the electron moves from n = 1 to n = 2, how much does the radius change?

(b) What is the distance travelled by the electron when it goes from n = 8 to n = 3?

Ans. (a) 1.587 $\mathring{A}$ (b) 29.095 $\mathring{A}$