ATOMIC STRUCTURE

PREFACE

Atom – Everything in this universe is made of atoms. Therefore, studying atom is considered to be the first step towards understanding chemistry.

This book includes the initial models discovering fundamental particles like electron, proton and neutrons to the result of quantum mechanical model; the introspection of the structure of atoms has opened a complete new dimension of science. The first challenge to Newtonian physics, the dual nature, the famous CAT experiment and the wave theory had left unprecedented impressions on the history of science.

An interesting aspect of this era was the Bohr- Einstein debates. The Bohr-Einstein debates were a series of public disputes about quantum mechanics between Albert Einstein and Neils Bohr, who were two of its founders. Their debates are still remembered because of their importance to the philosophy of the science. An account of them has been written by Bohr in an article titled "Discussions with Einstein on Epistemological Problems in Atomic Physics". Despite their differences of opinion regarding quantum mechanics, Bohr and Einstein had a mutual admiration throughout their lives.

In the gist, one thing is clear, the day we know completely about atoms is the day we will completely decode the code of science.

In this book, after regular intervals, we have included "**Illustrations**" to understand Concepts studied till then. Students are advised to kindly go through Illustrative Examples before jumping on to next articles.

To enhance your skills for various examinations consisting of objective questions, we suggest use of Education Studio App to generate Automated and Customized Test Papers.

A section of challenging questions has been provided in the "**Assignment Section of Application**".

We are sure; you will have fun while you go through this journey.

Best of Luck!!

Team Chemistry @ Education Studio Private Limited

ATOMIC STRUCTURE

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1. INTRODUCTION OF ATOM

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word '*a-tomio*' which means 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century.

1.1 DALTON'S ATOMIC THEORY

An English school teacher, John Dalton gave the first convincing argument about the existence of atoms. He relied upon a large number of experiments and measurements to measure the masses of elements that combined together, and assembled arguments that strangely indicated the existence of atoms.

Dalton, in 1808, proposed that matter was made up of extremely small, indivisible particles called atoms. (In Greek atom means which cannot be cut). This concept was accepted for many years.

Key postulates of Dalton's atomic theory are:

    (a) Matter is made up of small indivisible particles called atoms.

    (b) Atoms can neither be created nor destroyed. This means that a chemical reaction is just a simple rearrangement of atoms and the same number of atoms must be present before and after the reaction.

    (c) Atom is the smallest particle of an element which takes part in a chemical reaction.

    (d) Atoms of the same element are identical in all respects especially, size, shape and mass.

    (e) Atoms of different elements have different mass, shape and size. Atoms of different elements combine in a fixed ratio of small whole numbers to form compound atoms, called molecules.

Drawbacks of Dalton's Atomic Theory:

    (a) The discovery of isotopes and isobars revealed that atom of same element may have different atomic mass (isotopes) and atom of different elements may have same atomic masses (isobars).

    (b) Atoms can be split into more fundamental particles: electrons, protons and neutrons.

2   DISCOVERY OF SUBATOMIC PARTICLES

Dalton's atomic theory explained the law of conservation of mass, law of constant composition and law of multiple proportions very successfully. However, it failed to explain the results of many experiments; for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century. However, we will discuss about three fundamental particles, namely electron, proton and neutron.

2.1 CATHODE RAYS AND DISCOVERY OF ELECTRONS

Michael Faraday showed that chemical changes occur when electricity is passed through an electrolyte. He stated that electricity is made up of particles called atoms of electricity. G.J Stoney suggested the name of electron for the particles of electricity. However, the real credit for the discovery of electrons goes to J.J. Thomson. In 1850s many mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases was adjusted by evacuation.

When sufficiently high voltage is applied across the electrodes; current starts flowing as a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. After passing through anode, when these rays strike the zinc sulphide coating, a bright spot on the coating is developed (same thing happens in a television sets having cathode tube).
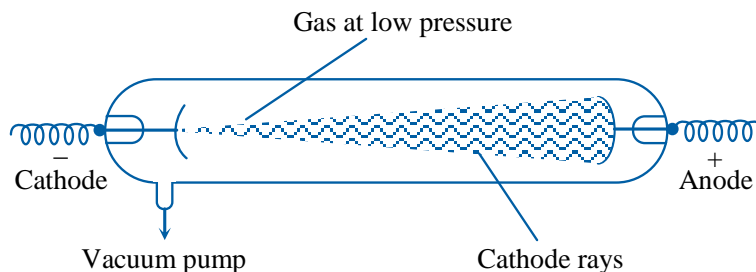
Observations of Cathode Ray Experiments:

    (i)   The cathode rays start from cathode and move towards the anode. These rays have particle nature was proved by placing a light fan in the path of cathode rays. Due to collision of these particles, mechanical effect is produced and wheel starts rotating.

    (ii)   These rays themselves are not visible but their behaviour can be observed with the help of certain kind of fluorescent or phosphorescent materials that glow when hit by them. Earlier television picture tubes were cathode ray tubes and television pictures resulted due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field, these rays travel in straight lines. When an object was placed between anode and cathode, its shadow was obtained towards anode.

(iv) When magnetic or electric field is applied, cathode rays deviates from straight path this indicate that cathode rays are charged particles. Further analysis of electric or magnetic field on the behaviour of cathode rays proved that they are negatively charged particles, called **electrons.**

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube. Thus, we can conclude that electrons are basic constituent of all the atoms.

(vi) Cathode rays produce heating effect. When these rays are made to strike on a metal foil, the latter gets heated.

(vii) Cathode rays produce X-rays when they strike on surface of hard metals such as tungsten, copper molybdenum etc.

(viii) Cathode rays can pass through thin foils of metals like aluminium. However, these are stopped if the foil is quite thick.

(ix) Cathode rays ionize the gas through which they pass.

Determination of Charge my Mass ratio:

Sir J.J. Thomson performed a series of experiments in which he was able to determine the **charge/mass** $\left(\dfrac{e}{m}\right)$ **ratio** of the particles that make up the cathode ray by measuring deflection of the rays with varying magnetic and electric fields. Thomson performed same experiment using different metals for cathode and anode as well as different gases inside the tube.

This value $\left(\dfrac{e}{m}\right)$ **is** 1.76×10^{11} **coulomb per kg.**

The e/m ratio for electron was found to be same irrespective of the nature of cathode and nature of gas taken in discharge tube. This shows that electrons are universal constituent of all matter.

Determination of Charge on Electron (Quantization of Charge):

R.A. Millikan through his oil drop experiments determined the charge on the electrons. Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge (e)

That is, $q = n$ e, where n = 1, 2, 3................ That means charge is quantized.

He found that the value of e is -1.6×10^{-19} C.
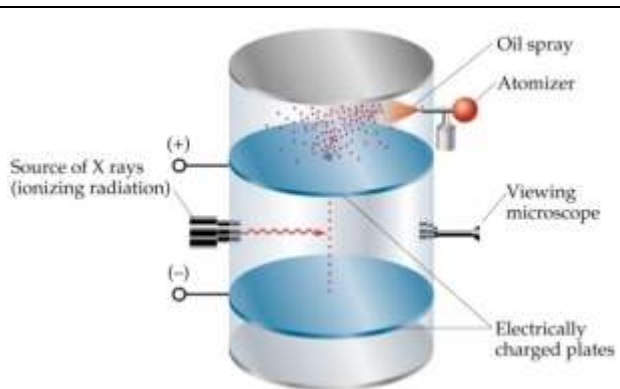
The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m ratio.

Calculation of mass of an electron: With the help of the experiments discussed above, it is possible to calculate the values of e/m ratio and also the charge *(e)* on the electron. The mass *(m)* of the electron can be calculated as follows.

$$\text{Mass of electron (m)} = \frac{e}{e/m} = \frac{(1.60 \times 10^{-19} C)}{(1.76 \times 10^{8} Cg^{-1})} = 9.10 \times 10^{-28} g = 9.10 \times 10^{-31} kg .$$

An electron may be defined as: **A fundamental particle present in an atom, which carries one unit negative charge** $(1.60 \times 10^{-19} C)$ **and negligible mass** $(9.1 \times 10^{-28} g)$ **which is 1/1837 of the mass of an atom of hydrogen.**

2.2.   THE PLUM PUDDING MODEL

Based on these discoveries J.J. Thompson proposed the plum pudding model. This model proposed that atoms are blobs of a positively charged jellylike material, with electrons suspended in it like raisins in a pudding.

This model is called the plum – pudding model after a type of Victorian dessert in which bits of plums were surrounded by matrix of pudding.

This model could not satisfactorily explain the results of scattering experiment carried out by Rutherford who worked with Thomson.
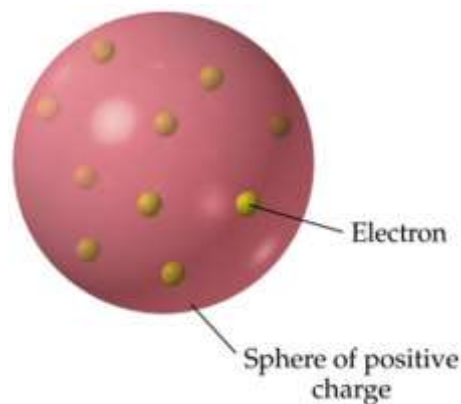

2.3 DISCOVERY OF PROTONS

We know that an atom is electrically neutral, if it contains negatively charged electrons it must also contain some positively charged particles. This was confirmed by **Goldstein** in his discharge tube experiment with perforated cathode. On passing high voltage between the electrodes of a discharge tube it was found that some rays were coming from the side of the anode which passed through the holes in the cathode. These anode rays (canal rays) consisted of positively charged particles formed by ionization of gas molecules by the cathode rays. The charge to mass ratio (e/m value) of positively charge particles was found to be maximum when the discharge tube was filled with hydrogen gas as hydrogen is the lightest element. This e/m varies with the nature of gas taken in the discharge tube. The positive particles are positive residues of the gas left when the gas is ionized.

2.4 DISCOVERY OF NEUTRONS

The neutral charge particle, neutron was discovered by **James Chadwick** by bombarding boron or beryllium with α–particles.

$$_4\text{Be}^9 + _2\alpha^4 \rightarrow _6\text{C}^{12} + _0\text{n}^1$$
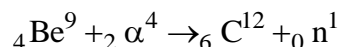
Total mass of electrons and protons in almost all the atoms (except hydrogen) was found to be much lesser than the mass or atom. This lead to conclusion that atom also consist of neutral particles (neutrons).

Table 1: Properties of Electrons, Protons & Neutrons

		ELECTRON (e)	PROTON (p)	NEUTRON (n)
MASS	AMU	0.000549	1.00727	1.00866
	GRAMS	9.11×10^{-28}	1.673×10^{-24}	1.675×10^{-24}
	RELATIVE	$\dfrac{1}{1837}$	1	1
CHARGE	COULOMBS	-1.602×10^{-19}	$+ 1.602 \times 10^{-19}$	Zero
	ESU	$- 4.8 \times 10^{-10}$	$+ 4.8 \times 10^{-10}$	Zero
	RELATIVE	-1	$+1$	Zero

The electron and proton have equal, but opposite electric charges while the neutron is uncharged.

3.   RUTHERFORD MODEL OF ATOM

In 1908, the plum pudding model was overthrown by a simple experiment. The New Zealander Ernest Rutherford asked two students to shoot α-particles (he knew that some element like Radon emit positively charged particles called alpha (α) particles) toward a piece of gold foil only a few atoms thick. If atoms were indeed like blobs of positively charged jelly, then all the α–particles would leave similar paths as they move through the foil.

What his students observed astonished everyone around them. Although almost all the α–particles did pass through (mostly straight), about 1 in 20,000 was deflected through more than 90°, and a few α–particles bounced straight back in the direction from which they had come. "It was almost incredible," said Rutherford, "as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you".

The fact that most of the α - particles passed straight through the metal foil indicates the most part of the atom is empty. The explanation was that atoms had to contain massive point like centers of positively charge surrounded by a large volume of mostly empty space. Rutherford called the point of positively charged region, the nucleus. He reasoned that closer the path of the α–particles to the nucleus of the atom, greater the deflection it experiences and the α–particles which directly hit on the molecules would rebound back.

The electrons are thinly distributed throughout the space around the nucleus. If the nucleus in a hydrogen atom were the size of a fly at the center of a cricket stadium, then the space occupied by the electron would be about the size of the entire cricket stadium.
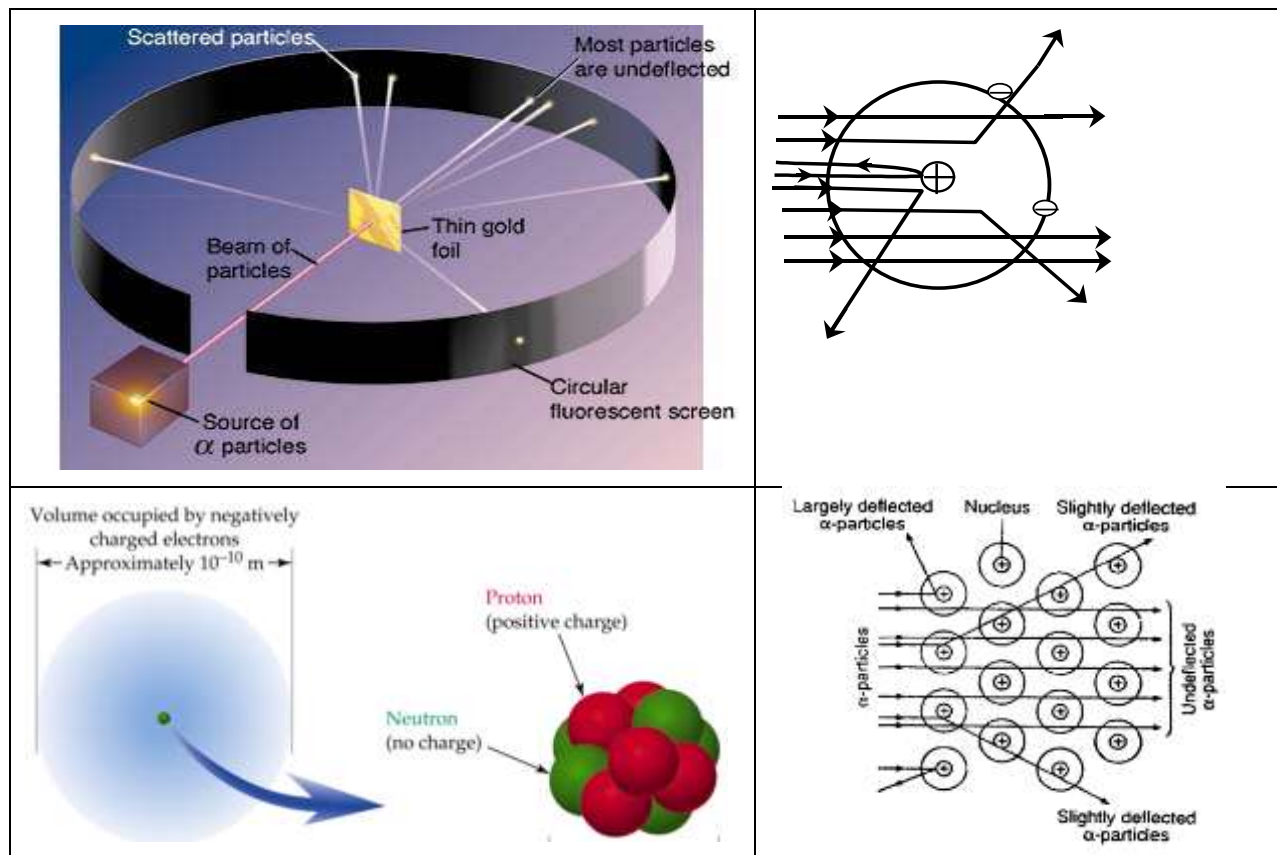
In an atom the positive charge of the nucleus exactly cancels the negative charge of the surrounding electrons. So, for each electron outside the nucleus, there must be a matching positively charged particle inside the nucleus called the proton.

Since electrons would be attracted by the nucleus and would eventually fall into it, Rutherford assumed that electron were not stationary and that they move in a circular path around the nucleus using the electrostatic force of attraction. This was analogues to the earth moving around the sun using the gravitational force of attraction.

3.1 Postulates of Rutherford's atomic model:

On the basis of the above observation, and having realized that the rebounding α-particles had met something even more massive than themselves inside the gold atom, Rutherford proposed an atomic model as follows.

(i)   All the protons (+ve charge) and the neutrons (neutral charge) i.e nearly all the mass of an atom is present in a very small region at the centre of the atom. The atom's central core is called nucleus.

(ii)   The size of the nucleus is very small in comparison to the size of the atom. Diameter of the nucleus is about 10^{-13} cm while the atom has a diameter of the order of 10^{-8} cm. So, the size of atom is 10^5 times more than that of nucleus.

(iii)   Most of the space outside the nucleus is empty.

(iv)   The electrons, equal in number to the net nuclear positive charge, revolve around the nucleus with fast speed in various circular orbits.

(v)   The centrifugal force arising due to the fast speed of an electron balances the electrostatic force of attraction of the nucleus and the electron remains stable in its path. Thus according to him atom consists of two parts (A) nucleus and (B) extra nuclear part.

3.2 Defects in Rutherford's atomic model:

(i)   *Distance of electrons:* The exact distance of the electrons from the nucleus are not mentioned.

(ii)   *Stability of the atom*: Neils Bohr pointed out that Rutherford's atom should be highly unstable. According to the law of electro–dynamics, any charged particle under acceleration should continuously lose energy. The electron should therefore, continuously emit radiation and lose energy. As a result of this a moving electron will come closer and closer to the nucleus and after passing through a spiral path, it should eventually fall into the nucleus.
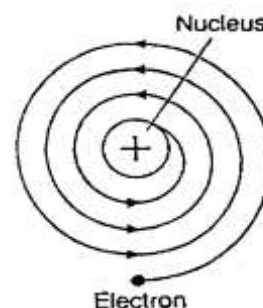
It was further calculated that the electron should fall into the nucleus in less than 10^{-8} sec. But it is known that electrons keep moving outside the nucleus. To solve this problem Neils Bohr later proposed an improved form of Rutherford's atomic model.

4.   GENERAL ATOMIC TERMS

(a)   ***Atomic Number* (Z):** The atomic number of an element is the number of protons contained in the nucleus of atoms of that element.

(b)   *Isotopes:* Atoms of the element with same atomic number but different mass number e.g. $_1H^1$, $_1H^2$, $_1H^3$. There are three isotopes of hydrogen.

(c)   ***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 (or its isotope).

(d)   **Nuclide:** Various species of atoms in general. A nuclide has specific value of atomic number and mass number.

(e)   *Nucleons:* Protons and neutrons are present in a nucleus. So, these fundamental particles are collectively called nucleons.

(f)   *Isobars:* Atoms having the same mass number but different atomic numbers, e.g. $_{15}P^{32}$ and $_{16}S^{32}$ are called isobars.

(g)   *Isotones:* Atoms having the same number of neutrons but different number of protons or mass number, e.g. $_6C^{14}$, $_8O^{16}$, $_7N^{15}$ are called isotones.

(h) **Isodiapheres:** Atoms having same difference between neutrons & protons are called isodiapheres. They have same value of N - Z or A - 2Z

$$\,_{92}^{238}U \ \& \ \,_{90}^{234}Th \qquad \text{or} \qquad \,_{1}^{3}H \ \& \ \,_{3}^{7}Li$$

(i) *Isoelectronic:* Molecules or ions having same number of electrons are called isoelectronic species. e.g. N_2, CO, CN^-.

(j) *Isosters:* Molecules having same number of atoms and also same number of electrons are called isosters.

e.g.,   (i) N_2 and CO   (ii) CO_2 and N_2O (iii)   HCl and F_2

(k) *Atomic mass unit:* Exactly equal to $\left(\dfrac{1}{12}\right)$ of the mass of $_6C^{12}$ atom

1 amu = 1.66×10^{-27} kg, If it is converted to energy then E= 931.5 MeV

5. ELECTROMAGNETIC WAVES

Wave theory was given by **C. Huygens.** A wave is a disturbance which originates from some vibrating source and travels outward as a continuous sequence of alternating crests and troughs. Every wave has five important characteristics: wavelength (λ), frequency (ν), velocity (C), wave number $(\bar{\nu})$ and amplitude (A).
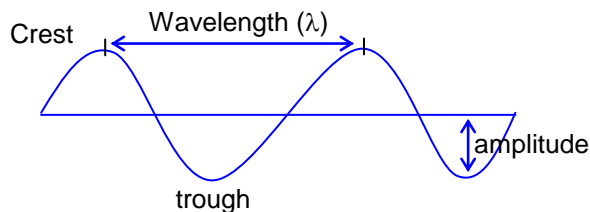
Ordinary light rays, X–rays, γ–rays, etc. are called electromagnetic radiations because similar waves can be produced by moving a charged body in a magnetic field or a magnet in an electric field. These radiations have wave characteristics and do not require any medium for their propagation.
Important characteristics of these waves are:
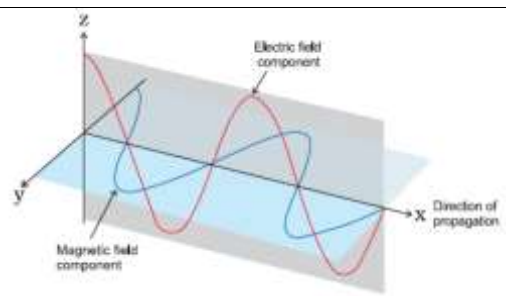
(i) **Wave length (λ):** The distance between two neighbouring troughs or crests is known as wavelength. It is denoted by λ. Different units used for wavelength are cm, m, nanometers (1nm = 10^{-9} m), Angstrom (1Å = 10^{-10} m); micron (1μ = 10^{-6} m), 1 milli micron (1mμ = 10^{-9} m), 1pm = 10^{-12} m.

(ii) **Frequency (ν):** Frequency of a wave is the number of times a wave passes through a given point in a medium in unit time. It is denoted by ν(nu) and is usually expressed in cycles per second (cps) or hertz (Hz) 1Hz = 1cps.

The frequency of a wave is inversely proportional to its wave length (λ) $\nu \propto \dfrac{1}{\lambda}$ or $\nu = \dfrac{c}{\lambda}$

(iii) **Velocity:** The distance travelled by wave in unit time is called its velocity. It is denoted by c and is usually expressed in m sec^{-1} or cm sec^{-1}.

If the frequency is ν, it means that to travel ν waves, it takes one second. Therefore, in one second it will travel $\nu\lambda$.

$$c = \nu\lambda \text{ or } \lambda = \dfrac{c}{\nu}$$

The velocity 'c' of all types of electromagnetic radiations including light is established experimentally. It is a constant in vacuum, equal to 3×10^8 ms^{-1}. Since all electromagnetic radiations travel with the same velocity, they differ from are another in their wavelengths and consequently their frequencies.

(iv) **Wave number** $(\bar{\nu})$**:** It is defined as number of wavelengths per unit length. It is denoted by $\bar{\nu}$ and is usually expressed in m^{-1} or cm^{-1}. $\bar{\nu} = \dfrac{1}{\lambda}$ (or) $\bar{\nu} = \dfrac{\nu}{c}$

(v) **Amplitude:** It is the height of the crest or depth of the trough of a wave and is denoted by A. It determines the intensity or brightness of the beam of light & is also expressed in the unit of length

6. PLANCK'S QUANTUM THEORY

A black body, on heating, emits thermal radiations of different wavelengths or frequency. To explain these radiations, Max Planck put forward a theory popularly known as Planck's Quantum Theory. The main points of Planck's Quantum Theory are:

(i) Substances radiate or absorb energy discontinuously in the form of small packets or bundles of energy called *quantum*. In case of light the quantum is known as *photon.*

(ii) The energy of a quantum is directly proportional to the frequency of the radiation.

$E \propto \nu$ (or) $E = h\nu$

Here ν is the frequency of radiation and h is Planck's constant

$h = 6.626 \times 10^{-27}$ erg-sec or 6.626×10^{-34} J-sec.

(iii) A body can radiate or absorb energy only in whole number multiples of a quantum. Hence it can be $h\nu$, $2h\nu$, $3h\nu$………..$nh\nu$. Where n is a positive integer.

(iv) Energy of photons can also be represented by $\dfrac{nhc}{\lambda}$ Joules .

Here, n = number of photons; h = $6.626 \times 10^{-34} \text{J}-\text{s}$; $C = 3 \times 10^8 \text{ m/s}$; Wavelength in 'm'.

In eV units: $E_{photon} = \dfrac{12400}{\lambda\left(in\ \overset{\circ}{A}\right)} eV$ where, $1eV = 1.6 \times 10^{-19}$ Joules

Illustration **1.**

Question: **A source of sound (velocity = 330 m/s) produces waves in the frequency range 500 Hz to 600 Hz. Find the wavelength range of sound produced.**

Solution: $V = \lambda.\nu = 330\,m/s$

$\lambda_{max} = \dfrac{V}{\nu_{min}} = \dfrac{330}{500} = 0.66\,m$ $\qquad\qquad \lambda_{min} = \dfrac{V}{\nu_{max}} = \dfrac{330}{6600} = 0.05m$

Illustration **2.**

Question: **Find the distance travelled by a wave of frequency 20 kHz in 2 minutes if its wavelength is 1.5 cm.**

Solution: $V = \lambda V = (1.5 \times 10^{-2}\,m) \times (20 \times 10^3\,Hz) = 300\,m/s$

$\therefore$ distance $= v \times t = 300 \times (120s) = $ **36 km**

Illustration **3.**

Question: **Find the energy range of photons belonging to the visible region.**

Given: $\lambda_{violet} \approx 4000$ Å **and** $\lambda_{Red} \approx 8000$ Å

Solution: Maximum energy (minimum wavelength)

$E_{max} = \dfrac{12400}{4000} eV = 3.1 eV$

Minimum energy (maximum λ) $\qquad E_{min} = \dfrac{12400}{8000 eV} = 1.55 eV$

Illustration **4.**

Question: **Two waves differ in frequency by 10^{15} Hz. If one wave has wavelength of 2000 Å. Find possible wavelength values of other wave.**

Solution: Given, $\lambda_1 = 2000$ Å $\qquad \therefore \upsilon_1 = \dfrac{c}{\lambda} = 1.5 \times 10^{15}$

$\therefore$ Possible λ_2 values = 0.5 x 10^{15} Hz, 0.5 x 10^{15} Hz

$\therefore \lambda_2$ values are:

(i) $\dfrac{C}{0.5 \times 10^{15}} = 6000$ Å $\qquad\qquad$ (ii) $\dfrac{C}{2.5 \times 10^{15}} = 1200$ Å

Illustration **5.**

Question: **Find the number of photons required to raise the temperature of 5 g of water from 20°C to 22°C, given that water has a specific heat capacity of 4.2 J/g/°C and wavelength = 5000 Å. It is also given that photon energy is 80% utilized to heat the water.**

Solution: Heat required $= m.s.\Delta T$

$$= 5g \times 4.2\,J\big/ g^{\circ}C \times 2^{\circ}C = 42\,J$$

i.e $42\,J = \dfrac{80}{100} \times E_{photon,total}$

$ie\left(n \times \dfrac{hc}{\lambda}\right) \times \dfrac{80}{100} = 42$

$\therefore n = \dfrac{42 \times 100 \times \left(5000 \times 10^{-10}\right)}{80 \times \left(6.626 \times 10^{-34} \times 3 \times 10^{8}\right)} = 1.32 \times 10^{20}$ photons

7. SPECTRUM

When visible light coming from a source is dispersed by a prism, light of different wavelength are deviated through different angles and get separated. This phenomenon is called dispersion of light and such a dispersed light may be received on a photo graphic plate or it may be viewed directly by eye. A collection of dispersed light (visible or otherwise) giving its wave length composition is called a spectrum.
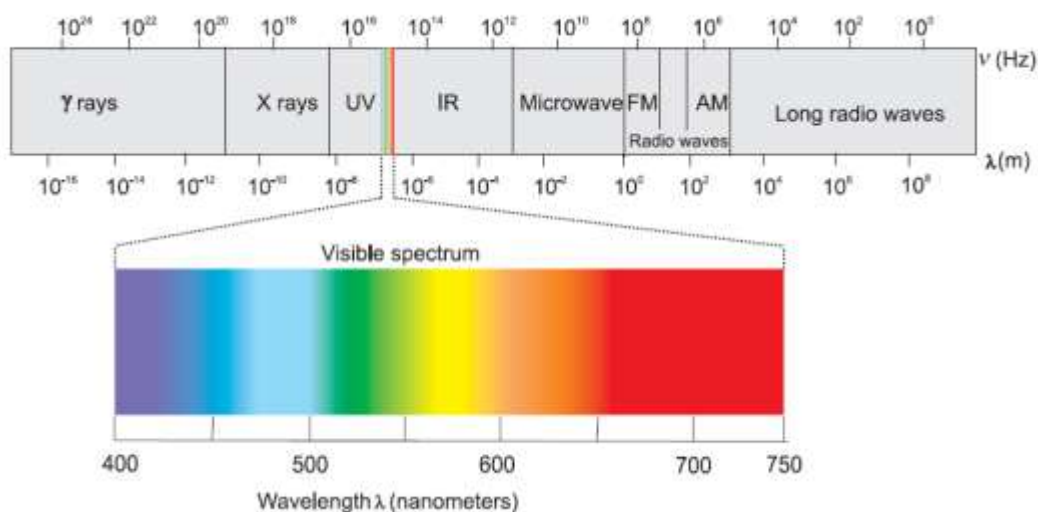
7.1 TYPES OF SPECTRUM

Emission Spectrum and Absorption Spectrum:

The spectrum of radiation emitted by a substance is called an *emission spectrum.* To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted (as the sample gives up the absorbed energy) is recorded. The arrangement of these emitted radiations is called **emission spectrum**. Emission spectrum can be recorded directly.

The spectrum of radiation absorbed by a substance is an *absorption spectrum.* However, it is not possible to directly arrange absorbed radiations. Therefore, it is recorded indirectly when radiations of all possible photon frequencies (or wavelength) are passed through a substance. Some of these frequencies are absorbed by the substance and the remaining are arranged. This arrangement is actually called **absorption spectrum** because by looking at the absent frequencies we can tell what frequencies are absorbed by the substance.
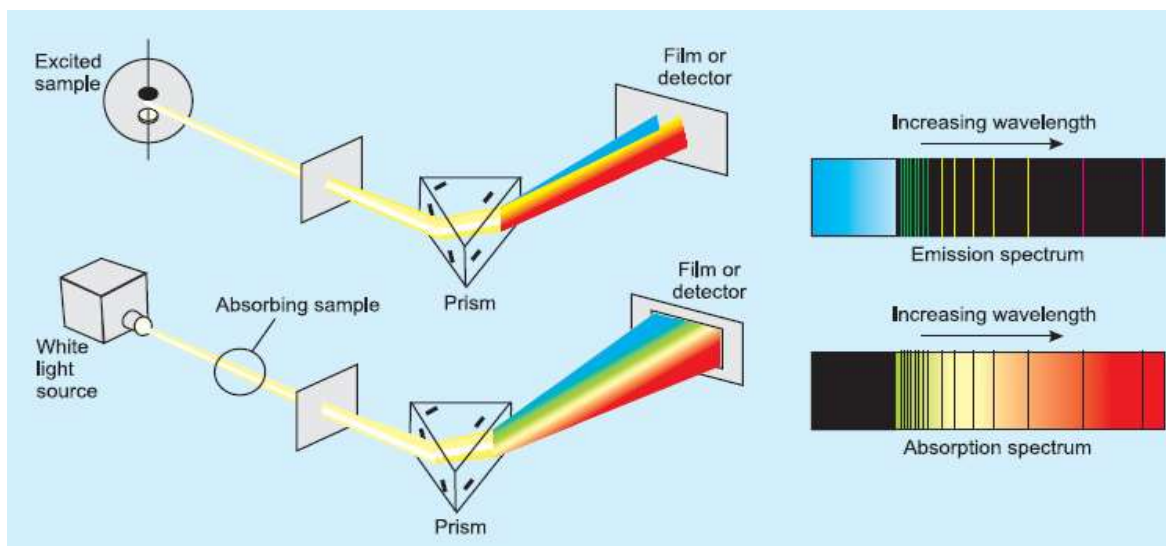
It was experimentally observed that absorption spectrum of a substance and emission spectrum of same substance are always complimentary to each other. This is because any substance can absorb only and only those radiations that it can emit.

Based on frequencies in the arrangement, there are two types of absorption / emission spectrum:

(i) **Continuous Spectrum:** When a particular spectrum consists of all possible frequencies of a particular range, it is called continuous spectrum. When white light is dispersed through prism, we get arrangement of light of all frequencies in visible range. This is a continuous visible spectrum. Rainbow is also an example of continuous spectrum obtained naturally by dispersion of white light.

Arrangement of all frequencies of electromagnetic radiations is also continuous spectrum called electromagnetic spectrum.

(ii) **Discontinuous Spectrum:** When a particular spectrum does not consist of all possible frequencies of a particular range, it is called discontinuous spectrum. When a bulb light is dispersed through prism, we get arrangement of light of some frequencies in visible range. This is a discontinuous visible spectrum.

Based on the appearance, there are again two types of absorption / emission spectrum:

(i) **Line Spectrum (For atoms)**: When a gas is heated, it emits light. If this emitted light is analysed in a spectrometer, the spectra obtained consists of a series of well-defined sharp lines, each line corresponding to a definite wavelength or frequency. The arrangement of these well-defined sharp lines in the emission spectrum is called line spectrum. These line spectra are characteristic of atoms.

(ii) **Band Spectrum (In molecules):** If the adjacent lines of emission spectra are very closely placed, we are unable to see distinct lines. In rainbow, we see bands of different colours instead of several lines of each colour. Such arrangement is called band spectrum. In other words band spectrum is condensed form of line spectrum.

Band Spectrum
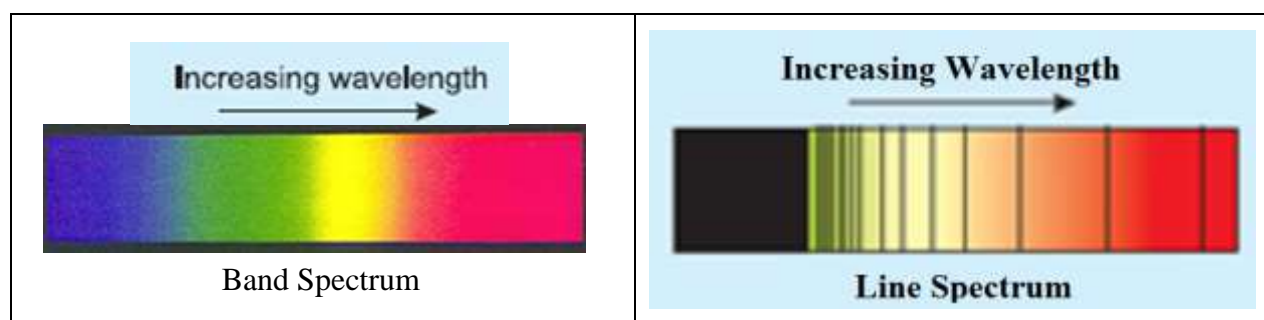
Line Spectrum

7.2 HYDROGEN SPECTRUM

If an electric discharge is passed through hydrogen gas taken in a discharge tube under low pressure, and the emitted radiation is analysed with the help of spectrograph, it is found to consist of a series of sharp lines in the UV, visible and IR regions. This series of lines is known as line or atomic spectrum of hydrogen. The lines in the visible region can be directly seen on the photographic film.

Each line of the spectrum corresponds to a light of definite wavelength. The entire spectrum consists of six series of lines, each series known after their discoverer as Lyman, Balmer, Paschen, Brackett, Pfund and Humphrey series. The wavelength of all these series can be expressed by a single formula which is attributed to Rydberg.

$$\frac{1}{\lambda} = \bar{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ Where,} \qquad \bar{v} = \text{wave number; } \lambda = \text{wave length}$$

R = Rydberg constant (109678 cm^{-1}) = 10967820m^{-1}

n_1 and n_2 have integral values as follows

Series	n_1	n_2	Main spectral lines
Lyman	1	2, 3, 4, etc	Ultra – violet
Balmer	2	3, 4, 5, etc	Visible

Paschen	3	4, 5, 6, etc	Infra – red
Brackett	4	5, 6, 7, etc	Infra – red
Pfund	5	6, 7, 8, etc	Infra – red

[**Note:** All lines in the visible region are of Balmer series but reverse is not true. i.e., all Balmer lines will not fall in visible region]

Total possible transitions for jump from n_2 to $n_1 = \sum_1^{n_2-n_1} i = \dfrac{\Delta n (\Delta n + 1)}{2}$, where $\Delta n = |n_2 - n_1|$.

This also gives us the number of spectral lines observed under the given circumstances. As discussed earlier, the above pattern of lines in atomic spectrum is characteristic of hydrogen**.**

8. BOHR'S MODEL (QUANTIZATION OF ANGULAR MOMENTUM)

In 1913 more than a decade before quantum mechanics was established, the Danish physicist Niels Bohr proposed that angular momentum (*mvr*) of an electron in an atom is quantized and a whole number multiple of (h/2π)

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

Bohr mathematically derived a model of the hydrogen atom based on the concept of quantization of angular momentum, Law of circular motion and Coulomb's Law of electrostatics. Although a fully developed quantum model later replaced Bohr's model, it nevertheless served as a powerful stimulus of later developments.

Bohr retained the Rutherford model of a central positively charged nucleus containing practically all the mass surrounded by a planetary system of electrons whose number is equal to the protons. To understand his work, let us first discuss Law of circular motion and Coulomb's Law of electrostatics.

Law of circular motion: An object can move in a circular path under the influence of a constant force towards the centre of the circle. For this to happen, the force (F) towards the centre must be equal to (mv^2/R). Here, m is mass of the object, v is the speed at which the object is moving and R is the radius of the circle in which the object is moving.

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

Coulomb's Law of Electrostatics: According to Coulomb's law of electrostatics, the force between two charges is directly proportional to the product of charges and inversely proportional to the square of the distance between the charges.

$$F \propto \frac{Q_1 Q_2}{d^2} \; ;$$

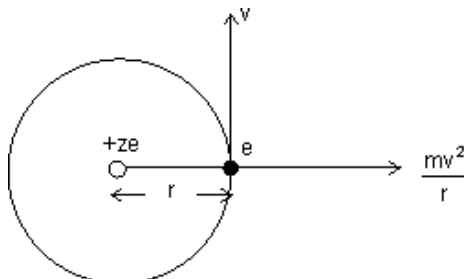$$F = K \frac{Q_1 Q_2}{d^2}$$

Here, K is the proportionality constant called Coulomb's constant.

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8.1 Derivation of Bohr Theory

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

For the system to be stable, the Coulomb's force of 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

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

Here,

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 constant $= \dfrac{1}{4\pi\varepsilon_\circ} = 9 \times 10^9 \dfrac{Nm^2}{C^2}$ in SI system and = 1 in CGS units.

The above equation becomes,

$$-\frac{K \cdot Ze^2}{r} = mv^2 \qquad \ldots\ldots\ldots(i)$$

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

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

Substituting in equation (i)

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

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. Based on this equation Bohr proposed that electron in an atom cannot move in a circular path of any arbitrary radius. Out of infinite circular paths only those are allowed for electron to revolve whose radius is satisfied by equation (iii). These allowed circular paths for electron in an atom are called Bohr Orbits (or Orbits). For hydrogen atom ($Z = 1$) in the ground state, $n = 1$ and substituting the values of the constants in equation (iii), we get

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

The radius of any other orbit in H atoms will be, $r_n = 0.529 \, n^2$ Å

Bohr also calculated the energy of the electron in an orbit. The total energy of the electron will be the sum of the potential and kinetic energies.

Total energy, $E = PE + KE$

The potential energy is the energy due to coulombic attraction and so $PE = \dfrac{-KZe^2}{r}$

Kinetic energy can be calculated from the velocity of the electron. $KE = \dfrac{1}{2}mv^2$

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

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

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

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

From equation (v), it can be seen that the magnitude of the potential energy is twice that of kinetic energy. The negative sign in the equation (vi) 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.

Substituting value of r from equation (iii) in (vi), we get

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

From equation (vii) Bohr proposed that electron in an atom cannot have any arbitrary value of energy and can have only that energy which is satisfied by equation (vii). This observation explained the stability of hydrogen atom as it put a restriction that electron will not lose energy

continuously while moving in a particular orbit. Because the energy of electron remains stationary as long as electron remains in a particular orbit, these orbits are also called **stationary state or energy state** of the electrons.

According to Bohr Theory, electron can jump from one energy state to any other energy state by absorbing or emitting energy exactly equal to the energy difference of two states.

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

$$E = \frac{-2 \times (3.14)^2 \times (9 \times 10^9) \times 1^2 \times 9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^4}{1^2 \times 6.626 \times 10^{-34}}$$

$E = -2.179 \times 10^{-18}$ 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.

$$E_n = E_H \times \frac{Z_2}{n^2}$$

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 ($n_2 > n_1$)

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

$$E_{n_2} = \frac{-2\pi^2 k^2 me^4}{n_2^2 h^2}$$

The difference in energy emitted is

$$h\nu = \frac{-2\pi^2 k^2 me^4}{h^2}\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$

$$\nu = \frac{-2\pi^2 k^2 me^4}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{2\pi^2 k^2 me^4}{h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

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

$$R = \frac{2\pi^2 k^2 me^4}{h^3 c} = 109737 \text{ cm}^{-1}$$

This empirical value of R deduced from Balmer, Lyman and other series agreed excellently with the experimental results. This is the triumph for Bohr's theory. From the foregoing discussion, we can understand that Bohr's theory has given an expression for the energy of the electron of hydrogen atom in the nth orbit as

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

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

8.2 IMPORTANT POSTULATES OF BOHR THEORY

❖ An atom consists of a dense stationary nucleus situated at the centre with the electron revolving around it in circular paths (called orbits) without emitting any energy. The force of attraction between the nucleus and an electron is equal to the centrifugal force on the moving electron.

❖ Out of many circular orbits around the nucleus, an electron can revolve only in those orbits whose angular momentum (mvr) is an integral multiple of factor $h/2\pi$

$mvr = \dfrac{nh}{2\pi}$;   where, m = mass of the electron; v = velocity of the electron; n = orbit number in which electron is present; r = radius of the orbit

❖ As long as an electron is revolving in such an orbit it neither loses nor gains energy. Hence these orbits are called **stationary states**. Each stationary state is associated with a definite amount of energy and it is also known as **energy state or energy level**. The greater the distance of the energy level from the nucleus, the more is the energy associated with it. The different energy levels are numbered as 1, 2, 3, 4…. (from nucleus onwards) or K, L, M, N ….. etc.

❖ Ordinarily an electron continues to move in a particular least possible energy stationary state without losing energy. Such a stable state of the atom is called as **ground state** or **normal state**.

❖ If energy is supplied to an electron, it may jump (excite) instantaneously from lower energy (say 1) to higher energy level (say 2, 3, 4, etc.) by absorbing one photon. This new state of electron is called as **excited state**. The quantum of energy absorbed is equal to the difference in energies of the two concerned levels.

Since the excited state is less stable, atom will lose its energy and come back to the ground state.

Energy absorbed or released in an electron jump, (ΔE) is given by $\Rightarrow \Delta E = E_2 - E_1 = h\upsilon$

Where E_1 and E_2 are the energies of the electron in the first and second energy levels, and υ is the frequency of radiation absorbed or emitted.

[**Note:** *If the energy supplied to hydrogen atom is less than 13.6 eV, it will accept or absorb only those quanta which can take it to a certain higher energy level i.e., all those*

photons having energy different from what is required for a particular transition will not be absorbed by hydrogen atom. But if energy supplied to hydrogen atom is more than 13.6 eV then all photons are absorbed and excess energy appears as kinetic energy of emitted photo electron].

Calculation of velocity of electron in atom:

We know that $mvr = \dfrac{nh}{2\pi}$; $\quad v = \dfrac{nh}{2\pi mr}$

By substituting for r we are getting; $v = \dfrac{2\pi KZe^2}{nh}$

Where excepting n and z all are constants; $\quad v = 2.18 \times 10^8 \dfrac{Z}{n}$ cm/sec.

Explanation for hydrogen spectrum by Bohr's theory:

According to the Bohr's theory electron neither emits nor absorbs energy as long as it stays in a particular orbit. However, when an atom is subjected to electric discharge or high temperature, and electron in the atom may jump from the normal energy level, i.e., ground state to some higher energy level i.e. excited state. Since the life time of the electron in excited state is short, it returns to the ground state in one or more jumps.

During each jump, energy is emitted in the form of a photon of light of definite wavelength or frequency. The frequency of the photon of light thus emitted depends upon the energy difference of the two energy levels concerned (n_1, n_2) and is given by

$$h\nu = E_{n_2} - E_{n_1} = \dfrac{-2\pi^2 mZ^2 e^4 K^2}{h^2}\left[\dfrac{1}{n_2^2} - \dfrac{1}{n_1^2}\right]; \quad \nu = \dfrac{2\pi^2 mZ^2 e^4 K^2}{h^3}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$$

The frequencies of the spectral lines calculated with the help of above equation are found to be in good agreement with the experimental values. Thus, Bohr's theory elegantly explains the line spectrum of hydrogen and hydrogen like species (single electron species).

Bohr had calculated Rydberg constant from the above equation.

$$\nu = \dfrac{c}{\lambda} = \dfrac{2\pi^2 mZ^2 e^4 K^2}{h^3}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]; \quad \dfrac{1}{\lambda} = \bar{\nu} = \dfrac{2\pi^2 mZ^2 e^4 K^2}{h^3 c}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$$

where $\dfrac{2\pi^2 me^4 K^2}{h^3 c} = 1.097 \times 10^{-7} m^{-1}$ or 109678 cm^{-1} i.e., Rydberg constant (R)
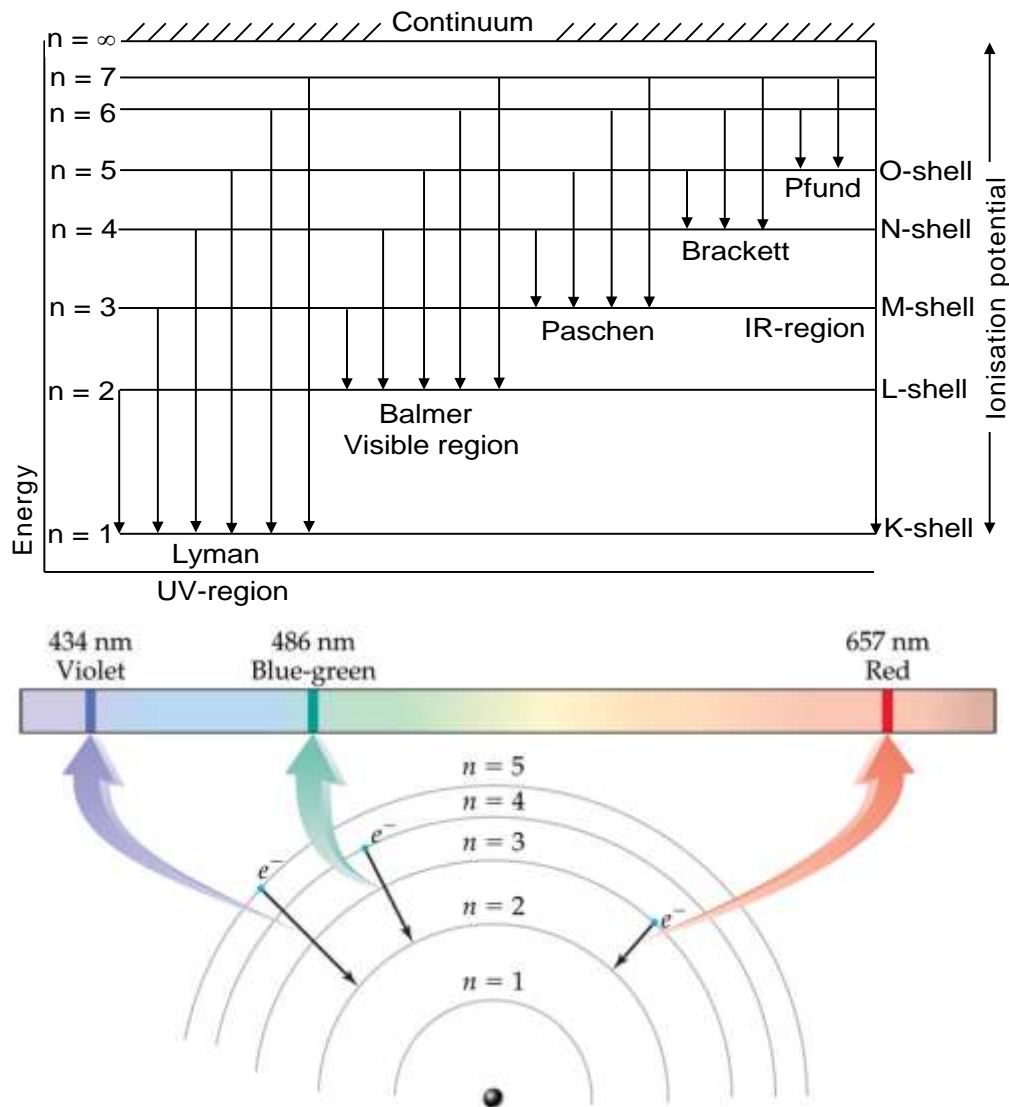
Further application of Bohr's work was made, to other one electron species (Hydrogen like ion) such as He^+ and Li^{2+}. In each case of this kind, Bohr's prediction of the spectrum was correct.

- Now after obtaining the explanation of Rydberg's equation from Bohr's theory we can derive what could be the equation for other one-electron species and the value of Rydberg's constant for He^{+1}, Li^{+2} etc.

8.3 MERITS AND LIMITATIONS OF BOHR'S MODEL

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+, Li^{2+}, Be^{3+} and so on).

Merits of Bohr's theory:

(i)   Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability of the atom by putting restriction over angular momentum of electron.

(ii)   The experimental value of radii and energies in hydrogen atom are in good agreement with that calculated on the basis of Bohr's theory.

(iii)   Bohr's concept of stationary state of electron explains the emission and absorption spectra of hydrogen like atoms.

(iii)   The experimental values of the spectral lines of the hydrogen spectrum are in close agreement with that calculated by Bohr's theory.

Limitations of Bohr's theory:

(i)   It does not explain the spectra of atoms having more than one electron.

(ii)   Bohr's atomic model failed to account for the effect of magnetic field (Zeeman Effect) or electric field (Stark effect) on the spectra of atoms or ions. It was observed that when the source of a spectrum is placed in a strong magnetic or electric field, each spectral line further splits into a number of lines. This observation could not be explained on the basis of Bohr's model.

(iii)   De Broglie Relationship suggested that electrons like light have dual character. It has particle and wave character. Bohr treated the electron only as particle.

(iv)   Another objection to Bohr's theory came from ***Heisenberg's Uncertainty Principle***. According to this principle ***"It is impossible to determine simultaneously the exact position and momentum of a small moving particle like an electron"***. The postulate of Bohr Theory that electrons revolve in well-defined orbits around the nucleus with well-defined velocities is thus not tenable.

8.4 IMPROVEMENT IN BOHR THEORY

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

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

Here μ is the reduced mass $= \dfrac{Mm}{M+m}$ whose M is the mass of the nucleus and m is the mass of the electron. This can explain the difference in various isotopes of an atom. The size of heavier isotope is found to be smaller.

***Illustration* 6.**

Question: **Find the distance between 2nd and 4th orbit in He$^+$.**

Solution: Required answer $= r_{4,He^+} - r_{2,He^+}$. Now, radius $= 0.529 \dfrac{n^2}{Z}$ Å

$$\therefore \textbf{Distance} = \dfrac{0.529}{2}(4^2 - 2^2)\,\text{Å} = 3.174\text{Å}$$

***Illustration* 7.**

Question: **Calculate the energy of an electron in 3rd Bohr orbit.**

Solution: $E_n = -\dfrac{13.6}{n^2}$ eV $= -\dfrac{13.6}{3^2} = -1.51$ eV $= -2.42 \times 10^{-19}$ J

***Illustration* 8.**

Question: **Calculate the energy in kJ per mole for an electron accelerated by a potential of 1 volt.**

Solution: Energy in joules = charge in coulombs × potential difference in volt

$= 1.6 \times 10^{-19} \times 6.02 \times 10^{23} \times 1;\ = 9.632 \times 10^4$ J or 96.32 kJ

***Illustration* 9.**

Question: **Find the time taken for half a revolution by electron in 3rd orbit of Li^{2+}.**

Solution: $\text{time} = \dfrac{distance}{\text{speed}} = 1/2 \times \dfrac{circumference}{velocity} = \dfrac{1}{2} \times \dfrac{2\pi r_3, Li^{2+}}{V_3, Li^{2+}}$

$r_3, Li^{2+} = \dfrac{0.529 \times 3^2}{3} = 1.587$ Å

$V_3, Li^{2+} = 2.18 \times 10^6 \left(\dfrac{Z}{n}\right) = 2.18 \times 10^6\ m/s$

$\therefore \text{Time} = \dfrac{\pi \times 1.587\ \mathring{A}}{2.18 \times 10^6\ m/s} = 2.287 \times 10^{-16} s$

***Illustration* 10.**

Question: **Find the wavelength of photon absorbed during transition of an electron from 4th orbit to 6th orbit in He$^+$.**

Solution: $E_{photon} = E_{6,He^+} - E_{4,He^+}$ But, $E_{n,Z} = -13.6\left(\dfrac{Z^2}{n^2}\right)eV$

$$\therefore E_{photon} = 13.6 \times 4 \times \left(\frac{1}{4^2} - \frac{1}{6^2}\right) = 1.89\,eV$$

$$\therefore \lambda = \frac{12400}{1.89}\,\mathring{A} = 65600\,\mathring{A}$$

Illustration **11.**

Question: **Find out the longest wavelength of absorption line for hydrogen gas containing atoms in ground state.**

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

For longest wavelength, ΔE should be least i.e. transition occurs from n = 1 to n = 2

i.e. $\dfrac{1}{\lambda} = 109678\text{ cm}^{-1} \times 1^2\left[\dfrac{1}{1} - \dfrac{1}{2^2}\right]$

$\therefore \dfrac{1}{\lambda} = 109678 \times \dfrac{3}{4}\text{ cm}^{-1}$

$\therefore \lambda = \dfrac{4}{3 \times 109678\text{cm}^{-1}} = 1.2157 \times 10^{-5}\text{ cm} = 121.6\text{ nm}$

Illustration **12**

Question: **The series limit for the Paschen series of hydrogen spectrum occurs at 8205.8Å. Calculate.**

(A) Ionization energy of hydrogen atom

(B) Wave length of the photon that would remove the electron in the ground state of the hydrogen atom.

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Solution: **(A)** Energy corresponding to 8205.8 Å = $\dfrac{6.626\times10^{-34}\times3\times10^8}{8205.8\times10^{-10}}$

$= 2.422\times10^{-19}$ J $= \dfrac{1240}{820.58} = 1.512$ eV; $\Delta E = E_1,H\times Z^2\left[\dfrac{1}{n_1^2}-\dfrac{1}{n_2^2}\right]$

1.512 eV $= E_{1,H}\times(1)^2\times\left(\dfrac{1}{3^2}-\dfrac{1}{\infty^2}\right)$; 1.512 eV $= \dfrac{E_{1H}}{9}$

$E_{1,H} = 13.608$ eV

∴ Ionisation energy of hydrogen atom = **13.6 eV**

(B) $\lambda = \dfrac{hc}{E} = \dfrac{6.626\times10^{-34}\times3\times10^8}{13.6\times1.602\times10^{-19}} = \dfrac{1240}{13.6}$ in nm = **91.6 nm**

Illustration **13**

Question: **Calculate frequency of the spectral line when an electron from 5th Bohr orbit jumps to the second Bohr orbit in a hydrogen atom.**

Solution: $\dfrac{1}{\lambda} = R\left[\dfrac{1}{n_1^2}-\dfrac{1}{n_2^2}\right] = 109673\left[\dfrac{1}{2^2}-\dfrac{1}{5^2}\right] = 2.304\times10^6\,m^{-1}$

∴ $v = \dfrac{C}{\lambda} = 2.304\times10^6\,m^{-1}\times2.998\times10^8\,m/s = 6.906\times10^{14}$ Hz

Illustration **14.**

Question: **What is highest frequency photon that can be emitted from hydrogen atom? What is wavelength of this photon?**

Solution: Highest frequency photon is emitted when electron comes from infinity to 1st energy level.

$E = -\dfrac{13.6Z^2}{1^2} = -13.6\,eV$

or $13.6\times1.6\times10^{-19}$ Joule $= 2.176\times10^{-18}$ Joule

$E = hv$ ∴ $v = \dfrac{E}{h} = \dfrac{2.176\times10^{-18}J}{6.626\times10^{-34}Js} = 0.328\times10^{16}$ Hz;

$v = \dfrac{C}{\lambda}$; ∴ $\lambda = \dfrac{3\times10^8}{0.328\times10^{18}} = 9.146\times10^{-8}$ m

Illustration **15.**

*Question***: Calculate the longest wavelength transition in the Paschen series of He⁺.**

Solution: $\bar{\upsilon} = R_H \times Z^2 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right]$;   For He; Z = 2; For Paschen series $n_1 = 3$

For longest wavelength $n_2 = 4$

$$\frac{1}{\lambda} = 109678 \times (2)^2 \times \left[\frac{1}{3^2} - \frac{1}{4^2} \right] = 109678 \times 4 \times \left[\frac{1}{9} - \frac{1}{16} \right] = 109678 \times 4 \times \frac{7}{144}$$

$\lambda = \mathbf{4689 \mathring{A}}$

Illustration 16

Question: **Calculate ratio of the wavelength of first and last line of Balmer series of Li^{2+}.**

Solution: wave number of first line of Balmer series, $\bar{\nu}_1 = RZ^2 \left[\dfrac{1}{2^2} - \dfrac{1}{3^2} \right] = \dfrac{5 \times 9R}{36} = \dfrac{5R}{4}$

$\therefore$ Wave length of first line of Balmer series $= \dfrac{4}{5R}$

Wave number of ultimate line of Balmer series, $\bar{\nu}_2 = RZ^2 \left[\dfrac{1}{2^2} - \dfrac{1}{\infty} \right] = \dfrac{9R}{4}$

$\therefore$ wave length of ultimate line of Balmer series $= \dfrac{4}{9R}$ $\therefore$ **Ratio** $= \dfrac{9}{5}$

Illustration 17

Question: **The energies of the electron in the second and third orbits of the hydrogen atom are −5.42 × 10^{-12} and − 2.41 × 10^{-12} ergs respectively. Calculate the wavelength of the emitted radiation when the electron drops from the third to the second orbit.**

Solution: The emitted radiation will have energy equal to the energy difference between the third and the second orbit.

$\Delta E \quad = E_3 - E_2$

$\qquad = -2.41 \times 10^{-12} - (-5.42 \times 10^{-12})$

$\qquad = 3.01 \times 10^{-12}$ ergs.

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

$\therefore \Delta E = 3.01 \times 10^{-19}$ J

This energy of radiation corresponds to a wavelength of

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

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3.01 \times 10^{-19}} = 6.6039 \times 10^{-7} \text{ m} = 6603.9 \times 10^{-10} \text{ m} = \mathbf{6603.9 \mathring{A}}$$

Illustration **18.**

Question: **Calculate the wavelength in Å of the photon that is emitted when an electron in the Bohr orbit n = 2 returns to the orbit n = 1 in the hydrogen atom. The ionization potential of the ground state of the hydrogen atom is -2.17×10^{-11} erg per atom.**

Solution: Energy of nth level in the hydrogen is inversely proportional to n^2.

$$E_n \propto \frac{1}{n^2}; \qquad E_n = \frac{-2.17 \times 10^{-11}}{n^2}$$

When electron falls from n = 2 to n = 1 the energy emitted would be,

$$E_1 = \frac{-2.17 \times 10^{-11}}{1^2}; \quad E_2 = \frac{-2.17 \times 10^{-11}}{2^2}$$

$$\Delta E = E_2 - E_1 = 2.17 \times 10^{-11} \left[1 - \frac{1}{2^2} \right]$$

$$= 2.17 \times 10^{-11} \times \frac{3}{4} \text{ erg /atom} = 2.17 \times 10^{-18} \times \frac{3}{4} \text{ J/atom}$$

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

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2.17 \times 10^{-18} \times \frac{3}{4}} = 1.22138 \times 10^{-7} \text{ m} = \mathbf{1221.38 \text{ Å}}$$

Illustration **19.**

Question: **The electron energy in hydrogen atom is given by $E = \frac{-21.7 \times 10^{-12}}{n^2}$ ergs. Calculate the energy required to remove an electron completely from n = 2 orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition?**

Solution: $E_n = \frac{-21.7 \times 10^{-12}}{n^2}$ ergs

$$E_2 = \frac{-21.7 \times 10^{-12}}{2^2}$$

Removing the electron completely from the atom implies that the electron has been exited to the level ∞.

$$\therefore \ E_\infty = \frac{-21.7 \times 10^{-12}}{\infty^2} = 0$$

$$\Delta E = E_\infty - E_2 = \frac{-21.7 \times 10^{-12}}{4} \, \text{ergs}$$

$$\Delta E = \frac{-21.7 \times 10^{-12}}{4} \times 10^{-7} \, \text{Joule} = \mathbf{5.425 \times 10^{-19} \, J}$$

$$\Delta E = \frac{hc}{\lambda}$$
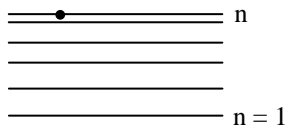
$$\therefore \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{5.425 \times 10^{-19}} = 3.66414 \times 10^{-7} \, \text{m.}$$

$$\therefore \lambda = \mathbf{3664.14 \, \text{Å}}$$

Illustration **20.**

Question: **There is a hydrogen atom in the ground state. It is exited to a higher energy level n. When the electron comes back to the ground state, it emits radiation. What is the maximum number of unique wavelengths it can emit?**

Solution:

Let us imagine the electron to be in the energy level n. When it comes to the ground state it can come in many no. of ways. Either it will directly come to n = 1, in which case it will emit only one wavelength (corresponding to n to 1) or it can fall to n =2 and then from n = 2 to n = 1, in which case it will emit two unique wavelengths (one corresponding to n to 2 and the other corresponding to n = 2 to n = 1) and so on. We have to find how the electron must come back by emitting maximum number of unique wavelengths. It is very clear that every jump of the electron would radiate a unique wavelength as

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

λ cannot be same for different sets of n_1 and n_2.

The only way maximum wavelengths can be emitted is when the electron comes back to ground state by maximum jumps. This means the electron must jump stepwise i.e., n to n − 1 to n − 2 to n −3 and so on. This means the total jumps would be n − 1 and so would be the number of unique wavelength.

$$\therefore \mathbf{n - 1}$$

Illustration **21.**

Question: **Show that the circumference of an orbit of Bohr hydrogen atom is an integral multiple of the de Broglie wavelength associates with the electron revolving round the nucleus.**

*Solution:* According to Bohr's postulates,

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

$\therefore$ the circumference, $2\pi r = \frac{nh}{mv}$

From de Broglie's equation, $\lambda = \frac{h}{mv}$

$\therefore$ **$2\pi r = n\lambda$**

9.   PHOTO ELECTRIC EFFECT

Sir J.J. Thomson observed that when a light of certain frequency strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is known as **photoelectric effect** and the ejected electrons are called photoelectrons. A few metals, which are having low ionisation energy like Cesium, show this effect under the action of visible light but many more show it under the influence of more energetic ultraviolet light.
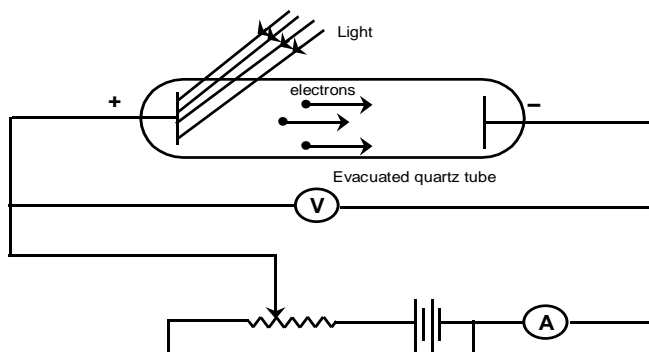
An evacuated tube contains two electrodes connected to a source of variable voltage, with the metal plate whose surface is irradiated as the anode. Some of the photoelectrons that emerge from this surface have enough energy to reach the cathode despite its negative polarity, and they constitute the measured current. The slower photoelectrons are repelled before they get to the cathode. When the voltage is increased to a certain value V_o, of the order of several volts, no more photoelectrons arrive, as indicated by the current dropping to zero. This extinction voltage is also referred as stopping potential corresponding to the maximum photoelectron kinetic energy i.e.,

$$eV_o = K.E._{max.} = \frac{1}{2} mv^2$$

The experimental findings are summarized as below:

(i)   Electrons come out as soon as the light (of sufficient frequency) strikes the metal surface.

(ii)   Light of any random frequency will not be able to cause ejection of electrons from a metal surface. A minimum frequency, called the threshold (or critical) frequency is required to cause the ejection. If frequency of light is increased beyond threshold frequency (higher energy); photoelectric current does not increase but the maximum kinetic energy of photoelectrons increases.

iii)   Photoelectric current is increased with increase in intensity of light of same frequency, if emission is permitted i.e., a bright light yields more photoelectrons than a dim light of the same frequency, but the maximum kinetic energy of photoelectron remains the same.

These experimental observations can be explained if light must have stream of energy particles or quanta of energy ($h\nu$). Suppose, the threshold frequency of light required to eject electrons from a metal is ν_o, when a photon of light of this frequency strikes a metal it imparts its entire energy ($h\nu_o$) to one electron.

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

$$h\nu = h\nu_o + (K.E)_{max} \quad ; \qquad h\nu = h\nu_o + \tfrac{1}{2}mv^2 \qquad ; \qquad \tfrac{1}{2}mv^2 = h\nu - h\nu_o$$
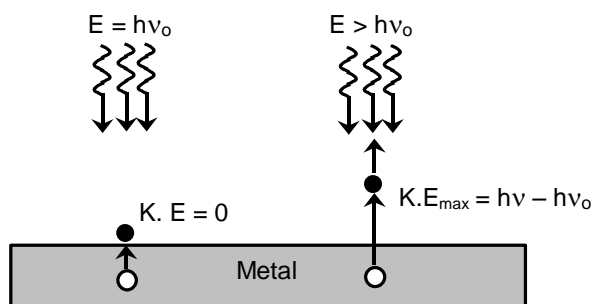
Where, ν = frequency of the incident light

ν_o = threshold frequency

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

The kinetic energy of the photoelectrons increases linearly with the frequency of incident light. Thus, if the energy of the ejected electrons is plotted as a function of frequency, it results in a straight line whose slope is negative and equal to Planck's constant 'h' and whose intercept is $-h\nu_o$.
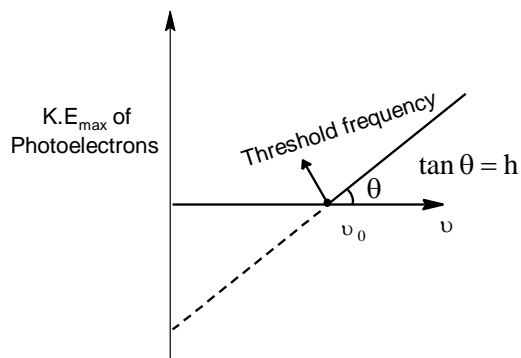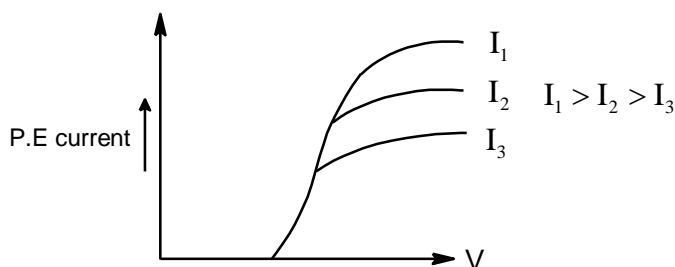
It is important to remember that the expression involves $(KE)_{max}$. In reality e⁻ will have K.E lesser than this also.

Total energy falling on plate = n hν,   photon intensity = $\dfrac{n}{At}$

Intensity of energy falling on the metal surface = $\dfrac{n\,h\,v}{At}$

Variation of P.E current vs voltage for different photon intensities I_1, I_2, I_3

Concept of Photon:

Observation of photoelectric effect made by Einstein had confirmed electromagnetic radiation as streams of particles. When we stop the radiations by any physical obstruction we cannot convert radiations into matter. Therefore rest mass of photons ought to be zero.

Besides according to Einstein's formula m = $\dfrac{m_o}{\sqrt{1-v^2/c^2}}$, a particle traveling with the speed of

light must be massless. Otherwise its effective mass during motion will be infinite.

$\therefore$ m_o (rest mass) = 0

Energy of a photon is denoted by 'hν'.

E = hν   Where ν is the frequency of the wave.

E = pc is valid for all the particles which are massless (traveling with the speed of light). Therefore photon behaves as a MECHANICAL PARTICLE which can exchange momentum with other particles.

Note: A photon is always absorbed or destroyed completely or remains intact.

10 DE BROGLIE WAVELENGTH (DUAL NATURE OF MATTER)

Nature abounds in symmetries of all kinds. If light can be both wave and particle, is it possible that matter can also have these properties? Can the electron, traditionally regarded as a particle since its discovery in 1898, also have a wave aspect? More specifically, can we assign a wavelength and a frequency to a moving electron?

A French physicist Prince Louis−Victure Broglie, motivated entirely by this symmetry argument, answered yes to these questions. He proposed that an electron of energy E and linear momentum 'p' could be defined by a matter wave whose wavelength and frequency are given by

$$\lambda = \frac{h}{p} \qquad \text{or} \qquad \lambda = \frac{h}{p}$$

Here h is the Planck's constant. The wavelength of a moving particle calculated above is called its de Broglie wavelength. De Broglie shared the 1929 Nobel Prize for his discovery of the wave nature of matter.

Objects such as marbles or cricket balls do not seem at all wave like. We can understand why this is so because the Planck's constant h is so small and the momentum p of even slowly moving macroscopic particles is so large that the calculated de Broglie wavelengths of such objects are extremely small indeed, being many orders of magnitude smaller than the size of an atomic nucleus.

11. HEISENBERG'S UNCERTAINITY PRINCIPLE

Uncertainty principle was first derived by the German physicist Werner Heisenberg, it. According to Heisenberg it is not possible to measure, simultaneously, the position and the momentum of a particle with unlimited precision.

If Δx is the uncertainty in position and Δp is uncertainty in momentum then,

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

The message of the uncertainty principle is that there is a limit to the extent to which the concept of "particle" can be extended from the Newtonian world to the quantum world. In the quantum world, it is incorrect to imagine that a particle really has a definite position and momentum but, for some reason, we are not able to measure it. It is incorrect to visualize a particle as a tiny mass point moving along a path, with its position and velocity well defined at every instant. The very notion of "trajectory" belongs to the Newtonian world, not to the quantum world.

Illustration **22.**

Question: **A photon of wavelength 5000 Å strikes a metal surface, the work function of the metal being 2.20 eV. Calculate (i) the energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and (iii) the velocity of the photo electron.**

Solution: (i) Energy of the photon

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6\times10^{-34}\,Js)(3\times10^8\,ms^{-1})}{5\times10^{-7}\,m} = 3.96\times10^{-19}\,J \quad (1\ eV = 1.6\times10^{-19}\ J)$$

$$\text{Therefore } E = \frac{3.96\times10^{-19}\,J}{6\times10^{-19}\,J/eV} = 2.475 eV$$

(ii)   Kinetic energy of the emitted photo electron

Work function = 2.20 eV

Therefore, KE = 2.475 – 2.20 = 0.275 eV = $4.4\times10^{-20}\,J$

(iii)   Velocity of the photo electron   ; $KE = \dfrac{1}{2}mv^2 = 4.4\times10^{-20}\ J$

$$\text{Therefore, velocity (v)} = \sqrt{\frac{2\times4.4\times10^{-20}}{9.1\times10^{-31}}} = 3.11\times10^5\ ms^{-1}$$

Illustration **23.**

Question: **When photons of wavelength 1240 Å strikes a metal surface, the photoelectrons of maximum KE has thrice as much KE as the fastest electrons ejected by a source of wavelength 2480 Å from the same metal surface.**

(a) Find work function of the metal

(b) Find threshold wavelength of the metal

(c) Find stopping potential if light of wavelength 3100 Å is incident on this meal.

Solution: **(a)** $KE_{1240Å} = E_{photon,1240Å} - \phi$ (work function)

$KE_{2480Å} = E_{photon,\,2480Å} - \phi$

Given, $KE_{1240Å} = 3(KE_{2480Å})$

ie $\dfrac{2400}{1240} - \phi = 3\left(\dfrac{12400}{2480} - \phi\right)$

or (10 – ϕ) eV or 3(5 – ϕ) eV   or $2\phi = (15 - 10)$ eV $\Rightarrow$ 2.5 eV

(b) $\lambda_0 = \dfrac{12400}{\phi} = 4960 Å$

(c) $KE_{max} = \dfrac{12400}{3100} - \phi = 1.5\,eV$

$\therefore$ Stopping potential = **- 1.5 volts**

Illustration **24.**

Question: **Two particles A & B are in motion. If the wavelength associated with particle A is 5×10^{-8} m, calculate the wavelength associated with particle B if its momentum is half of A.**

Solution: According to de Broglie equation

$\lambda_A = \dfrac{h}{p_A}$ and $\lambda_B = \dfrac{h}{p_B}$ $\qquad\qquad \dfrac{\lambda_A}{\lambda_B} = \dfrac{P_B}{p_A}$

But $p_B = \tfrac{1}{2}\, p_A$ (given)

$\dfrac{\lambda_A}{\lambda_B} = \dfrac{1/2\,p_A}{p_A} = 1/2 \quad \lambda_B = 2\lambda_A = 2 \times 5 \times 10^{-8}$ m = **10^{-7} m**

Illustration **25**

Question: **Calculate the de Broglie wavelength of a ball of mass 0.1kg moving with a speed of $60\,ms^{-1}$.**

Solution: $\lambda = \dfrac{h}{mv} = \dfrac{6.6 \times 10^{-34}}{0.1 \times 60}$

$\lambda = \mathbf{1.1 \times 10^{-34}\ m.}$

Illustration **26**

Question: If the uncertainty in the position of an electron is 0.33 pm, what will be uncertainty in its velocity?

Solution: $\Delta x = 0.33 \times 10^{-12}\, m$ $\qquad\qquad \Delta x \cdot \Delta p \geq \dfrac{h}{4\pi}$

$\Rightarrow \quad 0.33 \times 10^{-12} \times 9.1 \times 10^{-31} \times \Delta v = \dfrac{h}{4\pi}$

$\Rightarrow \quad \Delta v = \dfrac{6.6 \times 10^{-34}}{4 \times 3.14 \times .33 \times 10^{-12} \times 9.1 \times 10^{-31}} = 1.75 \times 10^{8}\, m/sec.$

Illustration **27**

Question: **Calculate the uncertainty in velocity of a ball of mass $\dfrac{132}{\pi}$ g if the uncertainty in position is of the order of 1 Å.**

Solution: $\Delta x . m . \Delta v \geq \dfrac{h}{4\pi}$

$$\Delta v = \frac{6.6 \times 10^{-34}}{4 \times 132 \times 10^{-3} \times 1 \times 10^{-10}} = 2.5 \times 10^{-23}\, m/sec$$

Illustration **28.**

Question: **(a) If a 1 g body is traveling along the *x*–axis with uncertainty of 1 cm/s in velocity, what is theoretical uncertainty in its position?**

(b) If an electron is traveling with uncertainty in velocity of 1 m/s, what is the theoretical uncertainty in its position?

Solution: (a) According the uncertainty

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

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

$$= \frac{6.626 \times 10^{-27}\, ergs\, sec}{4 \times 3.14 \times 1g \times 1cms^{-1}}$$

$$= 5.275 \times 10^{-28}\, cm = 5.275 \times 10^{-30}\, m$$

(b) $\Delta x = \dfrac{6.626 \times 10^{-34}\, Js}{4 \times 3.14 \times 9.1 \times 10^{-31}\, kg \times 1ms^{1}}$

$$= 5.797 \times 10^{-5}\, m.$$

12. QUANTUM MECHANICAL MODEL (CONCEPT OF ORBITAL)

Improving on the Bohr Model, Sommerfield, in order to account for the additional lines present in the spectra of atoms, assumed that each principal energy level contains a number of sub–levels, each of which possesses slightly different energy. The subsidiary orbits are designated s, p, d and f (these letters standing for the nature – sharp, principal, diffuse and fundamental – of the lines in the spectra). The number of sub–levels in any particular energy level is fixed. The various sub–levels in K, L, M, N etc., shells and the maximum number of electrons that may be present in each of them are given below:

Shell	K	L		M			N			
Sublevels	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
Max. no. of electrons	2	2	6	2	6	10	2	6	10	14

The principle quantum number, n can have values 1, 2, 3, ….., and is indicative of the major energy levels of the electron in an atom in a gross way. This is similar to the quantum levels in Bohr's theory. The azimuthal quantum number, *l*, has values from 0 to (n−1), for each value of n.

It is a measure of the angular momentum of the electron, which is $\dfrac{h}{2\pi}\sqrt{l(l+1)}$ in magnitude.

Values of l = 0, 1, 2, 3, ….., are designated by the letters s, p, d, f ….. The magnetic quantum number m is indicative of the component of the angular momentum vector in any one chosen direction, usually the z−axis. The values of m are from $−l$ to $+l$ including zero for any value of l. An electron can spin either in clockwise direction or in anticlockwise direction. Spin quantum number, 's' can have two values $+$ ½ and $−$ ½ and also represented by arrow pointing in opposite direction i.e. ↑ and ↓ for any particular value of magnetic quantum number.

From the above table we have derived the formula, to know the number of subshells/orbitals/electrons in a shell/subshell.

1. Total number of subshells in a particular shell = 'n'

2. Total number of orbitals in a particular subshell = $(2l + 1)$

3. Total number of orbitals in a particular shell = $\displaystyle\sum_{l=0}^{l=n-1}(2l+1) = n^2$

4. Maximum number of electrons in a particular subshell = $2(2l + 1)$

5. Maximum number of electrons in a particular shell = $2n^2$

Permissible values of the quantum numbers for various orbitals are mentioned in the table given ahead.

Table: Permissible values of quantum numbers for atomic orbital

Pr. Q. no. 'n'	Azimuthal Quantum no. 'l'	Magnetic Quantum no. 'm'	Spin Quantum no. 's'
1	$l = 0$; 1s subshell	m = 0; s orbital (1 orbital)	+ ½ & −½ (max.2
	No. of subshells = 1	**Total no. of orbitals = 1**	**Max. no. of e's = 2**
2	$l = 0$; 2s subshell	m = 0; s orbital	+ ½ & − ½
	$l = 1$; 2p subshell	m = −1; p_x / p_z m = 0; p_y	+ ½ & − ½ + ½ & − ½
	No. of subshells = 2	**Total no. of orbitals = 4**	**Max. no. of e's = 8**
3	$l = 0$; 3s subshell	m = 0; s orbital	+ ½ & − ½
	$l = 1$; 3p subshell	m = −1; p_x / p_z m = 0; p_y	+ ½ & − ½ + ½ & − ½
	$l = 2$; 3d subshell	m = −2 m = −1 m = 0	+ ½ & − ½ + ½ & − ½ + ½ & − ½
	No. of subshells = 3	**Total no. of orbitals = 9**	**Max. no. of e's = 18**
4	$l = 0$; 4s subshell $l = 1$; 4p subshell	m = 0; s orbital No. of orbitals = 1 m = −1; p_x / p_z m = 0; p_y m = +1; p_z / p_x No. of orbitals = 3	+ ½ & − ½ no. of e's in s−subshell = 2 + ½ & − ½ + ½ & − ½ + ½ & − ½ Max. no. of e's = 6

	$l = 2$; 4d subshell	m = –2	+ ½ & – ½
		m = –1	+ ½ & –½
		m = 0	+ ½ & – ½
		m = +1	+ ½ & – ½
		m = +2	+ ½ & – ½
		No. of orbitals = 5	Max. no. of e's = 10
	$l = 3$; 4f subshell	m = –3	+ ½ & – ½
		m = –2	+ ½ & – ½
		m = –1	+ ½ & – ½
		m = 0	+ ½ & – ½
		m = +1	+ ½ & – ½
		m = +2	+ ½ & – ½
		m = +3	+ ½ & – ½
		No. of orbitals = 7	Max. no. of e's = 14
	No. of subshells = 4	**No. of Orbitals = 1+3+5+7=16**	**Max no. of e's = 2+6+10+14=32**

12.1   SCHRÖDINGER EQUATION

The atomic model based on the particle and wave nature of the electron is known as wave or quantum mechanical model of atom. This was developed by Ervin Schrödinger in 1926. This model describes the electron as a three dimensional wave in the electronic field of positively charged nucleus. Schrödinger derived an equation which describes wave motion of an electron. The differential equation is

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$
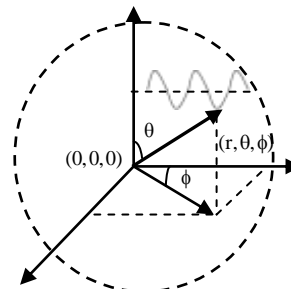
where x, y, z are certain coordinates of the electron, m = mass of the electron; E = total energy of the electron; V = potential energy of the electron; h = Planck's constant and ψ (psi) = wave function of the electron.

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels that electron can occupy and the corresponding wave function (ψ) of the electron associated with each energy level.

Actual view and properties of quantum mechanical model can be better understood in polar coordinates instead of normal Cartesian coordinate. In a polar coordinate any point in space can be represented in terms of r, θ and ϕ; where r = distance from the origin; θ and ϕ = angles from any of two Cartesian coordinates

ψ is Amplitude of electronic wave inside the atom. It can change if any of r, θ and ϕ changes. So ψ is a function of r, θ and ϕ. i.e.

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

This total wave function can also be written as multiplication of two different functions as

$$\psi_{(r, \theta, \phi)} = R_{(r)} \times A_{(\theta, \phi)}$$

Total Wave function

Radial Wave function

Angular Wave function

Where $R_{(r)}$, Radial Wave function depends only on distance from the nucleus and $A_{(\theta, \phi)}$, Angular Wave function depends only on the two angles.

Significance of ψ:

The wave function can be regarded as the amplitude function expressed in terms of coordinates x, y and z. The wave function can have positive or negative values depending upon the value of coordinates. The main aim of Schrödinger equation is to give solution for probability of electron. When the equation is solved, it is observed that for some regions of space the value of ψ is negative. The probability must be always positive and cannot be negative, it is thus, reasonable to use ψ^2 instead of ψ.

Significance of ψ^2:

ψ^2 represents the probability density (probability per unit volume) of electron. It represents the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is termed as orbital. The important point of the solution of the wave equation is that it provides a set of numbers called quantum numbers which describe energies of the electron in atoms, information about the shapes and orientations of the most probable distribution of electrons around nucleus.

12.2   NODE AND NODAL PLANE

Node is defined as a region within the orbital, where the probability of finding an electron is zero. Total number of nodes for an orbital = n - 1. Nodes can be of two types.

(a) Radial node or spherical node

(b) Angular node or planar node

Radial node or spherical node:

Radial node represent the distance (radius) from centre where the value of ψ or ψ^2 becomes zero. The number of radial nodes is always equal to 'n - l - 1' value.

Angular node or planar node:

Number of angular nodes is equal to 'l' value. It depends upon the shape of orbitals. For example, 's' orbitals are spherically symmetrical; so in s−orbital, no angular node exists. p−orbitals are not spherically symmetrical but the electron density is concentrated in one plane either x, y or z. So they have one angular node. Similarly electron density in d−orbital is concentrated in two planes i.e. xy, yz, zx etc. So the d−orbitals have two angular nodes.

Total no. of radial nodes = (n − l − 1)

Total no. of angular nodes = l

Total no. of nodes = (n − l − 1) + l = n −1

12.3 PROBABILITY DISTRIBUTION CURVE

It is known that wave functions (ψ) can be expressed as the product of two functions, one of which, the radial part R(r) depends only on the distance from the nucleus, the other being the angular part $f(\theta, \phi)$ depends only on the angles θ & ϕ.

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

Radial wave function   angular wave function

Hence, Probability distribution curves which give the variation of probability of finding the electron can also be classified into two types (i) one which give the variation of probability of finding the electron with *radial distance* (r), termed as *radial probability distribution curves,* and (ii) and one which give the variation of probability of finding the electron with *angle keeping the radial distance same (θ &* ϕ). Let us understand each of them separately.

Radial probability distribution curves:

We had already studied that $\psi_r{}^2$ gives the radial probability density of finding an electron at a point. *It refers to the radial probability of finding an electron in a unit volume in an atom at a radial distance of r from the nucleus*. Therefore, total radial probability in a spherical shell of thickness **dr** at a radial distance of **r** from the nucleus (which will have a volume of **$4\pi r^2$dr or dv**) is given by **$4\pi r^2 \psi_r{}^2$dr.** Sometimes, $\psi_r{}^2$ is often represented as **R^2.**

**Calculation of Radial probability distribution function:**

As stated above, the radial probability density at a radial distance r is R^2. Therefore radial probability of finding the election in a volume dv will be $R^2 dv$.

The radial probability is the probability of finding the election in a radial shell between spheres of radii r and r + dr, where dr is small radial distance.

Volume of spherical shell of thickness $dr = \dfrac{4}{3}\pi(r+dr)^3 - \dfrac{4}{3}\pi r^3$

$$= \dfrac{4}{3}\pi\left[r^3 + (dr)^3 + 3rdr(r+dr) - r^3\right]$$

$$= \dfrac{4}{3}\pi\left[(dr)^3 + 3r^2dr + 3r(dr)^2\right]$$
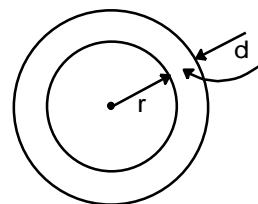
Since dr is very small, so the terms $(dr)^3$ and $3r(dr)^2$ can be neglected.

$$\Rightarrow dv = \dfrac{4}{3}\pi \times 3r^2 dr = 4\pi r^2 dr$$

Radial probability of finding an e^- in a shell of thickness dr at a distance 'r'

$$= R^2 4\pi r^2 dr = 4\pi r^2 R^2 dr$$

Examples of Radial Probability Density and Radial Probability Distribution Curves:

$4\pi^2 r^2 R^2(r)$

0.529 Å

→ r

Bohr rdius = 0.529 Å

(3 s)

$4\pi r^2 R^2$

node

→ r

(3 s)

$4\pi r^2 R^2$

→ r

(3 s)

R(r)

nodes

→ r

(3 p)

$R^2(r)$

→ r

(3 p)

$4\pi^2 r^2 R^2$

→ r

(3 p)

R(r)

→ r

(3 d)

$R^2(r)$

→ r

(3 d)

$4\pi^2 r^2 R^2(r)$

→ r

(3 d)

R(r)

→ r

$R^2(r)$

→ r

$4\pi^2 r^2 R^2(r)$

→ r
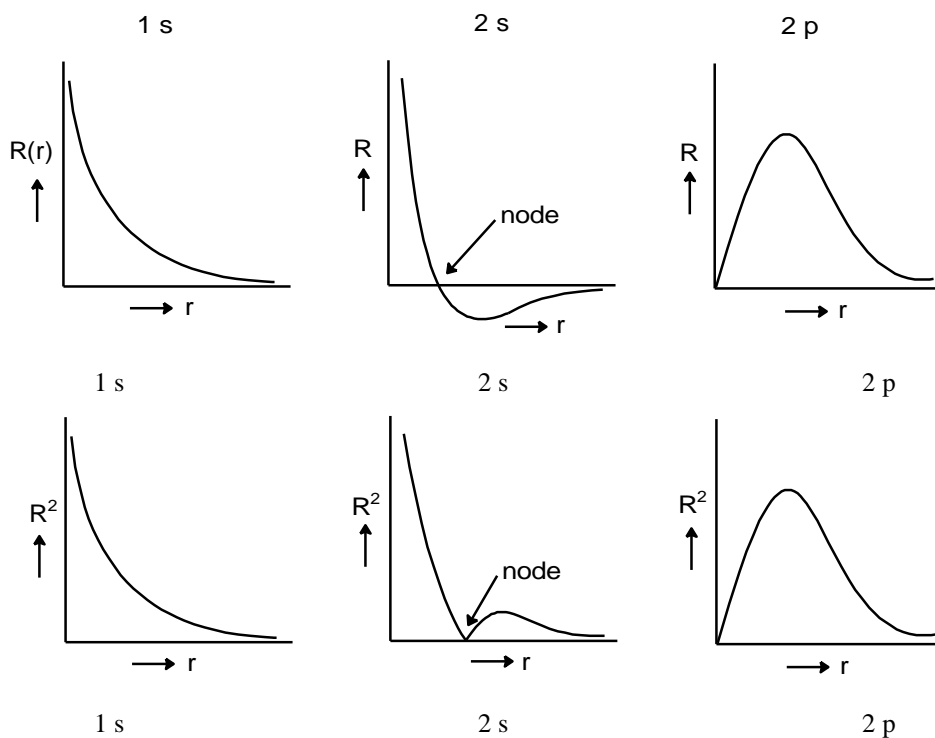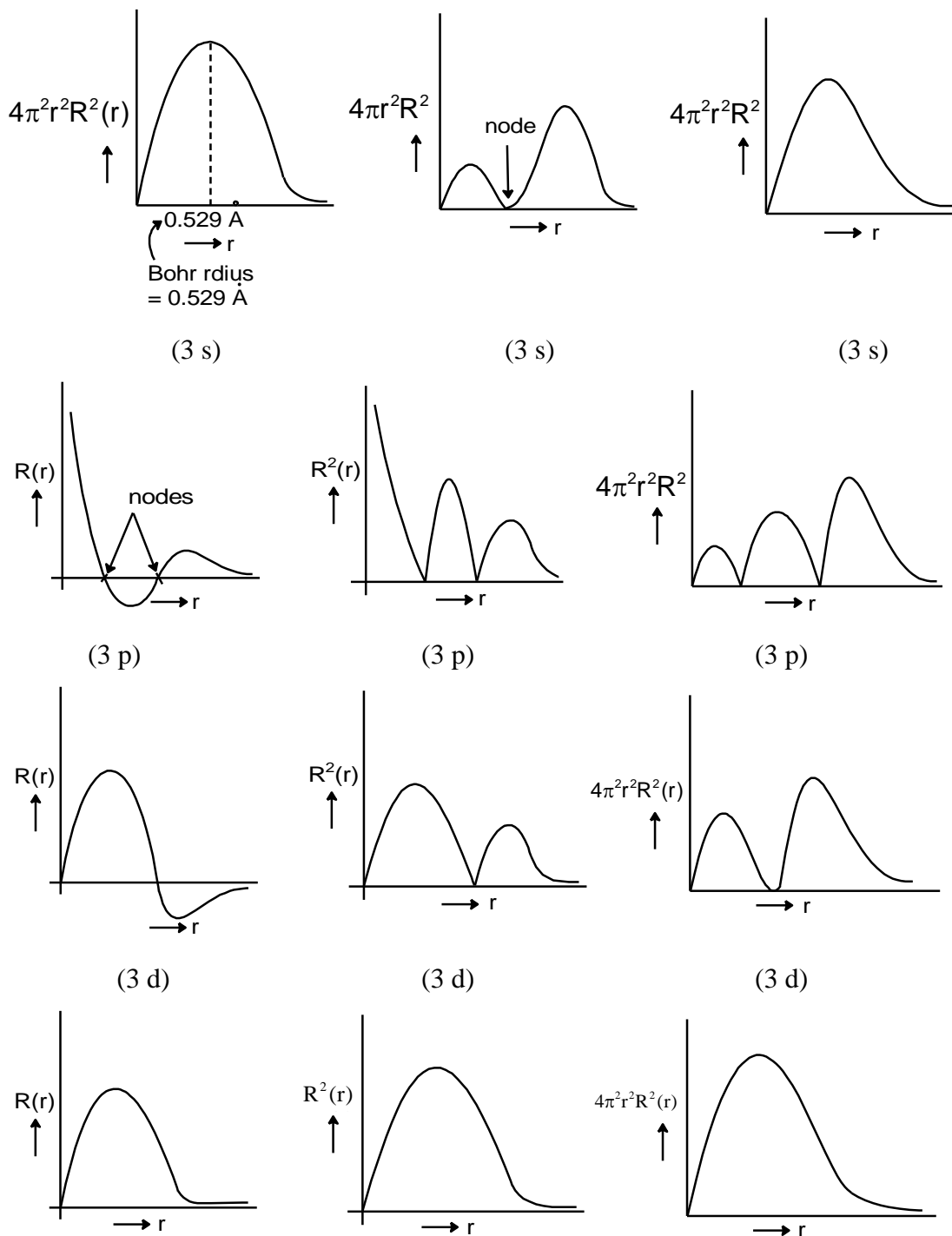
Radial Probability Density curves are between ψ_r^2 (also written as R^2) vs r whereas Radial Probability Distribution curves which would be more useful are between $4\pi r^2 \psi_r^2$ vs r.

Comparison between 3s, 3 p and 3d orbitals:

How to memorize above Graph:

1. Radial wave function (R) can have +ve as well as −ve values and changes sign at every radial node. Its value starts from maximum for s orbital and from 0 for p or d orbitals. The magnitude of successive peaks and troughs keep decreasing with increasing value of r. The value of R approaches 0 at infinite.
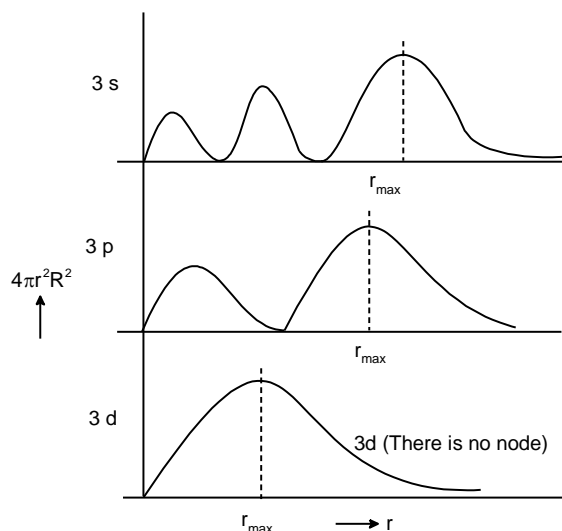
2. Radial probability density (R^2) is always +ve and becomes 0 at every radial node. Its value starts from maximum for s orbital and from 0 for p or d orbitals. The heights of successive peaks keep decreasing with increasing value of r. The value of R^2 approaches 0 at infinite.

3. Radial probability distribution ($R^2 4\pi r^2$) is always +ve and becomes 0 at every radial node. Its value starts from 0 for s, p or d orbitals. The heights of successive peaks keep increasing with increasing value of r. The value of $R^2 4\pi r^2$ approaches 0 at infinite.

4. For the same value of n, the distance of maximum probability, r_{max} of various orbitals is inversely dependent upon the value of ℓ.

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

    $(r_{max})_{3s} > (r_{max})_{3p} > (r_{max})_{3d}$

5. For the same value of ℓ, the distance of maximum probability, r_{max} of various orbitals increases with increasing value of n.

    $(r_{max})_{3s} > (r_{max})_{2s} > (r_{max})_{1s}$

6. Penetration power of an orbital is a measure of its closeness to the nucleus. Due to additional maxima in 3 s curve, electron in 3 s spends some of its time near the nucleus making it more penetrating than 3p which in turn is more penetrating than 3d.

    $$\xrightarrow{\hspace{2cm} 3s>3p>3d \hspace{2cm}}$$
    Decreasing order of penetration power

Important points to note about the $4\pi r^2 R^2$ vs. r plots:

(i) Radial probability is ALWAYS SMALL near the nucleus ($4\pi r^2$ is small near the nucleus).

ii) The maximum in the $4\pi r^2 R^2_{1s}$ vs. r plot occurs at 0.53Å - just the radius of the n = 1 orbit of the Bohr model.

iii) On average a 2s electron spends its most time at a greater distance from the nucleus than the 1s electron which is consistent with the observation that $(r_{1s})_{max} < (r_{2s})_{max}$

iv) The position of the principal (i.e. largest) maximum depends on n and *l*. For fixed *l*, as n increases, the position of the principal maximum moves to larger r values. (For fixed n, the position of the principal maximum moves to shorter r values as $\ell \uparrow$.)

i.e., $(r_{2p})_{max} < (r_{2s})_{max}$; $(r_{3d})_{max} < (r_{3p})_{max} < (r_{3s})_{max}$; $r_{2p\ max} < (r_{3p})_{max}$

Plots of Angular wave functions:

Angular probability density $f^2(\theta, \phi)$ determines the shape of orbitals and its orientation in space. $f(\theta, \phi)$ for s-orbitals does not depend upon angles θ & ϕ, for all other orbitals $f(\theta, \phi)$ will be a function in terms of θ & ϕ. The angular probability density curves are same as the shape and orientation of the orbital in space.
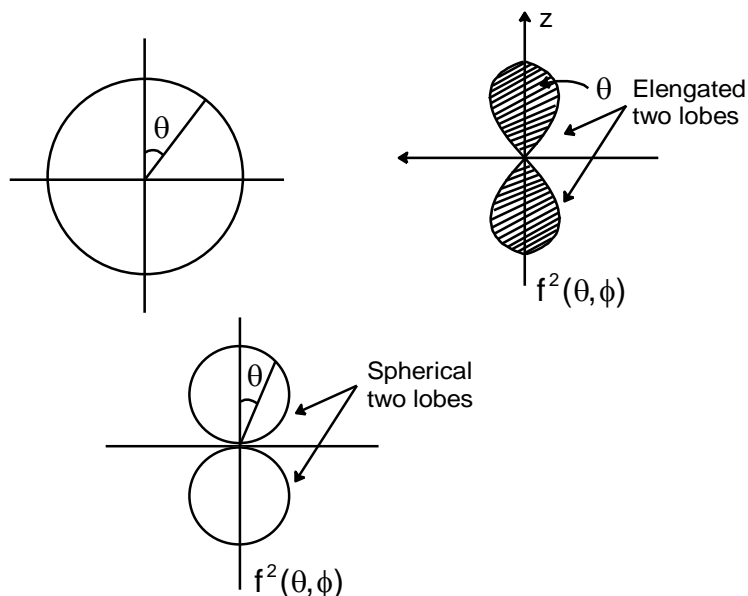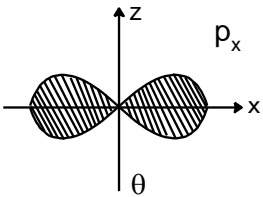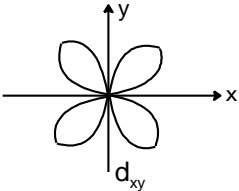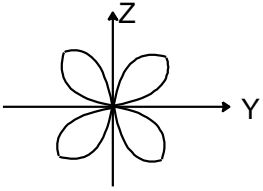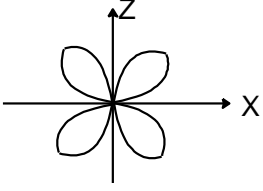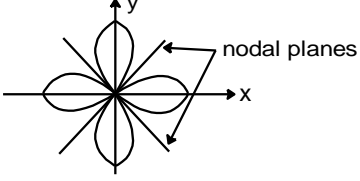
Angular nodes (Nodal Planes):

Total no. of angular nodes for any orbital = ℓ

For s orbital there will be no angular node.

For p_x orbital, $\ell = 1 \Rightarrow$ no. of angular nodal = 1 (yz plane) Similarly, For p_y orbital, nodal plane (xz plane) For p_z orbital, nodal plane (xy plane)	
For d_{xy} orbital, $\ell = 2$ therefore 2 nodal planes, nodal planes: xz & yz planes	
For d_{yz} orbital, xy & xz planes are nodal planes.	
For d_{zx} orbital, xy & yz planes are nodal planes.	
$d_{x^2-y^2}$	

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

no. of angular nodes = ℓ

total no. of nodes = $n - \ell - 1 + \ell = (n - 1)$

No. of peaks in ψ_r^2 vs r curve is $(n - \ell)$

ATOMIC STRUCTURE

12.4   SHAPES OF ATOMIC ORBITALS

An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (B > 90%). The shape of this region (electron cloud) gives the shape of the orbital. It is basically determined by the azimuthal quantum number ℓ, while the orientation of orbital depends on the magnetic quantum number (m). Let us now see the shapes of orbitals in the various subshells.

(i)   s−orbital: An electron is considered to be smeared out in the form of a cloud. The shape of the cloud is the shape of the orbital. The cloud is not uniform but denser in the region where the probability of finding the electron in maximum. The radius, at which the value of probability is maximum, is also called Bohr radius.

The orbital with the lowest energy is the 1s orbital. It is a sphere with its center at the nucleus of the atom. The s−orbital is said to spherical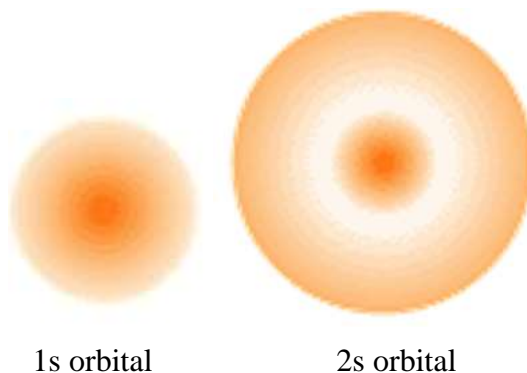ly symmetrical about the nucleus, so that the electronic charge is not concentrated in any particular direction. 2s orbital is also spherically symmetrical about the nucleus, but it is larger than (i.e., away from) the 1s orbital.

1s orbital   2s orbital

Shape of s−orbital

(ii)   p−orbitals: There are three p−orbitals: p_x, p_y and p_z. They are dumb−bell shaped, the two levels being separated by a nodal plane, i.e., a plane where there is no probability of finding the electron. The p−orbitals have a marked directional character, depending on whether p_x, p_y and p_z orbital is being considered. The p−orbitals consist of two lobes with the atomic nucleus lying between them. The axis of each p−orbital is perpendicular to the other two. The p_x, p_y and p_z orbitals are equivalent except for their directional property. They have the same energy. Orbitals having the same energy are said to be degenerate.
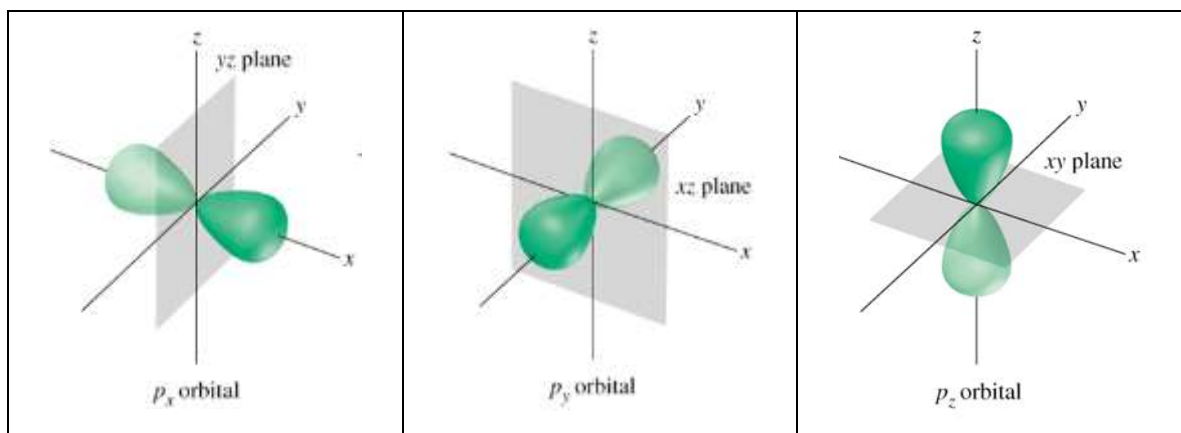
Shapes of p−orbital

(iii) **d–orbitals:** There are five d–orbitals. The shapes of four d–orbitals resemble four leaf cloves. The fifth d–orbital loops differently. The shapes of these orbitals are given below.
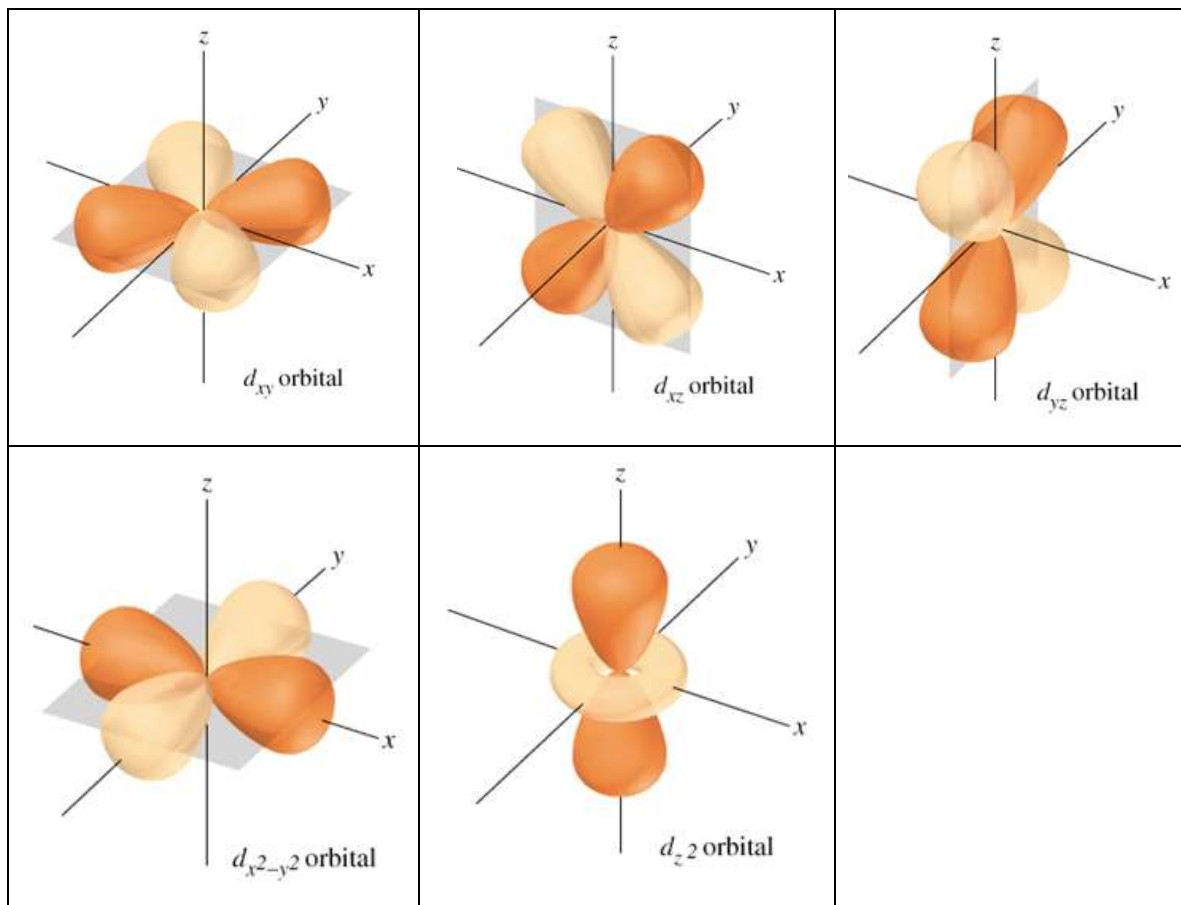
Shapes of d–orbital

13. ELECTRONIC CONFIGURATION

Electronic configuration of an atom is the particular distribution of electrons among available subshells. It is described by a notation that lists the subshell symbols, one after another. Each symbol has a superscript on the right giving the number of electrons in that subshell. For example, a configuration of the lithium atom (atomic number 3) with two electrons in the 1s subshell and one electron in the 2s subshell is written $1s^2 2s^1$. The notation for electron configuration gives the number of electrons in each subshell.

13.1 RULES FOR FILLING OF ELECTRONS IN VARIOUS ORBITALS

The atom is built up by filling electrons in various orbitals according to the following rules.

(i) *Aufbau Principle:* This principle states that the electrons are added one by one to the various orbitals in order of their increasing energy starting with the orbital of lowest energy. The increasing order of energy of various orbital is

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 5f < 6d < 7s < 5f < 6d < 7p < 8s ……

To make it simple to remember, here is given the method to write the increasing order of the orbitals. Starting from the top, the direction of the arrows gives the order of filling of orbitals.
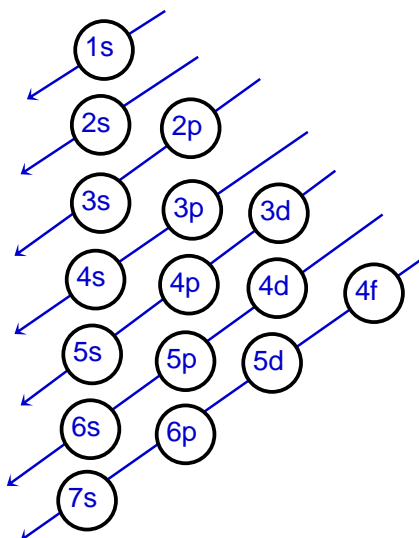
Alternatively, the order of increasing energies of the various orbitals can be calculated on the basis of (n+l) rule.

The energy of an orbital depends upon the sum of values of the principal quantum number (n) and the azimuthal quantum number (l). This is called (n+ l) rule. According to this rule,

"In neutral isolated atom, the lower the value of (n+ l) for an orbital, lower is its energy. However, if the two different types of orbitals have the same value of (n+ l), the orbitals with   lower value of n has lower energy''.

Illustration of (n + l) rule:

Type of orbitals	Value of n	Values of l	Values of (n+ l)	Relative energy
1s	1	0	1+0=1	Lowest energy
2s	2	0	2+0=2	Higher energy than 1s orbital
2p	2	1	2+1=3	2p orbital (n = 2) has lower
3s	3	0	3+1=3	energy than 3s orbital (n = 3)

(n + l) rule is applicable for multi electronic systems only. For uni-electronic system like H, order of energy of orbitals is not "significantly influenced" by l and depends only on the value of n.

(ii)   Pauli's Exclusion principle:

Pauli's Exclusion Principle states that no two electrons in an atom can have same values of all the four quantum number. Now because n, l and m value for one orbital are same, the electrons in an orbital must have different values of spin quantum number. There are only two different values of spin quantum number, one orbital can have maximum two electrons and that too with opposite spin.

Two electrons in an orbital can be represented by $\boxed{\uparrow\downarrow}$ or $\boxed{\downarrow\uparrow}$

(iii)   Hund's rule of maximum multiplicity:

Hund's rule of maximum multiplicity states that during filling of electrons, an atom tends to have maximum spin multiplicity. This rule deals with the filling of electrons in the orbitals of equal energy (degenerate degenerate) orbitals present in same sub shell (p, d and f). According to this rule, "Electron pairing in p, d and f orbitals cannot occur until each orbital of a given subshell contains one electron each or is singly occupied & that too with the same spin.

This is due to the fact that electrons being identical in charge, repel each other when present in the same orbital. This repulsion can, however, be minimized if two electrons move as far apart as possible by occupying different degenerate orbitals. All the electrons in a degenerate set of orbitals will have same spin.

- **Multiplicity is given by 2|S| + 1. Can you now comment why the rule is called Hund's rule of maximum multiplicity.**

13.2 ELECTRONIC CONFIGURATION OF ELEMENTS

Electronic configuration is the distribution of electrons into different shells, subshells and orbitals of an atom.

$$n\,l^{\,x}$$

Number of electrons in the subshell

Principal quantum number

Symbol of subshell or orbitals (s, p, d, f)
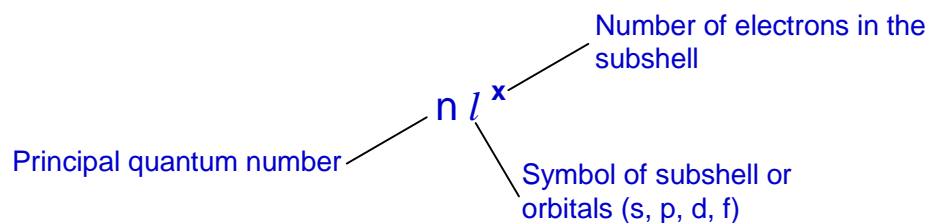
Alternatively, orbital can be represented by a box and an electron with its direction of spin by arrow. To write the electronic configuration, we need to know (i) the atomic number (ii) the order in which orbitals are to be filled (iii) maximum number of electrons in a shell, sub–shell or orbital.

(A)   Each orbital can accommodate two electrons

(B)   The number of electrons to be accommodated in a subshell is $2 \times$ number of orbitals in subshell.

Subshell	Maximum number of electrons

s	2
p	6
d	10
f	14

(C) The maximum number of electron in each shell (K, L, M, N…) is given by $2n^2$. Where n is the principal quantum number.

(D) The maximum number of orbitals in a shell is given by n^2 where n is the principal quantum number. Therefore, maximum number of electrons in a shell is $2n^2$.
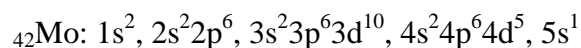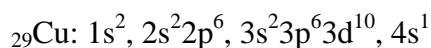
Some Exceptional electronic configuration:

$_{24}$Cr: $1s^2, 2s^22p^6, 3s^23p^63d^5, 4s^1$ $\qquad$ $_{47}$Ag: $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^{10}, 5s^1$

$_{29}$Cu: $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^1$ $\qquad$ $_{42}$Mo: $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^64d^5, 5s^1$
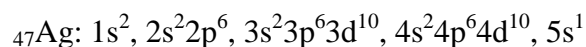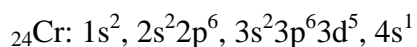
13.3 EXTRA STABILITY OF HALF-FILLED AND FULLY-FILLED SUB SHELL

The electronic configuration of most atoms follows the Aufbau's rule. However, in certain elements such a Cr, Cu etc. electron fills in 3d subshell in preference to 4s provided 3d subshell becomes either half-filled or fully filled.

It has been found that there is extra stability associated with these electronic configurations. This stabilization is due to the following two factors:

(i) Symmetrical distribution of electron:

It is well known that symmetry leads to stability. The completely filled or half-filled subshells have symmetrical distribution of electrons in them and are therefore more stable. This effect is more dominant in d and f-orbitals.

This means three or six electrons in p-subshell, 5 or 10 electrons in d-subshell, and 7 or 14 electrons in f-subshell forms a stable arrangement.

(ii) Exchange Energy:

This stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half-filled or full filled. As a result the exchange energy is maximum and so is the stability.

(1) 4-exchanges by electron 1   (2) 3-exchanges by electron 2   (3) 2-exchanges by electron 3   (4) 1-exchanges by electron 4
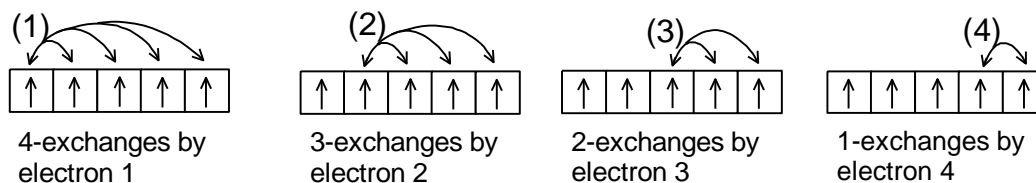
Total exchanges = 10

If n is the number of electron with parallel spins then can you calculate total number of possible exchanges?

$_{24}$Cr : ↑ ↑ ↑ ↑ ↑↓ Total exchanges possible are = 6

↑ ↑ ↑ ↑ ↑ ↑ Total exchanges possible are = 10

The stabilization due to exchange energy will compensate for the energy required for excitation from 4s to 3d.

13.4 ELECTRONIC CONFIGURATION OF IONS

Note that while filling electrons in various orbitals they are filled according to the three laws: Aufbau principle, Pauli's Exclusion Principle and Hund's rule. For removing electrons to form cations, electrons are removed from **outermost shell** as they are bound to the nucleus by weakest forces of attraction because of shielding effect.

For example for iron, $_{26}$Fe $\rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^6, 4s^2$ & the configuration of ions would be:

$Fe^{2+} \rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^6$ & $Fe^{3+} \rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^5$

Similarly for copper $_{29}$Cu $\rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^{10}, 4s^1$ & for its ions

$Cu^+ \rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^{10}$ & $Cu^{2+} \rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^9$

The anions are formed by adding electrons to the vacant orbital of lowest energy [(n + l) rule]

For example $_9$F $\rightarrow 1s^2, 2s^2\, 2p^5$ & that of its ion F$^-$ $\rightarrow 1s^2, 2s^2\, 2p^6$

Similarly for Chlorine $_{17}$Cl $\rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^5$ & that of Cl$^-$ $\rightarrow 1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6$
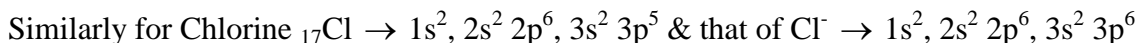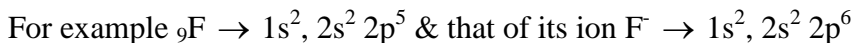
13.5 Application of Electronic Configuration

(i) Calculation of Magnetic Moment (μ): $\Rightarrow \mu = \sqrt{n(n+2)}$ Bohr Magneton

Where n $\rightarrow$ no. of unpaired electrons & 1 BM (Bohr Magneton) = $\dfrac{e.h}{4\pi m_e}$

When $\mu = 0$, Diamagnetic, repelled by magnetic field.

If $\mu \neq 0$, Paramagnetic, attracted by magnetic field.

(ii) Colour: It has been observed that the species having partially filled d sub-shell generally impart colour.

ATOMIC STRUCTURE

MIND MAP

1. According to the quantum theory, the radiant energy is emitted by atoms & molecules in small discrete amounts (quanta), rather than over a continuous range. The energy of each quanta is given by $E = h\nu$

2. According to Bohr model, the angular momentum of an electron is an integral multiple of $\dfrac{h}{2\pi}$. Bohr's model is applicable single electron species (hydrogen like species).

3. The radius of an orbit is given by $r = \dfrac{n^2h^2}{4\pi^2kZme^2}$. The velocity of an electron in an orbit is given by $v = \dfrac{nh}{2\pi mr}$ and the energy of an electron in an orbit is given by $E = \dfrac{-2\pi^2k^2Z^2me^4}{n^2h^2}$

9. In photoelectric effect, electrons are ejected from the surface of certain metal exposed to light of at least a certain minimum frequency called threshold frequency.
$h\nu = h\nu_\circ + K.E$

4. In Bohr model, an electron emits a photon when it drops from a higher energy state to a lower energy state.

ATOMIC STRUCTURE

8. Four quantum numbers characterize each electron in an atom. The principal quantum number(n) identifies the main energy level, the angular quantum number (l) indicates shape of orbital, the magnetic quantum number (m) specifies orientation of orbital in space and the spin quantum number (s) indicates the direction of the electron's spin on its axis.

5. The emission spectra of hydrogen is obtained when electron from an excited state is deexcited to the ground state. The release of specific amounts of energy in the form of photons accounts for the lines in the hydrogen spectrum. $\bar{\nu}$ of each line in the spectrum can be given by $\dfrac{1}{\lambda} = R_H z^2\left[\dfrac{1}{h_i^2} - \dfrac{1}{h_f^2}\right]$

7. An orbital may be defined as a region in space around the nucleus where the probability of finding the electron is maximum.

6. De Broglie extended Einstein's wave –particle description of light to all matters in motion. The wavelength of a moving particle of mass m and velocity ν is given by de Broglie equation, $\lambda = \dfrac{h}{m\nu}$.