03 Atomic Structure

Introduction:

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 'uncuttable' or '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. The atomic theory of matter was first proposed on a firm scientific basis by **John Dalton**, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter.

Dalton Atomic Theory:

(i) Atom is the smallest particle of any substance which cannot be divided further.

(ii) Atoms can neither be created nor be destroyed. Only the rearrangement of atoms occurs in chemical reactions.

(iii) All the atoms are hard and dense.

(iv) All the atoms of an element are identical but the atoms of different elements will be different.

(v) A compound is formed by the combinations of atoms of different elements in a fixed ratio by mass.

We start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into subatomic particles, i.e., electrons, protons and neutrons. a concept very different from that of Dalton. The major problems before the scientists at that time were:

- to account for the stability of atom after the discovery of sub-atomic particles,
- to compare the behaviour of one element from other in terms of both physical and chemical properties,
- to explain the formation of different kinds of molecules by the combination of different atoms and,
- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

Sub-atomic Particles:

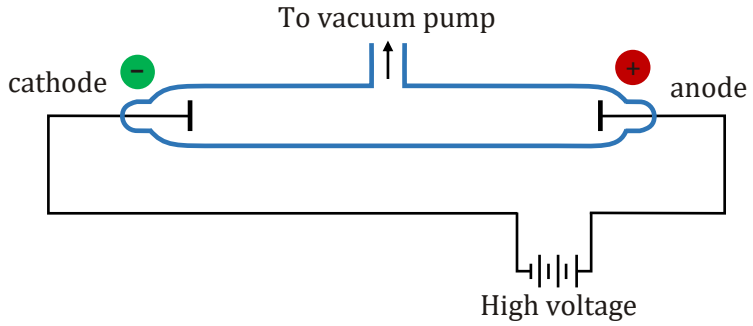
Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century.

Discovery of Electron:

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. These results suggested the particulate nature of electricity.

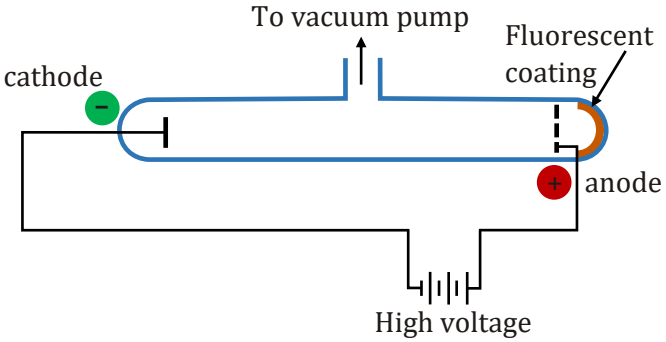
An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles: "Like charges repel each other and unlike charges attract each other".

In mid 1850 many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**.



A cathode ray discharge tube

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 could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, current starts flowing through 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 fluorescent or phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot on the coating is developed (same thing happens in a television set)



A cathode ray discharge tube with perforated anode

The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result 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.

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of 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.

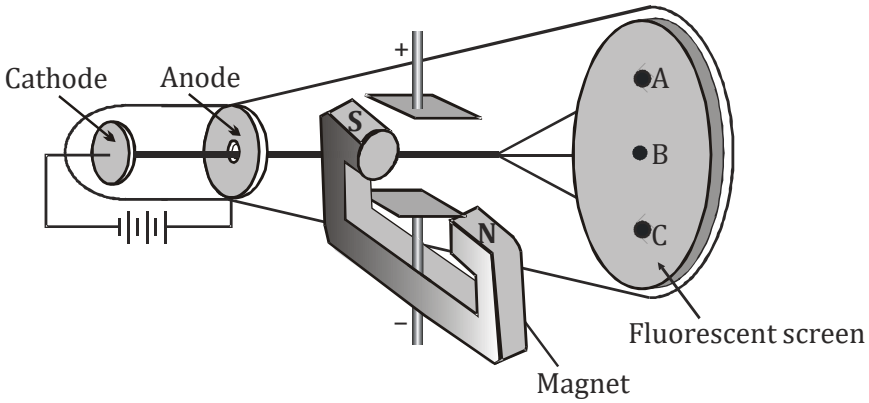
Charge to Mass Ratio of Electron:

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon :

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.

(ii) the mass of the particle lighter the particle, greater the deflection.

(iii) the strength of the electrical or magnetic field, the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.



The apparatus to determine the charge to the mass ratio of electron

When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly, when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path followed as in the absence of electric or magnetic field and they hit the screen at point B. By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/m_e as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\,C\,kg^{-1}$$

where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is –e.

Charge on the Electron:

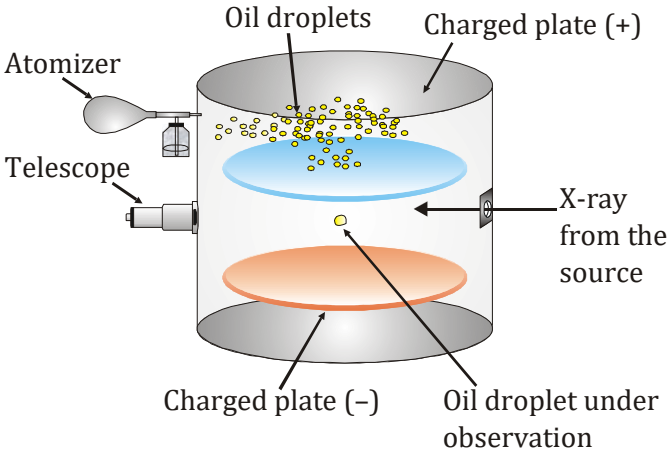
R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found that the charge on the electron to be -1.6×10^{-19} C. The present accepted value of electrical charge is -1.6022×10^{-19} C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.6022\times10^{-19}\,C}{1.758820\times10^{11}\,C\,kg^{-1}} = 9.1094\times10^{-31}\,kg$$

Millikan's Oil Drop Method:

In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micro meter eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, 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....

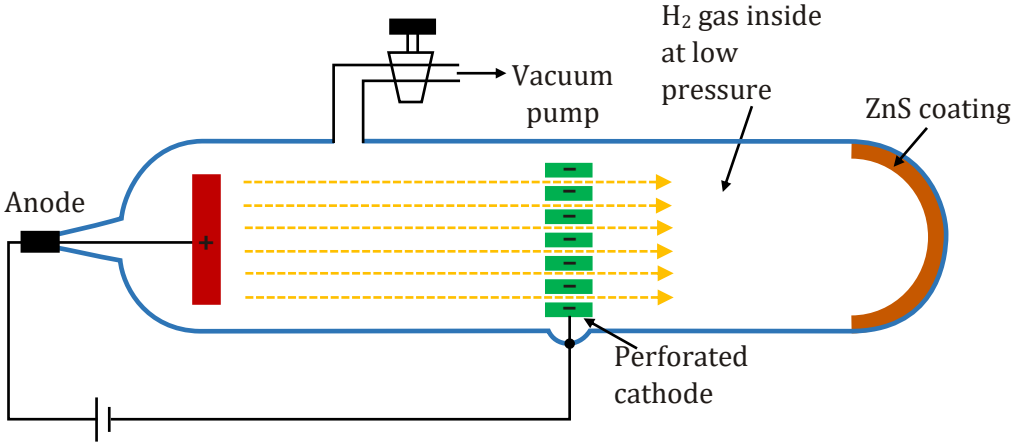
The highest common factor (HCF) of charges on oil droplet was taken as charge on electron.



The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electric field and a viscous drag force when the oil drop is moving.

Canal rays (or anode rays) – discovery of proton:

Atoms are electrically neutral. Hence after the discovery of the negatively charged constituent (electron) of an atom, attempts were made to discover the positively charged counterpart of electrons. By using a discharge tube containing a perforated cathode, ***Goldstein (1886)*** found that some rays passed through these holes in a direction opposite to that of the cathode rays.



Positive Rays or Canal Rays

Electrical discharge carried out in the modified cathode ray tube led to the discovery of particles carrying positive charge, also known as **canal rays**. The characteristics of these positively charged particles are listed below.

(i) Unlike cathode rays, the positively charged particles depend upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

(ii) The charge to mass ratio of the particles is found to depend on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen and was called proton. This positively charged particle was characterised in 1919.

The lightest positively charged particle is called a proton (P or $P^{\oplus}$). Positive rays are atomic or molecular cations from which some electrons have been removed. The removed electrons constitute the cathode rays and the positive cations form the positive or canal rays.

Discovery of neutron:

After the discovery of electron and proton ***Rutherford (1920)*** predicted the existence of a neutral fundamental particle. In ***1932, Chadwick*** bombarded the element Beryllium with α-particles and noticed the emission of a radiation having the following characteristics.

(i) The radiation was highly penetrating.

(ii) The radiation was unaffected by magnetic and electric fields which shows that it is electrically neutral.

(iii) It was found to have approximately the same mass as the protons.

The name 'neutron' was given to this sub-atomic particle. It is denoted by n or ${}_0n^1$. Bombardment of beryllium by α-particles results in the formation of carbon and also neutrons are emitted.

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

Mass of a neutron is 1.00867 amu (1.67493×10^{-24}g or 1.67493×10^{-27} kg)

Properties of fundamental particles:

Atoms are made up essentially, of three fundamental particles, which differ in mass and electric charge as follows :

	Electron	Proton	Neutron
Symbol	e or $e^{\ominus}$	P or $P^{\oplus}$	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	–1	+1	0
Mass in kg	9.10939×10^{-31}	1.67262×10^{-27}	1.67493×10^{-27}
Mass in amu	0.00054	1.00727	1.00867
Actual charge/C	-1.6022×10^{-19}	$+1.6022 \times 10^{-19}$	0

Illustration 1:

Arrange the particle in their increasing order of specific charge ratio.

(a) $e^{\oplus}$, P, n, α-particle (b) $Na^{\oplus}$, $Li^{\oplus}$, $F^{\ominus}$, $Mg^{2\oplus}$, $Al^{3\oplus}$

Solution:

(a) $\left(\frac{e}{m}\right)_e = \frac{1e}{\left(\frac{1}{1836}\right)amu}$

$\left(\frac{e}{m}\right)_P = \frac{1}{1} = 1 = \frac{1e}{1amu}$

$\left(\frac{e}{m}\right)_n = \frac{0}{1} = 0 = \frac{0e}{1amu}$

$\left(\frac{e}{m}\right)_\alpha = \frac{2}{4} = \frac{1}{2} = \frac{2e}{4amu}$

$n < \alpha < p < e^{\ominus}$

(b) $Na^{\oplus} = \frac{1}{23}$; $Li^{\oplus} = \frac{1}{7}$; $F^{\ominus} = \frac{1}{19}$; $Mg^{2\oplus} = \frac{2}{24} = \frac{1}{12}$; $Al^{3\oplus} = \frac{3}{27} = \frac{1}{9}$

$Na^{\oplus} < F^{\ominus} < Mg^{2\oplus} < Al^{3\oplus} < Li^{\oplus}$

Illustration 2:

Which of the following pairs have same specific charge $\left(\frac{e}{m}\right)$?

(a) electron & proton (b) electron & positron (c) proton & positron

(d) proton & deutron (e) α-particle & deutron

Solution:

(b) $\left(\frac{e}{m}\right)_e = \left(\frac{e}{m}\right)_{positron} = \frac{1}{1}$

(e) $\left(\frac{e}{m}\right)_\alpha = \frac{2}{4} = \frac{1}{2}$

$\left(\frac{e}{m}\right)_{deutron} = \frac{1}{2}$

Illustration 3:

Through what potential difference an α-particle should be accelerated to have speed 5×10^6 m/s.

Solution:

$qV = \frac{1}{2}mv^2$

$(2 \times 1.6 \times 10^{-19} \times V) = \frac{1}{2} \times 4 \times 1.66 \times 10^{-27} \times (5 \times 10^6)^2$

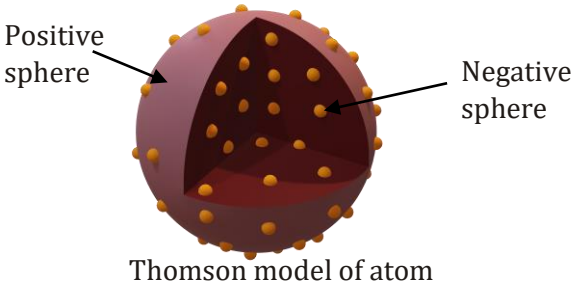
Atomic Models:

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, proposed by J. J. Thomson and Ernest Rutherford are discussed below.

Thomson Model of Atom:

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement. Many different names are given to this model, **for example, plum pudding, raisin pudding or watermelon**. This model can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments.

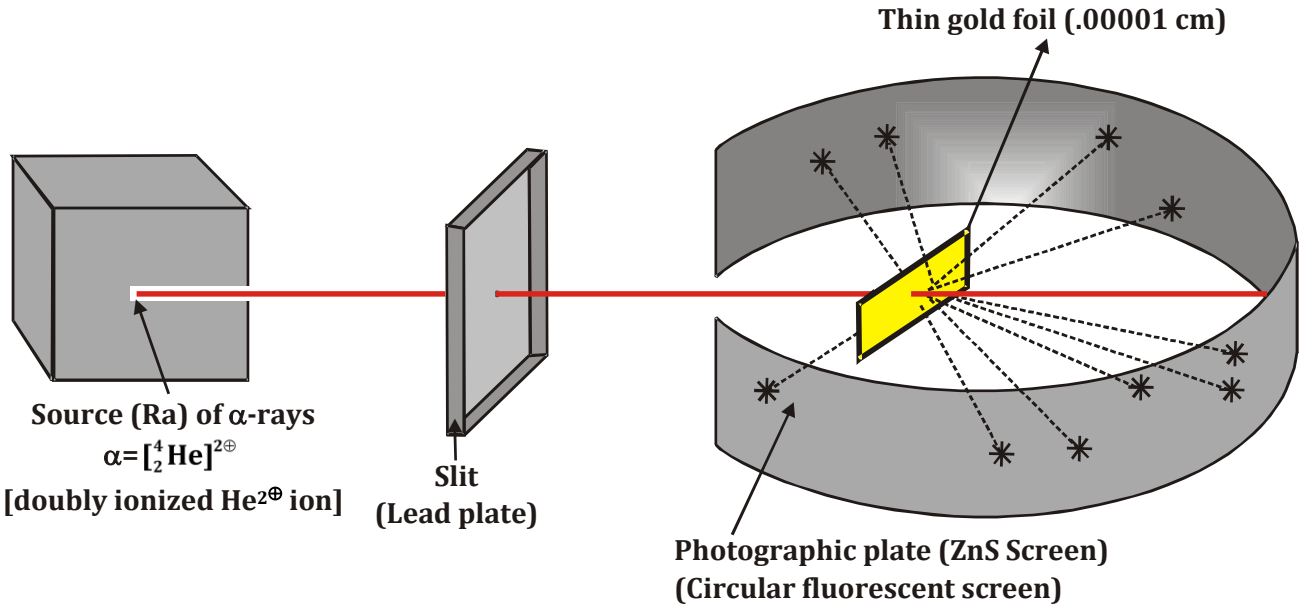
Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

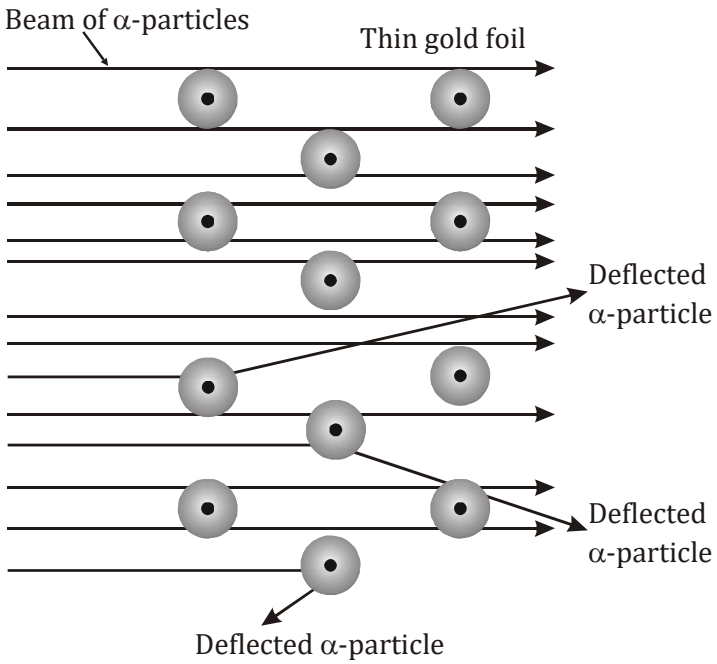


Thomson model of atom

Rutherford's Model:

Rutherford's α-scattering experiment





B. Schematic molecular view of the gold foil

Observations and conclusions:

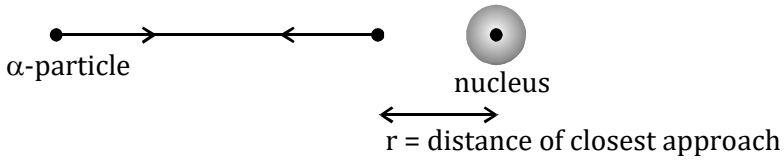
(i) Most of the α-particles passed through the gold foil undeflected. Hence, most of the space in the atom is empty.

(ii) A small fraction of α-particles was deflected by small angles. A very few α-particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α-particles. Rutherford given the name **nucleus** to this positively charged centre of atom.

(iii) The volume occupied by the nucleus is negligibly small as compared to the total volume of atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.

Rutherford estimated the size of nucleus by calculating the distance of closest approach.



The initial kinetic energy of α-particle must be equal to potential energy at distance of closest approach.

$$\text{K.E.} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{q_1\cdot q_2}{r} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{(2e)\cdot(Ze)}{r} \qquad \left\{\frac{1}{4\pi\varepsilon_0} = \text{coulamb's constant} = 9\times10^9\,\text{kgm}^3/\text{s}^2\text{c}^2\right\}$$

$$\boxed{r = \frac{2Ze^2}{(4\pi\varepsilon_0)(\text{K.E.})}}$$

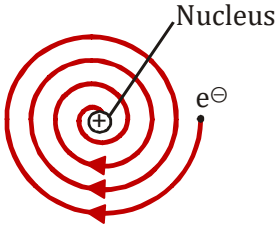
where Z = atomic number of elements used in foil.

(iv) Almost all mass of the atom is densely concentrated in extremely small region (nucleus).

(v) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks of Rutherford model:

(i) According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink.



Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.

(ii) It does not explain the arrangement of electrons revolving around nucleus.

(iii) It does not explain the stability of nucleus against strong repulsive forces.

(iv) It does not explain atomic spectrum.

Illustration 4:

An α-particles of kinetic energy of 5.4 MeV is projected towards gold nucleus. Calculate the distance of closest approach. (Atomic number of gold = 79, 1 eV = 1.6×10^{-19} J)

Solution:

$$\text{K.E.} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{q_1q_2}{r}$$

or $5.4 \times 10^6 \times 1.6 \times 10^{-19} = 9 \times 10^9 \times \dfrac{(2\times1.6\times10^{-19})\times(79\times1.6\times10^{-19})}{r}$

$\therefore$ $r = 4.21 \times 10^{-14}$ m

Illustration 5:

An α-particles is projected towards the following nucleus with same kinetic energy in different experiment the distance of closest approach is maximum for

(A) Na (Z = 11) (B) Ca (Z = 20) (C) Ag (Z = 47) (D) Au (Z = 79)

Ans. (D)

Solution:

r (distance of closest approach) $\propto$ Charge on the nucleus of the metal

$\therefore$ order : Na < Ca < Ag < Au

Illustration 6:

An α-particle, a proton, a deuteron and a neutron are projected towards the same nucleus with the same kinetic energy in different experiment. The distance of closest approach is minimum for

(A) α (B) P (C) d (D) n

Ans. (D)

Solution:

r (distance of closest approach) ∝ Charge on the particle

∴ neutron has least value of distance of closest approach.

Illustration 7:

An α-particle having K.E. = 7.7 MeV is scattered by gold (Z = 79) nucleus through 180°. Find distance of closest approach.

Solution:

K.E. = 7.7 M eV

$= 7.7 \times 10^{6} \times 1.6 \times 10^{-19}$ J

$= 1.23 \times 10^{-12}$ J

$$\text{K.E.} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r_0}$$

$$\frac{1}{4\pi\varepsilon_0} = 9\times10^{9}\,\text{Nm}^2\text{C}^{-2}$$

$$r_0 = \frac{9\times10^{9}\times2\times79\times(1.6\times10^{-19})^2}{1.23\times10^{-12}}$$

$r_0 = 3 \times 10^{-14}$ m

From the above example it is clear that nuclear dimension cannot be greater than 3×10^{-14} m.

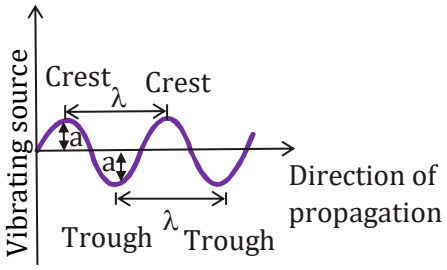
Wave Theory:

A wave is defined as a periodic disturbance in space or in a medium that involves elastic displacement of material particles or a periodic change in some physical quantities such as T, P, V etc. Thus, wave motion represents propagation of a periodic disturbance carrying energy. The wave travels at right angles to the vibratory motion of the object.

When an object moves up and down or vibrates continuously, energy in the form of waves is transmitted by a vibrating object to a distant place. For example, when a stone is thrown in a still water of a pond, a disturbance is produced at a place where the stone strikes the water.

This disturbance advances outwards in the same form and reaches the edges of the pond. Such a disturbance is called a ***mechanical wave***. The mechanical waves transmit only in a material medium. Besides the mechanical waves, there are waves which do not require any medium for their transmission. These waves are called ***electromagnetic waves*** or ***electromagnetic radiations.***

Wave Characteristics:



I. Wavelength (λ) :

It is defined as the distance between two nearest crests or nearest troughs.

It is measured in terms of a Å (Angstrom), pm (Picometre), nm (nanometres), cm(centimetre), m (metre)

1 Å = 10^{-10} m, 1 pm = 10^{-12} m, 1 nm = 10^{-9} m, 1 cm = 10^{-2} m

II. Frequency (ν) :

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

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

  1 Hertz = 1 sec^{-1}

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

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

IV. Velocity (c) :

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

$c = \lambda / T = \lambda\nu$ $\quad \nu = c/\lambda$ $\quad c = \nu\ (sec^{-1}) \times \lambda\ (m)$ $\quad c = \nu\lambda\ (m\ sec^{-1})$

Since c is constant for electromagnetic waves.

i.e. frequency is inversely proportional to λ

V. Wave number ($\bar{\nu}$) :

It is defined as number of waves per unit length. It is denoted by $\bar{\nu}$ & is expressed in cm^{-1}.

λ m $\rightarrow$ 1 wave

1 m $\rightarrow 1/\lambda$ waves

$\bar{\nu} = \frac{1}{\lambda}$ $\quad (1\ cm^{-1} = 100\ m^{-1})$

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

VI. Amplitude (a) :

It is the height of the crest or depth of the trough of a wave and is denoted by 'a'. It is half the vertical distance from the top of the wave to the bottom of the wave. It determines the intensity or brightness of the beam of light.

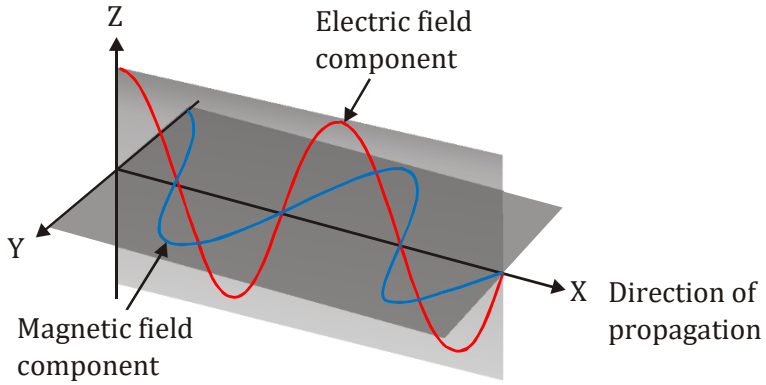
The amplitude of a wave in stretched string is the maximum displacement of the string from its normal position that of water waves is the maximum height of the water surface relative to its normal level, that of a sound wave is the maximum change in pressure relative to the normal pressure.

Electro Magnetic (EM) Waves:

James Maxwell (1870) suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted by it. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiations.

Main assumptions of Maxwell EM theory:

(i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.



(The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.)

(ii) Unlike sound waves or water waves, electromagnetic waves do not require medium and can move in vacuum. (However, speed changes in different mediums)

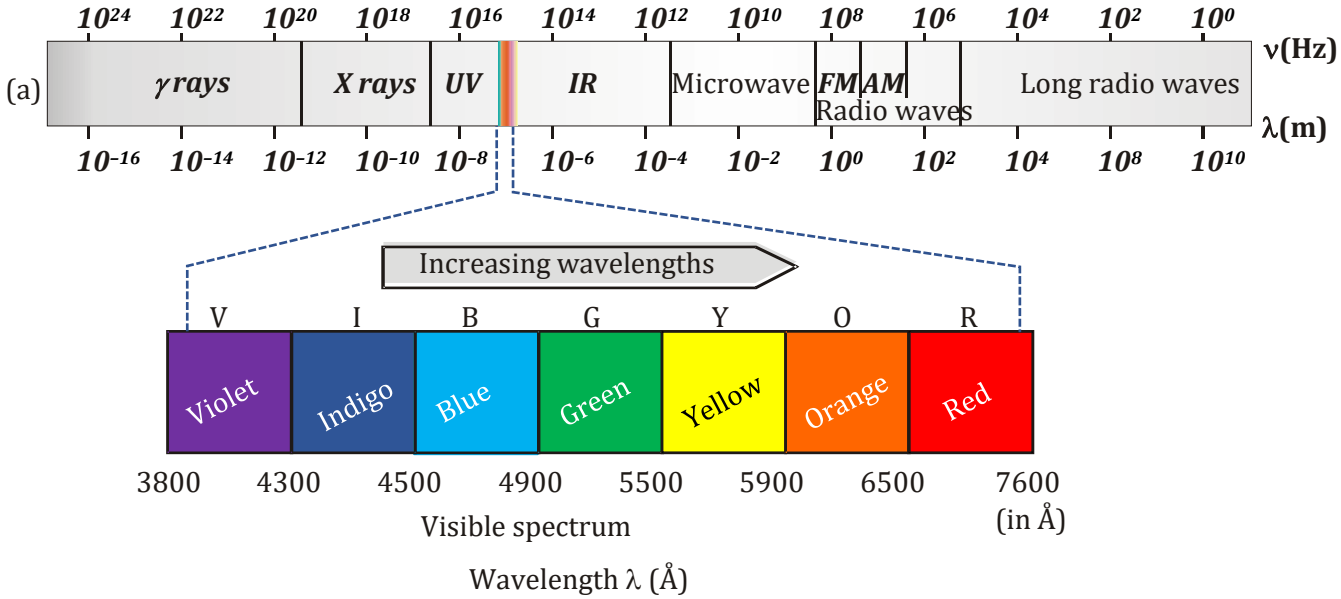
(iii) The EM waves travel with the velocity of light (3×10^8 m/sec) in vacuum.

(iv) Energy of EM waves depends on its amplitude not on its frequency or wavelength. (This assumption was later proved to be wrong in some situations).

Electromagnetic spectrum:

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelength or frequencies is known as electromagnetic spectrum. The wavelength decreases in the following order.

Radio waves > microwaves > Infrared > Television waves > Visible > Ultraviolet > X-rays > γ-rays > cosmic rays



(a) The spectrum of electromagnetic radiation (b) Visible spectrum
The visible region is only a small part of the entire spectrum.

Illustration 8:

Calculate the frequency of EMR (Electromagnetic radiation) of wave number 10^4 cm^{-1}.

Solution:

$\nu = \frac{c}{\lambda} = c\bar{\nu}$ = (3 × 10^8 m/s)(10^4 cm^{-1}) = (3 × 10^{10} cm/s)(10^4 cm^{-1}) = 3 × 10^{14} Hz.

Illustration 9:

A radio station radiates the radio waves of frequency 20kHz. What is meter band of that radio station?

Solution:

$20kHz = \frac{3\times10^8}{\lambda} \Rightarrow \lambda$ = 1.5 × 10^4 m

Black Body Radiation:

In 1900, Max Planck was the first to give a concrete explanation for the phenomenon of black body radiation. According to the Max Planck theory, an ideal body which is a perfect absorber and perfect emitter of radiation and is called a black body. The radiation emitted by such a body is called black body radiation. When such a body is heated, it emits radiation over a wide range of wavelengths.

For Example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. On heating further, the radiation emitted becomes white and then blue as the temperature becomes very high. In terms of frequency, it means that the radiation emitted goes from a lower frequency to a higher frequency as the temperature increases. The red colour lies in the lower frequency region while the blue colour belongs to the higher frequency region of the electromagnetic spectrum. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature. At a given temperature, the intensity of radiation emitted increases with a decrease in wavelength, reaches a maximum value at a given wavelength, and then starts decreasing with further decrease in wavelength, as shown in Figure.

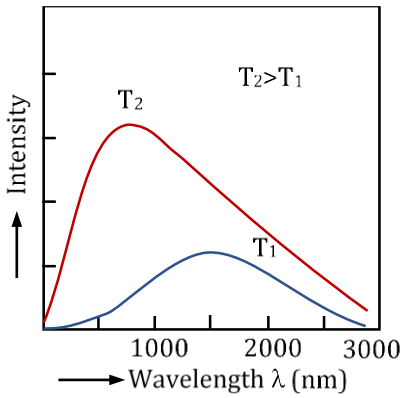


Figure : Wavelength-intensity relationship

The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. In 1900, Max Planck provided an explanation for this behavior. He said that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in an arbitrary amount or in a continuous manner (Figure) as was believed till then. Planck gave the name quantum to the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation. The energy of a quantum of radiation is proportional to its frequency and is expressed as

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

Where ν = frequency

$\bar{\nu}$ = wavenumber

λ = wavelength

c = velocity

The proportionality constant, h, is known as the Planck constant and has the value 6.626×10^{-34} J s. According to Planck's theory, energy is always emitted in integral multiples of hν, for example hν, 2hν, 3hν, etc. Planck, however, could not explain why energies should be quantized in this manner. However, with this assumption, Planck could explain the distribution of intensity in radiation from a black body as a function of frequency or wavelength at different temperatures.

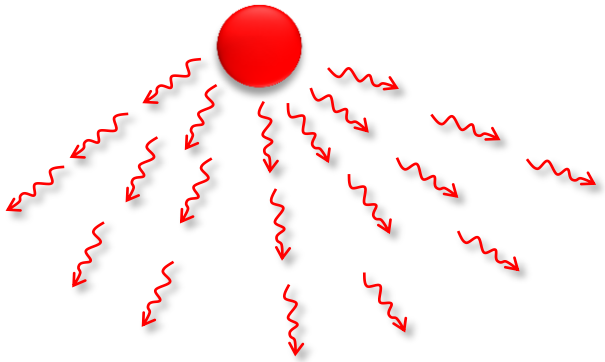


Figure : Heated iron ball emitting energy in discrete quantities

The assumptions of Planck's theory are listed below :

a. Each radiation is always associated with a definite amount of energy and is known as radiant energy.

b. Radiant energy is emitted or absorbed discontinuously in the form of small packets of energy called quanta.

Each wave packet or quantum is associated with a definite amount of energy. In case of light, the quantum of energy is called photon.

c. The amount of energy associated with a quantum of radiation is proportional to the frequency of radiation.

$E \propto \nu$

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

d. The energy emitted or absorbed by a body is always an integral multiple of quanta, i.e., E-nhν, where n = 1, 2, 3, ... etc.

Illustration 10:

Calculate and compare the energies of two radiations, one with a wavelength of 300 nm and the other with 600 nm.

Solution:

Energy of radiation (E) = $h\nu = \frac{hc}{\lambda}$

$$\therefore \quad E_1 = \frac{hc}{\lambda_1} = \frac{6.626\times10^{-34}\,\text{Js}\times3\times10^{8}\,\text{ms}^{-1}}{300\times10^{-9}\,\text{m}}$$

$= 6.626 \times 10^{-19}$ J

and $E_2 = \frac{hc}{\lambda_2} = \frac{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}}{600\times10^{-9}\,m}$

$= 3.313 \times 10^{-19}$ J

The ratio of E_1 and E_2 is

$$\frac{E_1}{E_2} = \frac{6.626\times10^{-19}\,J}{3.313\times10^{-19}\,J}$$

$\therefore \quad E_1 = 2E_2$

Illustration 11:

Calculate energy of one mole of photons of radiation whose frequency as 5×10^{14} Hz.

Solution:

$E = h\nu$

$= (6.626 \times 10^{-34}\ Js)\ (5 \times 1014\ s^{-1})$

$= (3.313 \times 10^{-19}\ J)$

Energy of one mole of photons

$= (3.313 \times 10^{-19}\ J)\ (6.022 \times 10^{23}\ mol^{-1})$

$= 199.51\ kJ\ mol^{-1}$

Illustration 12:

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

Solution:

Power of the bulb = 100 watt

$= 100\ Js^{-1}$

Energy of one photon :

$E = h\nu = hc/\lambda$

$= \frac{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}}{400\times10^{-9}\,m}$

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

Number of photons emitted = $\frac{100\ Js^{-1}}{4.969\times10^{-19}\ J} = 2.012 \times 10^{20}\ s^{-1}$

Illustration 13:

Calculate the number of protons emitted in 10 hours by a 60 W sodium lamp (λ of photon = 5893 Å)

Solution:

Energy emitted by sodium lamp in 1 s.

= Watt × second = 60 × 1 J

Energy of photon emitted = $\frac{hc}{\lambda}$

$= \frac{6.626\times10^{-34}\times3\times10^{8}}{5893\times10^{-10}}$

$= 3.37 \times 10^{-19}$ J

$\therefore$ Number of photons emitted per second = $\frac{60}{3.37\times10^{-19}}$

$\therefore$ Number of photons emitted in 10 hours $= 17.8 \times 10^{19} \times 10 \times 60 \times 60$

$= 6.41 \times 10^{24}$

Illustration 14:

An electromagnetic radiation of wave-length 242 nm is just sufficient to ionise a sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

Solution:

Energy associated with a photon of 242 nm

$$= \frac{6.625\times10^{-34}\times3.0\times10^{8}}{242\times10^{-9}}$$

$$= 8.21 \times 10^{-19}\ J$$

Since one atom of Na requires = 8.21×10^{-19} J for ionization, 6.023×10^{23} atoms of Na for ionization requires $8.21 \times 10^{-19} \times 6.023 \times 10^{-23} = 49.45 \times 10^{4}$ J

$$= 494.5\ kJ\ mol^{-1}$$

Illustration 15:

A bulb emits light of wavelength 4500 Å. The bulb is rated as 150 W and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second?

Solution:

A 150 W bulb emits 150 J of energy per second.

The energy emitted by the bulb as light is $150\times\frac{8}{100} = 12$ J

Let the bulb emit n photons per second.

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

$$\therefore \quad n = \frac{E\times\lambda}{c\times h}$$

$$= \frac{12\,J\times4500\times10^{-10}\,m}{3\times10^{8}\,m\,s^{-1}\times6.63\times10^{-34}\,Js}$$

$$= 2.715 \times 10^{19}$$

Particle Nature of Electromagnetic Radiations:

(Planck's Quantum Theory of Radiation)

Max Planck in 1901, put forward a theory known as **"Planck's Quantum Theory".** It regards electromagnetic radiations made up of particles. This was further extended by *Einstein* in 1905. The main points of the theory are :

(i) The radiant energy is emitted or absorbed by atoms or molecules discontinuously in the form of small energy packets called quanta. In case of light, these energy packets are known as photons.

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

$E \propto \nu$ or $E = h\nu = \frac{hc}{\lambda}$

Here h is a constant known as **Planck's constant.** Its value is 6.626×10^{-34} Joules sec.

(iii) The total amount of energy emitted or absorbed by a body is some whole number multiple of quantum i.e.,

$E = nh\nu$ (Here n is a positive integer : 1, 2, 3, 4 ..... etc.)

Thus, Planck for the first time has given a relationship between the frequency (or wavelength) of the radiations and the energy associated with them. Cosmic rays, gamma rays and X-rays are high energy radiations since they have very high frequency. At the same time, microwaves and radio waves with small frequency are regarded as low energy radiations.

Important features of Photon:

- Source of energy (light) emits radiation in the form of photons, which travel with speed of light.
- Energy of single photon, $E = h\nu = \frac{hc}{\lambda}$.
- All the photons in vacuum travel with speed 3×10^8 m/s but their speed is changed in different medium, however frequency remains same. Speed does not depend on energy.
- Photons travel as waves but are absorbed or emitted as particles.

Illustration 16:

Calculate the energy per quanta of an EMR of frequency 400 MHz.

Solution:

$E = 6.626 \times 10^{-34} \times 4 \times 10^6$ J/quanta

Illustration 17:

Calculate the energy per quanta of an EMR of wavelength 662.6 nm.

Solution:

$$E = n\frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^8}{662.6\times10^{-9}\,m} = 3 \times 10^{-19}\ J/quanta$$

Illustration 18:

Calculate the wavelength (in Å) of an EMR of energy 3.1 eV/quanta.

Solution:

$$E = h\nu = h\frac{c}{\lambda} \Rightarrow E(eV) \times 1.602 \times 10^{-19} = \frac{1\times6.62\times10^{-34}\times3\times10^8}{\lambda(Å)}$$

$$\boxed{E(eV) \approx \frac{12400}{\lambda(Å)} = \frac{1240}{\lambda(nm)}}$$

Illustration 19:

A bulb is rated as 110 watt. If it emits 25% of absorbed energy as red light (λ = 6626Å), how many photons are emitted out by the bulb per second.

Solution:

$$110\times\frac{25}{100} = n\times\frac{6.626\times10^{-34}\times3\times10^8}{6626\times10^{-10}}$$

Illustration 20:

The wavelength of microwave radiation is 0.08 m. How many moles of photons is needed to increase the temperature of 400 gm water from 25° to 45°C, assuming 25% efficiency.

Specific heat capacity = 4.2 J/K-gm

Solution:

$$\left(\frac{nhc}{\lambda}\right)\times\frac{25}{100} = ms\Delta t$$

$$n \times \frac{6.626\times10^{-34}\times3\times10^{8}}{0.08}\times\frac{25}{100} = 400 \times 4.2 \times 20$$

$\therefore$ Number of moles of photon $= \frac{n}{N_A}$

Illustration 21:

A dye absorbs the radiation of 4000 Å and fluoresces the radiation of 5000 Å. If only 40% of the absorbed energy is emitted out, calculate the ratio of number of quanta emitted out and the number of quanta absorbed.

Solution:

$$E_a \times \frac{40}{100} = E_e$$

$$n_a \times \frac{hc}{4000\text{Å}} \times \frac{40}{100} = n_e \times \frac{hc}{5000\text{Å}}$$

$$\frac{n_e}{n_a} = \frac{40}{100}\times\frac{5000}{4000} = \frac{1}{2}$$

Illustration 22:

The bond dissociation energy of Cl–Cl bond in chlorine gas is 240 kJ/mol. Calculate the longest wavelength of EMR needed to dissociate bond. Assume one photon may dissociate only one bond.

Solution:

$$\frac{240\times10^{3}}{6\times10^{23}} = \frac{1\times6.626\times10^{-34}\times3\times10^{8}}{\lambda}$$

Illustration 23:

A near ultra violet photon of wavelength 300 nm is absorbed by a gas and then emitted as two photons. One photon is of red light with wavelength 760 nm. What would be the wave length of the second photon ?

Solution:

It may be noted that energy of photon which adsorbed is emitted as sum of the energy of two photons.

Energy absorbed $h\nu = \frac{hc}{\lambda}$

According to available information,

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}; \frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}; \frac{1}{\lambda_2} = \left[\frac{1}{\lambda} - \frac{1}{\lambda_1}\right]$$

Now, λ = 300 nm ; λ_1 = 760 nm ; λ_2 can be calculated as :

$$\frac{1}{\lambda_2} = \left[\frac{1}{300} - \frac{1}{760}\right] = \frac{760-300}{300\times760}(\text{nm}^{-1})$$

$$\frac{1}{\lambda_2} = \frac{460}{760\times300}(\text{nm}^{-1})$$

or λ_2 = 496 nm.

Photoelectric effect:

Hertz in ***1887*** 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**.

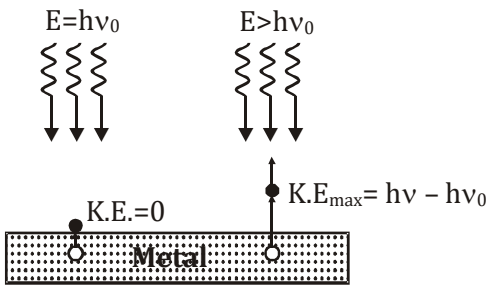
A few metals, which are having low ionisation energy like Caesium, show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light.

The experimental findings are summarized as below :

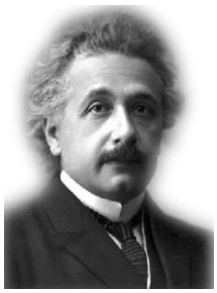
- Electrons come out as soon as the light (of sufficient energy) strikes the metal surface. There is no time lag between the two events.
- The light of any frequency will not be able to cause ejection of electrons from a metal surface. There is a minimum frequency, called the **threshold (or critical) frequency**, which can just cause the ejection. This frequency varies with the nature of the metal. The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light.
- Photoelectric current is increased with increase in intensity of light of same frequency, if emission is permitted, i.e. a bright light yields more photoelectrons than a dim one of the same frequency, but the electron energies remain the same.

Einstein's explanation:

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



This energy enables the electron to break away from the surface by overcoming the attractive influence of the nucleus. Thus, each photon can eject one electron. If the frequency of light is less than ν_0, there is no ejection of electron. If the frequency of light is higher than ν_0 (let it be ν), the photon of this light having higher energy ($h\nu$), will impart some energy to the electron that is needed to remove it away from the atom. Einstein proposed that light consisted of quanta, which we call photons with a frequency over a certain threshold would have sufficient energy to eject a single electron, producing the photoelectric effect.



Albert Einstein (1879 - 1955)

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, **Albert Einstein (1879 - 1955)** while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photo-electric effect.

Einstein's Equation for the Photoelectric Effect :

Einstein's interpretation of the photoelectric effect results in equation :

Energy of photon = Energy needed to remove an electron + Maximum Kinetic energy of the emitted electron.

The excess energy would give a certain velocity (i.e. kinetic energy) to the electron.

$$h\nu = h\nu_0 + K.E._{max.}$$

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

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

where ν = frequency of the incident light, ν_0 = threshold frequency

v = max. speed of photoelectron.

$h\nu_0$ is the **threshold energy** (or) the **work function** denoted by $\phi = h\nu_0$ (minimum energy of the photon to liberate electron). It is constant for particular metal.

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

Important conclusions from photoelectric effect :

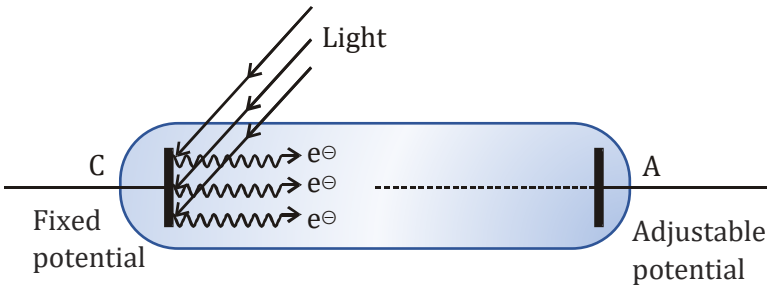
(i) Photoelectric effect demonstrates particle nature of radiation.

(ii) A photon is quanta of energy. Its rest mass is zero. This is why photon can give up its all energy to the particle it strikes.

(iii) There is no effect of frequency of incident light on the number of the emitted photoelectrons.

(iv) There is no effect of intensity of incident light on the K.E. of the emitted photoelectrons.

Saturation current & stopping potential



Case-I : $V_C = V_A$

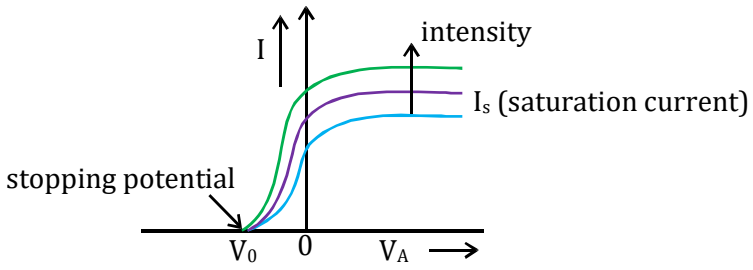
Some of the ejected electrons reach at electrode A resulting photocurrent.

Case-II : $V_C < V_A$

As electrode (A) is at high potential it attracts the electron & even a slower electron will reach at electrode A. It will result in increase in photocurrent. Further increase in the potential difference, a situation may result when the slowest photocurrent electron reaches the electrode. It results in maximum current called **saturation current.** Further increase in potential will not increase photocurrent.

Case-III : $V_C > V_A$

As electrode (A) is at low potential. It will repel electron resulting decrease in photocurrent. Further decrease in potential at electrode (A) may result a situation when the fastest electron just fails to reach at (A) and the photocurrent drops to zero. The potential of (A) relative to C to just stop photocurrent is called **stopping potential**.



Relative to V_C

$(V_A - V_C)$

On increasing the intensity of light, the stopping potential does not change because the maximum K.E. of photoelectron does not change. But the photocurrent increases, because the number of photons falling on the surface increase.

If the frequency of light is changed, the stopping potential will change.

$(KE)_{max} = eV_0$

$(KE)_{max} = h\nu - h\nu_0$

$$eV_0 = \frac{hc}{\lambda} - \phi$$

$$V_0 = \frac{hc}{e}.\frac{1}{\lambda} - \frac{\phi}{e}$$

$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$

$$y \quad m \quad x \quad c$$

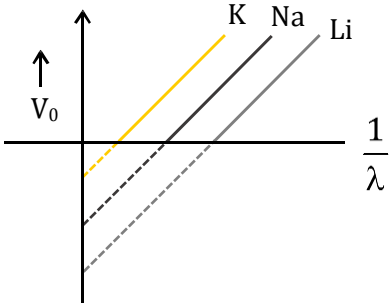


Illustration 24:

From a metal surface, photoelectron never comes out by orange light but comes from green light. Predict about the injection of photoelectron from the same metal by

(i) Red (ii) Blue (iii) Yellow light

Solution:

(i) Red light = No

(ii) Blue light = Yes

(iii) Yellow light = Can't say

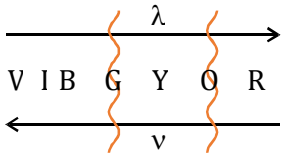


Illustration 25:

The work function of a metal is 3 eV. If EMR of 200 nm fall on the metal surface, calculate the maximum speed of photoelectron ejected.

Solution:

$$E = \frac{1240}{200} = 6.2eV$$

$$(KE)_{max} = h\nu - \phi$$

$$\frac{1}{2}mv^2 = (6.2 - 3)eV$$

$$\frac{1}{2} \times 9.1 \times 10^{-31} v_{max}^2 = 3.2 \times 1.6 \times 10^{-19}$$

Illustration 26:

When EMR of frequency 5×10^{15} Hz fall on a metal surface, the maximum kinetic energy of photoelectron is double than the photoelectron which emits when EMR of frequency 3×10^{15} Hz fall on the same metal. The threshold frequency for the metal is

Solution:

$(K.E.)_1 = h \times 5 \times 10^{15} - h\nu_0$

$(K.E.)_2 = h \times 3 \times 10^{15} - h\nu_0$

$2E_1 = E_2$

$\nu_0 = 1 \times 10^{15}$ Hz.

Illustration 27:

A photon of wavelength 3000 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

$$E = h\nu = \frac{hc}{\lambda} = \frac{\left(6.6\times10^{-34}\,Js\right)\left(3\times10^{8}\,ms^{-1}\right)}{3\times10^{-7}\,m} = 6.6 \times 10^{-19}\,J$$

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

$$\text{Therefore } E = \frac{6.6\times10^{-19}\,J}{1.6\times10^{-19}\,J/eV} = 4.125\ eV$$

(ii) Kinetic energy of the emitted photo electron

Work function = 2.20 eV

Therefore, KE = 2.475 – 2.20

= 1.925 eV = 3.08×10^{-19} J

(iii) Velocity of the photo electron

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

$$\text{Therefore, velocity (v)} = \sqrt{\frac{2\times3.08\times10^{-19}}{9.1\times10^{-31}}} = 8.22 \times 10^{5}\ ms^{-1}$$

Bohr's Atomic Model:

Bohr's model for hydrogen atom is based on the following postulates:

(i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

(ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.

(iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by :

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

(iv) The angular momentum of an electron in a given stationary state can be expressed as in equation

$$m_e vr = n\frac{h}{2\pi} \quad n = 1, 2, 3$$

Thus, an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed.

Niels Bohr
(1885-1962)

Niels Bohr, was a Danish physicist. After first world war, Bohr worked for peaceful uses of atomic energy. He was awarded the Nobel Prize in physics in 1922.

Application of Bohr's Model

When electron revolves in fixed circular orbit than electrostatic force of attraction and centrifugal force are equal.

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

Where, constant $K = 9 \times 10^9\ Nm^2/C^2$ (MKS) = 1 (CGS)

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

In balanced condition

Electrostatic force = Centrifugal force

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

Radius of various orbits (shell) :

According to Bohr model, $mvr = \frac{nh}{2\pi}$

$$v = \frac{nh}{2\pi mr} \qquad \text{...(ii)}$$

Now putting the value of v from eq.(ii) into eq.(i)

$$\frac{KZe^2}{r} = m\left(\frac{nh}{2\pi mr}\right)^2$$

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

$$r = \frac{n^2h^2}{4\pi^2mKZe^2} \quad \text{or} \quad r = \frac{n^2h^2}{4\pi^2mZe^2} \text{ (CGS K = 1)} \qquad \text{...(iii)}$$

Putting the value of π, h, m, K, & e (Constants) in the above eq. (iii)

$r = 0.529 \times 10^{-10} \times \frac{n^2}{Z}\ m$ $\{Å = 10^{-10}\ m = 10^{-8}\ cm\}$

or $\boxed{r_n = 0.529 \times \frac{n^2}{Z} Å}$

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

Velocity of electron in Bohr orbit :

According to Bohr postulate

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

$$v = \frac{nh}{2\pi mr} = \frac{nh}{2\pi m \times n^2h^2 / 4\pi^2 mKZe^2}$$

$$v = \frac{2\pi KZe^2}{nh} \quad \text{(MKS)} \qquad \ldots(iv)$$

$$v = \frac{2\pi Ze^2}{nh} \quad \text{(CGS)}$$

Putting the value of π, h, K, & e (Constants) in the above eq (iv)

$v = 2.18 \times 10^6 \frac{Z}{n} m/s$

Total energy of electron in Bohr orbit :

Total energy of an electron is the sum of kinetic and potential energy.

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

(i) Potential energy : $P.E. = \frac{Kq_1q_2}{r} = -\frac{KZe^2}{r} = -\frac{KZe^2}{r}$

(ii) Kinetic energy : $K.E. = \frac{1}{2}mv^2$

But $\frac{KZe^2}{r} = mv^2$ (By eq. i)

$K.E. = \frac{KZe^2}{2r}$

(iii) Total energy : T.E. = K.E.+ P.E.

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

Now putting the value of r from eq. (iii)

$T.E. = -\frac{KZe^2 \times 4\pi^2 mKZe^2}{2n^2h^2} \Rightarrow -\frac{2\pi^2 m \times K^2Z^2e^4}{n^2h^2}$

Now putting the value of π, K, e, m, h, we get :

T.E. $= -2.18\times10^{-18}\times\frac{Z^2}{n^2}$ J / atom $= -1312\times\frac{Z^2}{n^2}$ kJ/mol

$= -2.18\times10^{-11}\times\frac{Z^2}{n^2}$ erg/atom $= -313.6\times\frac{Z^2}{n^2}$ Kcal/mol

$= -13.6\times\frac{Z^2}{n^2}$ eV/atom $\Rightarrow E_n = -\frac{13.6Z^2}{n^2}$ eV / atom

Some extra points :

(i) K.E $= \frac{KZe^2}{2r}$ i.e. K.E. $\propto \frac{1}{r}$ On increasing radius, K.E. decreases.

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

(iii) T.E. $= -\frac{KZe^2}{2r}$ i.e. E. $\propto -\frac{1}{r}$ On increasing radius, total energy increases.

(iv) Relation between T.E., P.E. and K.E.

P.E = –2 KE

KE = –T.E.

P.E = 2 T.E.

Important Definitions :

(i) Ionization energy :

Minimum energy required to liberate an electron from the ground state of an isolated atom is called the ionization energy.

(ii) Separation energy :

Minimum energy required to remove an electron from its excited state is called as separation energy.

(iii) Excitation energy :

Amount of energy required to shift an electron from ground state to any excited state.

Note:

All these kinds of energy are always positive.

Illustration 28:

Calculate the radius of first 4 orbits of hydrogen atom

Solution:

$r_1 = 0.529\times\frac{1^2}{1} = 0.529\text{Å}$

$r_2 = 0.529\times\frac{2^2}{1} = 2.116\text{Å} = r_1\times 2^2$

$r_3 = 0.529\times\frac{3^2}{1} = 4.761\text{Å} = r_1\times 3^2$

$r_4 = 0.529 \times \frac{4^2}{1} = 8.464\text{Å}$

From this, for same Z : $r_n = r_1 \times n^2$

Illustration 29:

Calculate the ratio of radius of 2nd orbit of $Li^{2\oplus}$ atom & 3rd orbit $He^{\oplus}$ ion.

Solution:

$$\frac{r_{2,Li^{2\oplus}}}{r_{3,He^{\oplus}}} = \frac{0.529 \times \frac{4}{3}}{0.529 \times \frac{9}{2}} = \frac{8}{27}$$

Illustration 30:

Calculate the radius ratio of 3rd & 5th orbit of $He^{\oplus}$.

Solution:

$r = 0.529 \times \frac{n^2}{Z}$ Å

At. Number of He = 2

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

$r_5 = 0.529 \times \frac{(5)^2}{2} = 0.529 \times \frac{25}{2}$

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

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

Illustration 31:

Calculate the energy of $Li^{2\oplus}$ atom for 2nd excited state.

Solution:

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

$\because$ Z = 3 and $e^{\ominus}$ exist in 2nd excited state, means e^- present in 3rd shell i.e. n = 3

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

Illustration 32:

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

Solution:

(i) P.E. = – 2K.E.

– 6.8 = – 2K.E.

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

(ii) E. = – K.E.

= – 3.4 eV

(iii) Orbit = 2nd

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

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

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

i.e. n = 2

(iv) $r = 0.529 \times \frac{n^2}{Z}$ Å

$r = 0.529 \times \frac{(2)^2}{1}$ Å

= 0.529 × 4Å = 2.16 Å

Illustration 33:

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

Solution:

Ionization energy = 13.6 eV

i.e. 1st energy state = – 13.6 eV

Energy of 1st excited state

i.e. 2nd orbit = –3.4 eV

so, $E_2 - E_1 = -3.4 + 13.6 = 10.2$ eV

Illustration 34:

Calculate the amount of energy absorbed in the transition n = 1 to n = 3 in $Li^{2\oplus}$ ion.

Solution:

n_1 orbit $\rightleftarrows$ n_2 orbit

$$\Delta E = E_{n_2} - E_{n_1} = \left(-13.6\frac{z_1^2}{n_2^2}\right) - \left(-13.6\frac{z_2^2}{n_1^2}\right)$$

$$\Delta E = 13.6z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{eV}$$

$$\Delta E = 13.6\times 3^2\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = 108.8\text{eV}$$

Illustration 35:

Calculate the excitation energy of $Be^{3\oplus}$ ion in ground state.

Solution:

$$\Delta E = 13.6\times 16\left(\frac{1}{1} - \frac{1}{4}\right) = 163.2 \text{ eV}$$

Illustration 36:

The ionisation energy of $He^{\oplus}$ ion is x kJ/mole. Calculate ionisation energy of $Li^{2\oplus}$ ion.

Solution:

For I.E. $\Rightarrow n = 1 \longrightarrow n = \infty$

$$IE = 13.6z^2\left(\frac{1}{1^2}-\frac{1}{\infty^2}\right) = 13.6\ z^2\ eV$$

$$\frac{(I.E.)_{Li^{2\oplus}}}{(I.E.)_{He^{\oplus}}}=\frac{3^2}{2^2} \qquad \Rightarrow \qquad (I.E.)_{Li^{2\oplus}}=\frac{9}{4}x\ kJ/mol$$

Illustration 37:

The ionisation energy for a single electron system is 14.4 eV. Calculate the amount of energy released when electron jumps from 3rd orbits to 2nd orbit.

Solution:

$$\Delta E = (IE)\left(\frac{1}{n_1^2}-\frac{1}{n^2}\right)=14.4\times\left(\frac{1}{4}-\frac{1}{9}\right) = 2\ eV$$

Illustration 38:

Calculate the speed of an electron in the 3rd orbit of the $Li^{2\oplus}$ ion. Also calculate the number of revolutions per second that it makes around the nucleus.

Solution:

Radius of 3rd orbit = $r_1 x\frac{(n)^2}{Z} = 0.529 \times \frac{(3)^2}{3} = 1.587Å$

Velocity of electron in 3rd orbit, $v = 2.18 \times 10^6 \frac{Z}{n}$ m/sec $= 2.18 \times 10^6$ m/sec

$$\text{No. of revolutions/sec} = \frac{1}{2\pi r/v} = \frac{v}{2\pi r} = \frac{2.18\times10^6\ m/sec}{2\times3.14\times1.587\times10^{-10}\ m}$$

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

Rydberg Formula:

It an electron shows transition from n_2 to n_1 energy level then energy change ΔE will be.

$$\Delta E = En_2 - En_1$$

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

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

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

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

where $\frac{2\pi^2mK^2e^4}{ch^3}$ is a constant called Rydberg constant (R) (Assume nucleus is stationary)

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

value of $R = 109677\ cm^{-1} = 10967700 m^{-1}$

$\simeq 109700\ cm^{-1} \simeq 10970000\ m^{-1}$

$$\frac{1}{R} = 912Å$$

Illustration 39:

What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from the energy level with n = 4 to the energy level with n = 1 ?

Solution:

According to Rydberg's formula, $\bar{\nu}(cm^{-1}) = 109,677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

In the present case $n_2 = 4$ and $n_1 = 1$

$$\bar{\nu} = 109,677\left(\frac{1}{(1)^2} - \frac{1}{(1)^2}\right) = 109,677 \times \frac{15}{16} = 102822 cm^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{102822} cm = 9.7 \times 10^{-6} cm = 9.7 \times 10^{-6} \times 10^{7} nm = \mathbf{97\ nm.}$$

Limitation of the Bohr's Model:

(i) Bohr's theory does not explain the spectrum of multi electron atom.

(ii) Why the Angular momentum of the revolving electron is equal to $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.

(iii) Bohr inter-related quantum theory of radiation and classical law of physics without any theoretical explanation. This was the biggest drawback of this model.

(iv) Bohr's theory does not explain the fine structure of spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by a spectroscope of high resolving power.

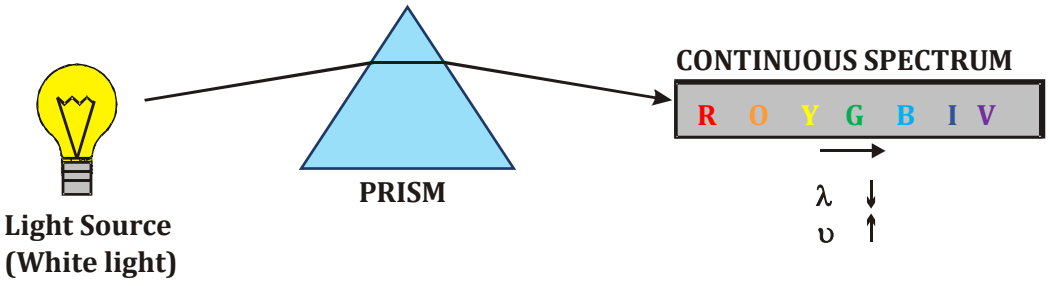
(v) Bohr's theory does not explain the splitting of spectral lines in the presence of magnetic field **(Zeeman effect)** or electric field **(Stark effect).**

Spectrum:

It is the impressions produced on any screen when a light falls on it after passing through prism or prism like material.

Classification of Spectrum:

(i) Continuous and discontinuous spectrum : In continuous spectrum, the impression produced on screen overlap each other, but in discontinuous spectrum, same gap exist between the impression. The spectrum of white light that we can see ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. This spectrum is called *continuous spectrum* because violet merges into blue, blue into green, and so on. A similar spectrum is produced when a rainbow forms in the sky. In a continuous spectrum, radiations corresponding to all the wavelengths are present.



(ii) Emission and Absorption Spectra : The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be **'excited'**. 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.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig).

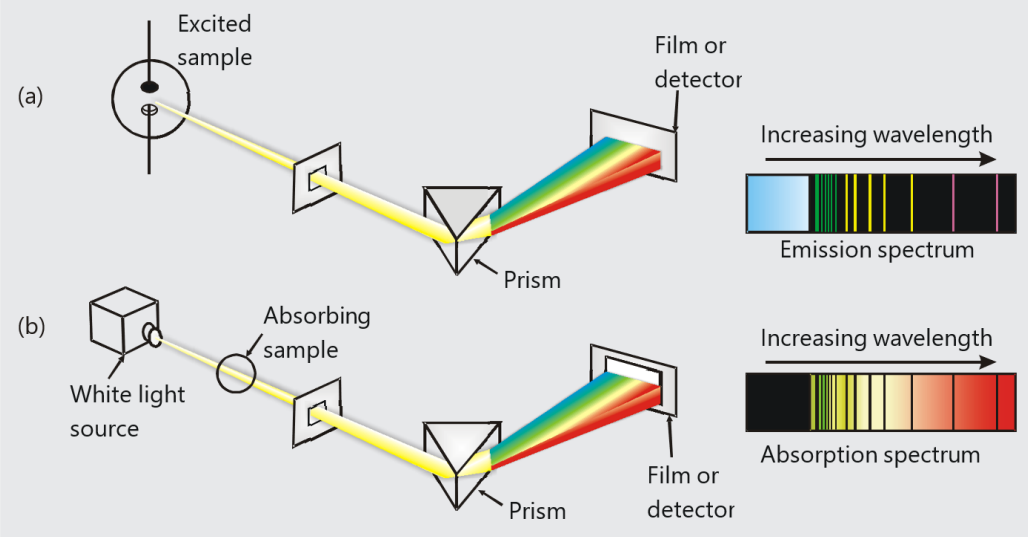


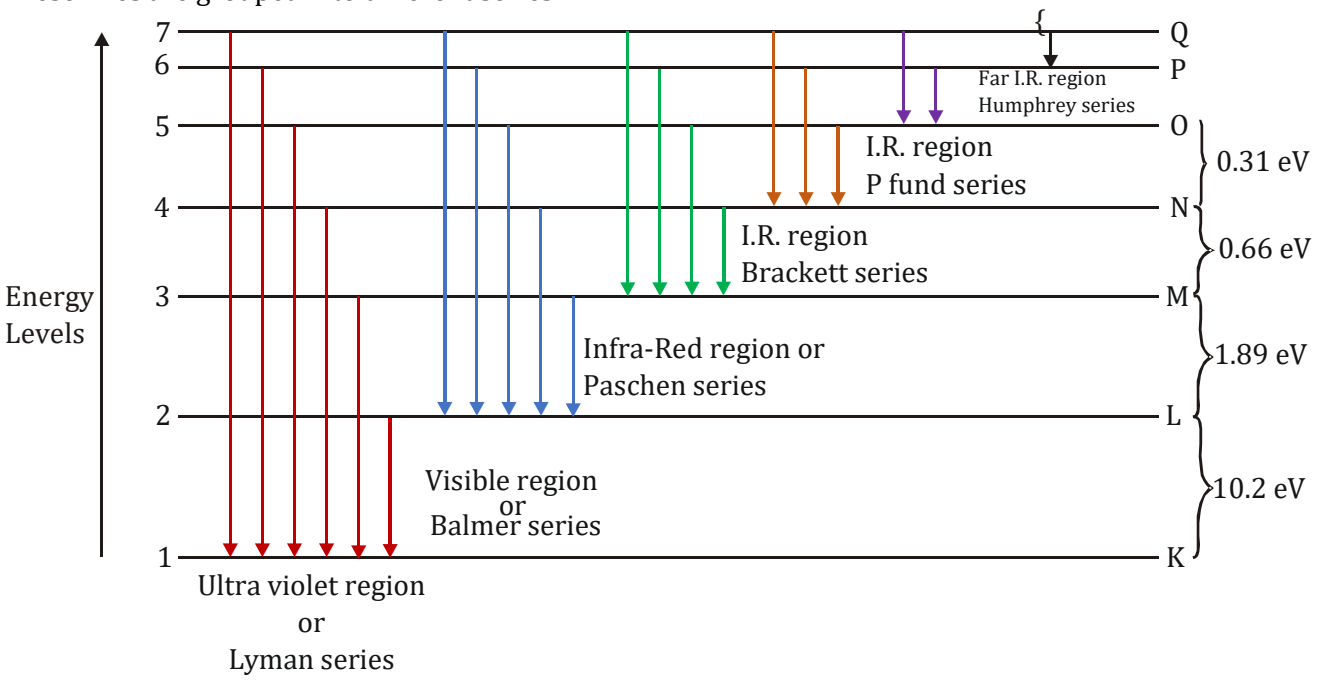
Fig. (a) Atomic emission. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus, an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. **(b) Atomic absorption**. When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Hydrogen line Spectrum:

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



Series	Discovered by	Regions	n_2	n_1
Lyman	Lyman	U.V. region	$n_2 = 2,3,4 ...$	$n_1=1$
Balmer	Balmer	Visible region	$n_2 = 3,4,5 ...$	$n_1=2$
Paschen	Paschen	Infra-Red (I.R.)	$n_2 = 4,5,6 ...$	$n_1=3$
Brackett	Brackett	I.R. region	$n_2 = 5,6,7 ...$	$n_1=4$
P fund	P fund	I.R. region	$n_2 = 6,7,8 ...$	$n_1=5$
Humphery	Humphery	Far I.R. region	$n_2 = 7,8,9 ...$	$n_1=6$

Key points:

- First line/Starting line/Initial line ($\lambda_{max.}$ and ν_{min})
- Last line/limiting line/Series limit (λ_{min} and $\nu_{max.}$)
- First line of any series = α line
  Second line of any series = β line
  Third line of any series = γ line
- Total no. of emission lines between n_2 & $n_1 = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$, $(n_2 > n_1)$

- For transition from any orbit 'n' to n = 1, total no. of emission lines $= \frac{n(n-1)}{2}$
- For an single isolated atom, only 1 line spectrum for 1 transition can be counted.

Illustration 40:

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

Solution:

Total number of lines = 4 + 3 + 2 + 1 + 0 = 10

Total number of lines = $\frac{(n_2-n_1)\left[(n_2-n_1)+1\right]}{2} = \frac{(6-2)(4+1)}{2} = 10$

Illustration 41:

In the spectrum of $He^{\oplus}$ ion the wavelength of α line of Balmer series is x Å. What is the wavelength of α line of Paschen series.

Solution:

$$\frac{1}{\lambda_1} = Rz^2\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$$

$$\frac{1}{\lambda_2} = Rz^2\left(\frac{1}{3^2}-\frac{1}{4^2}\right)$$

$$\frac{\lambda_2}{\lambda_1} = \frac{\frac{1}{2^2}-\frac{1}{3^2}}{\frac{1}{3^2}-\frac{1}{4^2}} \Rightarrow \frac{\lambda_2}{x\text{Å}} = \frac{5\times16\times9}{9\times4\times7} = \frac{20}{7}$$

$$\Rightarrow x = \frac{7}{20}\times\lambda_2$$

$$\lambda_2 = \frac{20x}{7}$$

Illustration 42:

A sample of $He^{\oplus}$ ions in ground state absorbs the radiation of x Å. subsequently, the sample emit radiation of 6 different wavelength. Calculate the value of x.

Solution:

$$\frac{1}{x} = R\left(\frac{1}{1^2}-\frac{1}{4^2}\right)\times 2^2$$

$$x = \frac{16}{15}\times\frac{912}{4}\text{Å}$$

Illustration 43:

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

Solution:

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

= 10

Total number of lines = $\frac{(n_2-n_1)\left[(n_2-n_1)+1\right]}{2} = \frac{(6-2)(4+1)}{2} \Rightarrow \frac{4\times5}{2} = 10$

Dual Behaviour of Matter & de Broglie Wavelength:

In 1923, a French physicist, ***Louis de Broglie*** suggested that, like light, matter also has dual character. It exhibits wave as well as particle nature. According to de Broglie, the wavelength λ of an electron is inversely proportional to its momentum p.

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

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

p = momentum of electron

∴ Momentum (p) = Mass (m) × Velocity (v)

The above relation can be derived for a photon as follows by using Einstein's equation, Planck's quantum theory and wave theory of light.

$E = mc^2$ (Einstein's equation) **...(i)**

Where E is energy, m is mass of a body and c is its velocity.

$E = h\nu = h \times \frac{c}{\lambda}$ (Planck's equation) $\left(\nu = \frac{c}{\lambda}\right)$ **...(ii)**

Combining (i) and (ii)

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

$$\boxed{\lambda = \frac{h}{mv} \text{ or } \lambda = \frac{h}{p}}$$

De Broglie' (1892-1987)

A French physicist, studied history as an undergraduate in the early 1910's. His interest turned to science as a result of his assignment to radio communications in world war 1. He was awarded the Nobel Prize in physics in 1929.

It is clear from the above equation that the value of λ decreases on increasing either m or v or both. The wavelength of many fast-moving objects like an aeroplane or a cricket ball, is very low because of their high mass. Thus, wave nature of macroscopic objects can be neglected but for microscopic particles like electrons, protons, atoms etc. wave nature is significant & cannot be neglected.

Derivation of Bohr's angular momentum quantization rule :

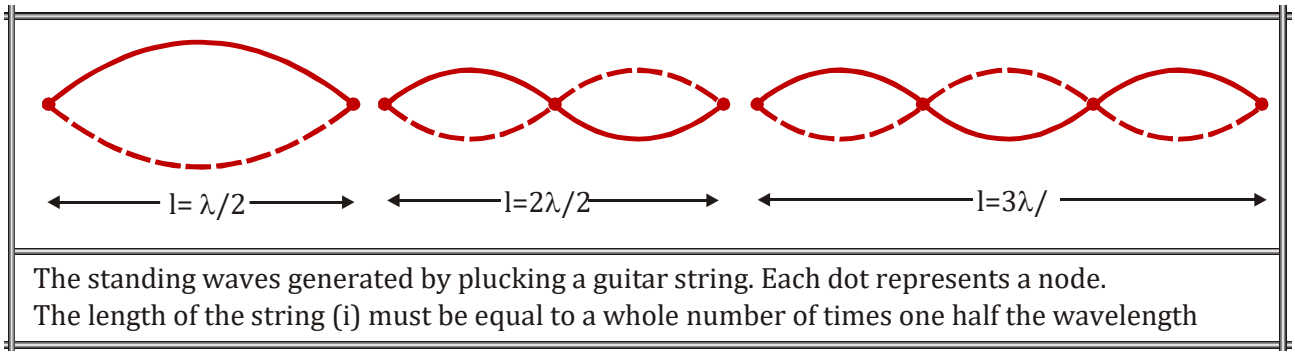
We know that according to Bohr theory, $mvr = \frac{nh}{2\pi}$

or $2\pi r = \frac{nh}{mv}$ ($\because$ mv = p momentum)

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

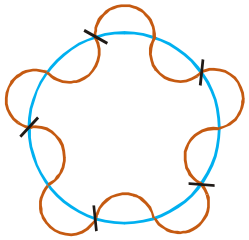
According to de Broglie, an electron bound to the nucleus behaves like a standing wave.

A standing wave – also known as a stationary wave – is a wave that remains in a constant position. Two opposing waves combine to form a standing wave. This phenomenon can occur because the medium is moving in the opposite direction to the wave, or it can arise in a stationary medium as a result of interference between two waves travelling in opposite directions.



The standing waves generated by plucking a guitar string. Each dot represents a node.
The length of the string (i) must be equal to a whole number of times one half the wavelength

For a circular standing wave to persist, a whole number of wavelengths must fit into the circumference of the circle (2π).

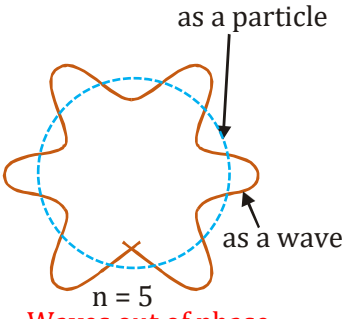


n = 5

$\therefore$ Waves made = 5

And if n number of waves of λ wavelength are present in this circle total circumference will be $n\lambda$.

$2\pi r = n\lambda$



Waves out of phase

n = Number of wave made by electron in one complete revolution.

According to de Broglie

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

$$2\pi r = n\frac{h}{mv}$$

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

Therefore in $2\pi r = n\lambda$, n = Number of shell

i.e., 2^{nd} shell $2\pi r = 2\lambda$

3^{rd} shell $2\pi r = 3\lambda$

Electron in n^{th} orbit of any uni-electron system can create 'n' waves in one complete revolution.

Illustration 44:

Calculate the de Broglie wavelength of a ball of mass 0.1 kg moving with a speed of 30 ms^{-1}.

Solution:

$\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}}{0.1\times30} = 2.2 \times 10^{-34}$ m

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

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

Illustration 45:

What should be the mass of the sodium photon if its wavelength is 5894 Å, the velocity of light is 3×10^8 metre/second and the value of h is 6.652×10^{-34} kg m^2/sec.?

(A) 3.746×10^{-26} (B) 3.746×10^{-30} (C) 3.746×10^{-34} (D) 3.746×10^{-36}

Ans. (D)

Solution:

$\lambda = \frac{h}{m\times c} \Rightarrow m = \frac{h}{c\lambda}$

($\because$ $\lambda = 5894Å = 5894 \times 10^{-10}$ m)

$m = \frac{6.652\times10^{-34}}{3\times10^{-8}\times5894\times10^{-10}}$ or $\frac{6.652}{17682}\times10^{-32}$

$= 0.0003746 \times 10^{-32} = 3.746 \times 10^{-36}$ kg

Illustration 46:

Calculate the de-Broglie wavelength when e^- is accelerated by the following voltage.

(i) 750 V (ii) 300 volt

Solution:

(i) $\lambda = \sqrt{\frac{150}{V}}Å = \sqrt{\frac{150}{750}}Å = \frac{1}{\sqrt{5}}Å$ (ii) $\lambda = \sqrt{\frac{150}{300}}Å = \frac{1}{\sqrt{2}}Å$

Illustration 47:

Find de-Broglie wavelength of electron with KE = 9.6×10^{-19} J.

Solution:

$KE = \frac{9.6\times10^{-19}}{1.6\times10^{-19}}eV = 6eV$

$\lambda = \sqrt{\frac{150}{6}}Å = 5Å$

KE of 6 eV means e^- is accelerated by 6 volt.

Illustration 48:

Calculate the ratio of de-Broglie wavelength of electron and α-particle.

(i) Moving at same speed

(ii) Moving at same momentum

(iii) Having same K.E.

(iv) Accelerated from rest through the same P.D.

Solution:

(i) $\lambda = \frac{n}{mv}$

$\lambda \propto \frac{1}{m}$

$\frac{\lambda_{electron}}{\lambda_{\alpha}} = \frac{m_{\alpha}}{m_e} = \frac{4\times1836}{1}$

(ii) $\frac{\lambda_{electron}}{\lambda_{\alpha}} = \frac{1}{1}$

(iii) $\frac{h}{\sqrt{2mE}}$

$\lambda = \frac{h}{\sqrt{2mE}} = \frac{\lambda_e}{\lambda_{\alpha}} = \sqrt{\frac{m_{\alpha}}{m_e}} = \sqrt{\frac{1836\times4}{1}}$

(iv) $\lambda = \frac{h}{\sqrt{2mqV}} = \frac{\lambda_e}{\lambda_{\alpha}} = \sqrt{\frac{(mq)_{\alpha}}{(mq)_e}} = \sqrt{\frac{4\times2}{1/1836\times1}}$

Illustration 49:

In $Li^{2\oplus}$ ion electron jumps from 2nd to 1st orbit. If the emitted radiation is absorbed by H atom. Calculate the de-Broglie wavelength of the ejected electron.

Solution:

$\Delta E = 13.6\times9\left(1-\frac{1}{4}\right) = 91.8eV$

Excess energy = 91.8 – 13.6 = 78.2 eV

$\lambda = \sqrt{\frac{150}{78.2}}Å = 1.38Å$

Illustration 50:

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

Solution:

K.E. = Quantum Energy – Threshold energy

$= \frac{6.626\times10^{-34}\times3\times10^{8}}{2000\times10^{-10}} - \frac{6.626\times10^{-34}\times3\times10^{8}}{4000\times10^{-10}}$

$= \frac{6.626\times10^{-34}\times3\times10^{8}}{10^{-10}}\left(\frac{1}{2000}-\frac{1}{4000}\right) = 4.969 \times 10^{-19}$ Joule.

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

$mv = 9.51 \times 10^{-25} \Rightarrow \lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}}{9.51\times10^{-25}} = 0.696 \times 10^{-9}$ m

Illustration 51:

Calculate the de-Broglie wavelength when proton is accelerated by the 750 V.

Solution:

(i) $\lambda = \sqrt{\frac{150}{V\times1836}}Å = \sqrt{\frac{150}{750\times1836}}Å$

Justification of dual nature of electrons :

I. Particle character :

(a) If an electron strikes a screen coated with ZnS, it produces a spot of light called scintillation, One electron produces only one scintillation point which means electron are localised not spread out like wave : Photoelectric effect also proves its particle nature.

(b) Electron possess definite mass, momentum & KE proving their particle nature.

II. Wave character :

- It was confirmed by phenomenon of diffraction, interference, reflection.
- Davisson and Germer showed that when high speed electron strike Ni crystal a diffraction pattern (having number of rings) is obtained like X-rays of electromagnetic spectrum.

Heisenberg Uncertainty Principle:

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

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

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

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

or $\mathbf{\Delta x.\Delta v^3 \frac{h}{4\pi m}}$

where h is Planck's constant.

$\Delta x\, \Delta v$ = uncertainty product

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

$$\Delta x \,.\, \Delta v \geq \frac{6.624\times10^{-27}}{4\pi m} \geq \frac{6.624\times10^{-27}}{4\times3.14\times9.10\times10^{-28}}$$

= 0.57 erg sec per gram approximately

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

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

Illustration 52:

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

Solution:

Mass of the ball = 40 g = 40×10^{-3} kg

The uncertainty in the speed,

$$\Delta v = 45 \times \frac{2}{100} = 0.9\,ms^{-1}$$

$$\Delta x = \frac{h}{4\pi m\,\Delta v} = \frac{6.626\times10^{-34}\,Js}{4\times3.14\times(40\times10^{-3}\,kg)(0.9\,ms^{-1})} = 1.46 \times 10^{-33}\ m.$$

Illustration 53:

Calculate the uncertainty in the velocity of a cricket ball of mass 150 g, if the uncertainty in its position in of the order of 1 Å. ($h = 6.626 \times 10^{-34}$ kg m^2 s^{-1})

Solution:

Mass of ball,

$m = 150\ g = 150 \times 10^{-3}\ kg = 0.150\ kg$

Uncertainty in position, $\Delta x = 1\ Å = 10^{-10}\ m$

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

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

$$= \frac{6.626 \times 10^{-34}\ kg\ m^2\ s^{-1}}{4 \times 3.14 \times 10^{-10}\ m \times 0.150\ kg} = 3.52 \times 10^{-24}\ m\ s^{-1}.$$

Quantum Mechanical Model of Atom

Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However, it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called **quantum mechanics.**

Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics.

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrodinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrodinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates wave-particle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes.

For a system (such as an atom or a molecule whose energy does not change with time) the Schrodinger equation is written as

$$H\psi = E\psi$$

is a mathematical operator called Hamiltonian. Schrodinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and ψ.

Hydrogen Atom and the Schrodinger Equation

Erwin Schrodinger, an Austrian physicist received his Ph.D.in theoretical physics from the University of Vienna in 1910. In 1927 Schrodinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrodinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrodinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrodinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933.

Erwin Schrodinger (1887-1961)

When Schrodinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers **(principal quantum number *n*, azimuthal quantum number *l* and magnetic quantum number** m_l) arise as a natural consequence in the solution of the Schrodinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron.

The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called **atomic orbitals**.

Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model.

Application of Schrodinger equation to multi-electron atoms presents a difficulty: the Schrodinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later, unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers *n* and *l*.

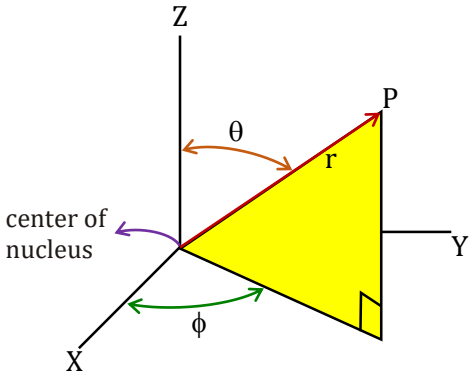
Important Features of the Quantum Mechanical Model of Atom :

Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrodinger equation to atoms. The following are the important features of the quantum mechanical model of atom:

1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms.
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrodinger wave equation.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom.

4. **An atomic orbital is the wave function ψ for an electron in an atom.** Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These "one electron orbital wave functions" or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function ψ and quantum mechanics makes it possible to extract this information out of ψ.
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as **probability density** and is always positive. **From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.**

Solution of Schrodinger Equation:



Spherical coordinate system

The solution in spherical coordinates may be represented as :

$\psi = R(r).\Theta(\theta).\Phi(\phi)$ R(r) : Radial function depends on n and l

$\Theta(\theta).\Phi(\phi)$: Angular function depends on l and m.

Radial part of solution :

1s $(n = 1, \ell = 0)$: $R_{1s}(r) = 2\cdot\left(\frac{z}{a_0}\right)^{3/2}\cdot e^{-\sigma/2}$

where $\sigma = \frac{2Zr}{na_0}$ a_0 = Ist Bohr's radius = 0.529Å

2s $(n = 2, \ell = 0)$: $R_{2s}(r) = \frac{1}{2\sqrt{2}}\cdot\left(\frac{Z}{a_0}\right)^{3/2}\cdot(2-\sigma)e^{-\sigma/2}$

2p $(n = 2, \ell = 1)$: $R_{2p}(r) = \frac{1}{2\sqrt{6}}\cdot\left(\frac{Z}{a_0}\right)^{3/2}\cdot\sigma\cdot e^{-\sigma/2}$

3s $(n = 3, \ell = 0)$: $R_{3s}(r) = \frac{1}{9\sqrt{3}}\cdot\left(\frac{Z}{a_0}\right)^{3/2}\cdot(6-6\sigma+\sigma^2)e^{-\sigma/2}$

3p $(n = 3, \ell = 1)$: $R_{3p}(r) = \frac{1}{9\sqrt{6}} \cdot \left(\frac{Z}{a_0}\right)^{3/2} \cdot \sigma(4-\sigma)e^{-\sigma/2}$

3d $(n = 3, \ell = 2)$: $R_{3d}(r) = \frac{1}{9\sqrt{30}} \cdot \left(\frac{Z}{a_0}\right)^{3/2} \cdot \sigma^2 \cdot e^{-\sigma/2}$

General form :

(Polynomial of order n – ℓ – 1)

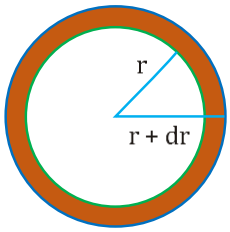
Radial probability distribution function (rpdf), $4\pi r^2\psi^2(r)$

It is often useful to know the likelihood of finding the electron in an orbital at any given distance away from the nucleus. This enables us to say at what distance from the nucleus the electron is most likely to be found, and also how tightly or loosely the electron is bound in a particular atom. This is expressed by the radial probability distribution function, $4\pi r^2\psi^2(r)$.

Radial distribution function is the measure of the probability of finding the electron in a spherical shell between thickness r and (r + dr) from the nucleus, irrespective of the direction.

Volume of radial shell :

$dV = \begin{bmatrix}\text{Volume of sphere}\\ \text{with radius}(r+dr)\end{bmatrix} - \begin{bmatrix}\text{Volume of sphere}\\ \text{with radius } r\end{bmatrix}$



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

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

(As dr represents an extremely small thickness, the higher powers of dr such as dr^2 and dr^3 may be neglected.)

$\therefore$ Volume of shell, $dV = \frac{4}{3}(\pi \times 3r^2dr) = 4\pi r^2dr$

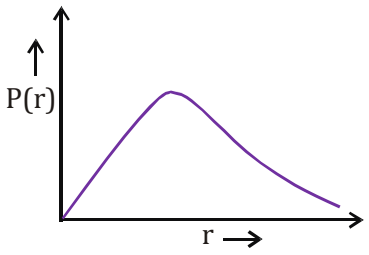
Now, radial probability density, $R^2(r) = \frac{P}{dV}$

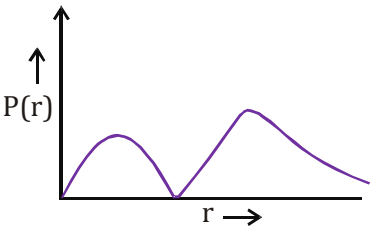
$\therefore$ Probability of finding electron in the volume element,

$P = R^2(r).\, dV = R^2(r).4\pi r^2.dr$

Now radial probability distribution function, $P(r) = \frac{P}{dr} = 4\pi r^2.R^2(r)$

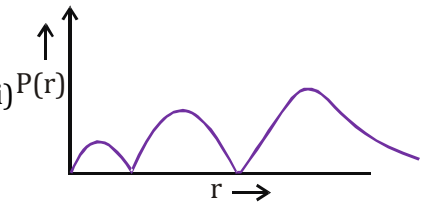
(i)



(ii) 

$n - \ell - 1 = 0$ $n - \ell - 1 = 1$

1s, 2p, 3d, 4f .....orbitals 2s, 3p, 4d, 5f .....orbitals

(iii) 

$n - \ell - 1 = 2$

3s, 5p, 5d, 6f ..... orbitals

Characteristics of radial distribution function:

(i) The number of maxima in radial distribution function plot are $(n - \ell)$.

(ii) The maximum probability of finding the electron, for the ground state hydrogen atom (1s) is found to be at a_0 (first Bohr radius).

(iii) For 2s, 3s, 3p orbitals, the number of maxima is more than one, indicating that there is maximum probability of finding the electron at the distance corresponding to the highest value of peak. However, there is lesser probability of finding the electron at the other peaks. It shows that in a certain state, the electron spends some portion of its time very close to the nucleus.

Angular part of solution:

(1) s-orbital :

$\ell = 0, m = 0$ $\Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{1}{4\pi}}$

As the probability of finding electron is not depending on angle (direction) then it must be same. In all direction and hence the shape of s-orbital is spherical.

(2) p-orbital :

p_x -orbital : $\ell = 1, m = +1$ $\Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \sin\theta\cos\phi$

p_y -orbital : $\ell = 1, m = -1$ $\Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \sin\theta\cos\phi$

p_z -orbital : $\ell = 1, m = 0$ $\Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{3}{4\pi}} \cdot \cos\theta$

(3) d-orbital :

d_{z^2} -orbital : $\ell = 2, m = 0$ $\quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$

$d_{x^2-y^2}$ -orbital : $\ell = 2, m = -2$ $\quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin^2\theta\cos 2\phi$

d_{xy} -orbital : $\ell = 2, m = +2$ $\quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin^2\theta\sin 2\phi$

d_{xz} -orbital : $\ell = 2, m = +1$ $\quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin\theta\cos\theta\sin 2\phi$

d_{yz} -orbital : $\ell = 2, m = +1$ $\quad \Theta(\theta) \cdot \Phi(\phi) = \sqrt{\frac{15}{4\pi}} \cdot \sin\theta\cos\theta \cdot \sin\phi$

Note:

Number of radial nodes = $n - \ell - 1$

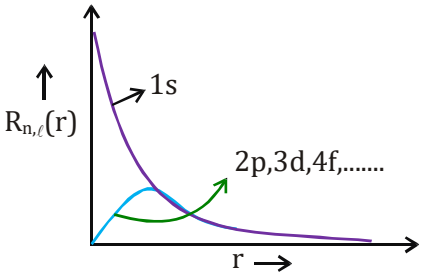
Number of angular nodes = ℓ

Total of number nodes = $n - 1$

Graph of radial function [R(r) or Ψ(r)] :

Only the graph of s-orbital does not start from origin.

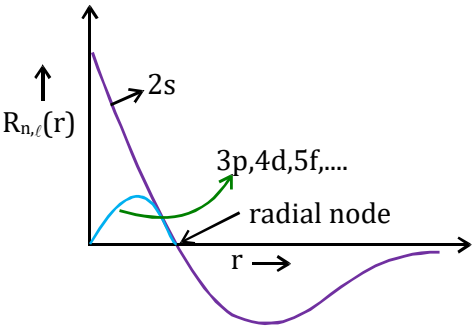
(i)



$n - \ell - 1 = 0$

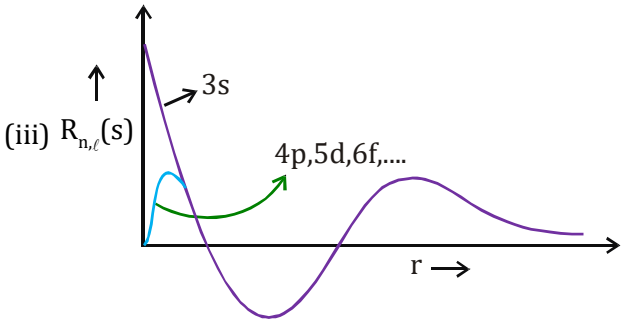
1s, 2p, 3d, 4f .....orbitals

(ii)



$n - \ell - 1 = 1$

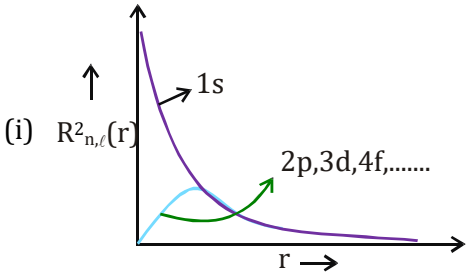
2s, 3p, 4d, 5f .....orbitals

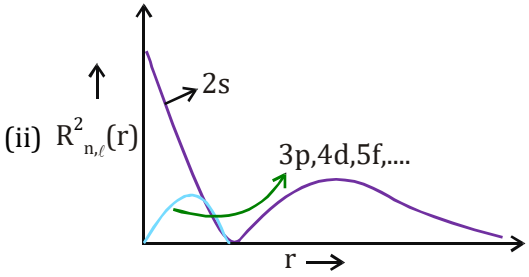


$n - \ell - 1 = 2$

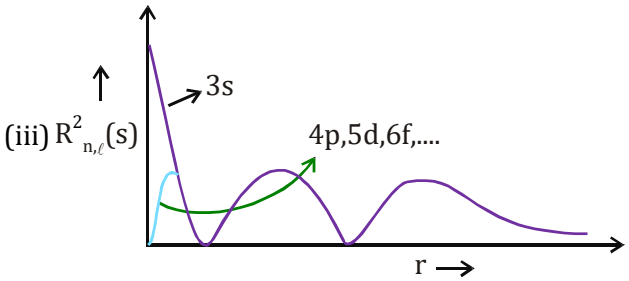
3s, 5p, 5d, 6f ..... orbitals

Graph of radial probability density function [$R^2(r)$ or $\psi^2(r)$] :





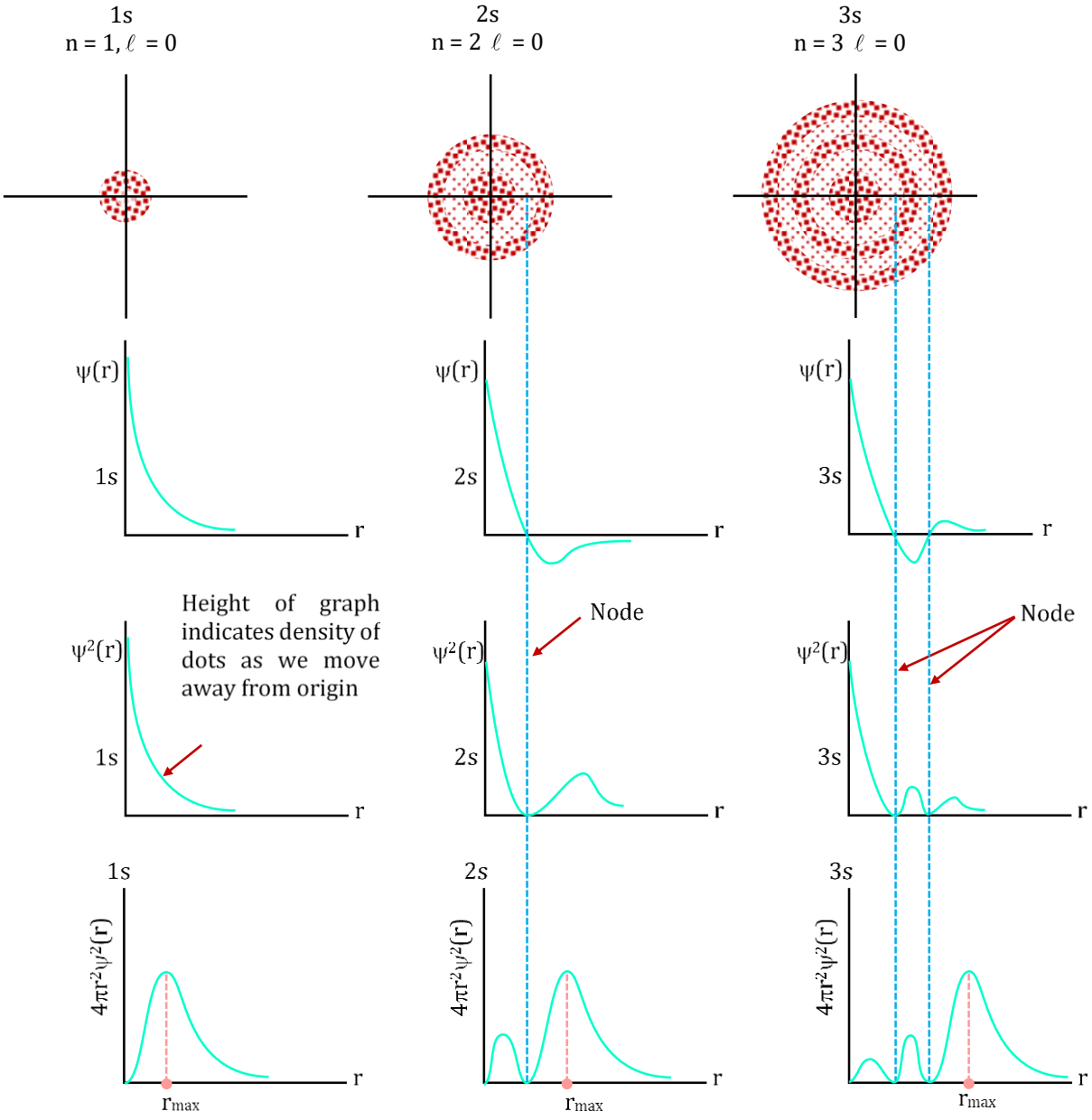
$n - \ell - 1 = 0$, (1s, 2p, 3d, 4f .....orbitals) $n - \ell - 1 = 1$ (2s, 3p, 4d, 5f .....orbitals)



$n - \ell - 1 = 2$ (3s, 5p, 5d, 6f ..... orbitals)

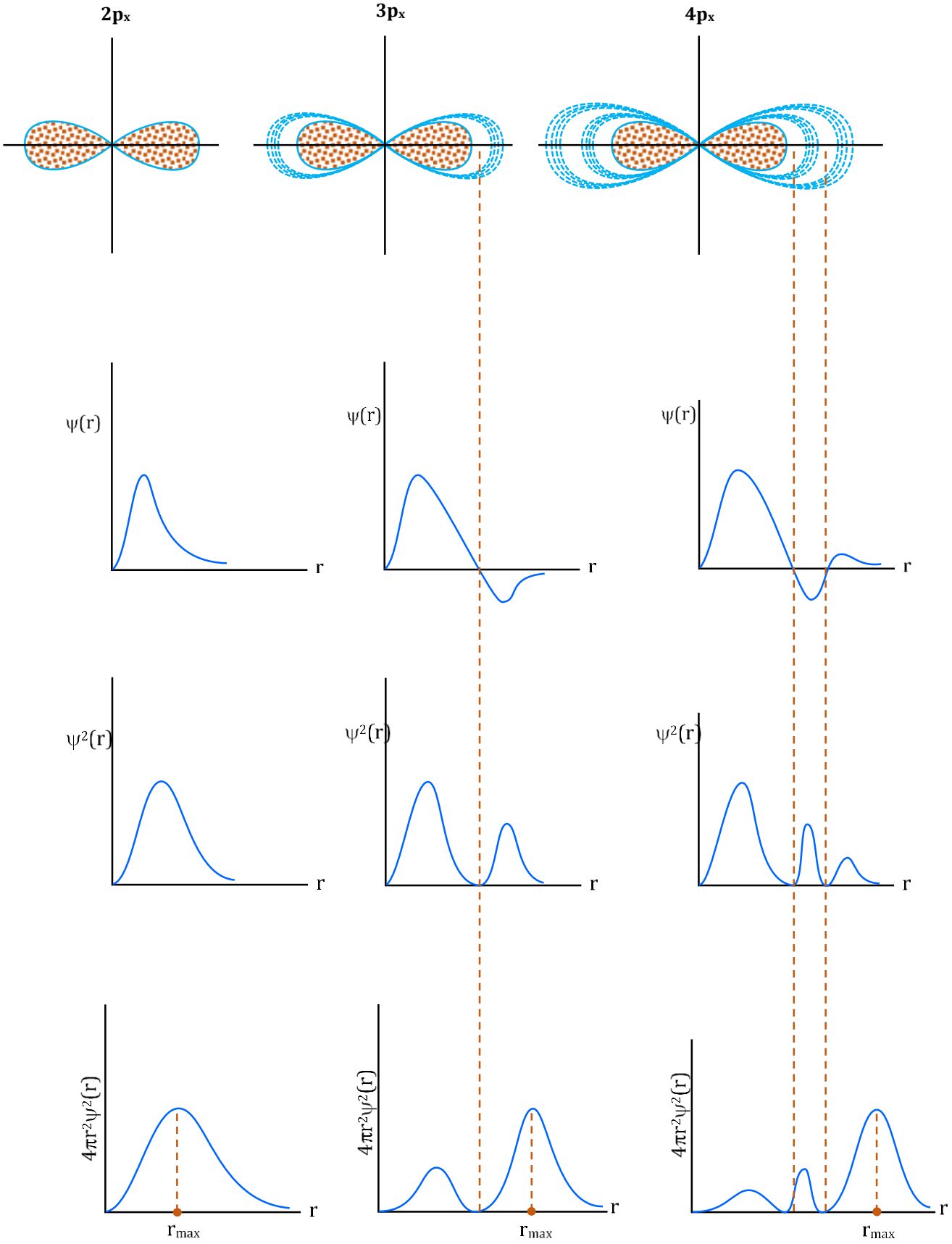
Electron-density distribution in 1s, 2s and 3s-orbitals.

The lower part of the fig. shows how the electron density, represented by ψ^2 varies as a function of distance from the nucleus. In the 2s and 3s - orbitals, the electron-density function drops to zero at certain distances from the nucleus. The spherical surfaces around the nucleus at which ψ^2 is zero are called nodes.



r_{max} = radius where the probability of finding an electron is maximum.

Electron-density distribution in $2p_x$, $3p_x$ and $4p_x$ orbitals :



Quantum Numbers:

Quantum numbers give complete information about an electron or orbital in an atom.

1. Principal Quantum number (n) :

(i) Permissible value of **$n \rightarrow 1$ to ∞**

(ii) It represents shell number/energy level

(iii) The energy states corresponding to different principal quantum numbers are denoted by letters K, L, M, N etc.

n :	1	2	3	4	5	6
Designation of shell :	K	L	M	N	O	P

(iv) It indicates the distance of an electron from the nucleus.

(v) It also determines the energy of the electron. In general, higher the value of 'n', higher is the energy of the electron.

(vi) It gives an idea of total number of orbitals & electron (which may) present in a shell & that equal to n^2 & $2n^2$ respectively.

2. Azimuthal Quantum number (ℓ) :

(i) The values of ℓ depends upon the value of 'n' and possible values are '0' to (n –1).

(ii) It gives the name of subshells associated with the energy level and number of subshells within an energy level.

(iii) The different value of 'ℓ' indicates the shape of orbitals and designated as follows :

Value	Notation	Name	Shape
$\ell = 0$	s	Sharp	Spherical
$\ell = 1$	p	Principal	Dumbell
$\ell = 2$	d	Diffused	Double Dumbell
$\ell = 3$	f	Fundamental	Complex

(iv) It also determines the energy of orbital along with n.

For a particular energy level/shell energy of subshell is in the following order $\rightarrow$ **s < p < d < f**

(v) It gives the total number of orbitals in a subshell & that equals to **$(2\ell + 1)$** and number of electrons in a subshell = **$2(2\ell + 1)$**

3. Magnetic Quantum number (m or m_l) :

(i) The value of m depends upon the value of ℓ and it may have integral value $-\ell$ to $+\ell$ including zero.

(ii) It gives the number of orbitals in a given subshell and orientation of different orbitals in space.

e.g. for n = 4, l = 0 to 3.

ℓ	0	1	2	3
m	0	–1, 0, +1	–2, –1, 0, +1, +2	–3,–2,–1,0+1,+2,+3
Possible Orientation	1	3	5	7
Orbitals	s	p_x, p_y, p_z	d_{z^2}, $d_{x^2-y^2}$ d_{xy}, d_{yz}, d_{xz}	Diffused *** Not in syllabus

(iii) The orbitals having same value of n and ℓ but different value of m, have same energy in absence of external electric & magnetic field. These orbitals having same energy of a particular subshell is known as Degenerate orbitals.

4. Spin Quantum number (s) OR Magnetic spin quantum number (m_s) :

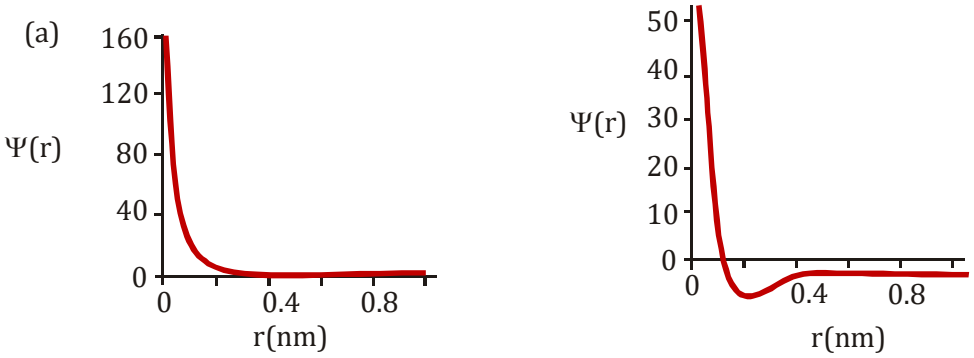
(i) While moving around the nucleus, the electron always spins about its own axis either clockwise or anticlockwise. The magnetic spin quantum number represents the direction of electron spin (rotation) around its own axis (clockwise or anticlockwise).

(ii) There are two possible values of $\mathbf{m_s}$ are $+\frac{1}{2}$ & $-\frac{1}{2}$ and represented by the two arrows ↑ (spin up) and ↓ (spin down).

Shapes of Atomic Orbitals:

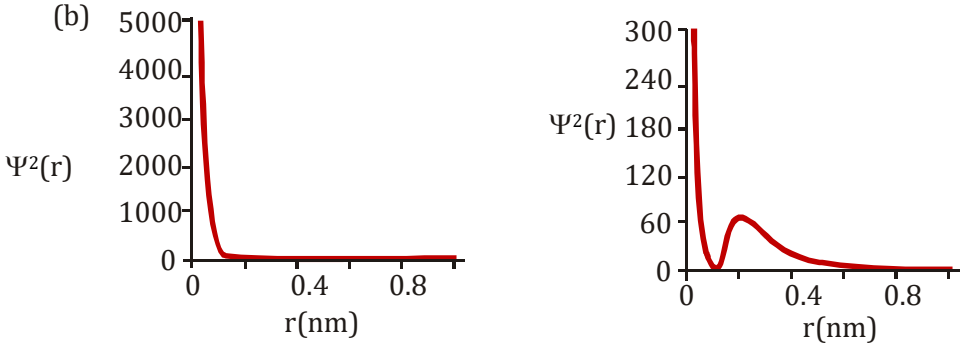
The orbital wave function or ψ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of corresponding wave functions as a function of r (the distance from the nucleus) are different. Such plots for 1s (n = 1, l = 0) and 2s (n = 2, l = 0) orbitals are

(a)



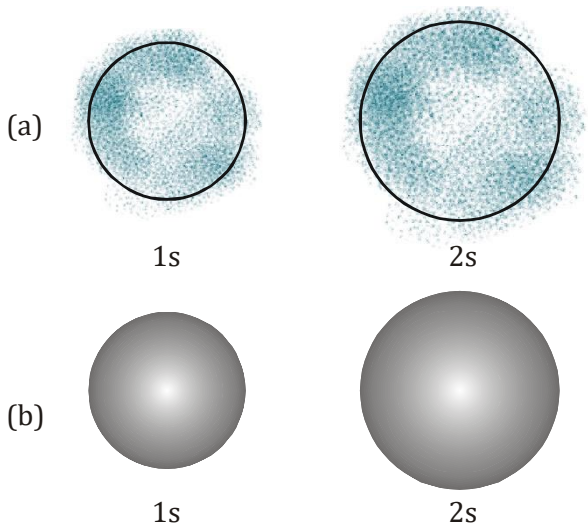
According to the German physicist, Max Born, the square of the wave function (i.e., ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ^2 as a function of r for 1s and 2s orbitals is given in fig. Here again, you may note that the curves for 1s and 2s orbitals are different.

(b)



It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maximum it decreases again and approaches zero as the value of r increases further. The region where this probability density function reduces to zero is called **nodal surfaces** or simply **nodes**. In general, it has been found that ns-orbital has (n – 1) nodes, that is, number of nodes increases with increase of principal quantum number n. In other words, number of nodes for 2s orbital is one, two for 3s and so on.

These probability density variations can be visualised in terms of charge cloud diagrams. In these diagrams, the density of the dots in a region represents electron probability density in that region.



(a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region.
(b) Boundary surface diagram for 1s and 2s orbitals.

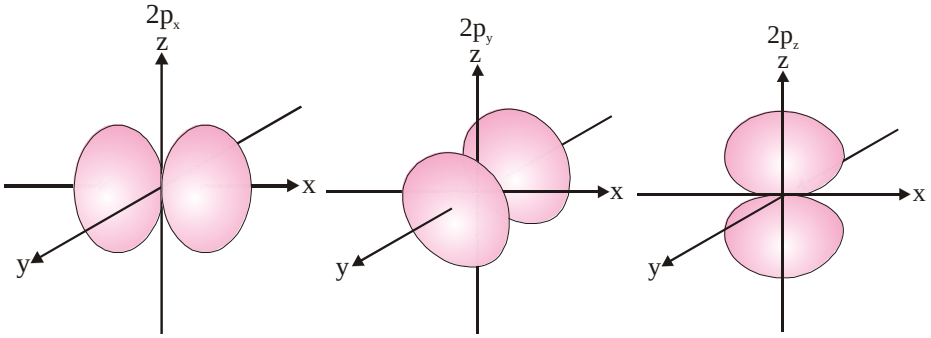
Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%.

The boundary surface diagram for 1s and 2s orbitals are given in figure, One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle.

It encloses a region in which probability of finding the electron is about 90%.

Thus, we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n, i.e. 4s > 3s > 2s > 1s and the electron is located further away from the nucleus as the principal quantum number increases.

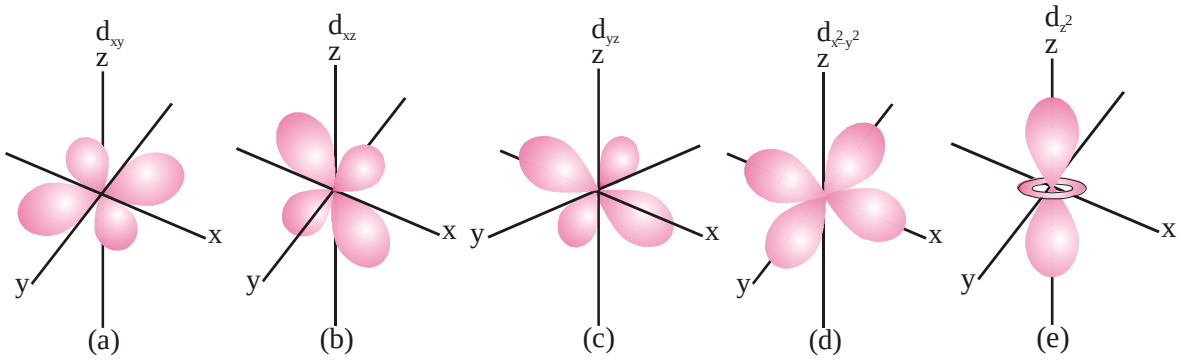
Boundary surface diagrams for three 2p orbitals (l = 1) are



Boundary surface diagrams of the three 2p orbitals.

In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$. It should be understood, however, that there is no simple relation between the values of m_l (–1, 0 and +1) and the x, y and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of m_l, there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is 4p > 3p > 2p. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the n – 2, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on.

For l = 2, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3. as the value of l cannot be greater than n – 1. There are five m_l values (–2, –1, 0, +1 and +2) for l = 2 and thus there are five d orbitals. The boundary surface diagram of d orbitals are



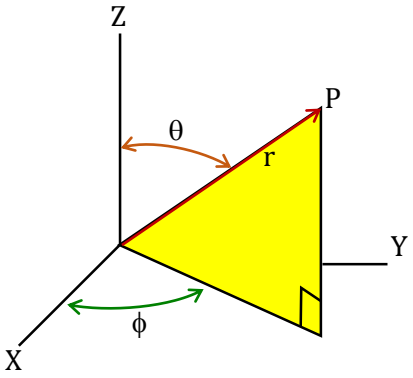
Boundary surface diagrams of the five 3d orbitals.

The five d-orbitals are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}. The shapes of the first four d-orbitals are similar to each other, where as that of the fifth one, d_{z^2}, is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size.

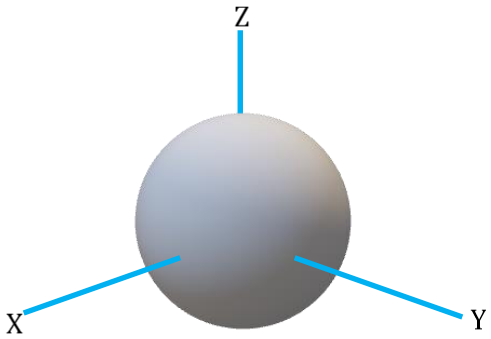
Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the np and nd orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of p_z orbital, xy-plane is a nodal plane, in case of d_{xy} orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis. These are called **angular nodes** and number of angular nodes are given by 'l', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals and so on.

The total number of nodes are given by (n–1), i.e., sum of ℓ angular nodes and (n – ℓ – 1) radial nodes.

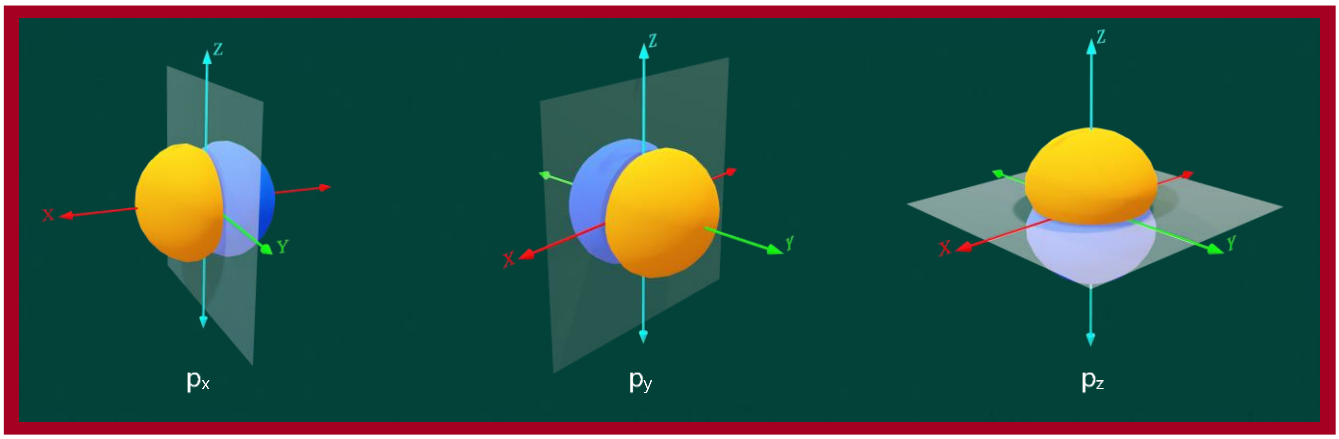
Shapes of Atomic Orbitals:

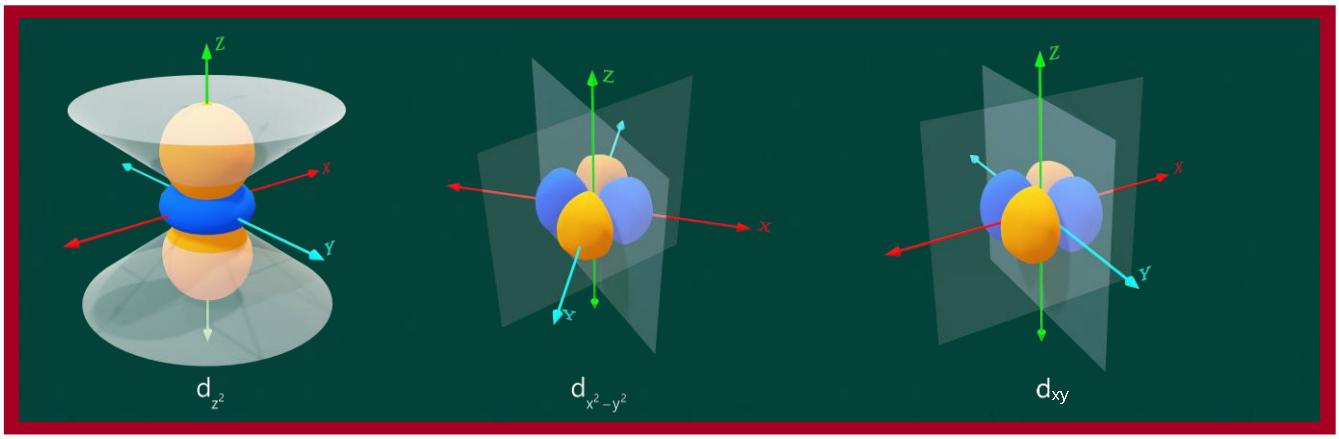


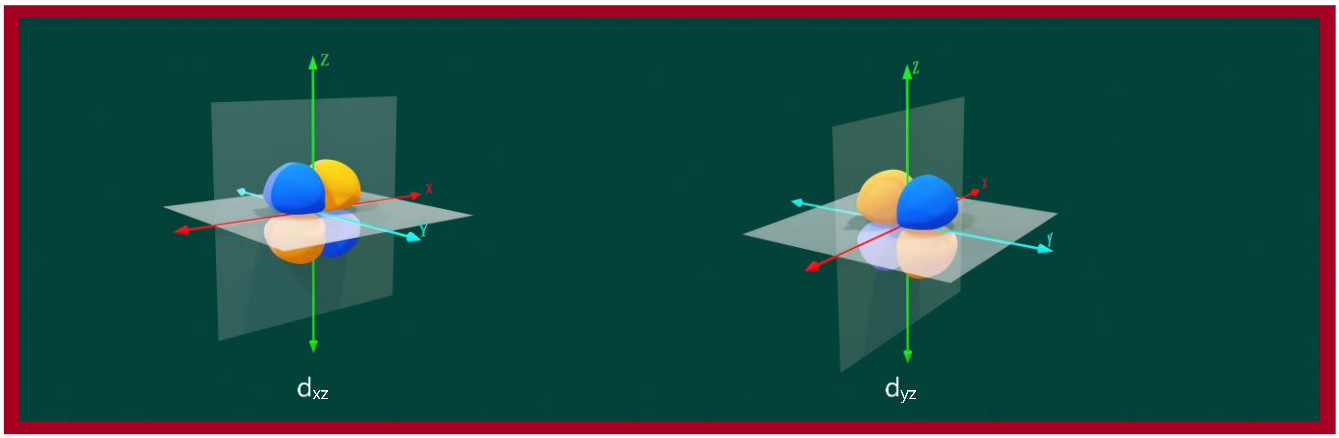
The spherical Polar Coordinates

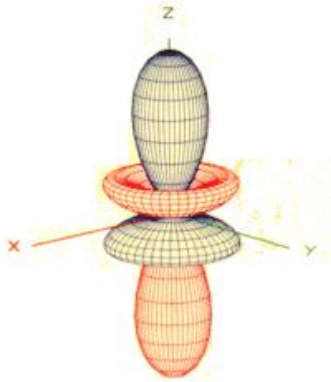


s

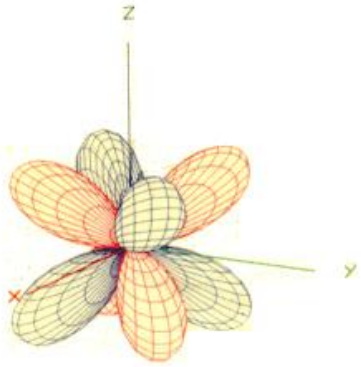




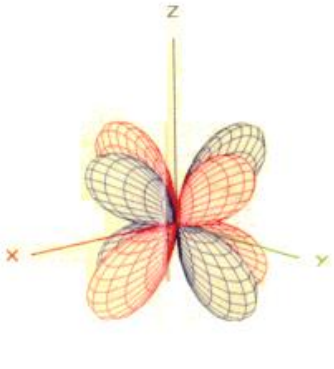




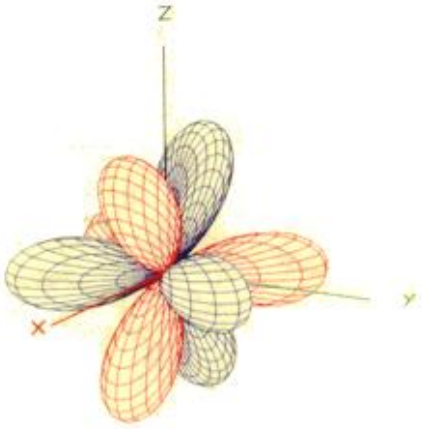
f_{z^3}



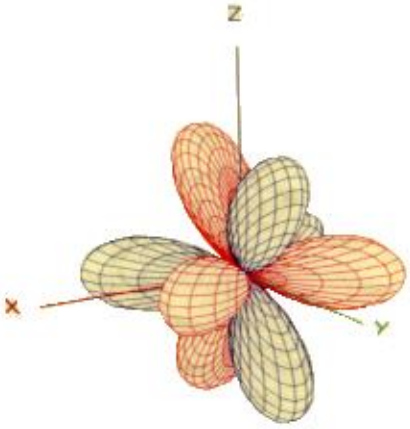
f_{xyz}



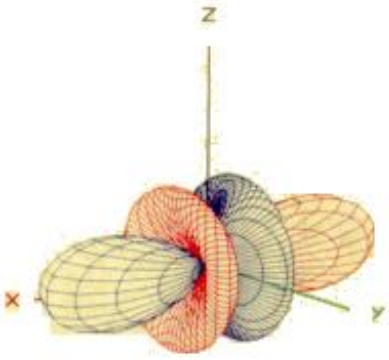
$f_{z(x^2-y^2)}$



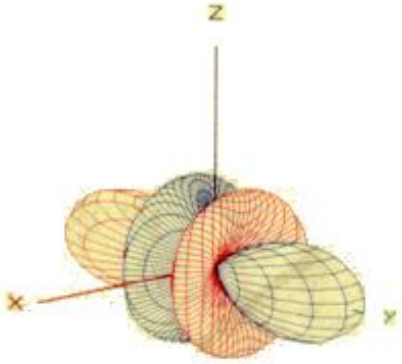
$f_{x(y^2-z^2)}$



$f_{y(z^2-x^2)}$



f_{x^3}



f_{y^3}

Note : Orbital angular momentum (L) $\rightarrow L=\sqrt{\ell(\ell+1)}\hbar$

$$\hbar=\frac{h}{2\pi}$$

Illustration 54:

Find the distance at which probability of finding electron is maximum for 1s orbital in a He atom. The wave function of orbital is given as.

$$\psi_{1s}=\frac{4}{a_0^{3/2}}.e^{-\frac{2r}{a_0}}$$

Solution:

Probability distribution function is $P(r) = \psi^2.4\pi r^2 = \left(\frac{16}{a_0^3}\right)e^{\left(-\frac{4r}{a_0}\right)}.4\pi r^2$

$\Rightarrow$ $P(r) = k \,.\, r^2.\, e^{\frac{-4r}{a_0}}$

differentiating $\frac{dP(r)}{dr} = 2r.e^{-\frac{4r}{a_0}} - \left(\frac{4}{a_0}\right)r^2.e^{-\frac{4r}{a_0}} = 0$

$\Rightarrow$ $1 = \frac{2r}{a_0} \Rightarrow r = \frac{a_0}{2}$

$\Rightarrow$ probability of finding electron is maximum at distance $\frac{a_0}{2}$ from nucleus.

Illustration 55:

Consider ψ (wave function) of 2s atomic orbital of H-atom is -

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\left[2-\frac{r}{a_0}\right]e^{-\frac{r}{2a_0}}$$

Find distance of radial node from nucleus in terms of a_0.

Solution:

$R(r) = 0$

$\left[2-\frac{r}{a_0}\right]e^{-\frac{r}{2a_0}} = 0 \Rightarrow 2-\frac{r}{a_0} = 0 \Rightarrow r = 2\,a_0$

Illustration 56:

The wave function of 2s electron is given by

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/a_0}$$

It has a node at $r = r_0$. Find the relation between r_0 and a_0.

Solution:

The wave function of 2s electron is

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/a_0}$$

Thus, the probability of finding of 2s electron at a point is

$$\psi^2_{2s} = \left[\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/a_0}\right]^2 = \frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3\left(2-\frac{r}{a_0}\right)^2 e^{-2r/a_0}$$

Node is the point at which the probability of finding an electron is zero. It means the value of ψ^2_{2s} is zero when $r = r_0$.

So, $\frac{1}{32\pi}\left(\frac{1}{a_0}\right)^3\left(2-\frac{r_0}{a_0}\right)^2 e^{-2r_0/a_0} = 0$

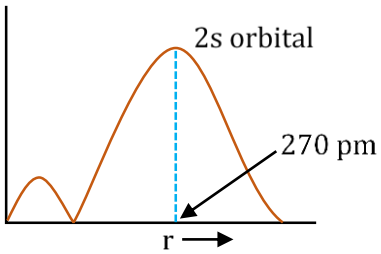
$\Rightarrow$ $2-\frac{r_0}{a_0} = 0$ $\qquad\qquad$ $\therefore$ $r_0 = 2a_0$

Illustration 57:

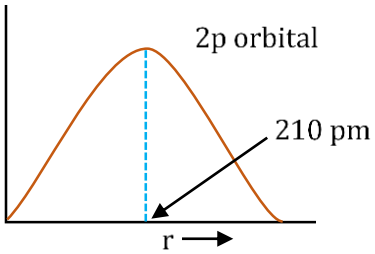
Draw the radial probability function curves for 2s and 2p electron orbitals and compare them.

Solution:

The radial probability distribution curves for 2s and 2p electron orbitals are given below :



Radial probability distribution curve for 2s electron orbital



Radial probability distribution curve for 2p electron orbital

Comparison of radial probability distribution curves for 2s and 2p electron orbitals : The following points are noteworthy when we compare the radial probability curves for different electron orbitals :

a. The radial probability distribution curve for 2s electron orbital shows two maxima – a smaller one near the nucleus and a bigger one away from it at a larger distance. In between two maxima, there is one minimum where the probability of finding the electron is almost at the nodal point.

b. Although the radius of maximum probability for 2p electron (210 pm) is slightly less than that for 2s electron (270 pm), because of the presence of a small additional maxima, 2s electron spends some more time near the nucleus than 2p electron. In other words, 2s electron is held more tightly by the nucleus than 2p electron. This is what we actually observe.

Illustration 58:

I. Choose the correct statements among the following:

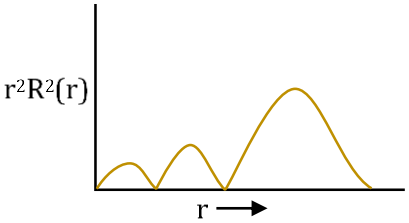
(1) A node is a point in space where the wave function (ψ) has zero amplitude.

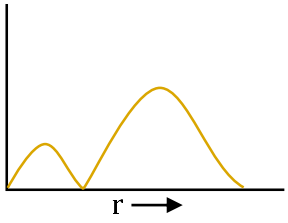
(2) The number of peaks in radial distribution is n – 1.

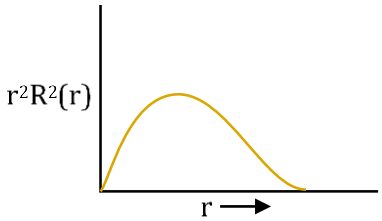
(3) Radial probability density $\pi_{n,\ell}(r) = 4\pi r^2 R^2_{n,\ell}(r)$.

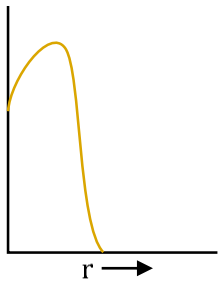
(4) ψ^2 represents the atomic orbital.

II. Which of the following radial distribution graphs corresponds to $\ell = 2$ for H atom for the least value of n for which $\ell = 2$ is allowed ?

(1) 

(2) 

(3) 

(4) 

III. For an electron in a hydrogen atom, the wave function ψ is proportional to e^{-r/a_0}, where a_0 is the Bohr's radius. What is the ratio of the probability of finding the electron at the nucleus to the probability of finding it at a_0 ?

(1) e (2) $1/e^2$ (3) e^2 (4) 0

IV. The wave function of atomic orbital of H-like atoms is given as under :

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} Z^{3/2}(2 - Zr)e^{Zr/2}$$

Given that the radius is in Å, then which of the following is the radius for nodal surface for $He^{\oplus}$ ion ?

(1) 1 au (2) 2 au (3) 2.5 au (4) 4 au

(au = atomic unit of radius)

Solution:

I. (1, 2, 3)

(Factual statement)

(4) is wrong as ψ represents atomic orbitals, ψ^2 represents probability density.

II. (3)

Option (3) represents the distribution of $\ell = 2$ for H atom.

(1) Two nodes : $(n - \ell - 1) = 2$, $(n - 2 - 1) = 2$

$\therefore$ $n = 5$ (High value of n)

(2) One node : $(n - 2 - 1) = 1$, $n = 4$.

(3) Zero node : $(n - 2 - 1) = 0$, $n = 3$. (Minimum value of n for which $\ell = 2$ is allowed)

(4) Graph does not correspond to any radial distribution curve.

III. (3)

Because probability at $r = a_0$ is proportional to $e^{-2r/a_0} = e^{-2}$

$$\frac{|\psi|^2_{r=0}}{|\psi|^2_{r=a_0}} = \frac{e^0}{e^{-2}} = e^2$$

$$[\because \quad P = |\psi|^2 \propto (e^{-r/a_0})^2]$$

IV. (1)

$(2 - Zr) = 0$

$(\because$ $Z = 2$ for $He^{\oplus})$

$\therefore$ $Zr = 2$

$$r = \frac{2}{Z} = \frac{2}{2} = 1 \text{ au}$$

Illustration 59:

I. Suggest the number of angular and spherical nodes in

a. 4p b. 3p c. 3s

II. The correct Schrodinger wave equation for an electron with E as total energy and V as potential energy is

(1) $\frac{\partial^2\psi}{dx^2}+\frac{\partial^2\psi}{dy^2}+\frac{\partial^2\psi}{dz^2}+\frac{\partial\pi^2}{mh^2}(E-V)\psi=0$ (2) $\frac{\partial^2\psi}{dx^2}+\frac{\partial^2\psi}{dy^2}+\frac{\partial^2\psi}{dz^2}+\frac{8\pi m}{h^2}(E-V)\psi=0$

(3) $\frac{\partial^2\psi}{dx^2}+\frac{\partial^2\psi}{dy^2}+\frac{\partial^2\psi}{dz^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$ (4) $\frac{\partial^2\psi}{dx^2}+\frac{\partial^2\psi}{dy^2}+\frac{\partial^2\psi}{dz^2}+\frac{8\pi m^2}{h}(E-V)\psi=0$

III. In an atomic orbital, the sign of lobes indicates the

(1) Sign of the probability distribution (2) Sign of charge

(3) Sign of the wave function (4) Presence or absence of electron

IV. The permissible solution to the Schrodinger wave equation gave an idea of ..... quantum numbers.

(1) 4 (2) 2 (3) 3 (4) 1

Solution:

I. Angular nodes = ℓ, spherical node = n – ℓ – 1

a. 1, 2 b. 1, 1 c. 0, 2

II. (3)

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

III. (3)

Sign of wave function

IV. (3)

3 (n, ℓ, m)

Illustration 60:

I. Which of the following d-orbitals has dough-nut shape?

(1) d_{xy} (2) d_{yz} (3) $d_{x^2-y^2}$ (4) d_{z^2}

II. The number of nodal planes d-orbital has

(1) Zero (2) One (3) Two (4) Three

III. The energy of state s_1 in units of the hydrogen atom ground state energy is

(1) 0.75 (2) 1.50 (3) 2.25 (4) 4.50

Solution:

I. (4) d_{z^2}

II. (3) Two

III. (3) 2.25

Spherically symmetrical state (i.e., s orbital) with one radial node = 2s = s_1

(n – ℓ – 1)

n = 2 $\longrightarrow$ s_2 (one radial node) $\equiv n_2$ and $(E_n)_{Li^{2+}}=(E)_{1H}$

$\Rightarrow \quad -13.6\times\frac{3^2}{n_2^2}=-13.6\times\frac{1^2}{1^2}$

$\Rightarrow$ $n_2 = 3$

$\Rightarrow$ $s_2 = 3p$

$\Rightarrow \quad \frac{E_{S_1}}{(E_H)_{n=1}}=\frac{-13.6\times\frac{3^2}{2^2}}{-13.6\times\frac{1^2}{1^2}} = 2.25$

Rules for filling Electrons:

1. Pauli's exclusion principle

'No two electrons in an atom can have same values of all the four quantum numbers.

An orbital accommodates two electrons with opposite spin. These two electrons have same values of principal, azimuthal and magnetic quantum number but the fourth, i.e. magnetic spin quantum number will be different. i.e.

For K, shell (n = 1)

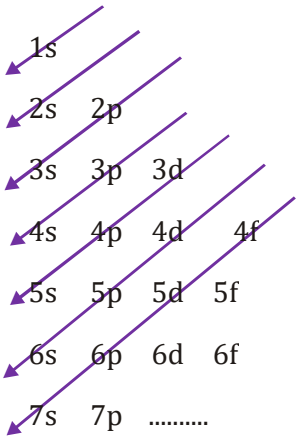
l = 0, m = 0

For 1st Electron n = 1, l = 0, m = 0, $m_s = +\frac{1}{2}$

For 2nd Electron n = 1, l = 0, m = 0, $m_s = -\frac{1}{2}$

2. Aufbau Principle (Means Building up) :

The electrons are added progressively to the various orbitals in the order of increasing energies starting with the orbital of the lowest energy



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

Alternatively, the order of increase of energy of orbitals can be calculated from (n + ℓ) rule.

(i) Lower the value of (n + ℓ) for an orbital, the lower will be its energy.

(ii) If two orbitals have the same (n + ℓ) value, then orbital with lower value of n has the lower energy.

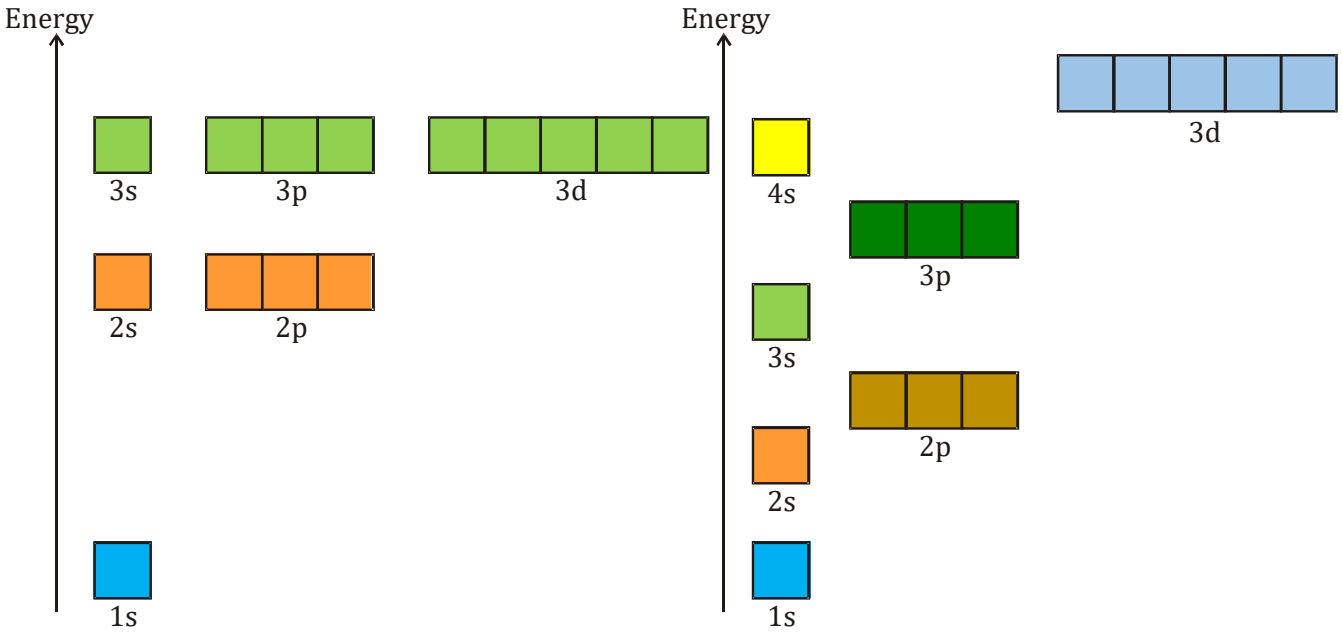
e.g. 2p & 3s

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

For 3s, n = 3, ℓ = 0, (n + ℓ) = 3 + 0 = 3

Then for 2p, n is lesser than for 3s, so 2p has lower energy than 3s.

(iii) 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f .... energy order of different orbitals for single electron system like H, $He^{\oplus}$, $Li^{2\oplus}$ etc. (used in Bohr model)



(A) For single electron or hydrogenic atom (B) Multi electronic atoms

Energy level diagram for few electronic shells

Illustration 61:

Write the increasing order of energies of 4s, 3p, 4p and 3d.

Solution:

For 4s, n = 4, l = 0, (n + l) = 4

For 3p, n = 3, l = 1, (n + l) = 4

For 4p, n = 4, l = 1, (n + l) = 5

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

$\Rightarrow$ 3p < 4s < 3d < 4p increasing order

3. Hund's rule of maximum multiplicity :

This rule deals with the filling of electrons into the orbitals belonging to the same subshell i.e. orbitals of equal energy, called degenerate orbitals.

"Electrons are distributed among the orbitals of a subshell in such a way so as to give the maximum number of unpaired electrons with parallel spins."

"Pairing of electrons in the orbitals belonging to the same subshell (p, d, f) does not take place until each orbital belonging to that subshell has got one electron each i.e. singly occupied. Moreover, the singly occupied orbitals must have the electrons with the parallel spin multiplicity"

Multiplicity = 2|S| + 1, where S = Total spin.

i.e. 

Find total spin & multiplicity

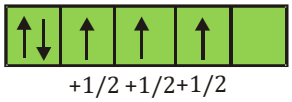
Total spin S = $\frac{1}{2}+\frac{1}{2}+\frac{1}{2}=\frac{3}{2}$

Multiplicity = $2\times\frac{3}{2}+1=4$

i.e. 

Total spin S = $\frac{1}{2}-\frac{1}{2}+\frac{1}{2}=\frac{1}{2}$

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

i.e. 

Total spin S = $\frac{1}{2}+\frac{1}{2}+\frac{1}{2}=\frac{3}{2}$

Multiplicity = $2\times\frac{3}{2}+1=4$

i.e. 

Total spin = $5\times\frac{1}{2}=\frac{5}{2}$

Multiplicity = $2\times\frac{5}{2}+1=6$

Electronic Configuration of Atoms:

The distribution of electrons in various shells, subshells and orbitals, in an atom of an element, is called its electronic configuration.

x ← no. of electrons in subshell

n*l*

↑↑ ——— represents subshell

(represents shell)

$2p^5$ ← no. of electrons in p-subshell

↑↑ ——— p subshell

Second shell

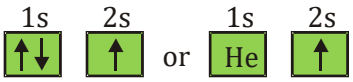
$_3Li$; $1s^2, 2s^1$ or [He] $2s^1$ or 

Illustration 62:

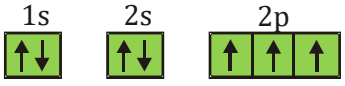
Write electronic configuration of Nitrogen.

Solution:

$_7N$: $1s^2, 2s^2\ 2p^3$ [Orbital notation method]

$1s^2, 2s^2\ 2p_x^1\ 2p_y^1 2p_z^1$

or



[Orbital diagram method]

or

[He] $2s^2\ 2p^3$ [Condensed form]

Extra stability of Half-filled and fully-filled orbitals.

The electronic configuration of most of the atoms follows the Aufbau's rule. However, in certain elements such as Cr, Cu etc. Where the two subshells (4s and3d) differ slightly in their energies (4s < 3d), an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half-filled.

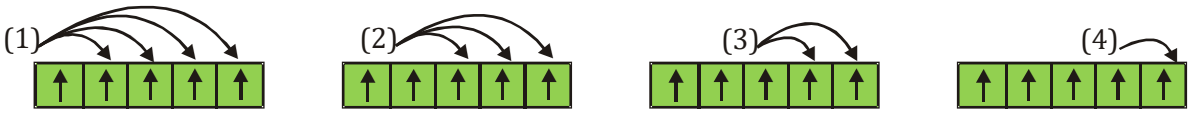
$_{24}Cr \rightarrow [Ar]\ 3d^5, 4s^1$ and not $[Ar]\ 3d^4\ 4s^2$

$_{29}Cu \rightarrow [Ar]\ 3d^{10}, 4s^1$ and not $[Ar]\ 3d^9\ 4s^2$

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 subshell have symmetrical distribution of electron 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 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 fully filled. As result the exchange energy is maximum and so is the stability.



4-exchanges by electron 1 | 3-exchanges by electron 2 | 2-exchanges by electron 3 | 1-exchanges by electron 4

Total exchange pairs = 10

$\frac{n(n-1)}{2} \rightarrow$ Number of exchange pairs

$n \rightarrow$ Number of electron with parallel spins.

e.g. 

Only 6 total exchange possible

Exceptional electronic configuration

S.No.	Element	Z	Configuration
1	Cr	24	**$[Ar]4s^1 3d^5$**
2.	Cu	29	**$[Ar]4s^1 3d^{10}$**
3.	Nb	41	**$[Kr]5s^1 4d^4$**
4.	Mo	42	**$[Kr]5s^1 4d^5$**
5.	Ru	44	**$[Kr]5s^1 4d^7$**
6.	Rh	45	**$[Kr]5s^1 4d^8$**
7.	Pd	46	**$[Kr]4d^{10}$**
8.	Ag	47	**$[Kr]5s^1 4d^{10}$**
9.	La	57	**$[Xe]6s^2 5d^1$**
10.	Pt	78	**$[Xe]6s^1 4f^{14} 5d^9$**
11.	Au	79	**$[Xe]6s^1 4f^{14} 5d^{10}$**
12.	Ac	89	**$[Rn]7s^2 6d^1$**
13.	**Th**	**90**	**$[Rn]7s^2 6d^2$**

Magnetic Properties:

Para magnetism :

(i) The substances which are weakly attracted by magnetic field are paramagnetic and this phenomenon is known as para magnetism.

(ii) Their magnetic character is retained till they are in magnetic field and lose their magnetism when removed from magnetic field.

Diamagnetism :

(i) The substances which are weakly repelled by magnetic field are diamagnetic and this phenomenon is known as diamagnetism.

(ii) Diamagnetic substances lack unpaired electrons and their spin magnetic moment is zero e.g., NaCl, N_2O_4 etc.

Spin magnetic moment :

The spin magnetic moment of electron (excluding orbit magnetic moment) is given by :

$\mu = \sqrt{n(n+2)}$ **B.M.**

Where n is number of unpaired electrons in species.

The magnetic moment is expressed in Bohr magneton (B.M.)

Illustration 63:

A compound of vanadium has magnetic moment of 1.73 BM. Work out the electronic configuration of vanadium ion in the compound.

Solution:

Vanadium belongs to 3d series with Z = 23. The magnetic moment of 3d series metal is given by spin only formula.

$\mu = \sqrt{n(n+2)}$ BM (BM = Bohr's magneton)

$\because \quad 1.73 = \sqrt{3}$

$\Rightarrow$ n(n+2) = 3 $\Rightarrow$ n = 1

$\Rightarrow$ Magnetic moment corresponds to one unpaired electron.

$\Rightarrow$ Electronic configuration of vanadium atom $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$.

For one unpaired electron 4 electron must be removed in which first 2 electron are lost from 4s orbital (outermost).

Electronic configuration of $V^{4\oplus}$

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^1$

Nodal Planes of different orbitals :

Nodal plane is a plane at which the probability of finding an electron becomes zero.

e.g.

Orbital	Nodal plane	Orbital	Nodal plane
s	None	d_{xy}	XZ & YZ planes
$\mathbf{p_x}$	YZ plane	d_{yz}	XZ & XY planes
$\mathbf{p_y}$	XZ plane	d_{xz}	XY & YZ planes
$\mathbf{p_z}$	XY plane	$d_{x^2-y^2}$	Planes perpendicular to XY plane, passing through origin (nucleus) and inclined at 45° to X & Y axis.
		d_{z^2}	None (two nodal cones are available)