ATOMIC STRUCTURE & NUCLEAR CHEMISTRY

SECTION (A) : DISCOVERY OF SUB ATOMIC PARTICLES, ATOMIC MODELS, NUCLEUS

INTRODUCTION:

Structure of Atom

Rutherford's Model | Bohr's Model | Wave mechanical model

Dalton's concept of the indivisibility of the atom was completely discredited by a series of experimental evidences obtained by scientists. A number of new phenomena were brought to light and man's idea about the natural world underwent a revolutionary change. The discovery of electricity and spectral phenomena opened the door for radical changes in approaches to experimentation. It was concluded that atoms are made of three particles: electrons, protons and neutrons. These particles are called the fundamental particles of matter.

Earlier efforts to reveal structure of atom:

CATHODE RAYS - DISCOVERY OF ELECTRON

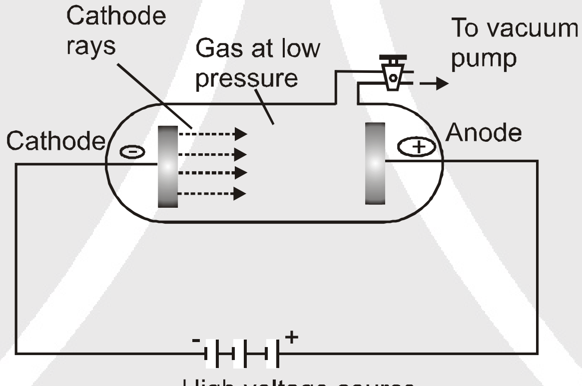


Figure-1

In 1859 **Julius Plucker** started the study of conduction of electricity through gases at low pressure (10^{-4} atm) in a discharge tube. When a high voltage of the order of 10,000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrode, these rays are called as cathode rays.

Properties of Cathode Rays:

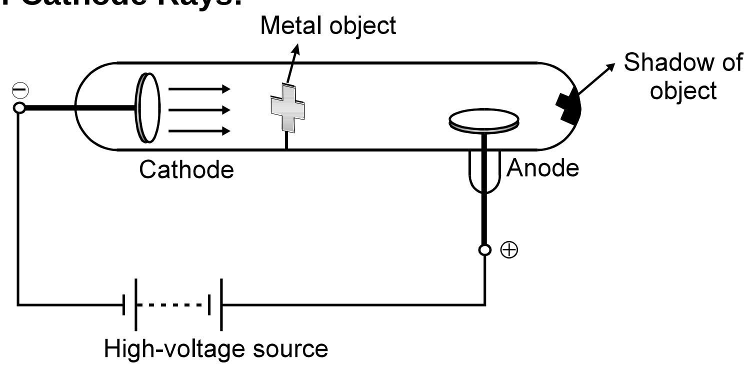


Figure-2

Cathode rays have the following properties.

(i) Cathode rays travel at a very high velocity on a straight path as it produces shadow of an object placed in its path.

(ii) Cathode rays produce mechanical effects. If small light paddle wheel is placed between the electrodes, it rotates. This indicates that the cathode rays consist of material particles.

(iii) When electric and magnetic fields are applied to the cathode rays in the discharge tube. The rays are deflected thus establishing that they consist of charged particles. The direction of deflection showed that cathode rays consist of negatively charged particles called **electrons**.

(iv) They produce a green glow when strike the glass wall beyond the anode. Bright spot is developed when they strike the zinc sulphide screen.

(v) Cathode rays penetrate through thin sheets of aluminum and metals.

(vi) They affect the photographic plates

(vii) The ratio of charge(e) to mass(m) i.e. charge/mass is same for all cathode rays irrespective of the gas used in the tube. $e/m = 1.76 \times 10^{11}\ Ckg^{-1}$

Thus, it can be concluded that electrons are basic constituent of all the atoms.

(viii) Cathode rays are invisible.

Production of Anode rays (Discovery of Proton):

Goldstein (1886) repeated the experiment with a discharge tube filled with a perforated cathode and found that new type of rays came out through the hole in the cathode.

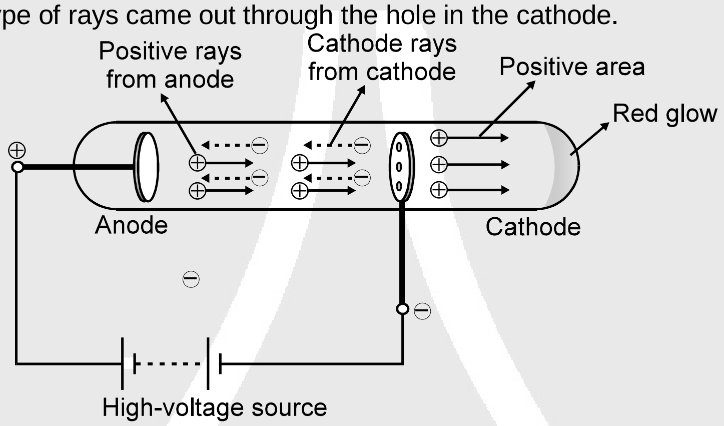


Figure-3

When this experiment is conducted, a faint red glow is observed on the wall behind the cathode. Since these rays originate from the anode, they are called anode rays (canal rays).

Properties of Anode Rays :

- ***Anode rays travel along straight paths*** and hence they cast shadows of object placed in their path.
- ***They rotate a light paddle wheel placed in their path.*** This shows that anode rays are made up of material particles.
- They are deflected towards the negative plate of an electric field. This shows that these rays are positively charged.
- For different gases used in the discharge tube, the charge to mass ratio (e/m) of the positive particles constituting the positive rays is different. When hydrogen gas is taken in the discharge tube, the e/m value obtained for the positive rays is found to be maximum. Since the value of charge (e) on the positive particle obtained from different gases is the same, the value of m must be minimum for the positive particles obtained from hydrogen gas. Thus, the positive particle obtained from hydrogen gas is the lightest among all the positive particles obtained from different gases. This particle is called the proton.

Discovery of Neutron :

Later, a need was felt for the presence of electrically neutral particles as one of the constituent of atom. These particles were discovered by Chadwick in 1932 by bombarding a thin sheet of Beryllium with α-particles, when electrically neutral particles having a mass slightly greater than that of the protons were emitted. He named these particles as neutrons.

$$^{9}_{4}Be + {}^{4}_{2}He \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n$$

The NUCLEUS :

Electrons, protons & neutrons are the fundamental particles present in all atoms,(except hydrogen)

Table : 1

Particles	Symbol	Mass	Charge	Discoverer
Electron	$_{-1}e^0$ or β	9.10939×10^{-31} kg 0.00054 u	-1.6022×10^{-19} Coulombs -4.803×10^{-10} esu	J.J. Thomson Stoney Lorentz 1887
Proton	$_1H^1$	1.6722×10^{-27} kg 1.00727 u	$+1.6022 \times 10^{-19}$ Coulombs $+4.803 \times 10^{-10}$ esu	Goldstein Rutherford1907
Neutron	$_0n^1$	1.67493×10^{-27} kg 1.00867 u 1 amu $\approx 1.66 \times 10^{-27}$ kg	Neutral 0	James Chadwick 1932

Atomic Models :

(A) Thomson's Model of the atom :

An atom is electrically neutral. It contains positive charges (due to the presence of protons) as well as negative charges (due to the presence of electrons). It assumes that mass is equally distributed in the atom. Hence, J.J. Thomson assumed that an atom is a uniform sphere of positive charges with electrons embedded in it.

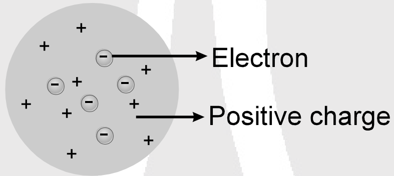


Figure-4

(B) Rutherford's Experiment :

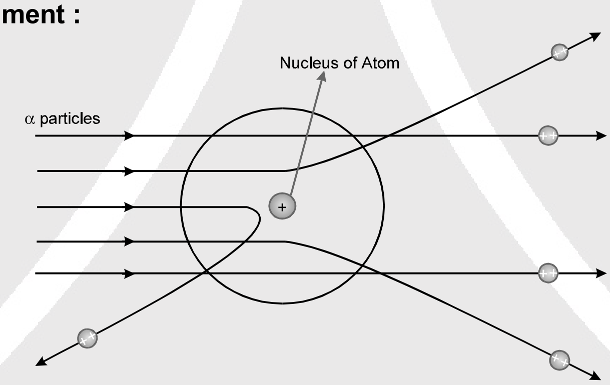


Figure-5

Observation :

1. Most of the α-particles passed straight through the gold foil undeflected.

2. A few of them were deflected through small angles, while a very few were deflected to a large extent.

3. A very small percentage (1 in 20000) was deflected through angles ranging from nearly 180°.

Rutherford's nuclear concept of the atom.

(i) The atom of an element consists of a small positively charged 'nucleus' which is situated at the centre of the atom and which carries almost the entire mass of the atom.

(ii) The electrons are distributed in the empty space of the atom around the nucleus in different concentric circular paths, called orbits.

(iii) The number of electrons in orbits is equal to the number of positive charges (protons) in the nucleus. Hence, the atom is electrically neutral.

(iv) The volume of the nucleus is negligibly small as compared to the volume of the atom.

(v) Most of the space in the atom is empty.

Drawbacks of rutherford's model :

1. This was not according to the classical theory of electromagnetism proposed by Maxwell. According to this theory, every accelerated charged particle must emit radiations in the form of electromagnetic waves and loses it total energy.
Since energy of electrons keep on decreasing, so radius of the circular orbits should also decrease and ultimately the electron should fall in nucleus.

2. It could not explain the line spectrum of H-atom.

3. It says nothing about the electronic structure of atom i.e. how the e^- are distributed around the nucleus and what are the energies of these e^-.

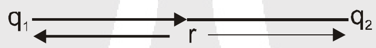
Properties of charge :

F1

1. Q = ne (charge is quantized)

2. Charge are of two types :
(i) Positive charge
(ii) Negative Charge
$e = -1.6 \times 10^{-19}$
$p = +1.6 \times 10^{-19}$C

This does not mean that a proton has a greater charge but it implies that the charge is equal and opposite.
Same charge repel each other and opposite charges attract each other.
3. Charge is a SCALAR Qty. and the force between the charges always acts along the line joining the charges.



The magnitude of the force between the two charge placed at a distance 'r' is given by

$$F_E = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r^2}$$

(electrical force)

4. If two charge q_1 and q_2 are separated by distance r then the potential energy of the two charge system is given by.

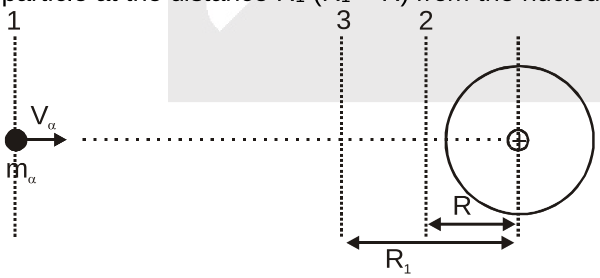
F2 $$P.E. = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r}$$

5. If a charged particle q is placed on a surface of potential V then the potential energy of the charge is q × V.

Estimation of closest distance of approach (derivation)

Der.1 An α-particle is projected from infinity with the velocity V_0 towards the nucleus of an atom having atomic number equal to Z then find out (i) closest distance of approach (R) (ii) what is the velocity of the α-particle at the distance R_1 ($R_1 > R$) from the nucleus.

Sol.



From energy conservation $P.E_1 + KE_1 = P.E_2 + KE_2$

$\Rightarrow$ $$0 + \frac{1}{2}m_\alpha V_\alpha^2 = \frac{K(Ze)(2e)}{R} + 0$$

$$R = \frac{4KZe^2}{m_\alpha V_\alpha^2}$$ (closest distance of approach)

Let velocity at R_1 is V_1.

From energy conservation $P.E_1 + KE_1 = P.E_3 + KE_3$ $\Rightarrow$ $$0 + \frac{1}{2}m_\alpha V_\alpha^2 = \frac{K(Ze)(2e)}{R_1} + \frac{1}{2}m_\alpha V_1^2$$

Size of the nucleus:

The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.

Thus, diameter (size) of the atom is 100,000 times the diameter of the nucleus.

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

F3 $R = R_0\,(A)^{1/3}$ cm

where R_0 can be 1.1×10^{-13} to 1.44×10^{-13} cm ; A = mass number ; R = Radius of the nucleus.

Nucleus contains protons & neutrons except hydrogen atoms which does not contain neutron in the nucleus.

Atomic number (Z) and Mass number (A) :

D1

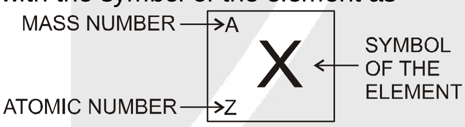
- **Atomic number (Z) of an element**
  = Total number of protons present in the nucleus
  = Total number of electrons present in the atom

- Atomic number is also known as proton number.
- Since the electrons have negligible mass, the entire mass of the atom is mainly due to protons and neutrons only. Since these particles are present in the nucleus, therefore they are collectively called **nucleons**.
- As each of these particles has one unit mass on the atomic mass scale, therefore the sum of the number of protons and neutrons will be nearly equal to the mass of the atom.

F4

- **Mass number of an element = No. of protons (Z) + No. of neutrons (n).**

- The mass number of an element is nearly equal to the atomic mass of that element. However, the main difference between the two is that mass number is always a whole number whereas atomic mass is usually not a whole number.
- The atomic number (Z) and mass number (A) of an element 'X' are usually represented along with the symbol of the element as



e.g. ${}^{23}_{11}Na$, ${}^{35}_{17}Cl$ and so on.

D2

1. **Isotopes:** Such atoms of the same element having same atomic number but different mass numbers are called isotopes.
   ${}^{1}_{1}H$, ${}^{2}_{1}D$ and ${}^{3}_{1}T$ named as protium, deuterium (D) and tritium (T) respectively. Ordinary hydrogen is protium.

D3

2. **Isobars :** Such atoms of different elements which have same mass numbers (and of course different atomic numbers) are called isobars. e.g. ${}^{40}_{18}Ar$, ${}^{40}_{19}K$, ${}^{40}_{20}Ca$.

D4

3. **Isotones :** Such atoms of different elements which contain the same number of neutrons are called isotones. e.g. ${}^{14}_{6}C$, ${}^{15}_{7}N$, ${}^{16}_{8}O$.

D5

4. **Isoelectronic :** The species (atoms or ions) containing the same number of electrons are called isoelectronic. e.g., O^{2-}, F^{-}, Na^{+}, Mg^{2+}, Al^{3+}, Ne all contain 10 electrons each and hence they are isoelectronic.

Solved Example

Example 1 Complete the following table :

Particle	Mass No.	Atomic No.	Protons	Neutrons	Electrons
Nitrogen atom	–	–	–	7	7
Calcium ion	–	20	–	20	–
Oxygen atom	16	8	–	–	–
Bromide ion	–	–	–	45	36

Solution. **For nitrogen atom.**

No. of electron = 7 (given)
No. of neutrons = 7 (given)
$\therefore$ No. of protons = Z = 7 ($\therefore$ atom is electrically neutral)
Atomic number = Z = 7
Mass No. (A) = No. of protons + No. of neutrons = 7 + 7 = 14

For calcium ion.

No. of neutrons = 20 (Given)
Atomic No. (Z) = 20 (Given)
$\therefore$ No. of protons = Z = 20 ;
No. of electrons in calcium atom = Z = 20
But in the formation of calcium ion, two electrons are lost from the extra nuclear part according to the equation $Ca \rightarrow Ca^{2+} + 2e^{-}$ but the composition of the nucleus remains unchanged.
$\therefore$ No. of electrons in calcium ion = 20 – 2 = 18
Mass number (A) = No. of protons + No. of neutrons = 20 + 20 = 40.

For oxygen atom.

Mass number (A) = No. of protons + No. of neutrons = 16 (Given
Atomic No. (Z) = 8 (Given)
No. of protons = Z = 8,
No. of electrons = Z = 8
No. of neutrons = A – Z = 16 – 8 = 8

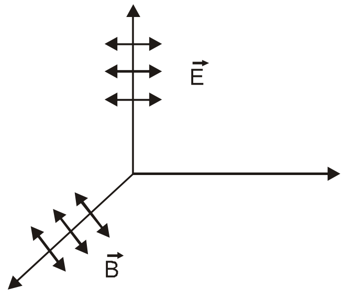
For bromide ion.

No. of neutrons = 45 (given)
No. of electrons = 36 (given)
But in the formation of bromide ion, one electron is gained by extra nuclear part according to equation
$Br + e^{-} \rightarrow Br^{-}$, But the composition of nucleus remains unchanged.
$\therefore$ No. of protons in bromide ion = No. of electrons in bromine atom = 36 – 1 = 35
Atomic number (Z) = No. of protons = 35
Mass number (A) = No. of neutrons + No. of protons = 45 + 35 = 80.

SECTION (B) : QUANTUM THEORY OF LIGHT & PHOTOELECTRIC EFFECT

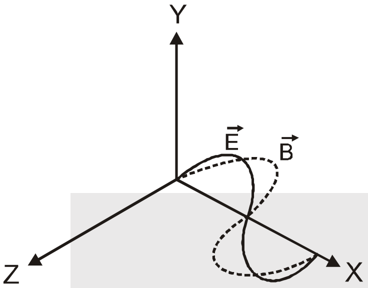
ELECTROMAGNETIC WAVE RADIATION :

D6 The oscillating electrical/magnetic field are electromagnetic radiations.
Experimentally, the direction of oscillations of electrical and magnetic field are perpendicular to each other.
These rays don't require medium for their propagation.
In vacuum all types of EM radiations, regardless of λ, travel at the same speed i.e., 2.997925×10^{8} m/s called the speed of light.



$\vec{E}$ = Electric field, $\vec{B}$ = Magnetic field

Figure-6



Direction of wave propagation

Figure-7

Some important characteristics of a wave :

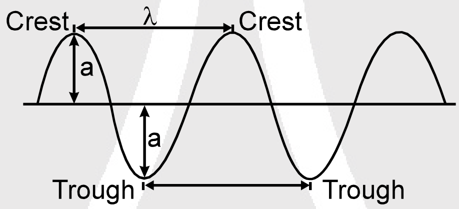


Figure-8

D7 **Wavelength** of a wave is defined as the distance between any two consecutive crests or troughs. It is represented by λ (lambda) and is expressed in Å or m or cm or nm (nanometer) or pm (picometer).

1 Å = 10^{-8} cm = 10^{-10} m

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

D8 **Frequency** of a wave is defined as the number of waves passing through a point in one second. It is represented by ν (nu) and is expressed in Hertz (Hz) or cycles/sec or simply sec^{-1} or s^{-1}.

1 Hz = 1 cycle/sec

D9 **Velocity** of a wave is defined as the linear distance travelled by the wave in one second. It is represented by v and is expressed in cm/sec or m/sec (ms^{-1}).

D10 **Amplitude** of a wave is the height of the crest or the depth of the trough. It is represented by 'a' and is expressed in the units of length.

D11 **Wave number** is defined as the number of waves present in 1 cm length. Evidently, it will be equal to the reciprocal of the wavelength. It is represented by $\bar{\nu}$ (read as nu bar).

F5 $\bar{\nu} = \dfrac{1}{\lambda}$

If λ is expressed in cm, $\bar{\nu}$ will have the units cm^{-1}.

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

F6 $v = \nu \times \lambda$

Order of wavelength in Electromagnetic spectrum

Cosmic rays < γ – rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction and interference can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained

(i) The nature of emission of radiation from hot bodies (black - body radiation)
(ii) Ejection of electrons from metal surface when radiation strikes it (photoelectric effect)
(iii) Variation of heat capacity of solids with respect to temperature.
(iv) Line spectrum of Hydrogen.

Black Body Radiation:

When solids are heated they emit radiation over a wide range of wavelengths.
The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. 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.

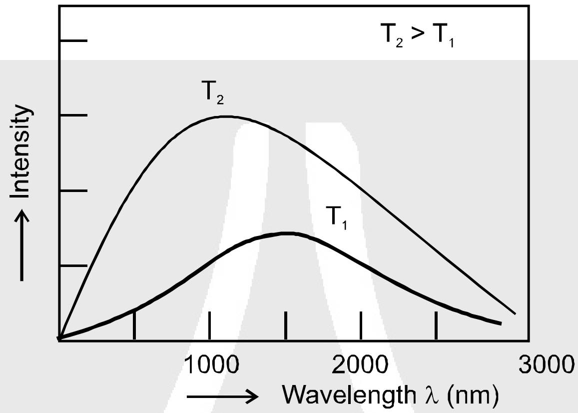


Figure-9

In the graph, there's a peak intensity but as per the Rayleigh-Jeans law (A mathematical formula for waves), there must be an infinite peak. So, the wave theory failed to explain this experimental graph.
Later, Plank's equation, which considered that atoms and molecules could emit (or absorb) energy only in discrete quantities (called quantum) and not in continuous manner, tallied with the graph proving even the particle nature of light.

Quantum theory of light:

D12 The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation is called as quantum of light.
According to Planck, the light energy coming out from any source is always an integral multiple of a smallest energy value called quantum of light.
Let quantum of light be = E_0(J), then total energy coming out is = nE_0 (n = Integer)
Quantum of light = Photon (Packet or bundle of energy)
Energy of one photon is given by

F7 $E_0 = h\nu$ (ν - Frequency of light)
$h = 6.626 \times 10^{-34}$ J-Sec (h - Planck const.)

F8 $E_0 = \frac{hc}{\lambda}$ (c - speed of light)
(λ - wavelength)

Order of magnitude of $E_0 = \frac{10^{-34} \times 10^{8}}{10^{-10}} = 10^{-16}$ J

Solved Example

Example 1 Certain sun glasses having small of AgCl incorporated in the lenses, on exposure to light of appropriate wavelength turns to gray colour to reduce the glare following the reactions:

$$AgCl \xrightarrow{h\nu} Ag(Gray) + Cl$$

If the heat of reaction for the decomposition of AgCl is 248 kJ mol^{-1}, what maximum wavelength is needed to induce the desired process?

Solution. Energy needed to change = 248×10^3 J/mol

If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon. Therefore, $\therefore$ $N_A . \frac{hc}{\lambda} = 248 \times 10^3$

$$\lambda = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^{8} \times 6.023 \times 10^{23}}{248 \times 10^{3}} = 4.83 \times 10^{-7} \text{ m}$$

D13 **One electron volt (e.v.) :** Energy gained by an electron when it is accelerated from rest through a potential difference of 1 volt.

Note: Positive charge always moves from high potential to low potential and –ve charge always. Moves from low potential to high potential if set free.

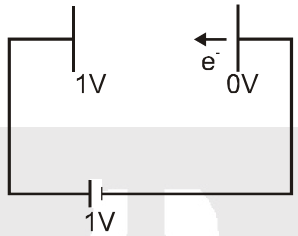


Figure-10

Der.2 From Energy conservation principle, $P.E._i + K.E._i = P.E._f + K.E._f$

$(-e)\,0 + 0 = (-e)\,(1V) + \frac{1}{2} mV_f^2$; $K.E. = \frac{1}{2} mV_f^2 = e\,(1 \text{ volt})$

If a charge 'q' is accelerated through a potential difference of 'V' volt then its kinetic energy will be increased by q.V.

$1eV = 1.6 \times 10^{-19}$ C x 1 volt $\therefore$ $1eV = 1.6 \times 10^{-19}$J

Photoelectric Effect :

D14 When certain metals (for example Potassium, Rubidium, Caesium etc.) were exposed to a beam of light electrons were ejected as shown in Fig.

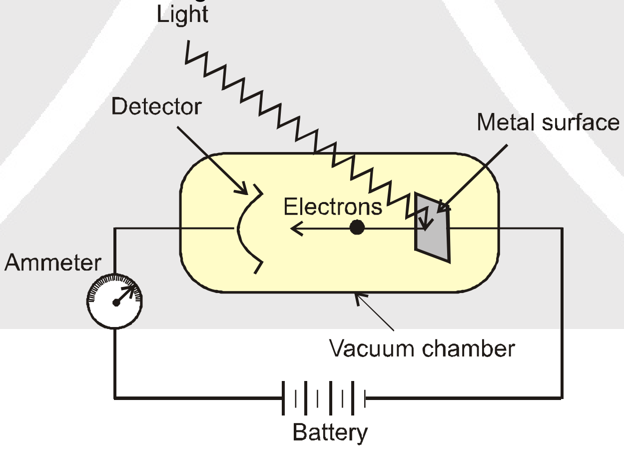


Figure-11

The phenomenon is called **Photoelectric effect**. The results observed in this experiment were :

(i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.

(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, ν_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (is also called work function, W_0) then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation

F9 $$h\nu = h\nu_0 + \frac{1}{2}m_e v^2$$

where m_e is the mass of the electron and v is the velocity associated with the ejected electron.

(iv) A more intense beam of light (consists of larger number of photons), ejected more e^- so it proved particle nature of light.

Solved Example

Example 1 The threshold frequency ν_0 for a metal is 6×10^{14} s^{-1}. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.1 \times 10^{15}$ s^{-1} hits the metal.

Solution. K.E. = $\frac{1}{2}m_e V^2 = h(\nu - \nu_0)$

$\therefore$ K.E. = $(6.626 \times 10^{-34})\ (1.1 \times 10^{15} - 6 \times 10^{14})$

$\therefore$ K.E. = $(6.626 \times 10^{-34})\ (5 \times 10^{14}) = 3.313 \times 10^{-19}$ J

SECTION (C) : BOHR MODEL

Bohr's Atomic Model :

It is based on quantum theory of light.

Assumptions of Bohr's model :

- There are certain orbits around the nucleus such that if electron will be revolving in these orbit, then it does not emit any electromagnetic radiation. These are called stationary orbit for the e^-. The necessary centripetal force is produced by attraction forces of nucleus.

F10 $$\frac{mv^2}{r} = \frac{Ke^2Z}{r^2}$$

- Angular momentum of the electron in these stationary orbit is always an integral multiple of $\frac{h}{2\pi}$.

F11 $$mvr = \frac{nh}{2\pi}$$

- Electron can make jump from one stationary orbit to another stationary orbit by absorbing or emitting a photon of energy equal to difference in the energies of the stationary orbit i.e. energy change does not take place in continuous manner.

F12 $\frac{hc}{\lambda} = \Delta E$ ΔE – difference in the energy of orbit

F13 $\upsilon = \frac{\Delta E}{h}$ This is Bohr's frequency rule.

Mathematical forms of Bohr's Postulates :

Der.3 **Calculation of the radius of the Bohr's orbit :** Suppose that an electron having mass 'm' and charge 'e' revolving around the nucleus of charge 'Ze' (Z is atomic number & e = charge) with a tangential/linear velocity of 'v'. Further consider that 'r' is the radius of the orbit in which electron is revolving.

According to Coulomb's law, the electrostatic force of attraction (F) between the moving electron and nucleus is :

$F = \frac{KZe^2}{r^2}$ where : K = constant = $\frac{1}{4\pi\varepsilon_0}$ = 9×10^9 Nm^2/C^2

and the centrifugal force $F = \frac{mv^2}{r}$

For the stable orbit of an electron both the forces are balanced.

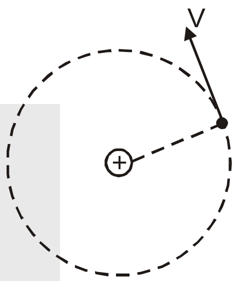


Figure-12

i.e $\frac{mv^2}{r} = \frac{KZe^2}{r^2}$

then $v^2 = \frac{KZe^2}{mr}$ .... (i)

From the postulate of Bohr,

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

On squaring $v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$ .... (ii)

From equation (i) and (ii)

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

On solving, we will get

F14 $r = \frac{n^2h^2}{4\pi^2mKZe^2}$

On putting the value of e, h, m the radius of n^{th} Bohr orbit is given by :

F15 $r_n = 0.529 \times \frac{n^2}{Z}$ Å

Solved Example

Example 1 Calculate radius ratio for 2^{nd} orbit of He^+ ion & 3^{rd} orbit of Be^{3+} ion.

Solution. r_1 (radius of 2^{nd} orbit of He^+ ion) = $0.529\left(\frac{2^2}{2}\right)$ Å

r_2 (radius of 3^{rd} orbit of Be^{3+} ion) = $0.529\left(\frac{3^2}{4}\right)$ Å

Therefore $\frac{r_1}{r_2} = \frac{0.529 \times 2^2/2}{0.529 \times 3^2/4} = \frac{8}{9}$

Der.4 **Calculation of velocity of an electron in Bohr's orbit :**

Angular momentum of the revolving electron in n^{th} orbit is given by

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

$v = \frac{nh}{2\pi mr}$ .... (iii) put the value of 'r' in the equation (iii)

then, $v = \dfrac{nh \times 4\pi^2 mZe^2K}{2\pi mn^2h^2}$

F16 $v = \dfrac{2\pi Ze^2K}{nh}$

on putting the values of π, e^-, h and K

F17 velocity of electron in n^{th} orbit $v_n = 2.18 \times 10^6 \times \dfrac{Z}{n}$ m/sec; $v \propto Z$; $v \propto \dfrac{1}{n}$

F18 T, Time period of revolution of an electron in its orbit = $\dfrac{2\pi r}{v}$

F19 f, Frequency of revolution of an electron in its orbit = $\dfrac{v}{2\pi r}$

Der.5 **Calculation of energy of an electron :**

The total energy of an electron revolving in a particular orbit is

T.E. = K.E. + P.E.

where : P.E. = Potential energy , K.E. = Kinetic energy , T.E. = Total energy

The K.E. of an electron = $\dfrac{1}{2}mv^2$

and the P.E. of an electron $= -\dfrac{KZe^2}{r}$

Hence, T.E. $= \dfrac{1}{2}mv^2 - \dfrac{KZe^2}{r}$

We know that, $\dfrac{mv^2}{r} = \dfrac{KZe^2}{r^2}$ or $mv^2 = \dfrac{KZe^2}{r}$

Substituting the value of mv^2 in the above equation:

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

So, T.E. $= -\dfrac{KZe^2}{2r}$

Substituting the value of 'r' in the equation of T.E.

Then $\text{T.E.} = -\dfrac{KZe^2}{2} \times \dfrac{4\pi^2Ze^2m}{n^2h^2} = -\dfrac{2\pi^2Z^2e^4m\ \ K^2}{n^2h^2}$

Thus, the total energy of an electron in n^{th} orbit is given by

F20 $\text{T.E.} = E_n = -\dfrac{2\pi^2me^4k^2}{h^2}\left(\dfrac{z^2}{n^2}\right)$ ... (iv)

Putting the value of m, e, h and π we get the expression of total energy

F21 $E_n = -13.6\ \dfrac{Z^2}{n^2}$ eV / atom $n\uparrow$ T.E. $\uparrow$; $Z\uparrow$ T.E.$\downarrow$

F22 $E_n = -2.18 \times 10^{-18}\ \dfrac{Z^2}{n^2}$ J/atom

F23 T.E. = $\dfrac{1}{2}$P.E.

F24 T.E. = – K.E.

Note: The P.E. at the infinite = 0; The K.E. at the infinite = 0

Conclusion from equation of energy :

(a) The negative sign of energy indicates that there is attraction between the negatively charged electron and positively charged nucleus.

(b) All the quantities on R.H.S. in the energy equation are constant for an element having atomic number Z except ‘n’ which is an integer such as 1, 2, 3, etc. i.e. the energy of an electron is constant as long as the value of ‘n’ is kept constant.

(c) The energy of an electron is inversely proportional to the square of ‘n’ with negative sign.

(d) Negative charge of the energy of e^- in the atom indicates that the energy of e^- in the atom is at lower energy than the energy of a free e^- at rest (which is taken to be zero).

Solved Example

Example 1 What are the frequency and wavelength of a photon emitted during a transition from n = 5 state to the n = 2 state in the hydrogen atom ?

Solution. Since n_i = 5 and n_f = 2, this transition gives rise to a spectral line in the visible region of the Balmer series.

$$\Delta E = 2.18 \times 10^{-18}\ \text{J} \left[\frac{1}{5^2} - \frac{1}{2^2}\right] = -4.58 \times 10^{-19}\ \text{J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h} = \frac{4.58 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{Js}} = 6.91 \times 10^{14}\ \text{Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{8}\ \text{ms}^{-1}}{6.91 \times 10^{14}\ \text{Hz}} = 434\ \text{nm}$$

Failures / limitations of Bohr’s theory:

(a) He could not explain the line spectra of atoms containing more than one electron.

(b) He also could not explain the presence of doublet i.e. 2 closely spaced lines.

(c) He was unable to explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect)

(d) No conclusion was given for the principle of quantisation of angular momentum.

(e) He was unable to explain the de-Broglie’s concept of dual nature of matter.

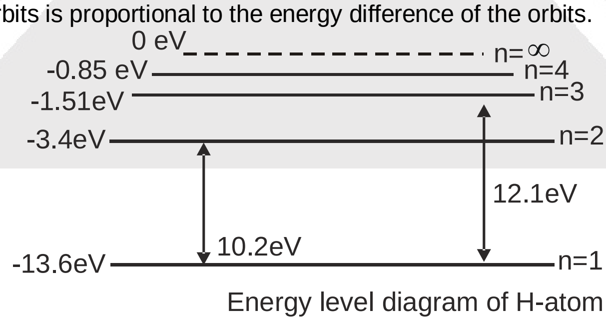
(f) He could not explain Heisenberg’s uncertainty principle.

(g) Could’t explain the ability of atoms to form molecules by chemical bonds.

Energy Level Diagram :

(i) Orbit of lowest energy is placed at the bottom, and all other orbits are placed above this.

(ii) The gap between two orbits is proportional to the energy difference of the orbits.



Energy level diagram of H-atom

Figure-13

Definition valid for single electron System :

D15

(i) **Ground state :**

Lowest energy state of any atom or ion is called ground state of the atom. For it n = 1.

Ground state energy of H–atom = – 13.6 eV

Ground state energy of He^+ Ion = – 54.4 eV

D16

(ii) Excited State :

States of atom other than the ground state are called excited states :

n = 2 first excited state
n = 3 second excited state
n = 4 third excited state
n = n + 1 n^{th} excited state

D17

(iii) Ionisation energy (IE) :

Minimum energy required to move an electron from ground state to
n = ∞ is called ionisation energy of the atom or ion.
Ionisation energy of H–atom = 13.6 eV
Ionisation energy of He^+ ion = 54.4 eV
Ionisation energy of Li^{+2} ion = 122.4 eV

D18

(iv) Ionisation Potential (I.P.) :

Potential difference through which a free electron must be accelerated from rest, such that its kinetic energy becomes equal to ionisation energy of the atom is called ionisation potential of the atom.
I.P. of H atom = 13.6 V, I.P. of He^+ Ion= 54.4 V

D19

(v) Excitation Energy :

Energy required to move an electron from ground state of the atom to any other state of the atom is called
excitation energy of that state.
Excitation energy of 2^{nd} state = excitation energy of 1^{st} excited state = 1^{st} excitation energy = 10.2 eV.

D20

(vi) Excitation Potential :

Potential difference through which an electron must be accelerated from rest to so that its kinetic energy
become equal to excitation energy of any state is called excitation potential of that state.
Excitation potential of third state = excitation potential of second excited state = second excitation potential = 12.09 V.

D21

(vii) Binding Energy 'or' Separation Energy :

Energy required to move an electron from any state to n = ∞ is called binding energy of that state.
Binding energy of ground state = I.E. of atom or Ion.

Solved Example

Example 1 A single electron system has ionization energy 11180 kJ mol^{-1}. Find the number of protons in the nucleus of the system.

Solution. $I.E. = \dfrac{Z^2}{n^2} \times 21.69 \times 10^{-19}$ J

$$\frac{11180 \times 10^3}{6.023 \times 10^{23}} = \frac{Z^2}{1^2} \times 21.69 \times 10^{-19}$$

Ans. Z = 3

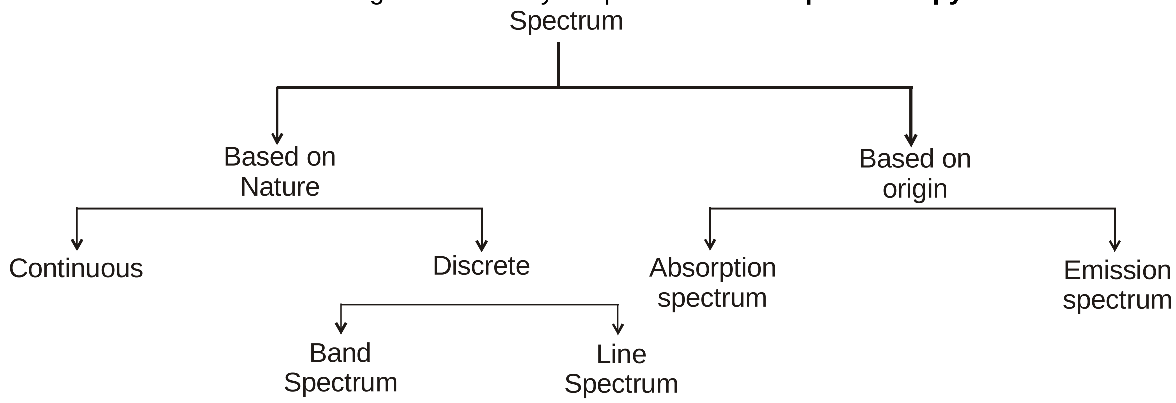
SECTION (D) : SPECTRUM

Hydrogen Spectrum :

Study of Emission and Absorption Spectra :

An instrument used to separate the radiation of different wavelengths (or frequencies) is called spectroscope or a spectrograph. Photograph (or the pattern) of the emergent radiation recorded on the film is called a spectrogram or simply a spectrum of the given radiation.

D22 The branch or science dealing with the study of spectra is called **spectroscopy**.



D23 **Emission spectra :**

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

Depending upon the source of radiation, the emission spectra are mainly of two type :

D24

(a) Continuous spectra :

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

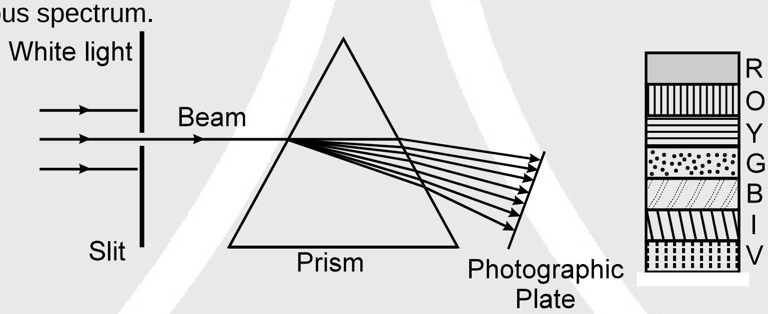


Figure-14

(b) Discrete spectra : It is of two type

(i) **Band spectrum**

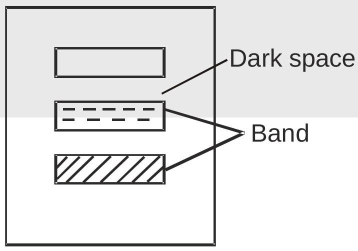


Figure-15

Band spectrum contains colourful continuous bands sepearted by some dark space.
Generally, molecular spectrum are band spectrum.

(ii) **Line Spectrum :**

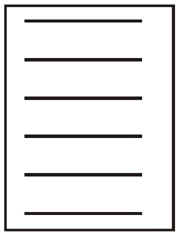


Figure-16

D25 This is the ordered arrangement of lines of particular wavelength separated by dark space eg. Hydrogen spectrum.
Line spectrum can be obtained from atoms.

D26 **Absorption spectra :**
When white light from any source is first passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, it is observed that some dark lines are obtained in the continuous spectrum. These dark lines are supposed to result from the fact that when white light (containing radiations of many wavelengths) is passed through the chemical substance, radiations of certain wavelengths are absorbed, depending upon the nature of the element.

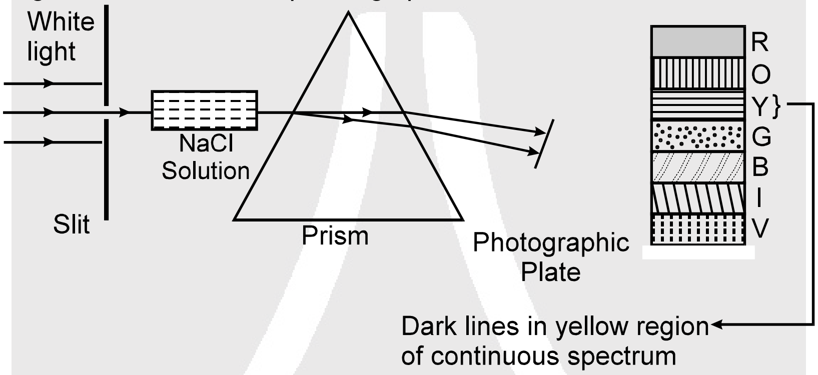


Figure-17

D27 **EMISSION SPECTRUM OF HYDROGEN :**

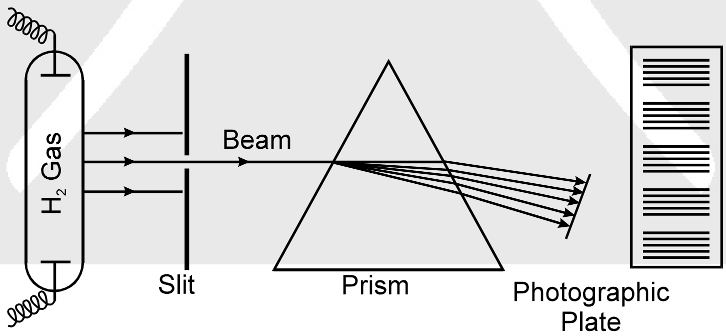
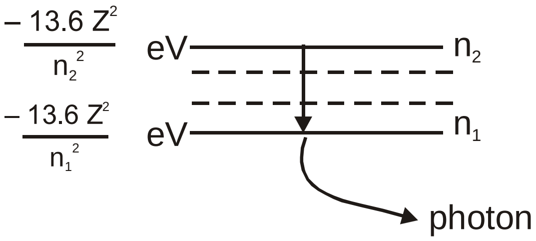


Figure-18

When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen.

Line Spectrum of Hydrogen :

Line spectrum of hydrogen is observed due to excitation or de-excitation of electron from one stationary orbit to another stationary orbit
Let electron make transition from n_2 to n_1 ($n_2 > n_1$) in a H-like sample



Der.6 Energy of emitted photon $= (\Delta E)_{n_2 \to n_1} = \dfrac{-13.6Z^2}{n_2^2} - \left(\dfrac{-13.6Z^2}{n_1^2}\right) = 13.6Z^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

Wavelength of emitted photon

$$\lambda = \frac{hc}{(\Delta E)_{n_2 \to n_1}}$$

$$\lambda = \frac{hc}{13.6Z^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)}$$

$$\frac{1}{\lambda} = \frac{(13.6)z^2}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

F25 Wave number, $\dfrac{1}{\lambda} = \bar{\nu} = RZ^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

R = Rydberg constant = $1.09678 \times 10^7 m^{-1}$; $R \approx 1.1 \times 10^7\ m^{-1}$;

$R = \dfrac{13.6eV}{hc}$; R ch = 13.6 eV

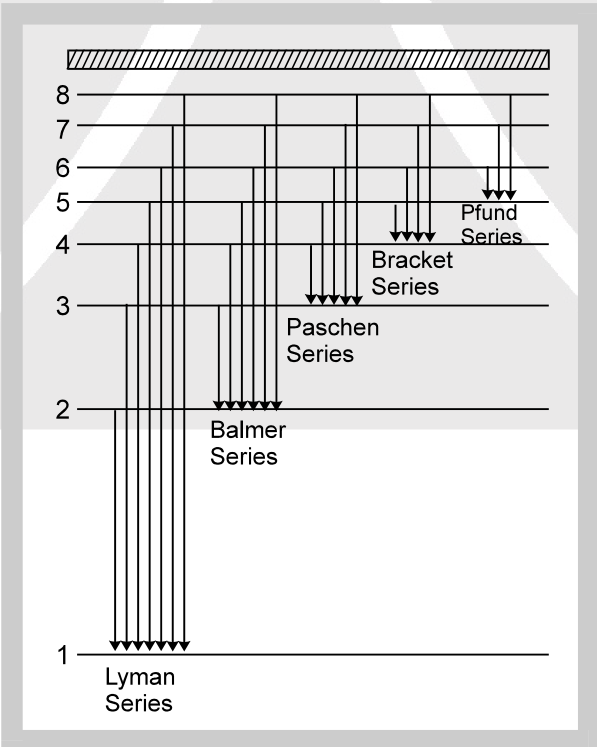


Figure-19

Solved Example

Example 1 Calculate the wavelength of a photon emitted when an electron in H- atom maker a transition from n = 2 to n = 1

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

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

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

Spectra lines of Hydrogen Atom :

LYMAN SERIES

* It is first spectral series of H.
* It was found to be in ultraviolet region by Lyman in 1898.
* For it value of $n_1 = 1$ and $n_2 = 2, 3, 4$ where 'n_1' is ground state and 'n_2' is called excited state of electron present in a H - atom.
* $\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 1$ always.
* The wavelength of marginal line (i.e. $n_2 = \infty$) = $\frac{n_1^2}{R_H}$ for all series. So for Lyman series $\lambda = \frac{1}{R_H}$.
* Ist line of lyman series $\Rightarrow 2 \to 1$
  IInd line of lyman series = $3 \to 1$
  Last line of lyman series = $\infty \to 1$
  [10.2 eV $\le (\Delta E)_{lyman} \le 13.6$ eV]
  $\frac{12400}{13.6} \le \lambda_{lyman} \le \frac{12400}{10.2}$ Å
* **Longest line :** longest wavelength line $\lambda_{longest}$ or $\lambda_{max.} = \frac{12400}{(\Delta E)_{min}}$
* **Shortest line :** shortest wavelength line $\lambda_{shortest}$ or $\lambda_{min} = \frac{12400}{(\Delta E)_{max}}$
* First line of any spectral series is the longest (λ_{max}) line.
* Last line of any spectral series is the shortest (λ_{min}) line.

Series limit :

It is the last line of any spectral series.

Wave no of Ist line of Lyman series = $\frac{1}{\lambda} = \bar{\nu} = R \times 1^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$

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

$\bar{\nu} = \frac{R \times 3}{4} = \frac{3R}{4}$

$\therefore \left[\lambda = \frac{4}{3R}\right]$

Wave no of last line of Lyman series

$\bar{\nu} = R \times 1^2\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$

$\bar{\nu} = R$

For Lyman series,

$$\lambda_{\text{longest}} = \frac{12400}{(\Delta E)_{2-1}}, \quad \lambda_{\text{shortest}} = \frac{12400}{(\Delta E)_{\infty \to 1}}$$

Balmer series :

* It is the second series of H-spectrum.
* It was found to be in visible region by Balmer in 1892.
* For it value of $n_1 = 2$ and $n_2 = 3, 4, 5,$.............
* The wavelength of marginal line of Balmer series = $\frac{n_1^2}{R_H} = \frac{2^2}{R_H} = \frac{4}{R_H}$
* $\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$ where $n_2 > 2$ always.

$1.9 \le (\Delta E)_{\text{balmer}} \le 3.4$ eV.

All the lines of balmer series in H spectrum are not in the visible range. Infact only Ist 4 lines belongs to visible range.

$\frac{12400}{3.4}$ Å $\le \lambda_{\text{balmer}} \le \frac{12400}{1.9}$ Å

3648 Å $\le \lambda_{\text{balmer}} \le$ 6536 Å

Lines of balmer series (for H atom) lies in the visible range.

Ist line of balmer series = $3 \to 2$

last line of balmer series = $\infty \to 2$

$(\bar{\nu})$ 1st line $= R \times 1\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R}{36}$

$(\bar{\nu})$ last line $= R\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) = \frac{R}{4}$

Paschen series :

(a) It is the third series of H - spectrum.
(b) It was found to be in infrared region by Paschen.
(c) For it value of $n_1 = 3$ and $n_2 = 4, 5, 6$ ....
(d) The wavelength of marginal line of Paschen series = $\frac{n_1^2}{R_H} = \frac{3^2}{R_H} = \frac{9}{R_H}$.
(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 3$ always.

Brackett series :

(a) It is fourth series of H - spectrum.
(b) It was found to be in infrared region by Brackett.
(c) For it value of $n_1 = 4$ and $n_2 = 5, 6, 7$ ....
(d) The wavelength of marginal line of brackett series = $\frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$
(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 4$ always.

Pfund series :

(a) It is fifth series of H- spectrum.
(b) It was found to be in infrared region by Pfund.
(c) For it value of $n_1 = 5$ and $n_2 = 6, 7, 8$ .... where n_1 is ground state and n_2 is excited state.

(d) The wavelength of marginal line of Pfund series = $\frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$

(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{5^2}-\frac{1}{n_2^2}\right]$ where $n_2 > 5$ always.

Humphry series :

(a) It is the sixth series of H-spectrum.
(b) It was found to be in infrared region by Humphry.
(c) For it value of $n_1 = 6$ and $n_2 = 7, 8, 9$ ....

(d) The wavelength of marginal line of Humphry series = $\frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$

(e) $\frac{1}{\lambda} = R_H\left[\frac{1}{6^2}-\frac{1}{n_2^2}\right]$ where $n_2 > 6$.

Solved Example

Example 1 Calculate wavelength for 2nd line of Balmer series of He^+ ion

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

$n_1 = 2 \quad n_2 = 4$

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

$\frac{1}{\lambda} = \frac{3R}{4} \qquad \lambda = \frac{4}{3R}$ **Ans.**

No. of photons emitted by a sample of H atom :

If an electron is in any higher state n = n and makes a transition to ground state, then total no. of different photons emitted = $\frac{n \times (n-1)}{2}$.

F26 If an electron is in any higher state $n = n_2$ and makes a transition to another excited state $n = n_1$, then total no. of different photons emitted = $\frac{\Delta n \quad (\Delta n + 1)}{2}$, where $\Delta n = n_2 - n_1$

F27 **Note:** In case of single isolated atom if electron make transition from n^{th} state to the ground state then max. number of spectral lines observed = (n-1)

Solved Example

Example 1 If electron make transition from 7th excited state to 2nd state in H atom sample find the max. number of spectral lines observed.

Solution. $\Delta n = 8 - 2 = 6$

spectral lines = $6\left(\frac{6+1}{2}\right) = 6 \times \frac{7}{2} = 21$

SECTION (E) : DE-BROGLIE WAVELENGTH AND HEISENBERG UNCERTAINITY PRINCIPLE

Dual nature of electron (de-Broglie Hypothesis):

(a) Einstein had suggested that light can behave as a wave as well as like a particle i.e. it has dual character.

(b) In 1924, de-Broglie proposed that an electron behaves both as a material particle and as a wave.

(c) This proposed a new theory, the wave mechanical theory of matter. According to this theory, the electrons protons and even atom when in motion possess wave properties.

(d) According to de-Broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation,

F28 $\lambda = \frac{h}{mv}$ where h is Planck's constant

Der.7

(e) This can be derived as follows according to Planck's equation.

$E = h\nu = \frac{h.c}{\lambda}$

Energy of photon on the basis of Einstein's mass energy relationship

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

Equating both we get

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

Which is same as de - Broglie relation.

This was experimentally verified by Davisson and Germer by observing diffraction effects with an electron beam.

Let the electron is accelerated with a potential of V then the K.E. is

Der.8 $\frac{1}{2}mv^2 = eV$

$m^2v^2 = 2emV$

$mv = \sqrt{2emV}$ = p (momentum)

F29 $\lambda = \frac{h}{\sqrt{2emV}}$

If we associate Bohr's theory with de - Broglie equation then

$2\pi r = n\lambda$ or $\lambda = \frac{2\pi r}{n}$

From de-Broglie equation

$\lambda = \frac{h}{mv}$ therefore $\frac{h}{mv} = \frac{2\pi r}{n}$ so, $mvr = \frac{nh}{2\pi}$

m = dynamic mass = $\frac{m_0}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$

m_0 = rest mass of particle

Depended on velocity

c = velocity of light

If velocity of particle is zero then :

Dynamic mass = rest mass

Rest mass of photon is zero that means photon is never at rest

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

m (K.E.) = $\frac{1}{2}m^2v^2$ multiplied by mass on both side

$\Rightarrow$ m.v. = $\sqrt{2m(K.E.)}$

$\lambda = \dfrac{h}{\sqrt{2m(K.E.)}}$

If a charge q is accelerated through a potential difference of 'V' volt from rest then K.E. of the charge is equal to: " q.V"

$\Rightarrow \quad \lambda = \dfrac{h}{\sqrt{2m(q.V)}}$

* If an electron is accelerated through a potential difference of 'V' volt from rest then:

$\Rightarrow \quad \lambda = \dfrac{h}{\sqrt{2m_e(eV)}}$

$\Rightarrow \quad \lambda = \left(\dfrac{150}{V}\right)^{\frac{1}{2}}$ Å (on putting values of h, m_e and e)

F30 $\lambda = \dfrac{12.3}{\sqrt{V}}$ Å (V in volt)

* $mvr = n \times \dfrac{h}{2\pi}$

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

$mv = \dfrac{h}{\lambda}$ putting this in $mvr = \dfrac{nh}{2\pi}$

$\therefore \quad \dfrac{h}{\lambda} r = \dfrac{nh}{2\pi} \Rightarrow \left[\lambda = \dfrac{2\pi r}{n}\right]$ de Broglie wavelength

Solved Example

Example 1 What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

Solution. According to de Broglie equation

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34}\,Js)}{(0.1\,kg)\ \ (10\,ms^{-1})} = 6.626 \times 10^{-34}\ m\ (J = kg\ m^2\ s^{-2}).$$

Heisenberg's Uncertainty Principle :

The exact position and momentum of a fast moving particle cannot be calculated precisely at the same moment of time. If Δx is the error in the measurement of position of the particle and if Δp is the error in the measurement of momentum of the particle, then:

F31 $\Delta x.\Delta p \geq \dfrac{h}{4\pi}$ or $\Delta x.(m\Delta v) \geq \dfrac{h}{4\pi}$

where, Δx = uncertainty in position, Δp = uncertainty in momentum
h = Plank's constant, m = mass of the particle
Δv = uncertainty in velocity

Der.9 If the position of a particle is measured precisely, i.e. $\Delta x \to 0$ then $\Delta p \to \infty$.
If the momentum of the particle is measured precisely. i.e. $\Delta p \to 0$ then $\Delta x \to \infty$.
This is because of a principle of optics that if a light of wavelength 'λ' is used to locate the position of a particle then maximum error in the position measurement will be $\pm\lambda$. i.e. $\Delta x = \pm\lambda$
If $\Delta x \to 0$; $\lambda \to 0$
But, $p = \dfrac{h}{\lambda} \Rightarrow p \to \infty$
So, to make $\Delta x \to 0$, $\lambda \to 0$ a photon of very high energy is used to locate it.
When this photon will collide with the electron then momentum of electron will get changed by a large amount.

* $\Delta p.\Delta x \geq \dfrac{h}{4\pi}$ (multiplied & divided by Δt)

$\frac{\Delta P}{\Delta t}\,\Delta t.\Delta x \geq \frac{h}{4\pi}$ $\qquad$ ($\frac{\Delta P}{\Delta t}$ = rate of change in momentum = F)

$F.\Delta x.\Delta t \geq \frac{h}{4\pi}$; $\qquad$ $\Delta E.\Delta t \geq \frac{h}{4\pi}$

$\Delta E \longrightarrow$ uncertainty in energy ; $\Delta t \longrightarrow$ uncertainty in time

☞ In terms of uncertainty in energy ΔE, and uncertainty in time Δt, this principle is written as,

F32 $\Delta E.\Delta t \geq \frac{h}{4\pi}$.

☞ Heisenberg replaced the concept of definite orbits by the concept of probability.

Solved Example

Example 1 A golf ball has a mass of 40 g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

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

Using the equation, $\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 40 \times 10^{-3}\ (0.9\ \ ms^{-1})} = 1.46 \times 10^{-33}$ m

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

SECTION (F) : QUANTUM MECHANICAL MODEL OF ATOM, SHRODINGER WAVE EQUATION AND ORBITAL CONCEPT ORBITAL :

D28 An orbital may be defined as the region of space around the nucleus where the probability of finding an electron is maximum (90% to 95%)

Orbitals do not define a definite path for the electron, rather they define only the probability of the electron being in various regions of space around the nucleus.

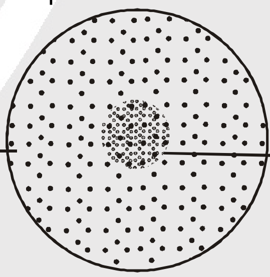


Figure-20

Difference between orbit and orbitals

	Orbit	Orbitals
1	It is well defined circular path followed by revolving electrons around the nucleus.	It is the region of space around the nucleus where electron is most likely to be found.
2	It represents planar motion of electron.	It represents 3 dimensional motion of an electron around the nucleus.
3	The maximum no. of electron in an orbits is $2n^2$ where n stands for no. of orbit.	Orbitals cannot accommodate more than 2 electrons.
4	Orbits are circular in shape.	Orbitals have different shape e.g. s-orbital is spherical, p-orbital is dumb-bell shaped.
5	Orbit are non-directional in character. Hence, they cannot explain shape of molecules.	Orbitals (except s-orbital) have directional character. Hence, they can account for the shape of molecules.
6	Concept of well-defined orbit is against Heisenberg's uncertainty principle.	Concept of orbitals is in accordance with Heisenberg's principle.

Shape of the orbitals :

Shape of the orbitals are related to the solutions of Schrodinger wave equation, and gives the space in which the probability of finding an electron is maximum.

s-orbital : **Shape $\rightarrow$ spherical**

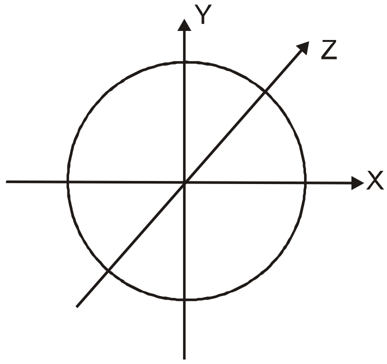
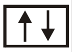


Figure-21

s-orbital is non directional and it is closest to the nucleus, having lowest energy.
s-orbital can accommodate maximum no. of two electrons.



n s

p-orbital : Shape $\rightarrow$ dumb bell

Dumb bell shape consists of two lobes which are separated by a region of zero probability called node.

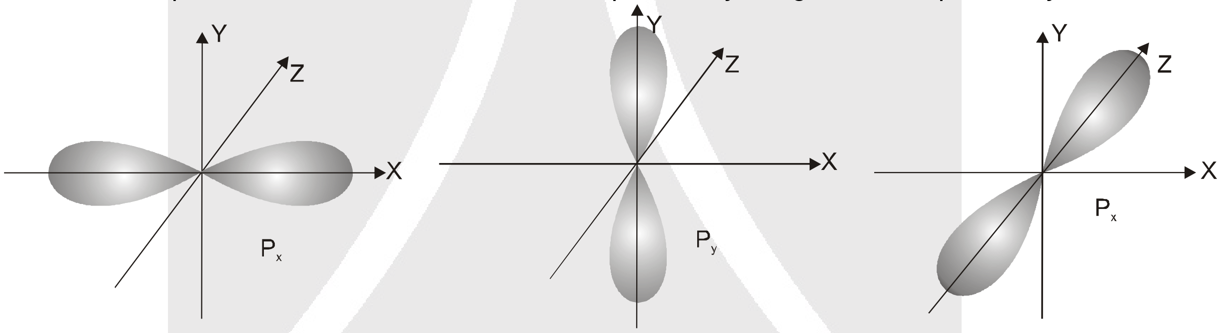
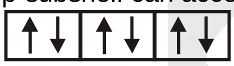


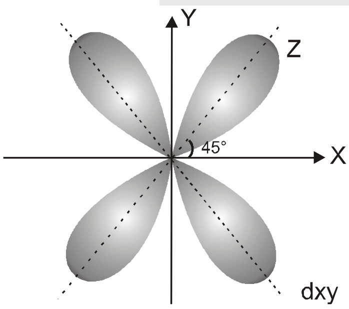
Figure-22

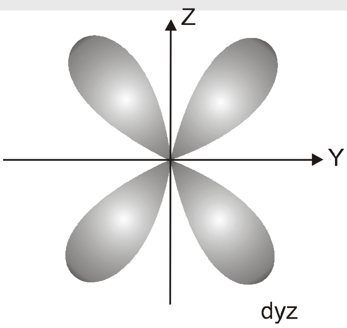
p-subshell can accomodate maximum no. of six electrons.



p_x p_y p_z

d-Orbital : **Shape $\rightarrow$ double dumb bell**





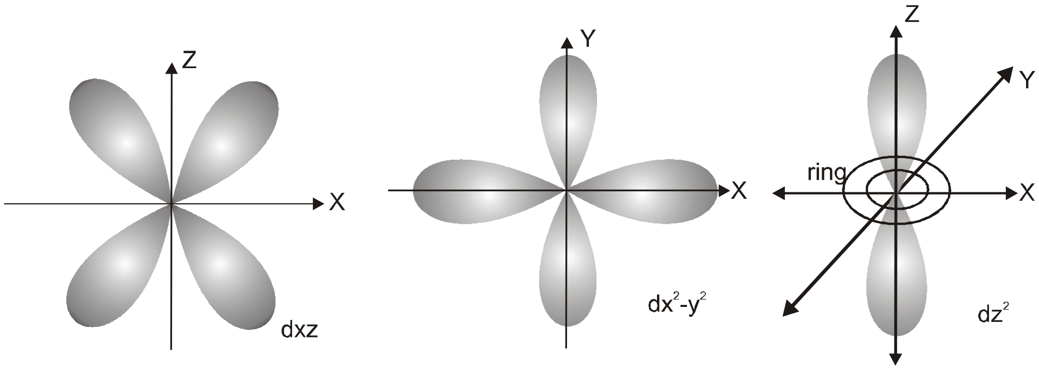


Figure-23

d-subshell can accommodate maximum no. of 10 electrons.

↑↓	↑↓	↑↓	↑↓	↑↓
dxy	dyz	dz^2	dx^2-y^2	dxz

f-orbital : **Shape → leaf like**

↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

f-subshell can accommodate maximum no. of 14 electrons.

Schrodinger Wave Mechanical model

Ervin Schrodinger developed a model which is based on the particle and wave nature of the electron, known as Wave Mechanical Model of atom. The equation determines the behaviour of the wave function that describes the wave like properties of subatomic system. It is solved to find the different energy levels of the system.

Schrodinger applied the equation to the hydrogen atom and predicted many of its properties with remarkable accuracy. The differential wave equation is as follows :

F-33 $$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0$$

where m is mass of electron, ψ is wave function, E is total energy of electron, V is potential energy and h is Planck's constant.

- Wave function has no actual physical meaning but the value of ψ^2 describes the probability distribution of an electron.
- When we solve the Schrodinger equation, it is observed that for some region of space, the value of ψ is positive and for other, it is negative. But the probability must be positive, so it is proper to use ψ^2 in place of ψ.
- The Schrodinger equation is said to have been solved for a particular atomic system. The details of, how this is done, are beyond the syllabus, but the consequences of its solution are extremely important to us.

The important point of the solution of this equation is that it provides a set of numbers called quantum numbers. Quantum numbers are required to describe the distribution of electrons in atoms. Quantum numbers derived from the solution of Schrodinger equation are called principal quantum number, azimuthal quantum number and magnetic quantum number. These quantum numbers are used to describe the atomic orbitals.

Orbital : The locations in space at which the probability of finding the electron is maximum.

Node and Nodal Plane : Node represents the region where probability of finding an electron is zero (i.e., ψ and ψ^2 = 0). Similarly nodal plane represents the plane having zero probability of finding electron.

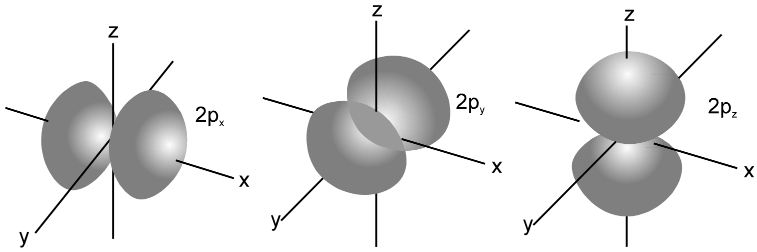
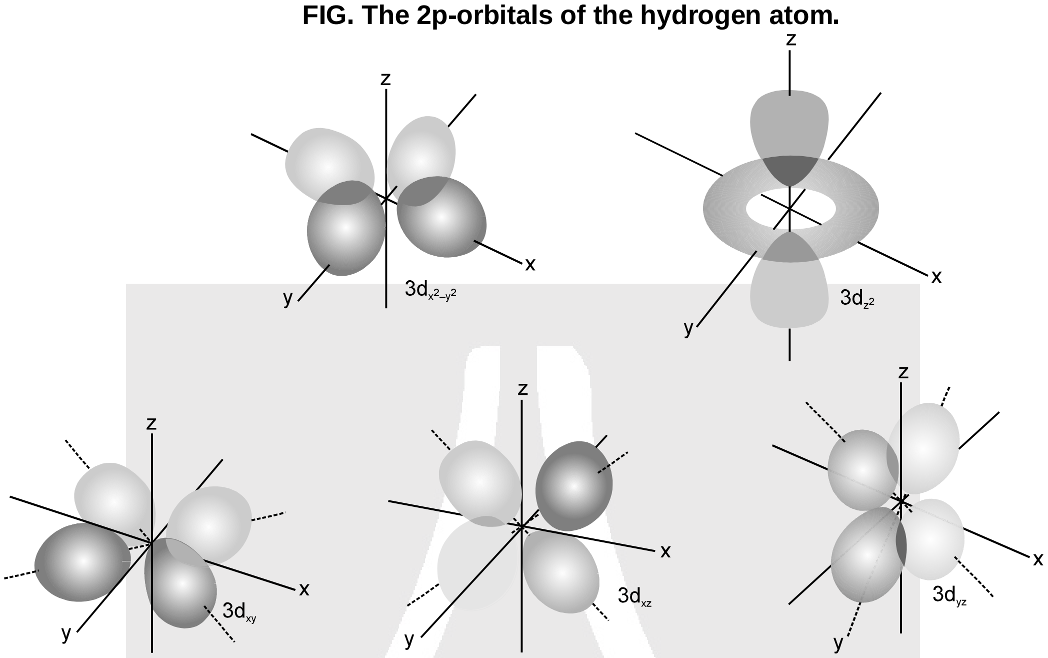


FIG. The 2p-orbitals of the hydrogen atom.



The 3d-orbitals of the hydrogen atom. Note the relation between the labeling of the d-orbitals and their orientations in space.

Nodes are of two types : (a) Radial node (b) Angular node

A radial node is the spherical region around nucleus having ψ and ψ^2 equal to zero. An orbital having higher number of nodes has more energy.

Calculation of number of nodes :

F34 Radial nodes = n – ℓ – 1,

F35 Angular nodes = ℓ,

F36 Total nodes = n – 1, where n and ℓ are principal and azimuthal quantum numbers.

e.g. In 3p-orbital, Radial nodes = 3 – 1 – 1 = 1 (= n – ℓ – 1)
Angular nodes = 1 (= ℓ)
Total nodes = 2 (one radial, one angular)

- $\psi_{(r)}$ i.e. radial part of wave function depends upon quantum number n and l and decides the size of an orbital.
- Angular part of wave function $\psi_{(\theta - \phi)}$, depends upon quantum numbers l and m and describes the shape of orbital.

For the sake of convenience the $\psi_{(r)}$ vs. r and $\psi_{(\theta , \phi)}$ vs. angle are plotted separately.

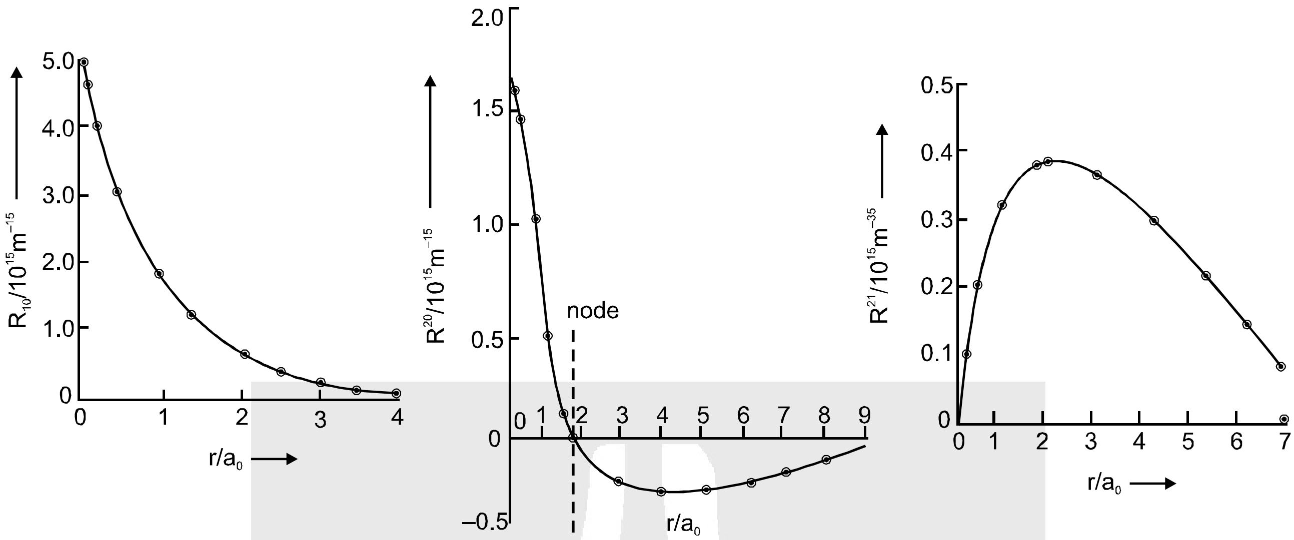
An atomic orbital is a one electron wave function Ψ (r, θ, ϕ) obtained from the solution of the Schrodinger equation. The orbital wave function Ψ has no physical significance but its square (Ψ^2) has a physical significance it measures the electron probability density at a point in an atom.

Plots of the Radial wave function R :

The plots of the radial wave function R, radial probability density R^2 and radial probability function $4\pi r^2 R^2$ for 1s, 2s & 2p atomic orbitals as a function of the distance r from the nucleus are shown in fig.

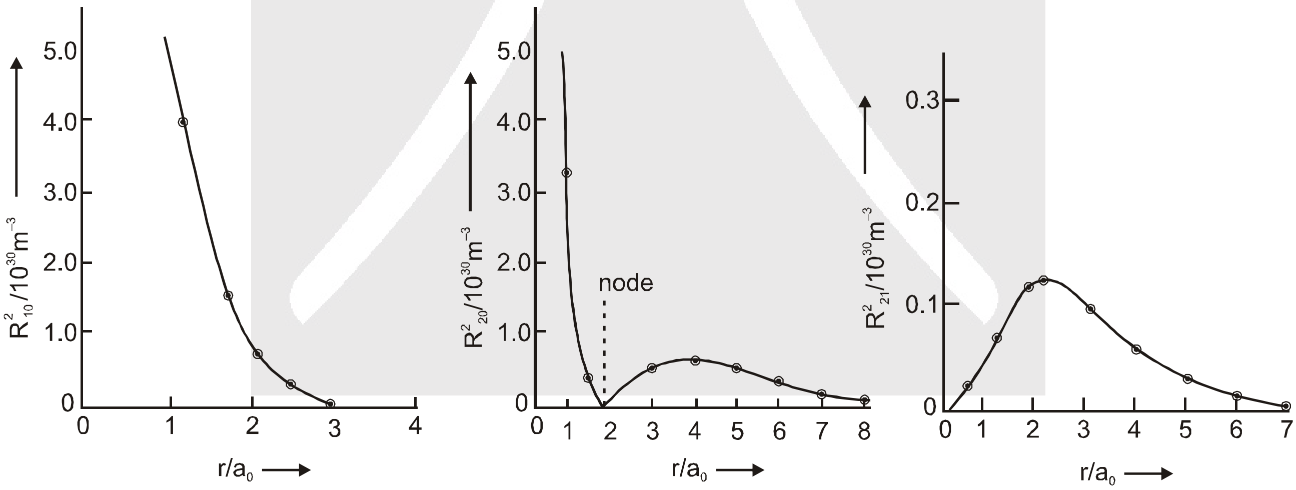
(i) Radial wave function (R) [Fig. (A)] :

In all cases R approaches zero as r approaches infinity. We finds that there is a node in the 2s radial function. At the node the value of the radial function changes from positive to negative. In general, it has been found that ns-orbitals have (n–1) radial nodes and np-orbitals have (n–2) radial nodes etc.

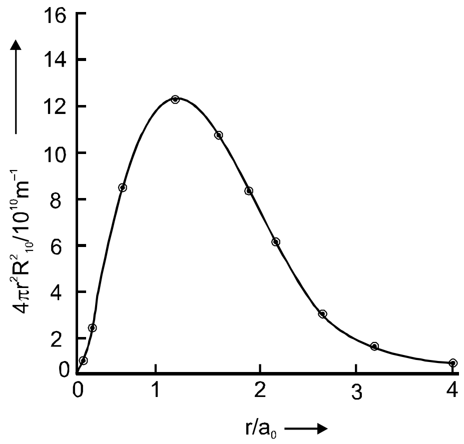


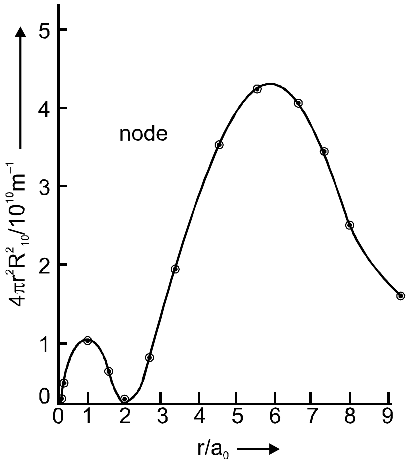
(ii) Radial Probability density (R^2) [Fig. (B)] :

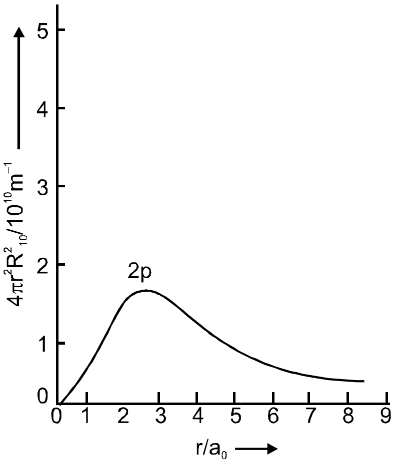
The radial density R^2 gives the probability density of finding the electron at a point along a particular radius line. Plots in fig. (B) give useful information about probability density or relative electron density at a point as a function of radius. It may be noted that for s-orbitals the maximum electron density is at the nucleus while all other orbitals have zero electron density at the nucleus. Its zero value (R^2 = 0) indicates zero probability of finding an electron.

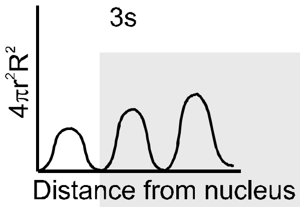


(iii) Radial probability function $4\pi r^2R^2$ [Fig.(C)] : Since the atoms have spherical symmetry, It is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radius (r + dr) and r. The volume of the shell is equal to $4/3\pi(r + dr)^3 - 4/3\pi r^3 = 4\pi r^2dr$.









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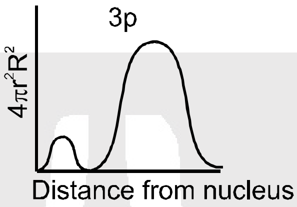

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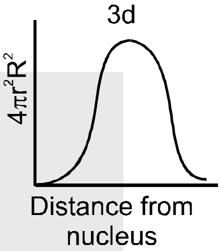
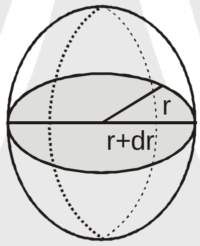


This probability which is independent of direction is called radial probability and is equal to [$4\pi r^2drR^2$]. It gives the probability of finding the electron at a distance r from the nucleus regardless of direction.



SECTION (G) : QUANTUM NUMBERS & ELECTRONIC CONFIGURATION

D29 QUANTUM NUMBERS :

The set of four numbers required to define an electron completely in an atom are called quantum numbers. The first three have been derived from Schrodinger wave equation.

(i) Principal quantum number (n) : (Proposed by Bohr)

It describes the size of the electron wave and the total energy of the electron. It has integral values 1, 2, 3, 4 ...., etc., and is denoted by K, L, M, N. ..., etc.

F37 Number of subshell present in n^{th} shell = n

n	**subshell**
1	s
2	s, p
3	s, p, d
4	s, p, d, f

F38 Number of orbitals present in n^{th} shell = n^2 .

F39 The maximum number of electrons which can be present in a principal energy shell is equal to $2n^2$. No energy shell in the atoms of known elements possesses more than 32 electrons.

F40 Angular momentum of any orbit $= \dfrac{nh}{2\pi}$

(ii) Azimuthal quantum number (ℓ) : (Proposed by Sommerfield)

It describes the shape of electron cloud and the number of subshells in a shell.

* It can have values from 0 to (n – 1)
* **value of ℓ** **subshell**

value of ℓ	subshell
0	s
1	p
2	d
3	f

F41 Number of orbitals in a subshell = $2\ell + 1$

F42 Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$

F43 Orbital angular momentum L = $\frac{h}{2\pi}\sqrt{\ell(\ell+1)} = \hbar\sqrt{\ell(\ell+1)}$ $\left[\hbar = \frac{h}{2\pi}\right]$

i.e. Orbital angular momentum of s orbital = 0, Orbital angular momentum of p orbital = $\sqrt{2}\frac{h}{2\pi}$,

Orbital angular momentum of d orbital = $\frac{\sqrt{6}h}{2\pi}$

(iii) Magnetic quantum number (m) : (Proposed by Linde)

It describes the orientations of orbitals with respect to standard set of coordinate axes. It can have values from $-\ell$ to $+\ell$ including zero, i.e., total $(2\ell + 1)$ values. Each value corresponds to an orbital. s-subshell has one orbital, p-subshell three orbitals (p_x, p_y and p_z), d-subshell five orbitals $(d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2})$ and f-subshell has seven orbitals.

F44 The total number of orbitals present in a main energy level is 'n^2'.

(iv) Spin quantum number (s) : (Proposed by Goldsmith & Uhlenbeck)

It describes the spin of the electron. It has values +1/2 and –1/2. Signifies clockwise spinning and anticlockwise spinning.

F45 Spin magnetic moment $\mu_s = \frac{eh}{2\pi mc}\sqrt{s(s+1)}$ or $\mu = \sqrt{n(n+2)}$ B.M. (n = no. of unpaired electrons)

F46 It represents the value of spin angular momentum which is equal to $\frac{h}{2\pi}\sqrt{s(s+1)}$.

F47 Maximum spin of atom = $\frac{1}{2}$ × No. of unpaired electron.

Electronic configuration :

Pauli's exclusion principle :

No two electrons in an atom can have the same set of all the four quantum numbers, i.e., an orbital cannot have more than 2 electrons and the three quantum numbers (principal, azimuthal and magnetic) at the most may be same but the fourth must be different, i.e. their spins must be in opposite directions.

Aufbau principle :

Aufbau is a German word meaning building up. The electrons are filled in various orbitals in order of their increasing energies. An orbital of lowest energy is filled first. The sequence of orbitals in order of their increasing energy is :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, ...

The energy of the orbitals is governed by $(n + \ell)$ rule.

$(n + \ell)$ Rule :

The relative order of energies of various sub-shell in a multi electron atom can be predicated with the help of '$n + \ell$' rule

❖ The sub-shell with lower value of $(n + \ell)$ has lower energy and it should be filled first.

eg. 3d: $(n + \ell) = 3 + 2 = 5$ 4s: $(n + \ell) = 4 + 0 = 4$

Since, $(n + \ell)$ value of 3d is more than 4s therefore, 4s will be filled before 3d.

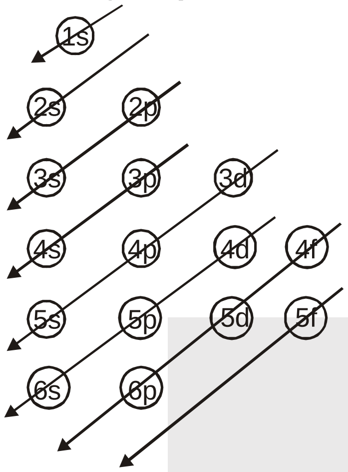
❖ If two sub-shell has same value of $(n + \ell)$ then the sub-shell with lower value of n has lower energy and it should be filled first.

eg. 3d 4p

$(n + \ell) = 3 + 2 = 5$ $(n + \ell) = 4 + 1 = 5$

3d is filled before 4p.

Memory Map :



Hund's rule :

No electron pairing takes place in the orbitals in a sub - shell until each orbital is occupied by one electron with parallel spin. Exactly half filled and fully filled orbitals are observed to be more stable, i.e., p^3, p^6, d^5, d^{10}, f^7 and f^{14} configuration are most stable probably because of the following reasons :

(i) relatively small shielding

(ii) larger exchange energy

(iii) smaller coulombic repulsion energy.

Solved Example

Example 1 Write the electronic configuration and find the no. of unpaired electrons as well as total spin for the following atoms :

(i) $_6C$ (ii) $_8O$ (iii) $_{15}P$ (iv) $_{21}Sc$

(v) $_{26}Fe$ (vi) $_{10}Ne$

Solution. (i) $_6C \rightarrow 1s^2, 2s^2, 2p^2$

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

No. of unpaired electrons $\rightarrow$ 2.

Total spin = $\frac{+2}{2}$ or $\frac{-2}{2}$

(ii) $_8O \rightarrow 1s^2, 2s^2, 2p^4$

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

1s 2s 2p

$\therefore$ No. of unpaired electrons = 2

Total spin = $\frac{+2}{2}$ or $\frac{-2}{2}$

(iii) $_{15}P \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

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

3s 3p

$\therefore$ No. of unpaired electrons = 3

Total spin = $\frac{+3}{2}$ or $\frac{-3}{2}$

(iv) $_{21}Sc \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$

or [Ar] $4s^2\ 3d^1$

[Ar] $3d^1\ 4s^2$

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

3d 4s

∴ No. of unpaired electrons = 1

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

(v) $_{26}Fe \rightarrow 1s^2,\ 2s^2\ 2p^6, 3s^2, 3p^6, 4s^2\ 3d^6$

or [Ar] $4s^2, 3d^6$

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

4s 3d

No. of unpaired electrons = 4

∴ Total spin = $\frac{+4}{2}$ or $\frac{-4}{2}$

(vi) $_{10}Ne \rightarrow 1s^2, 2s^2\ 2p^6$

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

No. of unpaired electrons = 0

Total spin = 0

Example 2 Write down the four quantum numbers for fifth and sixth electrons of carbon atom.

Solution. $_6C : 1s^2, 2s^2\ 2p^2$

fifth electron : n = 2 ℓ = 1 m = – 1 or +1 s = $+\frac{1}{2}$ or $-\frac{1}{2}$

sixth electron : n = 2 ℓ = 1 m = 0 s = $+\frac{1}{2}$ or $-\frac{1}{2}$

Example 3 Calculate total spin, magnetic moment for the atoms having at. no. 7, 24 and 36.

Solution. The electronic configuration are

$_7N$: $1s^2, 2s^2\ 2p^3$ unpaired electron = 3

$_{24}Cr$: $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$ unpaired electron = 6

$_{36}Kr$: $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6$ unpaired electron = 0

∴ Total spin for an atom = ± 1/2 × no. of unpaired electron

For $_7N$, it is = ± 3/2 ; For $_{24}Cr$, it is = ± 3 ; For $_{36}Kr$, it is = 0

Also magnetic moment = $\sqrt{n\,(n+2)}$

For $_7N$, it is = $\sqrt{15}$; For $_{24}Cr$, it is = $\sqrt{48}$; For $_{36}Kr$, it is = $\sqrt{0}$.

Exceptions :

(1) $_{24}Cr$ = [Ar] $4s^2, 3d^4$ (Not correct)

[Ar] $4s^1, 3d^5$ (correct : as d^5 structure is more stable than d^4 structure)

(2) $_{29}Cu$ = [Ar] $4s^1, 3d^{10}$ (correct : as d^{10} structure is more stable than d^9 structure).

SECTION (H) : NUCLEAR CHEMISTRY

D30 Spontaneous disintegration of nuclei due to emission of radiations like α, β, γ is called radioactivity.

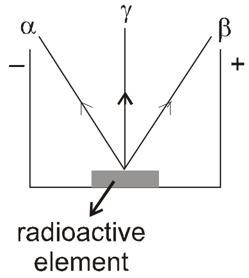
Radioactivity is a nuclei phenomenon.

Radioactivity is not dependent on external conditions like temperature, pressure etc.

Radioactivity of a substance is independent to its physical state.

x(s), x(l), x(g), $(x)^+(g)$, $(x)^-(g)$ in all form, x is radioactive.

$^{14}CO_2$, $^{14}_{6}C(s)$, $^{14}_{6}C(g)$ is radioactive.



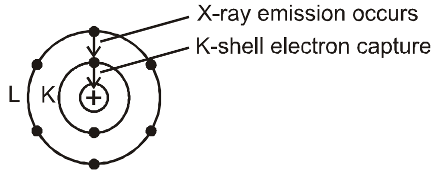
Radiations :

α : $_2He^4$ ($_2^4He^{2+}$) (nucleus of He-atom)
β or β^- : $_{-1}e^0$ (fast moving electron emitted from nucleus)
γ : $_0\gamma^0$ (electromagnetic radiation (waves) of high frequency)
speed : $\gamma > \beta > \alpha$
penetrating power : $\gamma > \beta > \alpha$
ionisation power : $\alpha > \beta > \gamma$

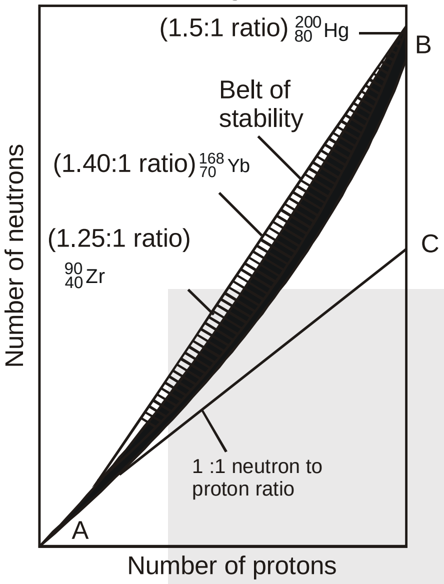
S.No.	Emission of rays	Usual condition	Effect	Process representation/ example
1	α	Z > 83	n/p ratio increases	$_ZX^A \rightarrow {}_{Z-2}X'^{A-4} + {}_2He^4$ $_{92}U^{238} \rightarrow {}_{90}Th^{234} + {}_2He^4$
2	β	If $\frac{n}{p}$ ratio is high eg. $_6C^{12}$ (stable) $\frac{n}{p} = \frac{6}{6}$ $_6C^{14}$ (radioactive) $\frac{n}{p} = \frac{8}{6}$ (high) eg. $_{11}Na^{24}$ (radioactive) $\frac{n}{p} = \frac{13}{11}$ (high) $_{11}Na^{23}$ (stable) $\frac{n}{p} = \frac{12}{11}$ $_{11}Na^{22}$ $\frac{n}{p} = \frac{11}{11}$ ($\frac{n}{p}$ ratio low)	$\frac{n}{p}$ ratio decreases	$_ZY^A \rightarrow {}_{Z+1}Y^A + {}_{-1}e^0$ $_6C^{14} \rightarrow {}_7N^{14} + {}_{-1}e^0$ $\frac{n}{p} = \frac{8}{6}$ $\frac{n}{p} = \frac{7}{7}$ $_0n^1 \rightarrow {}_1p^1 + {}_{-1}e^0$ (from nucleus)
3	γ	If nucleus energy level is high	nucleus energy level decreases	$_{43}Tc^{99} \rightarrow {}_{43}Tc^{99} + \gamma$ high nucleus energy (metastable) / low nucleus energy
4	**(a)** Positron emission ($_{+1}e^0$)	If $\frac{n}{p}$ ratio is low	$\frac{n}{p}$ ratio increases	$_ZY^A \rightarrow {}_{Z-1}Y'^A + {}_{+1}e^0$ $_{11}Na^{22} \rightarrow {}_{10}Ne^{22} + {}_{+1}e^0$ $_1p^1 \rightarrow {}_0n^1 + {}_{+1}e^0$ (from nucleus)
5	**(b)** Electron capture (EC) or K-shell	If $\frac{n}{p}$ ratio is low	$\frac{n}{p}$ ratio increases	$_ZX'^A + \underset{\text{K–shell}}{{}_{-1}e^0} \rightarrow {}_{Z-1}X''^A$ $_{80}Hg^{197} + {}_{-1}e^0 \rightarrow {}_{79}Au^{197}$

Electron capture

$$_1p^1 + {}_{-1}e^0 \longrightarrow {}_0n^1$$
(K – shell)



Nuclear stability belt :



β-emission

$_0n^1 \rightarrow {}_1p^1 + {}_{-1}e^0$

- * Z upto 20 : nuclei stable with n/p ratio nearly 1 : 1
- * Z > 20 : n/p ratio increases with Z in stable nuclei region.
- * More number of neutrons are required to reduce repulsion between protons.
- * $_{83}Bi^{209}$: Stable with largest n/p ratio

$$\frac{n}{p} = \frac{1.52}{1}$$

Even-odd rule :

no. of n	no. of p	no. of stable nuclei
even	even	155 (max)
even	odd	55
odd	even	50
odd	odd	5 (min)

Expected pairing of nucleus

Magic Numbers :

Nuclei in which nucleons have magic no. (2, 8, 20, 28, 50 ....) are more stable.

e.g. $_2He^4$, $_8O^{16}$

Group displacement law : (Given by Soddy and Fajan)

* When 1α emission takes place from a nuclei, new formed nuclei occupy two position left in periodic table.
* When 1β emission takes place from a nuclei, new formed nuclei occupy one position right in periodic table.

Due to emission of 1β particle; isobars are formed.
Due to emission of 1α particle; isodiaphers are formed.
Due to emission of 1α and 2β ; isotopes are formed.

Isotopes : same number of proton eg. $_6C^{14}$ and $_6C^{12}$
Isobars : same mass number eg. $_6C^{14}$ and $_7N^{14}$
Isotones : same number of neutron eg. $_2He^4$ and $_1H^3$

D31 **Isodiaphers :** Same (n – p) difference
e.g. $_9F^{19}$ and $_{19}K^{39}$; (n – p) = 10

D32 **Isosters :** Same number of atoms and electrons
e.g. N_2 and CO
N_2O and CO_2

Artifical nuclear reaction :

$$(\underset{\text{striking particle}}{\alpha}\ ,\ \underset{\text{emitted particle}}{p})$$

specific nuclei + stricking particle ⟶ New nuclei + emitted particle

eg.

1. (α, p type) $_7N^{14}$ + $\underset{\text{(s.p.)}}{_2He^4}$ $\longrightarrow$ $_8O^{17}$ + $\underset{\text{(e.p.)}}{_1p^1}$ (or $_1H^1$)
2. (n, γ type) $_{11}N^{23}$ + $_1n^0$ $\longrightarrow$ $_{11}Na^{24}$ + γ
3. (D, p type) $_{13}Al^{27}$ + $_1H^2$ $\longrightarrow$ $_{13}Al^{28}$ + $_1H^1$
4. (p, α type) $_3Li^7$ + $_1H^1$ $\longrightarrow$ $_2He^4$ + $_2He^4$

Nuclear fission and nuclear fusion:

In both processes, large amount of heat evolved due to conversion of some mass into energy.

D33 **Nuclear fission:** Is a process where heavy nuclei splits into large nuclei.

$$_{92}U^{235} + {_0n^1} \longrightarrow {_{92}U^{*236}} \rightarrow \text{various nuclie and neutrons}$$

eg. atom bomb is based on fission.

D34 **Nuclear fusion :**
Is a process where light nuclei fused together to form heavy nuclei.

$$_1H^2 + {_1H^3} \longrightarrow {_2He^4} + {_0n^1}$$
$$_1H^2 + {_1H^2} \longrightarrow {_2He^4}$$

Hydrogen bomb is based on fusion. Very high temperature is required in this process.

Solved Example

Example 1 ^{23}Na is the most stable isotope of Na. Find out the process by which $^{24}_{11}Na$ can undergo radioactive decay.

Solution. n/p ratio of ^{24}Na is 13/11 and thus greater than one. It will therefore decay following β-emission.

$$^{24}_{11}Na \longrightarrow {^{24}_{12}Mg} + {^{0}_{-1}e}$$

Example 2 The number of β-particle emitted during the change $^{c}_{a}X \longrightarrow {^{b}_{d}Y}$ is :

(A) $\dfrac{a-b}{4}$ (B) $d + \left(\dfrac{a-b}{2}\right) + c$ (C) $d + \left(\dfrac{c-b}{2}\right) - a$ (D) $d + \left(\dfrac{a-b}{2}\right) - c$

Solution. $^{c}_{a}X \longrightarrow {^{b}_{d}Y} + m\,{^{4}_{2}He} + n\,{^{0}_{-1}e}$

$\therefore$ c = b + 4m ......(i)
and a = d + 2m – n ......(ii)
by (i) & (ii)

$$n = d + \left(\frac{c-b}{2}\right) - a.$$ **Ans. (C)**

Example 3 The decay product of $^{13}_{7}N$ is :

(A) $^{13}_{8}O + ^{0}_{-1}e$ (B) $^{13}_{6}C + ^{0}_{+1}e$

(C) $^{13}_{6}C$ + K electron capture (D) $^{9}_{5}Be + ^{4}_{2}He$

Solution. $^{13}_{7}N$ is positron emitter ; $\frac{n}{p}$ ratio is low. **Ans. (B)**

Example 4 A radioactive element X has an atomic numbers of 100. It decays directly into an element Y which decays directly into an element Z. In both processes a charged particle is emitted. Which of the following statement would be true?

(A) Y has an atomic number of 102. (B) Z has an atomic number of 101.

(C) Z has an atomic number of 97. (D) Z has an atomic number of 99.

Solution. X and Y can decay one α each or one β each or X-decays, 1 α, Y-decays 1 β or X-decays 1 β or Y-decays 1 α. In either case (A), (B) and (C) cannot be true. **Ans. (D)**

ATOMIC STRUCTURE

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

2. According to Bohr model, the angular momentum of an electron is an integral multiple of h/2π.Bohr's model is applicable to single electron species (hydrogen like species).

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

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

5. The emission spectra of hydrogen is obtained when electron from an excited state is de-excited to the ground state. The release of specific amounts of energy in the form of photons accounts for the lines in the hydrogen spectrum. λ of each line in the spectrum can be given by $1/\lambda = R_Hz^2[(1/n^2_1) - (1/n^2_2)]$

6. de-Broglie extended Einstein's wave particle description of light to all matters in motion. The wavelength of a moving particle of mass m and velocity v is given by de Broglie equation, λ = h/mv.

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

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

9. In photoelectric effect, electrons are ejected from the surface of certain metal exposed to light of at least a certain minimum frequency.
$h\nu = h\nu_0 + K.E_{max}$.

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

Problem 1 The ratio of ($E_2 - E_1$) to ($E_4 - E_3$) for He^+ ion is approximately equal to (where E_n is the energy of n^{th} orbit)

(A) 10 (B) 15 (C) 17 (D) 12

Solution.
$$\frac{13.6\ (2)^2\left[\frac{1}{(1)^2}-\frac{1}{(2)^2}\right]}{13.6\ (2)^2\left[\frac{1}{(3)^2}-\frac{1}{(4)^2}\right]} = 15$$
Ans. (B)

Problem 2 If the binding energy of 2nd excited state of a hydrogen like sample is 24 eV approximately, then the ionisation energy of the sample is approximately

(A) 54.4 eV (B) 24 eV (C) 122.4 eV (D) 216 eV

Solution. $\frac{13.6(Z)^2}{(3)^2} = 24$

I.E. = $13.6(Z)^2 = (24 \times 9) = 216$ eV **Ans. (D)**

Problem 3 The ionisation energy of H atom is 21.79×10^{-19} J. Then the value of binding energy of second excited state of Li^{2+} ion

(A) $3^2 \times 21.7 \times 10^{-19}$ J (B) 21.79×10^{-19} J

(C) $\frac{1}{3} \times 21.79 \times 10^{-19}$ J (D) $\frac{1}{3^2} \times 21.79 \times 10^{-19}$ J

Solution. B.E. = $\frac{21.79 \times 10^{-19}(3)^2}{(3)^2} = 21.79 \times 10^{-19}$ J **Ans. (B)**

Problem 4 The wave number of the first line in the Balmer series of hydrogen is $15200 cm^{-1}$. What would be the wavenumber of the first line in the Lyman series of the Be^{3+} ion?

(A) $2.4 \times 10^5 cm^{-1}$ (B) $24.3 \times 10^5 cm^{-1}$ (C) $6.08 \times 10^5 cm^{-1}$ (D) $1.313 \times 10^6 cm^{-1}$

Solution. Given $15200 = R(1)^2\left[\frac{1}{(2)^2} - \frac{1}{(3)^2}\right]$ ..... (1)

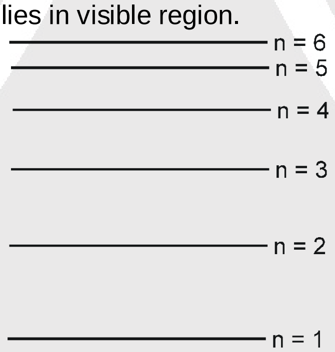
Then $\bar{\nu} = R(4)^2\left[\frac{1}{(1)^2} - \frac{1}{(2)^2}\right]$ ..... (2)

from (1) and (2) equation

$\bar{\nu} = 1.313 \times 10^6 cm^{-1}$ **Ans. (D)**

Problem 5 What would be the maximum number of emission lines for atomic hydrogen that you would expect to see with the naked eye if the only electronic energy levels involved are those as shown in the Figure?

Hint: Balmer series lines lies in visible region.



(A) 4 (B) 6 (C) 5 (D) 15

Solution. Only four lines are present in visible region, $6 \rightarrow 2$, $5 \rightarrow 2$, $4 \rightarrow 2$ & $3 \rightarrow 2$.

Ans. (A)

Problem 6 The de Brogile wavelength of an electron moving in a circular orbit is λ. The minimum radius of orbit is

(A) $\frac{\lambda}{\pi}$ (B) $\frac{\lambda}{2\pi}$ (C) $\frac{\lambda}{4\pi}$ (D) $\frac{\lambda}{3\pi}$

Solution. We know, $2\pi r = n\lambda$

For minimum radius n = 1

$2\pi r_{min} = \lambda$

$r_{min} = \frac{\lambda}{2\pi}$ **Ans. (B)**

Problem 7 Uncertainty in position of a hypothetical subatomic particle is 1Å and uncertainty in velocity is $\frac{3.3}{4\pi} \times 10^5$ m/s then the mass of the particle is approximately [h = 6.6 × 10^{-34} Js]

(A) 2 × 10^{-28} kg (B) 2 × 10^{-27} kg (C) 2 × 10^{-29} kg (D) 4 × 10^{-29} kg

Solution. $\Delta x \times m \times \Delta v \geq h/4\pi$

$1 \times 10^{-10} \times m \times \frac{3.3}{4\pi} \times 10^5 \geq \frac{6.6 \times 10^{-34}}{4 \times \pi}$ m = 2 × 10^{-29} kg **Ans. (C)**

Problem 8 Which of the following set of quantum numbers is not valid.

(A) n = 3, ℓ = 2, m = 2, s = $+\frac{1}{2}$ (B) n = 2, ℓ = 0, m = 0, s = $-\frac{1}{2}$

(C) n = 4, ℓ = 2, m = –1, s = $+\frac{1}{2}$ (D) n = 4, ℓ = 3, m = 4, s = $-\frac{1}{2}$

Solution. Not valid **Ans. (D)**

Problem 9 What is the total spin value in case of $_{26}Fe^{3+}$ ion.

(A) +1 or –1 (B) +2 or –2 (C) + 2.5 or – 2.5 (D) +3 or –3

Solution. Total spin = no. of unpaired e^- × $\left(\pm\frac{1}{2}\right)$ = 5 × $\left(\pm\frac{1}{2}\right)$ = $\pm\frac{5}{2}$

Ans. (C)

CHECK LIST

Definitions (D)

D1 Atomic number (Z) of an element ☐
D2 Isotopes ☐
D3 Isobars ☐
D4 Isotones ☐
D5 Isoelectronic ☐
D6 Electromagnetic wave radiation ☐
D7 Wavelength ☐
D8 Frequency ☐
D9 Velocity ☐
D10 Amplitude ☐
D11 Wave number ☐
D12 Quantum of light ☐
D13 One electron volt (e.v.) ☐
D14 Photoelectric Effect ☐
D15 Ground state ☐
D16 Excited State ☐
D17 Ionisation energy (IE) ☐
D18 Ionisation Potential (I.P.) ☐
D19 Excitation Energy ☐
D20 Excitation Potential ☐
D21 Binding Energy ‘or’ Separation Energy ☐
D22 Spectroscopy ☐
D23 Emission spectra ☐
D24 Continuous spectra ☐
D25 Line spectrum ☐
D26 Absorption spectra ☐
D27 Emission spectrum of Hydrogen ☐
D28 Orbital ☐
D29 Quantum Numbers ☐
D30 Radioactivity ☐
D31 Isodiaphers ☐
D32 Isosters ☐
D33 Nuclear fission ☐
D34 Nuclear fusion ☐

Formulae (F)

F1 Quantization of charge ☐
F2 Potential energy of two point charges ☐
F3 Size of nucleus ☐
F4 Mass number of an element ☐
F5 Wave number ☐
F6 Energy of emf waves ☐
F7 Speed of light ☐
F8 Energy in terms of wavelength (λ) ☐
F9 Photoelectric effect ☐
F10 Centripetal force ☐
F11 Angular momentum of a Bohr orbit ☐
F12 Photo energy ☐
F13 Frequency ☐
F14 Radius of Bohr orbit ☐
F15 Radius of Bohr orbit in term of calculation. ☐
F16 Velocity of electron in Bohr orbit (expanded) ☐
F17 Velocity of electron in Bohr orbit ☐
F18 Time period of a Bohr orbit ☐
F19 Frequency in a Bohr orbit ☐
F20 Total energy of a Bohr orbit ☐
F21 Total energy of in eV/atom ☐
F22 Total energy of in J/atom ☐
F23 Relation between total energy and potential energy ☐
F24 Relation between total energy and kinetic energy ☐
F25 Wave number ☐
F26 Number of spectral lines ☐
F27 Single isolated atom maximum number of spectral lines ☐
F28 de-Broglie Wavelength in form of velocity ☐
F29 de-Broglie Wavelength in term of kinetic energy ☐
F30 de-broglies in terms of voltage ☐
F31 Heisenberg principle ☐
F32 Heisenberg in terms of ΔE & ΔT ☐
F33 Schordinger’s equation ☐
F34 Radial nodes ☐
F35 Angular nodes ☐
F36 Total nodes ☐
F37 Number of subshell present in n^{th} shell ☐
F38 Number of orbitals present in n^{th} shell ☐
F39 The maximum number of electrons in a principal energy shell ☐
F40 Angular momentum of any orbit ☐
F41 Number of orbitals in a subshell ☐
F42 Maximum number of electrons in particular subshell ☐
F43 Angular orbital momentum ☐
F44 Orbitals present in a main energy level is ‘n^2’. ☐
F45 Magnetic moment ☐
F46 Spin angular momentum ☐
F47 Maximum spin of atom ☐

Derivations (Der.)

Der1 Distance of closest approach ☐
Der2 Value of one electron volt☐
Der3 Calculation of the radius of the Bohr’s orbit ☐
Der4 Calculation of velocity of an electron in Bohr’s orbit ☐
Der5 Calculation of energy of an electron ☐
Der6 Wave number ☐
Der7 de-Broglie wavelength ☐
Der8 de-Broglie wavelength in relation to voltage ☐
Der9 Heisenberg principle In terms of uncertainty in energy E & Δt ☐