Section (A) : Calculation related to nucleus

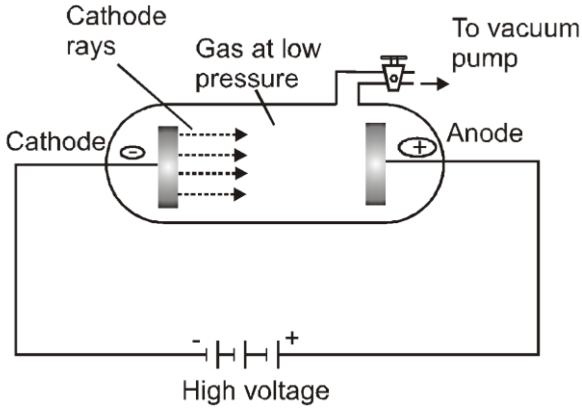
INTRODUCTION :

Structure of Atom

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

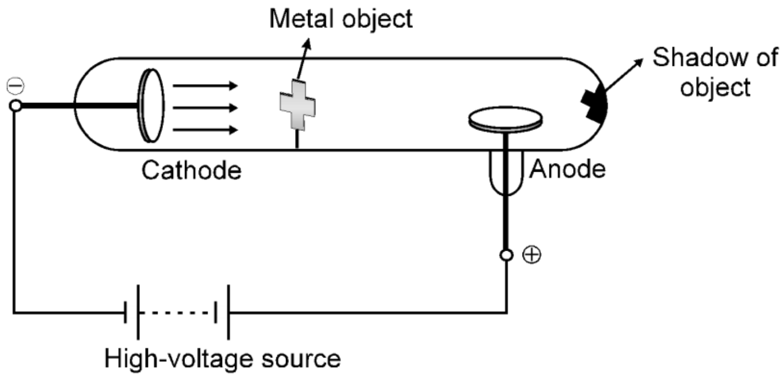
Dalton’s concept of the indivisibility of the atom was completely discredited by a series of experimental evidences obtained by scientists. A number of new phenomenone were brought to light and man’s idea about the natural world underwent a revolutionary change. The discovery of electricity and spectral 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.

CATHODE RAYS - DISCOVERY OF ELECTRON :



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 :



Cathode rays have the following properties :

(i) Path of travelling is straight from the cathode with a very high velocity as it produces shadow of an object placed in its path

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

(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. Light is emitted when they strike the zinc sulphide screen.

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

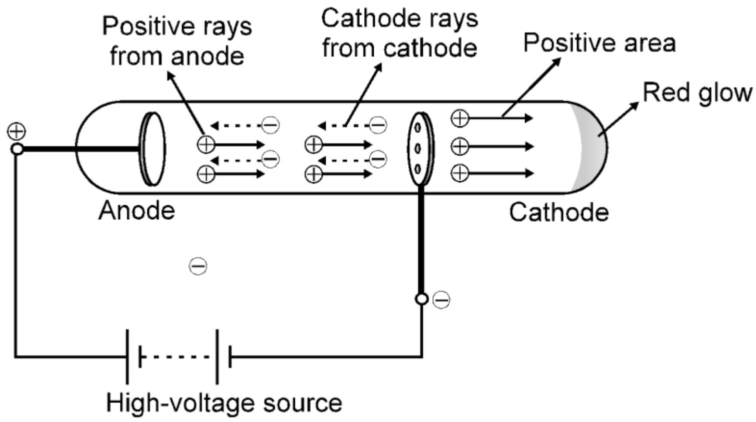
(vi) They affect the photographic plates

(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.

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.



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.

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 :

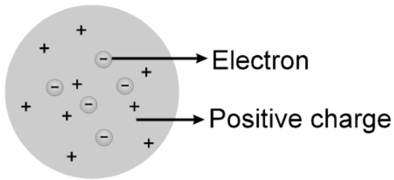
Later, a need was felt for the presence of electrically neutral particles as one of the constituent of atom. These particles were discovered by Chadwick in 1932 by bombarding a thin sheet of Beryllium with α-particles, when electrically neutral particles having a mass slightly greater than that of the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

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

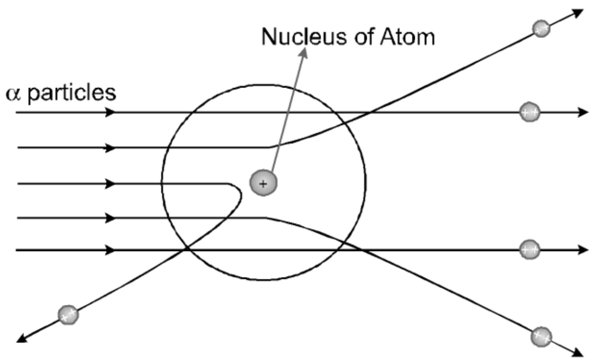
ATOMIC MODELS :

THOMSON'S MODEL OF THE ATOM :

An atom is electrically neutral. It contains positive charges as well as negative charges (due to the presence of electrons). Hence, J J Thomson assumed that an atom is a uniform sphere of positive charges with electrons embedded in it. The magnitude of total positive charge on sphere is equal to total negative charge of embedded electrons.



RUTHERFORD'S EXPERIMENT :



- Most of the α-particles passed straight through the gold foil without suffering any deflection from their original path.
- A few of them were deflected through small angles, while a very few were deflected to a large extent.
- A very small percentage (1 in 100000) was deflected through angles ranging from 90° to 180°.

Rutherford's nuclear concept of the atom.

- 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.
- The electrons are distributed in the empty space of the atom around the nucleus in different concentric circular paths, called orbits.
- The number of electrons in orbits is equal to the number of positive charges (protons) in the nucleus. Hence, the atom is electrically neutral.
- The volume of the nucleus is negligibly small as compared to the volume of the atom.
- Most of the space in the atom is empty.

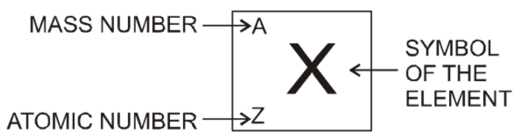
NUCLEUS :

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

Particles	Symbol	Mass	Charge	Discoverer
Electron	${}_{-1}e^0$ or β	9.1096×10^{-31} kg 0.000548 amu	-1.602×10^{-19} Coulombs -4.803×10^{-10} esu	J.J. Thompson Stoney Lorentz 1887
Proton	${}_1H^1$	1.6726×10^{-27} kg 1.00757 amu	$+1.602 \times 10^{-19}$ Coulombs $+4.803 \times 10^{-10}$ esu	Goldstein Rutherford 1907
Neutron	${}_0n^1$	1.6749×10^{-27} kg 1.00893 amu 1 amu ≈ 1.66×10^{-27} kg	Neutral 0	James Chadwick 1932

ATOMIC NUMBER AND MASS NUMBER :

- **Atomic number 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 because the charge on the nucleus depends upon the number of protons.
  - 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.
- **Mass number of an element = No. of protons + No. of neutrons.**
  - 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 alongwith the symbol of the element as



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

IMPORTANT DEFINATIONS :

1. ISOTOPES :

(i) First proposed by soddy.
(ii) The isotopes have same atomic number but different atomic weight.
(iii) They have same chemical properties because they have same atomic number.
(iv) They have different physical properties because they have different atomic masses.

eg. ${}_8O^{16}$, ${}_8O^{17}$, ${}_8O^{18}$; ${}_6C^{12}$, ${}_6C^{13}$, ${}_6C^{14}$; ${}_7N^{14}$, ${}_7N^{15}$

eg.	$_1H^1$	$_1H^2$	$_1H^3$
	Protium	deuterium	Tritium
Z =	1	1	1
A =	1	2	3

Average atomic weight = $\dfrac{m_1x_1 + m_2x_2 + ...}{x_1 + x_2 + ...}$

where m_1, m_2 .... are atomic weight of isotopes.

x_1, x_2 .... are ratio of percentage abundance of isotopes.

2. ISOBAR :

The different atoms which have same atomic masses but different atomic number are called as Isobar.

eg.	$_{18}Ar^{40}$	$_{19}K^{40}$	$_{20}Ca^{40}$
Atomic mass	40	40	40
Atomic number	18	19	20

3. ISOTONE :

Elements which contain same no. of neutron are called as Isotones.

eg.	$_{14}Si^{30}$	$_{15}P^{31}$	$_{16}S^{32}$
Number of neutrons	16	16	16

4. ISOELECTRONIC :

Ion or atom or molecule or species which have the same number of electrons are called as isoelectronic species.

eg.	$_{17}Cl^-$	$_{18}Ar$	$_{19}K^+$	$_{20}Ca^{+2}$
No. of electron	18	18	18	18

Solved Examples

Ex-1. The triad of nuclei that is isotonic -

(1) $_6C^{14}$, $_7N^{15}$, $_9F^{17}$ (2) $_6C^{12}$, $_7N^{14}$, $_9F^{19}$ (3) $_6C^{14}$, $_7N^{14}$, $_9F^{17}$ (4) $_6C^{14}$, $_7N^{14}$, $_9F^{19}$ **Ans. (1)**

Ex-2. 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

Sol. **For nitrogen atom.**

No. of electron = 7 (given)

No. of neutrons = 7 (given)

∴ No. of protons = Z = 7 (∴ 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 extranuclear 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,

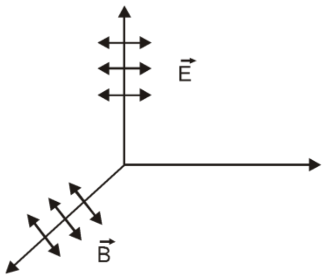
No. of electrons = Z = 8

No. of neutrons = A – Z = 16 – 8 = 8

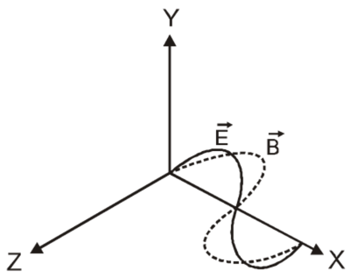
Section (B) : Quantum theory of light and photoelectric Effect

ELECTROMAGNETIC WAVE RADIATION :

The oscillating electrical/magnetic field are electromagnetic radiations. Experimentally, the direction of oscillations of electrical and magnetic field are prependicular to each other.



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



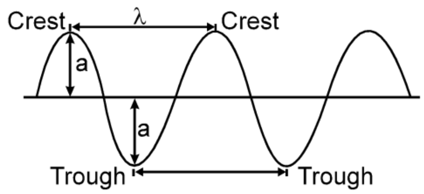
Direction of wave propogation.

Some important characteristics of a wave :

- **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



- **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

- **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}).

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

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

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

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. Thus

$$v = \nu \times \lambda$$

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 :

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)

QUANTUM THEORY OF LIGHT :

The light energy from any source is always an integral multiple of a smallest energy value called quantum of light.

Quantum of light is called as photon.

Energy of one photon = $h\nu$

h = plank's constant = 6.625×10^{-34} Js

ν = frequency of light

$\nu = \frac{c}{\lambda}$ (λ – wavelength)

(c- speed of light)

Energy, $E = \frac{hc}{\lambda}$

SOME IMPORTANT FORMULAE :

1. A = Z + N (Number of neutrons)

2. dynamic mass of particle $m = m_0 / [1 - (v/c)^2]^{1/2}$

3. Radius of nucleus $R = R_0 (A)^{1/3}$, $R_0 = 1.2 \times 10^{-15}$ m

4. $c = \upsilon\lambda$

5. wave number $\bar{\upsilon} = 1 / \lambda$

6. $E = h\upsilon = hc / \lambda = hc\,\bar{\upsilon}$

7. $F = \frac{q_1 \; q_2}{r^2} K$; $K = \frac{1}{4\pi\varepsilon_0} = 9.0 \times 10^9\ Nm^2/C^2$

8. $\Delta E = h\upsilon = E_2 - E_1$

Solved Examples

Ex-3. Calculate number of photon coming out per sec. from the bulb of 100 watt. If it is 50% efficient and wavelength coming out is 600 nm.

Sol. Energy = 100J

Energy of one photon = $\frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{600 \times 10^{-9}} = \times 10^{-19}$

no. of photon = $\frac{100}{6.625} \times 10^{19} = 15.09 \times 10^{19}$

Ex-4. Certain sun glasses having small of AgCl incorporated in the lenses, on exposer 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?

Sol. 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, $\therefore$ $N_A.\frac{hc}{\lambda} = 248 \times 10^3$

$$\lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8 \times 6.023 \times 10^{23}}{248 \times 10^3} = 4.83 \times 10^{-7}\ m$$

Section (C) : Bohr model

BOHR'S ATOMIC MODEL :

It is based on quantum theory of light.

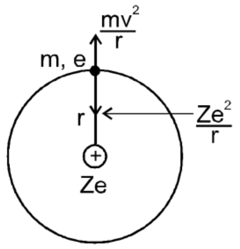
(A) Main Postulates :

(i) The electrons revolve around the nucleus with high velocities in certain fixed orbits, called levels.

There are two forces acting on it.

(a) Electrostatic force of attraction of nucleus, which provides centripetal force. It's magnitude is equal to Ze^2/r^2. Where Z = atomic number, e = electronic charge, r = radius of orbit.

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



where, m = mass of electron, v = velocity of electron, r = radius of that orbit. Both these forces balance each other to keep electron moving in circular path.

Centrifugal force = Centripetal force (Electrostatic force of attraction)

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad .... (1)$$

(ii) Energy of an electron remains constant as long as it stays in same orbit called **STATIONARY ORBIT**. Hence a fixed amount of energy is associated with each stationary orbit and hence it is called **Energy level or main energy level** these are represented as K,L,M,N .... etc.

(iii) When an electron jumps from one orbit to another, it emits or absorbs a definite amount of energy. This emission or absorption occurs in discrete energy levels.

$$\Delta E = E_{n_2} - E_{n_1} = h\nu \quad .... (2)$$

where ΔE = Emitted or absorbed energy, E_{n_2} = Energy of stationary n_2 orbit

E_{n_1} = Energy of stationary n_1 orbit, ν = Frequency of radiation emitted or absorbed

h = Planck's constant

When, $E_{n_2} - E_{n_1} > 0$ or $E_{n_2} > E_{n_1}$, energy is emitted.

It means when electron jumps to higher energy level from lower energy level, energy is abosorbed. When electron jumps to lower energy level from higher energy level, energy is emitted.

(iv) Permissible orbits are those for which angular momentum is an integral multiple of $h/2\pi$. i.e $mvr = nh/2\pi$ where n = 1,2,3,4.......... etc. This is also called **QUANTIZATION** of angular momentum, n is some number (principal quantum number) of that orbit e.g. n for K orbit is 1, for L is 2, for M is 3 etc.

$$mvr = n\frac{h}{2\pi} \quad .... (3)$$

(B) Application of Bohr's atomic model :–

(i) Radius of the Bohr's orbit :

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

In C.G.S. unit K = 1

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

Where $h = 6.62 \times 10^{-27}$ erg. sec. $m = 9.1 \times 10^{-28}$ g, $e = 4.8 \times 10^{-10}$ esu

on putting the value of e, h, m and constants.

then $r = 0.529 \times \frac{n^2}{Z}$ Å $\quad r \propto n^2$ & $r \propto \frac{1}{Z}$

(ii) Velocity of an electron in Bohr's orbit :

$$v = \frac{2\pi Ze^2}{nh}$$

on putting the values of all constants. Then–

$$v = 2.188 \times 10^8 \times \frac{Z}{n} \text{ cm/sec.}$$

$v \propto z$; $v \propto$

(iii) Energy of an electron :

$E_n = -\dfrac{2\pi^2 Z^2 e^4 m}{n^2 h^2}$ T.E. $= \dfrac{P.E.}{2} = -$ K.E.

Where T.E. = Total energy, K.E. = Kinetic energy, P.E. = Potential energy

(a) T.E. $= -13.6 \times \dfrac{Z^2}{n^2}$ eV/atom (b) T.E. $= -21.8 \times 10^{-19} \times \dfrac{Z^2}{n^2}$ J/atom

(c) T.E. $= -21.8 \times 10^{-12} \times \dfrac{Z^2}{n^2}$ erg/atom (d) T.E. $= -313.6 \times \dfrac{Z^2}{n^2}$ Kcal/mole

Solved Examples

Ex-5. What is the orbit number of H atom if electron having energy is – 3.4 eV? Also report the angular momentum of electron.

Sol. E_1 for H = – 13.6 eV

Now $E_n = \dfrac{E_1}{n^2}$ ∴ $-3.4 = \dfrac{-13.6}{n^2}$ ∴ n = 2

Now, Angular momentum (mvr) = $n \cdot \dfrac{h}{2\pi} = \dfrac{2 \times 6.626 \times 10^{-34}}{2 \times 3.14} = 2.1 \times 10^{-34}$ J - sec^{-1}

Ex-6. A single electron system has ionization energy 11180 kJ mol^{-1} . Find the number of protons in the nucleus of the system.

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

$\dfrac{11180 \times 10^3}{6.023 \times 10^{23}} = \dfrac{Z^2}{1^2} \times 21.69 \times 10^{-19}$ **Ans. Z = 3**

Ex-7. Which state of the triply ionized Beryllium (Be^{3+}) has the same orbit radius as that of the ground state of hydrogen atom ?

Sol. Radius of ground state of hydrogen atom = 0.529 Å

$0.529 = 0.529 \times \dfrac{n^2}{Z}$

$0.529 = 0.529 \times \dfrac{n^2}{4}$

∴ n = 2 **Ans.** n = 2

Ex-8. The excitation energy of first excited state of a hydrogen like atom is 40.8 eV. Find the energy needed to remove the electron to form the ion.

Sol. $40.8 = (\Delta E)_{2 \to 1} \times Z^2$ ⇒ $40.8 = 10.2 \times Z^2$ ⇒ $Z^2 = 4$ or Z = 2

IE = 13.6 Z^2 = 13.6 × 4 = 54.4 eV **Ans.** 54.4 eV

DEFINITION VALID FOR SINGLE ELECTRON SYSTEM :

1. Ground state (G.S.) : In any single electron species n = 1 is called ground state.

Ground state energy of H–atom = – 13.6 ev

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

2. **Excited state (E.S.) :** In single electron species $n > 1$ is called excited state.

$n = 2$, called first excited state
$n = 3$, called second excited state
$n = 4$, called third excited state

For the n^{th} shell = $(n - 1)^{th}$ excited state.

3. **Excitation energy :** Energy required to excite an electron from its ground state to any excited state is called excitation energy.

$E_2 - E_1 =$ first excitation energy
$E_3 - E_1 =$ second excitation energy
$E_4 - E_1 =$ third excitation energy

4. **Binding Energy or Seperation energy :** Energy required to move an electron from any state to $n = \infty$ is called binding energy of that state.

Binding energy of ground state = I.E. of atom or Ion.

$E_\infty - E_2 = 0 - E_2 = -E_2$ = first seperation energy
$E_\infty - E_3 = 0 - E_3 = -E_3$ = second seperation energy
$E_\infty - E_4 = 0 - E_4 = -E_4$ = third seperation energy

5. **Ionization energy (I.E) :** Energy required to remove an electron from its ground state.

For single electron species I.E. $= 0 - E_1 = - E_1$

For multi electron species

Ionisation energy of H–atom = 13.6 ev
$I.E._1 < I.E._2 < I.E._3$ .... Ionisation energy of He^+ ion = 54.4 ev
Ionisation energy of Li^{+2} ion = 122.4 ev

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

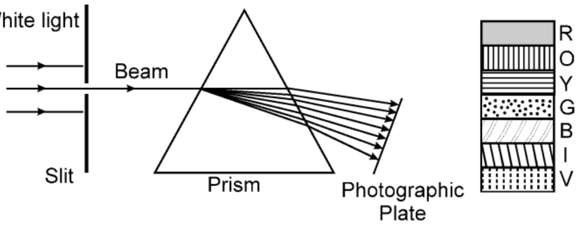
Emission spectra :

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 :

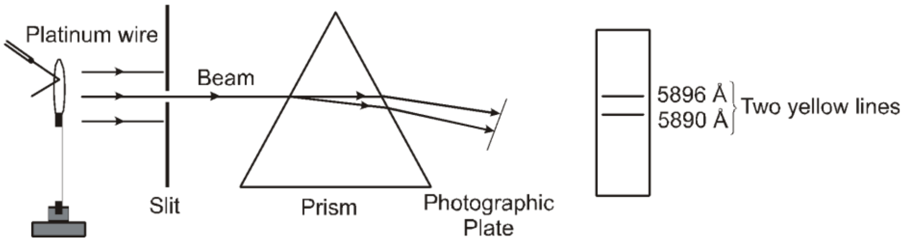
- **Continuous spectra :**

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.



- **Line spectra :**

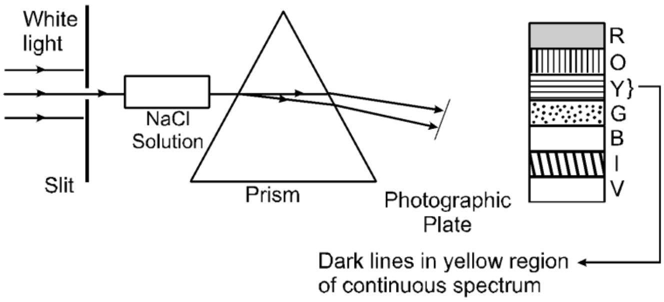
When some volatile salt (e.g., sodium chloride) is placed in the Bunsen flame or an electric discharge is passed through a gas at low pressure, light emitted depends upon the nature of substance.



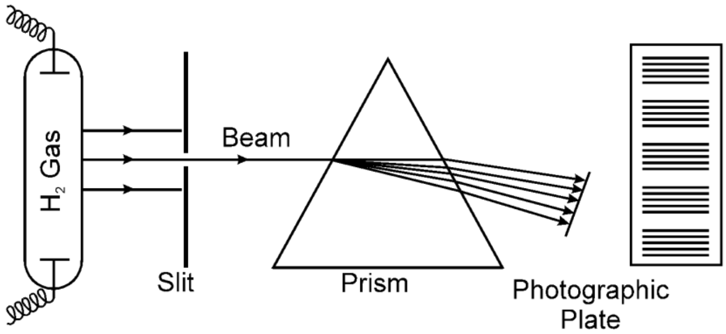
It is found that no continuous spectrum is obtained but some isolated coloured lines are obtained on the photographic plate separated from each other by dark spaces. This spectrum is called 'Line emission spectrum' or simply Line spectrum.

- **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 substance.



- **Emission spectrum of Hydrogen :**



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.

Spectra lines of Hydrogen Atom :

Series	n_1	$n_2 > n_1$	Region of Spectrum
Lyman	1	2,3,.....∞	Ultraviolet (2 → 1) H_α, (3 → 1) H_β & so on.
Balmer	2	3,4,.....∞	Visible (3 → 2) H_α, (4 → 2) H_β & so on.
Paschen	3	4,5......∞	Infrared (4 → 3) H_α, (5 → 3) H_β & so on.
Brackett	4	5,6,.....∞	Infrared (5 → 4) H_α, (6 → 4) H_β & so on.
Pfund	5	6,7,.....∞	Infrared (6 → 5) H_α, (7 → 5) H_β & so on.
Humphry	6	7,8,.....∞	Infrared (7 → 6) H_α, (8 → 6) H_β & so on.

- $\frac{n\ (n-1)}{2}$ = Max. no of spectral lines possible when an electron returns to ground state from n^{th} orbit.
- $\frac{1}{\lambda} = \bar{v} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$

Limitations of Bohr's theory :

(i) Fails to explain spectra of atoms with more than one electron. It can only explain spectra of hydrogen and single electron species like He^+, Li^{2+}, Be^{3+}, Na^{+10} etc.

(ii) Does not explain fine structure of spectral lines.

(iii) Does not explain **Zeeman effect** (splitting up of spectral lines in presence of a magnetic field) & **Stark effect** (Splitting up of spectral lines in presence of an electric field).

(iv) Fails to recognise wave property of electron established by De Broglie in 1923.

Solved Examples

Ex-9. The ionisation energy of He^+ is 19.6×10^{-18} J per ion. Calculate the energy of the first stationary state of Li^{2+}.

Sol. The ionisation energy of He^+ is 19.6×10^{-18} .

∴ Energy of the first orbit of He^+ (Z = 2) = 19.6×10^{-18} J.

∴ Energy of the first orbit of H^+ (Z = 1) = $\frac{19.6 \times 10^{-18}}{4}$ J

∴ Energy of the first orbit of Li^{2+} (Z = 3) = $\frac{19.6 \times 10^{-18}}{4} \times 9$ = 4.41×10^{-17} J.

Ans. 4.41×10^{-17} J.

Ex-10. The ionization energy of a hydrogen like Bohr atom is 4 Rydberg. What is the radius of the first orbit of this atom? (Bohr radius of hydrogen = 5×10^{-11} m; 1 Rydberg = 2.2×10^{-18} J)

Sol. $-13.6\ \frac{Z^2}{n^2} = 4R = 4 \times 2.2 \times 10^{-18}$ J.

$Z^2 = \frac{4 \times 2.2 \times 10^{-18}\ J}{13.6 \times 1.6 \times 10^{-19}} = 4$; Z = 2.

$r = 0.529\ \frac{n^2}{Z} \times 10^{-10}$ m. $r = 0.529 \times 10^{-10} \times \frac{1}{2} = 2.645 \times 10^{-11}$ m.

Ans. 2.65×10^{-11} m.

Ex-11. If the binding energy of II excited state of a hypothetical atom is 12 eV, then :

(1) I excitation potential = 81 V
(2) II Excitation energy = 96 eV
(3) Ionisation potential = 192 V
(4) Binding energy of 2^{nd} state = 27 eV

Sol. BE for (n = 3) = 1.51 Z^2 = 12 eV (given)
$Z^2 = 12/1.51$
I Excitation potential = 10.2 Z^2 = 10.2 × (12/1.51) = 81V
II Excitation potential = 12.09 Z^2 = 12.09 × (12/1.51) = 96eV
Ionisation potential = 13.6 Z^2 = 13.6 (12/1.51) = 108 V
BE of (n = 2) = 3.4 Z^2 = 3.4 x (12/1.51) = 27eV
Ans. (1, 2, 4)

Ex-12. What electron transition in the He^+ spectrum would have the same wavelength as the first Lyman transition of hydrogen.

Sol. $\frac{1}{\lambda_H} = R(1)^2\left[\frac{1}{1^2}-\frac{1}{2^2}\right]$ & $\frac{1}{\lambda_{He^+}} = R\,(2)^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

But $\lambda_H = \lambda_{He+}$

∴ from above 2 equations, $n_1 = 2$ & $n_2 = 4$.

Ans. n = 4 to n = 2

Development leading to quantum or wave mechanical model of atom :

In view of the short comings of Bohr model of atom, efforts were made to develop a new model of atom which could overcome the limitations of Bohr model. The development of new model was mainly based on following two concepts that had been put forward :

(1) De-Broglie concept (dual nature of matter)

(2) Heisenberg uncertainty principle.

The new branch of science which was developed taking into consideration the above two concepts is known as quantum mechanics or wave mechanics. That is why the new model of atom is known as quantum or wave mechanical model of atom.

Thus, just as Bohr model of atom was developed on the basis of planck’s quantum theory, the quantum mechanical model of atom has been developed on the basis of quantum mechanics. It is therefore, important to first understand the above two concepts as explained below.

Section (E) : De broglie wavelength & Uncertainity principle

De–Broglie Relation (Dual nature of matter and radiation) :

$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

De–Broglie pointed out that the same equation might be applied to material particle by substituting m for the mass of the particle instead of the mass of photon and replacing c, the velocity of the photon, by v, the velocity of the particle.

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

- From the De–Broglie equation it follows that wavelength of a particle decrease with increase in velocity of the particle. Moreover, lighter particles would have longer wavelengths than heavier particles, provided the velocity is equal.

- If a charged particle Q is accelerated through potential difference V from rest then De–broglie wavelength is

$$\lambda = \frac{h}{\sqrt{2mQV}}$$

- De–Broglie concept is more significant for microscopic or sub–micrscopic particles whose wavelength can be measured.
- The circumference of the nth orbit is equal to n times the wavelength of the electron.
  $2\pi r_n = n\lambda$.
- Wavelength of electron is always calculated using De–Broglie calculation.

HEISENBERG'S UNCERTAINITY PRINCIPLE :

It is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainity.

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

where, Δx = uncertainity in position

Δp = uncertainity in momentum

h = Plank's constant

m = mass of the particle

Δv = uncertainity in velocity

- ❍ In terms of uncertainity in energy ΔE, and uncertainity in time Δt, this principle is written as,

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

- ❍ Heisenberg replaced the concept of definite orbits by the concept of probability.

Solved Examples

Ex-13. Alveoli are the tiny sacs of air in the lungs whose average diameter is 50 pm. Consider an oxygen molecule trapped within a sac. Calculate uncertainty in the velocity of oxygen molecule?

(1) $1.98 \times 10^{-2}\ ms^{-1}$ (2) $19.8\ ms^{-1}$ (3) $198 \times 10^{-4}\ ms^{-1}$ (4) $19.8 \times 10^{-6} ms^{-1}$

Sol. $\Delta x = 50$ pm

So $$\Delta v = \frac{h}{4\pi.m\Delta x} = \frac{6.625 \times 10^{-34} \times 6.022 \times 10^{23}}{4 \times 3.14 \times 32 \times 10^{-3} \times 50 \times 10^{-12}} \text{ m/sec}$$

$= 0.0019853 \times 10^4$ m/sec = 19.853 m/sec

Ans. **(2)**

Ex-14. Determine the de-Broglie wavelength associated with an electron in the 3rd Bohr's orbit of He^+ ion?

(1) 10 Å (2) 2 A (3) 5 Å (4) 1 Å

Sol. $n\lambda = 2\pi r$

so $$\lambda = \frac{2\pi r}{3} = \frac{2\pi}{3} \times (53\text{ pm}) \times \frac{9}{2} \simeq 5\text{Å}$$

Ans. **(3)**

Ex-15. If the light of wavelength 5.77×10^{-10} cm is used to detect an electron then the uncertainly in velocity (approximately) will be ($h = 6.6 \times 10^{-34}$ Js, $m_e = 9.1 \times 10^{-31}$ kg).

(1) 10^5 m/s (2) 10^6 m/s (3) 10^7 m/s (4) None of these

Sol. $\Delta V = \frac{h}{4\pi m\Delta x} = \frac{6.6\times10^{-34}}{4\times3.14\times9.1\times10^{-31}\times5.77\times10^{-12}} = 10^7$ m/s

Ans. **(3)**

Ex-16. The uncertainty in position and velocity of the particle are 0.1 nm and 5.27×10^{-24} ms^{-1} respectively then the mass of the particle is : ($h = 6.625 \times 10^{-34}$Js)

(1) 200 g (2) 300 g (3) 100 g (4) 1000 g

Sol. $m = \frac{h}{4\pi\Delta x} = \frac{6.6\times10^{-34}}{4\times3.14\times10^{-10}\times5.27\times10^{-24}} \simeq 100$ g. **Ans.** **(3)**

THE SCHRODINGER EQUATION :

This equation determines the probability of position and energy of electron which is moving around the nucleus.

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

Where ∇ = Laplacian operator, E = Total energy of the electron.
V = Potential energy of the electron, y = Wave function or wave amplitude
y^2 = Probability density (probability of finding an electron in an atom)

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 electron 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 (Heisenberge 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 orbial. Since many such wave functions are possible for an electron, there are many atomic orbitals wave functions or orbitals from the basis of the electronic structure of atom. 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 stroed 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 porportional 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.

Hydrogen atom and the schrodinger Equation :

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 function of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave function 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 hydrogen atom successfully predict all aspect 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 system. This difficulty can be overcome by using approximate methodes such calculation 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 principle difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Unlike orbitals of hydrogen or hydrogen like species, whose energies depends only on the quantum number n, the energies of the orbitals in multi-electron atoms depends on quantum numbers n and ℓ.

Section (F) : Quantum numbers & Electronic configuration

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.

* 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

* Number of orbitals present in n^{th} shell = n^2 .
* 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.
* Angular momentum of any orbit = $\frac{nh}{2\pi}$

(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
0	s
1	p
2	d
3	f

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

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

* 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 = $\sqrt{3}\frac{h}{2\pi}$

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

It describes the orientations of the subshells. 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. The total number of orbitals present in a main energy level is 'n^2'.

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

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

* 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)

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

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

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 because three quantum numbers (principal, azimuthal and magnetic) at the most may be same but the fourth must be different, i.e., spins must be in opposite directions.

Aufbau principle :

Aufbau is a German word meaning builiding 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 + l) Rule :

This rule states that electrons are filled in orbitals according to their $(n + \ell)$ values. Electrons are filled in increasing order of their $(n + \ell)$ values. When $(n + \ell)$ is same for sub energy levels, the electrons first occupy the sublevels with lowest "n" value.

Energy level diagram :

The representation of relative energy levels of various atomic orbital is made in terms of energy level diagrams.

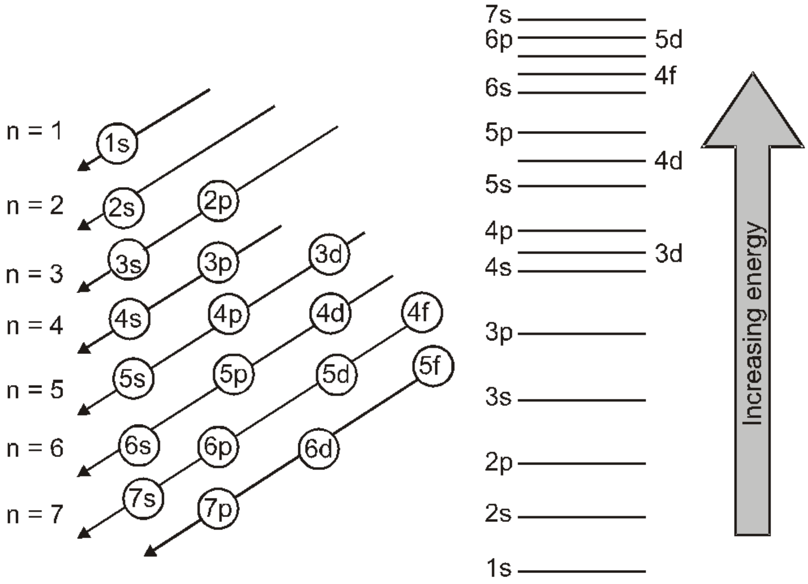


Fig. Sequence of filling of electrons in orbitals belonging to different energy levels

Hund's rule :

No electron pairing takes place in the orbitals in a subshell until each orbital is occupied by one electron with parallel spin. Exactly half filled and fully filled orbitals make the atoms more stable, i.e., p^3, p^6, d^5, d^{10}, f^7 and f^{14} configuration are most stable.

- Total no. of e^- in main energy shell = $2n^2$

  Total no. of e^- in a subshell = $2(2\ell + 1)$

  Maximum no. of e^- in an orbital = 2

  Total no. of orbitals in a subshell = $(2\ell + 1)$

  No. of subshells in main energy shell = n

  No. of orbitals in a main energy shell = n^2

- Orbital angular momentum L = $\frac{h}{2\pi}\sqrt{\ell(\ell+1)}$

- Spin angular momentum S = $\frac{h}{2\pi}\sqrt{S(S+1)}$; S = $\frac{1}{2}$

  $\mu = \sqrt{n(n+2)}$ B.M. (n = no. of unpaired electrons)

- Orbital magnetic moment $\mu_s = \frac{eh}{4\pi m_e} \times \sqrt{\ell(\ell+1)}$

Solved Examples

Ex-17. Calculate total spin, magnetic moment for the atoms having at. no. 7, 24 and 36.

Sol. 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 = $\sqrt{0}$

Ex-18. Write down the four quantum numbers for fifth and sixth electrons of carbon atom.

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

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 – $\frac{1}{2}$

Ex-19. Given below are the sets of quantum numbers for given orbitals. Name these orbitals.

(a) n = 3	(b) n = 5	(c) n = 4	(d) n = 2	(e) n = 4
ℓ = 1	ℓ = 2	ℓ = 1	ℓ = 0	ℓ = 2

Ans. 3p, 5d, 4p, 2s, 4d

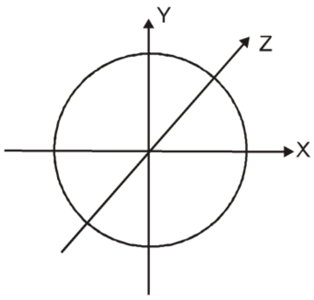
Sol. (a) n = 3 , ℓ = 1 ⇒ 3p (b) n = 5 , ℓ = 2 ⇒ 5d (c) n = 4 , ℓ = 1 ⇒ 4p

(d) n = 2 , ℓ = 0 ⇒ 2s (e) n = 4 , ℓ = 2 ⇒ 4d

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 → spherical**

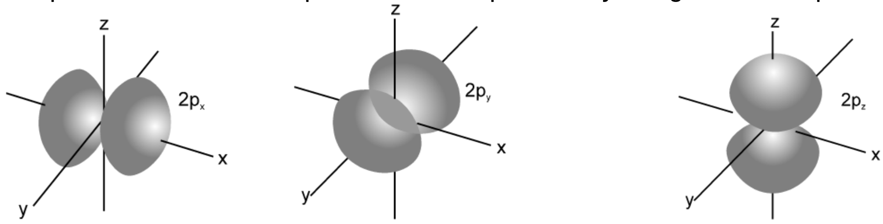


s- orbital is non directional and it is closest to the nucleus, having lowest energy.
s-orbital can accomodate maximum no. of two electrons.

↑↓
n s

p-orbital : Shape dumb bell

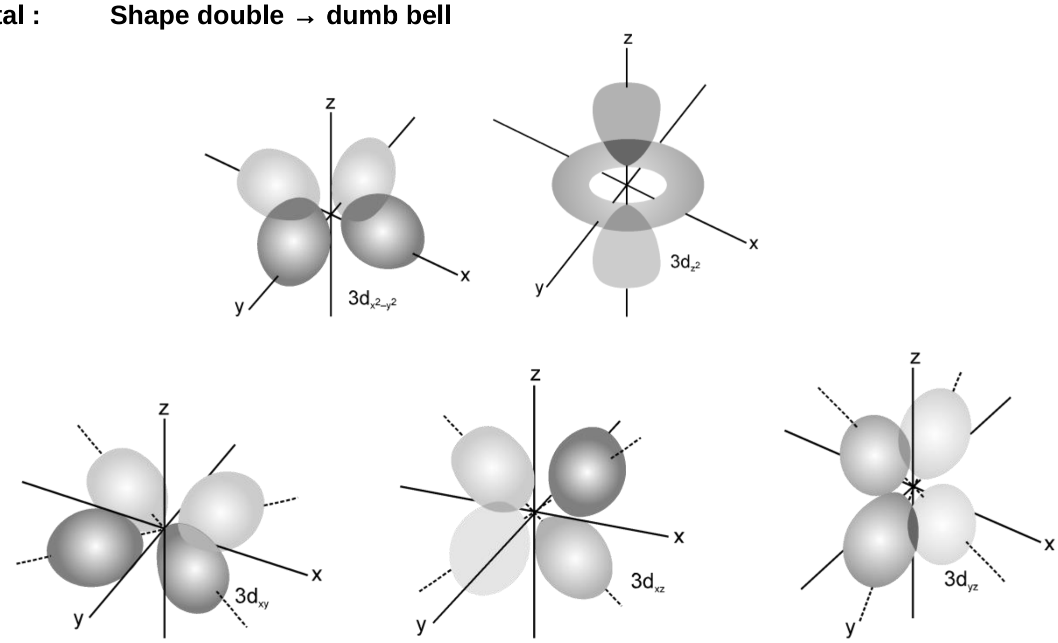
Dumb bell shape consists of two loops which are separated by a region of zero probability called node.



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

↑↓	↑↓	↑↓
p_x	p_y	p_z

d-orbital : **Shape double → dumb bell**



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

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

f-orbital : **Shape leaf like**

↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

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

(i) total nodes = n – 1,

(ii) angular nodes = l,

(iii) radial nodes = n – l – 1.

Nuclear Chemistry

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.

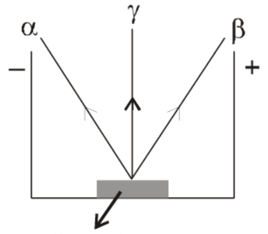
$^{14}CO_2$, $^{14}{}_6C(s)$, $^{14}{}_6C(g)$ is radioactive.

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 : $\gamma > \beta > \alpha$

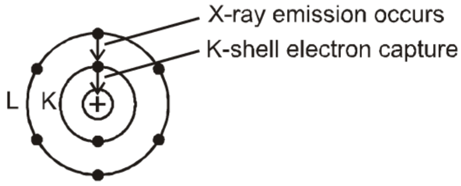
ionisation power : $\alpha > \beta > \gamma$

	Emission of rays	Usual condition	Effect	Process representation / example
1.	α	$Z > 83$	$\frac{n}{p}$ 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.	$\frac{n}{p}$ ratio decreases	$_ZY^A \rightarrow {}_{Z+1}Y'^{A-4} + {}_{-1}e^0$
	eg.	$_6C^{12}$ (stable) $\frac{n}{p} = \frac{6}{6}$		$_6C^{14} \rightarrow {}_7N^{14} + {}_{-1}e^0$
		$_6C^{14}$ (radioactive) $\frac{n}{p} = \frac{8}{6}$ (high)		$\frac{n}{p} = \frac{8}{6}$ $\frac{n}{p} = \frac{7}{7}$
	eg.	$_{11}Na^{24}$ (radioactive) $\frac{n}{p} = \frac{13}{11}$ (high)		$_0n^1 \rightarrow {}_1p^1 + {}_{-1}e^0$(from nucleus)
		$_{11}Na^{23}$ (stable) $\frac{n}{p} = \frac{12}{11}$		
		$_{11}Na^{22}$ $\frac{n}{p} = \frac{11}{11}$ ($\frac{n}{p}$ ratio low)		
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	If $\frac{n}{p}$ ratio is low	$\frac{n}{p}$ ratio increases	$_ZY^A \rightarrow {}_{Z-1}Y'^A + {}_{+1}e^0$

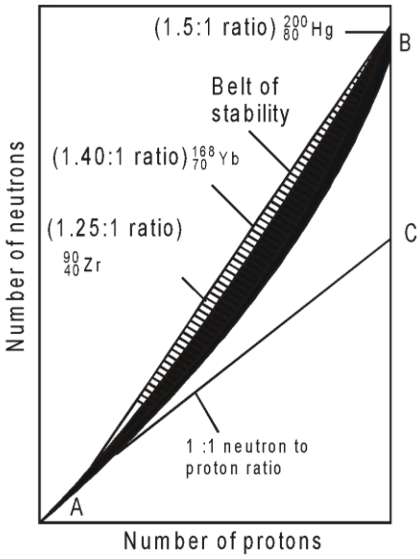
($_{+1}e^0$)			$_{11}Na^{22} \rightarrow {}_{10}Ne^{22} + {}_{+1}e^0$ $_1p^1 \rightarrow {}_0n^1 + {}_{+1}e^0$(from nucleus)
(b) Electron capture (EC) or K-shell	If $\frac{n}{p}$ ratio is low	$\frac{n}{p}$ ratio increases	$_ZX'^A + \underset{K-\text{shell}}{{}_{-1}e^0} \rightarrow {}_{Z-1}X''^A$ $_{80}Hg^{197} + {}_{-1}e^0 \rightarrow {}_{79}Au^{197}$

Electron capture

$$\boxed{{}_1p^1 + \underset{(K-\text{shell})}{{}_{-1}e^0} \longrightarrow {}_0x^1}$$



Nuclear stability belt :



Artifical nuclear reaction :

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

* specific nuclei + stricking particle $\longrightarrow$ New nuclei + emitted particle

eg.	1.	(α, p type)	$_7N^{14}$	+	$_2He^4$ (s.p.)	$\longrightarrow$	$_8O^{17}$	+	$_1p^1$ (e.p.)	(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.

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

$${}_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{92}U^{*236} \longrightarrow \text{various nuclie and neutrons}$$

eg. atom bomb is based on fission.

Nuclear fusion :

Is a process where light nuclei fused together to form heavy nuclei.

$${}_{1}H^{2} + {}_{1}H^{3} \longrightarrow {}_{2}He^{4} + {}_{0}n^{1}$$

$${}_{1}H^{2} + {}_{1}H^{2} \longrightarrow {}_{2}He^{4}$$

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

Solved Examples

Ex.20 ^{23}Na is the most stable isotope of Na. Find out the process by which $^{24}_{11}Na$ can undergo radioactive decay.

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

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

Ex.21 The number of β-particle emitted during the change ${}^{c}_{a}X \longrightarrow {}^{b}_{d}Y$ is :

(1) $\frac{a-b}{4}$ (2) $d + \left(\frac{a-b}{2}\right) + c$ (3) $d + \left(\frac{c-b}{2}\right) - a$ (4) $d + \left(\frac{a-b}{2}\right) - c$

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

∴ c = b + 4m ......(i) and a = d + 2m – n ......(ii)

by (i) & (ii)

$n = d + \left(\frac{c-b}{2}\right) - a$. **Ans. (3)**

Ex.22 The decay product of ${}^{13}_{7}N$ is :

(1) ${}^{13}_{8}O + {}^{0}_{-1}e$ (2) ${}^{13}_{6}C + {}^{0}_{-1}e$

(3) ${}^{13}_{6}C$ + K electron capture (4) ${}^{9}_{5}Be + {}^{4}_{2}He$

Sol. ${}^{13}_{7}N$ is positron emitter ; $\frac{n}{p}$ ratio is low. **Ans. (2)**

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. calculate the wavelength and energy of radiation emitted for the electronic transition from infinity to stationary state one of the hydrogen atom.

Sol. $\frac{1}{\lambda} = 109678\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 109678\left[\frac{1}{(1)^2} - \frac{1}{\infty}\right] = 109678\ cm^{-1}$

$\lambda = \frac{1}{109678}$ cm = 9.1 × 10^{-6} cm = 9.1 × 10^{-8} m = 91 nm.

$E = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\,J.s \quad \times 3\times10^{8}\,ms^{-1}}{9.1\times10^{-8}\,m} = 2.186 \times 10^{-18}$ J

2. The ionization energy of He^+ is 19.6 × 10^{-18} J/atom. Calculate the energy of the first stationary state of Li^{2+}.

Sol. For H–like species

I.E. = I.E.$_{(H)}$ × Z^2

∴ I.E.$_{(He^+)}$ = Z^2 × I.E.$_{(H)}$

19.6 × 10^{-18} J = $(2)^2$ × I.E.$_{(H)}$

$$I.E._{(H)} = \frac{19.6\times10^{-18}}{4} J$$

$$I.E._{(Li^{+2})} = Z^2 \times I.E._{(H)} = \frac{(3)^2\times19.6\times19^{-18}}{4} = 4.41 \times 10^{-17} \text{ J/atom}$$

$$I.E._{(Li^{+2})} = E_\infty - E_1$$

$4.41 \times 10^{-17} = 0 - E_1$

$E_1 = -4.41 \times 10^{-17}$ J/atom.

3. Calculate the wavelength of the radiation emitted, producing a line in the Lyman series when an electron falls from fourth stationary state in hydrogen atom ($R_H = 1.1 \times 10^7 \text{ m}^{-1}$)

Sol. For Lyman series $n_1 = 1$

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] = 1.1 \times 10^7 \text{ m}^{-1}\left[\frac{1}{(1)^2}-\frac{1}{(4)^2}\right] = 1.1 \times 10^7 \times \frac{15}{16}$$

$\lambda = 9.7 \times 10^{-8}$ m = 97 nm

4. Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen.

Sol. The shortest wavelength transition corresponds to $n_2 = \infty$ to $n_1 = 2$ transition

$$\bar{v} = 109678\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\text{cm}^{-1} = 109678\left[\frac{1}{(2)^2}-\frac{1}{\infty}\right] = \frac{109678}{4} = 27419.5 \text{ cm}^{-1}$$

5. If the energy of an electron in 3rd Bohr orbit is –E, what is the energy of the electron of the electron in (i) 1st Bohr orbit (ii) 2nd Bohr orbit ?

Sol. According to Bohr's model,

$$E_n = \frac{E_1}{n^2} \quad \Rightarrow \quad E_3 = \frac{E_1}{(3)^2} = -E \text{ (given)}$$

$$\therefore \quad E_1 = -9E \quad ; \quad E_2 = \frac{E_1}{(2)^2} = -\frac{9E}{4} = 2.25\ E$$

6. Sodium street lamp gives off a characteristic yellow light of wavelength 588 nm. Calculate the energy mole (in kJ/mol) of these photons.

Sol. $\lambda = 588 \text{ nm} = 588 \times 10^{-9}$ m

$c = 3 \times 10^8 \text{ ms}^{-1}$

$$E = N_0h\nu = N_0\, h\frac{c}{\lambda} = \frac{6.02\times10^{23}\times6.63\times10^{-34}\times3\times10^8}{588\times10^{-9}}$$

$= 2.04 \times 10^5 \text{ J mol}^{-1} = 2.04 \times 10^2 \text{ kJ mol}^{-1}$

7. A moving electron has 5×10^{-25} J of kinetic energy. What is the de-broglie wavelength ?

Sol. Mass of the electron $m = 9.1 \times 10^{-31}$ kg

$$K.E. = \frac{1}{2}mv^2 = 5 \times 10^{-25} \text{ J}$$

$$\lambda = \frac{h}{\sqrt{2m\times K.E.}} = \frac{6.626\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times5\times10^{-25}}} = 6.95 \times 10^{-7} \text{ m.}$$

8. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å

Sol. $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}}$

Where E is kinetic energy of the electron

$\lambda^2 = \frac{h^2}{2mE}$

$E = \frac{h^2}{2m\lambda^2} = \frac{(6.63\times10^{-34})^2}{2\times9.1\times10^{-31}\times(1.54\times10^{-10})^2} = 1.02 \times 10^{-17}$ J

But $E = V \times e = V \times 1.6 \times 10^{-19}$

$V = \frac{E}{1.6\times10^{-19}} = \frac{1.02\times10^{-17}}{1.6\times10^{-19}} = 63.75$ volts

9. Find the wavelength of 100 g particle moving with velocity 100 ms^{-1}

Sol. $\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,kg\ \ m^2s^{-1}}{0.1\ \ kg\ \ \times100\ \ ms^{-1}} = 6.626 \times 10^{-35}$ m.

10. The energy of the electron in the second and third Bohr orbits of hydrogen atom is -5.42×10^{-12} ergs and -2.41×10^{-12} ergs respectively. Calculate the wavelength of the emitted ratiation when electron drops from third to second orbits.

Sol. $\Delta E = E_3 - E_2 = -2.41 \times 10^{-12} - (-5.42 \times 10^{-12})$ ergs $= -2.41 \times 10^{-12} + 5.42 \times 10^{-12}$ ergs $= 3.01 \times 10^{-12}$ ergs

Now $h = 6.63 \times 10^{-27}$ ergs s,

$c = 3 \times 10^{10}$ cm/s

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

$\lambda = \frac{hc}{\Delta E} = \frac{6.63\times10^{-27}\,ergs.s\ \ \times3\times10^{10}\,cms^{-1}}{3.01\times10^{-12}\,ergs} = 6.6 \times 10^{-5}$ cm $= 6.6 \times 10^3$ Å

11. Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum. ($R_H = 1.1 \times 10^7\ m^{-1}$)

Sol. $\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] = 1.1 \times 10^7\ m^{-1}\left[\frac{1}{(2)^2}-\frac{1}{(3)^2}\right] = 1.1 \times 10^7 \times \frac{5}{36}\ m^{-1}$

$\lambda = 6.545 \times 10^{-7}$ m.

Energy emitted per atom, $E = \frac{hc}{\lambda} = \frac{6.62\times10^{-34}\,J.s\ \ \times3\times10^8\times ms^{-1}}{6.545\times10^{-7}\,m} = 3.03 \times 10^{-19}$ J

1.0 g atom hydrogen contains 1 mole hydrogen atoms

Energy emitted by 1.0 g atom of hydrogen

$N_A \times 3.03 \times 10^{-19}\ J = 6.02 \times 10^{23} \times 3.03 \times 10^{-19}\ J = 1.82 \times 10^5$ J

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

Sol. A 150 watt bulb emits 150 J of energy per second.

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

suppose the bulb emits n photons per second

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

$n = \frac{E \times \lambda}{c \times h} = \frac{12J \times 4500 \times 10^{-10} m}{3 \times 10^{8} ms^{-1} \times 6.63 \times 10^{-34} Js} = 2.715 \times 10^{19}$

13. Wavelength of highest energy transition of H-atoms is 91.2 nm. Calculate the corresponding wavelength of He^+ ion.

Sol. For hydrogen like species

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

For H atom, Z = 1 $\therefore$ $\frac{1}{\lambda_H} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \times 1^2$

For He^+ ion, Z = 2.

Hence for the same transition,

$\frac{1}{\lambda_{He^+}} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \times 2^2$ $\therefore$ $\frac{1/\lambda_H}{1/\lambda_{He^+}} = \frac{1^2}{2^2} = \frac{1}{4}$ or $\frac{\lambda_{He^+}}{\lambda_H} = \frac{1}{4}$

$\therefore$ $\lambda_{He^+} = \frac{\lambda_H}{4} = \frac{9.12}{4} = 22.8$ nm.

14. 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)

(1) 10 (2) 15 (3) 17 (4) 12

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

15. If the binding energy of 2^{nd} excited state of a hydrogen like sample is 24 eV approximately, then the ionisation energy of the sample is approximately

(1) 54.4 eV (2) 24 eV (3) 122.4 eV (4) 216 eV

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

I.E. = $13.6(Z)^2 = (24 \times 9) = 216$ ev **Ans. (4)**

16. 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

(1) $3^2 \times 21.7 \times 10^{-19}$ J (2) 21.79×10^{-19} J

(3) $\frac{1}{3} \times 21.79 \times 10^{-19}$ J (4) $\frac{1}{3^2} \times 21.79 \times 10^{-19}$ J

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

17. 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?

(1) $2.4 \times 10^5 cm^{-1}$ (2) $24.3 \times 10^5 cm^{-1}$ (3) $6.08 \times 10^5 cm^{-1}$ (4) $1.313 \times 10^6 cm^{-1}$

Sol. 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

$\bar{\nu} = 1.313 \times 10^6 cm^{-1}$

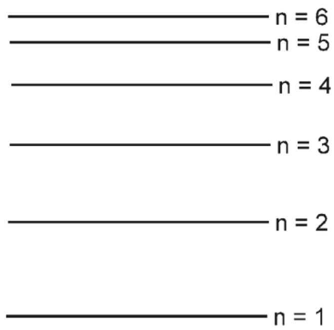
Ans. (4)

18. 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.

(1) 4 (2) 6

(3) 5 (4) 15



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

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

(1) $\frac{\lambda}{\pi}$ (2) $\frac{\lambda}{2\pi}$ (3) $\frac{\lambda}{4\pi}$ (4) $\frac{\lambda}{3\pi}$

Sol. We know $2\pi r = n\lambda$

For minimum radius n = 1

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

Ans. (2)

20. An electron, practically at rest, is initially accelerated through a potential difference of 100 volts. It then has a de Broglie wavelength = λ_1 Å. It then get retarded through 19 volts and then has a wavelength λ_2 Å. A further retardation through 32 volts changes the wavelength to λ_3, What is $\frac{\lambda_3 - \lambda_2}{\lambda_1}$?

(1) $\frac{20}{41}$ (2) $\frac{10}{63}$ (3) $\frac{20}{63}$ (4) $\frac{10}{41}$

Sol. $\lambda_1 = \sqrt{\frac{150}{100}}$ Å .... (1) $\lambda_2 = \sqrt{\frac{150}{81}}$ Å .... (2)

$\lambda_3 = \sqrt{\frac{150}{49}}$ Å .... (3)

From (1), (2) and (3)

$\frac{\lambda_3 - \lambda_2}{\lambda_1} = \frac{20}{63}$

Ans. (3)

21. 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 [$h = 6.6 \times 10^{-34}$ Js]

(1) 2×10^{-28} kg (2) 2×10^{-27} kg (3) 2×10^{-29} kg (4) 4×10^{-29} kg

Sol. $\Delta x \times m \times \Delta v$ h/4π

$1 \times 10^{-10} \times m \times \frac{3.3}{4\pi} \times 10^5 \geq \frac{6.6\times10^{-34}}{4\times\pi}$ m = 2×10^{-29} kg **Ans. (3)**

22. Which of the following set of quantum numbers is not valid.

(1) n = 3, l = 2, m = 2, s = +1/2 (2) n = 2, l = 0, m = 0, s = –1/2

(3) n = 4, l = 2, m = –1, s = +1/2 (4) n = 4, l = 3, m = 4, s = –1/2

Sol. Not valid **Ans. (4)**

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

(1) +1 or –1 (2) +2 or –2 (3) + 2.5 or – 2.5 (4) +3 or –3

Sol. Total spin = no. of unpaired e^- × $\left(\pm\frac{1}{2}\right)$ = 5 × $\left(\pm\frac{1}{2}\right)$ = ± $\frac{5}{2}$ **Ans. (3)**