ATOMIC STRUCTURE & NUCLEAR CHEMISTRY

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

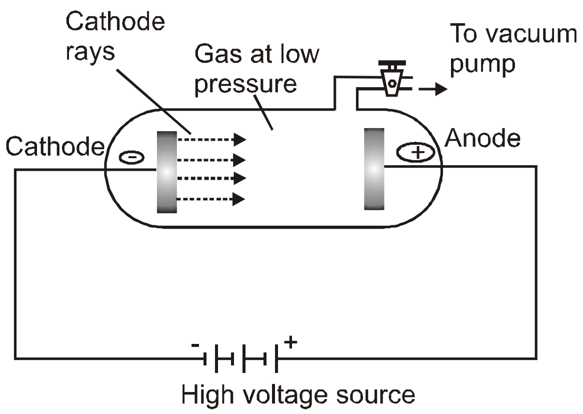


Figure-1

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 :

Table-2 : Different oxidation states of first transition series.

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, (+4), (+5), +6
Mn	$3d^5 4s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^7 4s^2$	+2, +3, (+4)
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

Oxidation states given in parenthesis are unstable.

Table-3 :Different oxidation states of elements of second transition series.

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	(+3)	(+2)	+2	+2	+2	+2	+2	+1	+2
	+4	(+3)	+3	(+4)	+3	+3	(+3)	(+2)	
		(+4)	+4	(+5)	+4	+4	+4	(+3)	
		+5	+5		(+5)	(+6)			
			+6		(+6)				
					(+7)				
					(+8)				

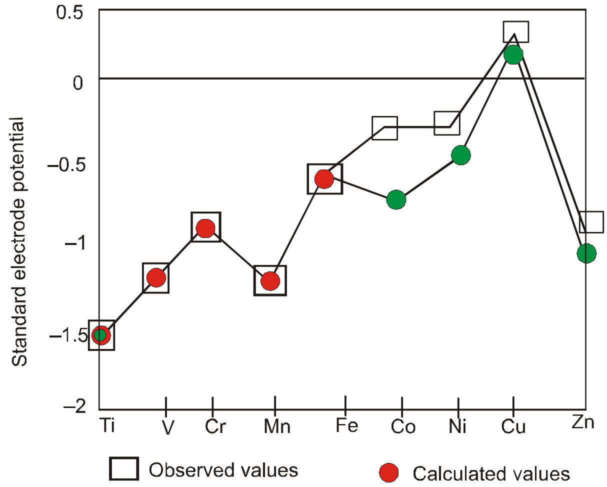
Table-4 : Different oxidation states of elements of third transition series.

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	(+3)	(+2)	+2	(-1)	+2	+2	+2	+1	+1
	+4	(+3)	(+3)	(+1)	+3	+3	(+3)	+3	+2
		(+4)	+4	(+2)	+4	+4	+4		
		+5	+5	+3	+6	(+6)	(+5)		
			+6	+4	+8		(+6)		
				+5					
				(+6)					
				+7					

It may be noted that the stability of a given oxidation state depends upon the nature of the elements with which the metal is combined. The highest oxidation states are found in compounds of fluorides and oxides because fluorine and oxygen are most electronegative elements.

The examination of the common oxidation states exhibited by different transition metals reveals the following facts :

The observed values of $E^\ominus$ and those calculated using the data are compared in the following figure.



Thermochemical data (kJ mol⁻¹) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of M^{II} to M

Table-6 :

Element (M)	$\Delta_a H^\ominus$ (M)	$\Delta_i H_1^\ominus$	$\Delta_i H_2^\ominus$	$\Delta_{hyd} H^\ominus (M^{2+})$	$E^\ominus$ /V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

The results lead to the following conclusions :

(i) There is no regular trend in these values. This is attributed to the irregular variation of ionisation enthalpies ($IE_1 + IE_2$) and the sublimation energies in the period.

(ii) It may be noted that the electrode potentials of transition metals are low in comparison to elements of group 2 (e.g., Ca = –2.87 V). Compared to group 2 elements, the transition elements have fairly large ionisation enthalpies and very large enthalpies of atomisation. These reduce their electrode potentials though their hydration enthalpies are large.

(iii) Zinc has low enthalpy of atomisation and fairly large hydration energy. But it has also low electrode potential (–0.76 V) because of its very high ionisation enthalpy ($IE_1 + IE_2$).

(iv) It is clear from above table and figure that copper has positive reduction potential, $E^\ominus$ (0.34 V) and this shows that copper is least reactive metal out of the first transition series. This unique behaviour (+ve) E value of copper) also accounts for its inability to liberate H_2 from acids. It has been observed that only oxidizing acids (such as nitric acid and hot concentrated sulphuric acid) react with copper in which the acids are reduced. The high energy required to convert Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy.

(v) In general, the value becomes, less negative across the series. This is related to the general increase in the sum of first and second ionisation enthalpies. It is interesting to note that the values of E" of Mn, Ni and Zn are more negative than expected from the general trend. The relatively more negative values of $E^\ominus$ for Mn and Zn are due to stability of half filled d-sub-shell in Mn^{2+} ($3d^5$) and the completely filled ($3d^{10}$) configuration in Zn^{2+}. The exceptionally high $E^\ominus$ value of Ni from regular trend is related to the highest negative enthalpy of hydration of Ni^{2+} ion.

Trends in the M^{3+} | M^{2+} Standard Electrode Potentials

Except copper and zinc, all other elements of first transition series show +3 oxidation states also to form M^{3+} ions in aqueous solutions. The standard reduction potentials for M^{3+} | M^{2+} redox couple are given below :

Table-7 :

	Ti	V	Cr	Mn	Fe	Co
$E^\ominus$ (M^{3+}(aq) | M^{2+}(aq) (in Volt)	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97

These values reveal the following facts :

(i) The low value of scandium reflects the stability of Sc^{3+} which has a noble gas configuration.

(ii) The comparatively high value for Mn shows that Mn^{2+} (d^5 configuration) is particularly stable. On the other hand comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5 configuration).

(iii) The comparatively low value of V is related to the stability of V^{2+} (due to half filled t_{2g}^3 energy level of 3d orbitals in octahedral crystal field spitting).

(iv) The E° value for Mn^{3+}/Mn^{2+} couple much more positive than for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}. This is because of the much larger III[rd] 'ionisation energy of Mn (removal of electron from d^5 configuration).

Trends in Stability of Higher Oxidation States

Standard electrode potential data provide valuable information about the stabilities of different oxidation states shown by an element. The highest oxidation states are shown generally among halides and oxides.

1. In metal halides. The transition elements react with halogens at high temperatures to form transition metal halides. These reactions have very high heat of reaction. But once the reaction starts, the heat of reaction is sufficient to continue the reaction. The halogens react in the following decreasing order ; $F_2 > Cl_2 > Br_2 > I_2$

Table-8 : Halides of first transition series

Oxidation Number	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+6				CrF_6						
+5			VF_5	CrF_5						
+4		TiX_4	VX_4^a	CrF_4	MnF_4					
+3	ScX_3	TiX_3	VX_3	CrF_3	MnF_3	FeX_3^a	CoF_3			
+2		TiX_2	VX_2^c	CrF_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^b	ZnX_2
+1									CuX^c	
	where X = F, Cl, Br, I, X^a = F, Cl, Br, X^b = F, Cl, X^c = Cl, Br, I									

Within each of the transition groups 3 - 12, there is a difference in the stability of the various oxidation states. In general, the second and third transition series elements exhibit higher coordination number and their higher oxidation states are more stable than the corresponding first transition series elements. The following trends are observed from table regarding transition metal halides :

(i) In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable difluorides and the other chlorides are also known.

(ii) Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in TiX_4 (tetrahalides, X = F, Cl, Br and I), VF_5 and CrF_6.

(iii) The +7 oxidation state for Mn is not shown by simple halides. However, MnO_3F is known in which the oxidation state of Mn is +7.

(iv) After Mn, the tendency to show higher oxidation states with halogens are uncommon. Iron and cobalt form trihalides FeX_3 (X = F, Cl or Br) and CoF_3.

(v) The tendency of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in case of CoF_3 or higher bond enthalpy due to higher covalent bonds e.g., VF_5 and CrF_6.

(vi) V(V) is shown by VF_5 only. However, the other halides undergo hydrolysis to form oxohalides, VOX_3.

(vii) Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only VX_2 (X = Cl, Br or I) and copper can form CuX (X = Cl, I). All copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidises I^- to I_2.

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2(s) + I_2$$

It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ($\Delta_{hyd}H^{\circ}$) of Cu^{2+} (aq) than Cu^+, which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

Example-10 Zinc does not show variable valency because of :

(A) complete 'd' sub-shell (B) inert pair effect (C) $4s^2$ sub-shell (D) none.

Solution $_{30}Zn = [Ar]^{18}\ 3d^{10}\ 4s^2$. Zinc has completely filled d-sub-shell so removal of electron from completely filled 4d sub-shell would be quite difficult. Thus it does not show variable valency.

Therefore, (A) option is correct.

Formation of Coloured Ions :

Most of the compounds of transition metals are coloured in the solid form or solution form. The colour of the compounds of transition metals may be attributed to the presence of incomplete (n – 1) d-sub-shell. In the case of compounds of transition metals, the energies of the five d-orbitals in the same sub-shell do not remain equal. Under the influence of approaching ions towards the central metal ion, the d-orbitals of the central metal split into different energy levels. This phenomenon is called crystal field splitting. For example, when the six ions or molecules approach the metal ion (called octahedral field), the five d-orbitals split up into two sets : one set consisting of two d-orbitals ($d_{x^2-y^2}$, d_{z^2}) of higher energies and the other set consisting of three d-orbitals (d_{xy}, d_{yz}, d_{zx}) of lower energies.

In the case of the transition metal ions, the electron can be easily promoted from one energy level to another in the same d-sub-shell. These are called d-d transitions. The amount of energy required to excite some of the electrons to higher energy states within the same d-sub-shell corresponds to energy of certain colours of visible light. Therefore, when white light falls on a transition metal compound, some of its energy corresponding to a certain colour, is absorbed and the electron gets raised from lower energy set of orbitals to higher energy set of orbitals as shown below :

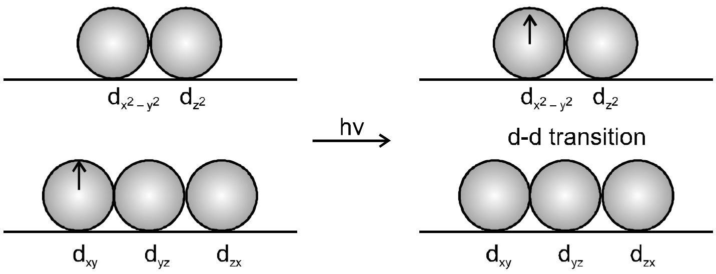


Figure showing electronic transition from t_{2g} to e_g orbitals.

The excess of other colours constituting white light are transmitted and the compound appears coloured. The observed colour of a substance is always complementary colour of the colour which is absorbed by the substance. For example, Ti^{3+} compounds contain one electron in d-sub-shell (d^1). It absorbs green and yellow portions from the white light and blue and red portions are emitted. Therefore, Ti^{3+} ions appear purple. Similarly, hydrated cupric compounds absorb radiations corresponding to red light and the transmitted colour is greenish blue (which is complementary colour to red colour). Thus, cupric compounds have greenish-blue colour.

Table-10 : Colour of different hydrated transition metal ions.

Ion	Outer Configuration	Colour of the ion
Sc (III), Ti (IV)	$3d^0$	Colourless
Ti (III)	$3d^1$	Purple
V (IV)	$3d^1$	Blue
V (III)	$3d^2$	Green
Cr (III)	$3d^3$	Green
Mn (III)	$3d^4$	Violet
Cr (II)	$3d^4$	Blue
Mn (II)	$3d^5$	Pink
Fe (III)	$3d^5$	Yellow
Fe (II)	$3d^6$	Green
Co (III)	$3d^6$	Blue
Co (II)	$3d^7$	Pink
Ni (II)	$3d^8$	Green
Cu (II)	$3d^9$	Blue
Cu (I)	$3d^{10}$	Colourless
Zn (II)	$3d^{10}$	Colourless

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.

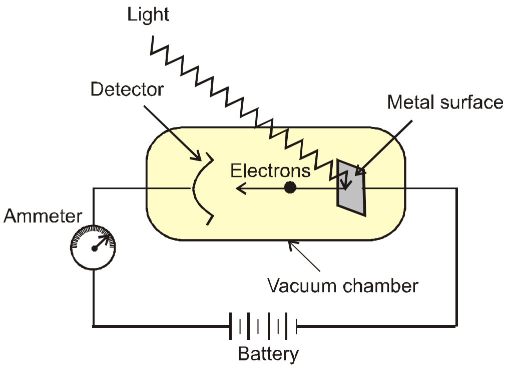


Figure-11

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 Examples

Ex-3. 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.

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

$\therefore$ 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

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 neccessary centripetal force is produced by attraction forces of nucleus.

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

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

F11 $\boxed{mvr = \dfrac{nh}{2\pi}}$

- 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 $\boxed{\dfrac{hc}{\lambda} = \Delta E}$ ΔE – difference in the energy of orbit

F13 $\boxed{\upsilon = \dfrac{\Delta E}{h}}$ 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 :

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

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

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

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

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

From the postulate of Bohr,

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

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

From equation (i) and (ii)

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

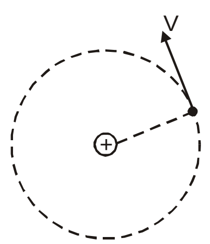


Figure-12

On solving, we will get

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

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

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

Solved Examples

Ex-4. Calculate radius ratio for 2^{nd} orbit of He^+ ion & 3^{rd} orbit of Be^{+++} ion.

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

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

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

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

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

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

put the value of 'r' in the equation (iii)

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

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

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

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

we know that, $\frac{mv^2}{r} = \frac{KZe^2}{r^2}$ or $mv^2 = \frac{KZe^2}{r}$

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

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

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

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

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

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

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

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

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

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

F23 T.E. = $\frac{1}{2}$ 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 [Eq. iv] 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 indictes 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 Examples

Ex-5 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 ?

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

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

It is an emission energy

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

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

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

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.

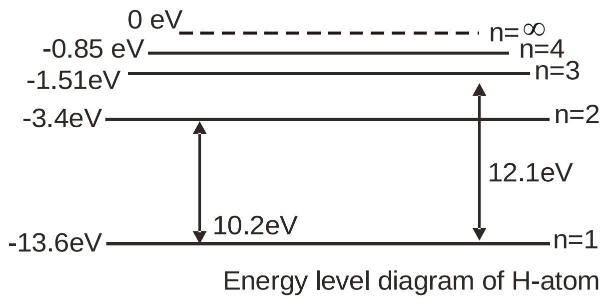


Figure-13

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 $n = \infty$ 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 2nd state = excitation energy of 1st excited state = 1st 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 exicited state = second excitation potential = 12.09 V.

D21 (vii) 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.

Solved Examples

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

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

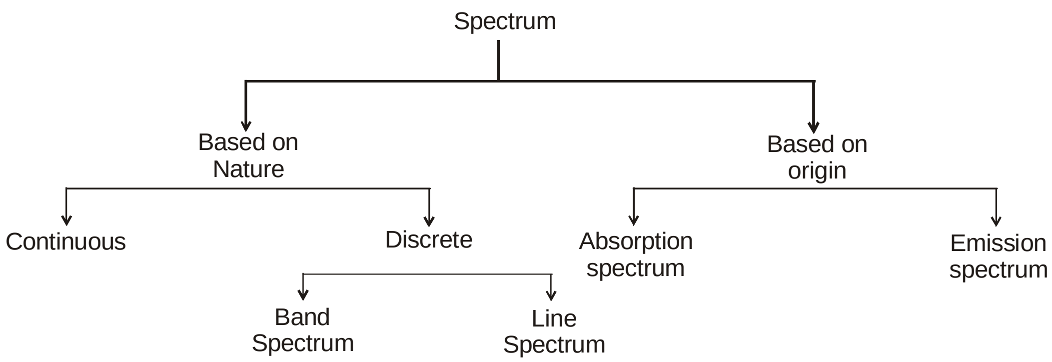
Ans. Z = 3

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.

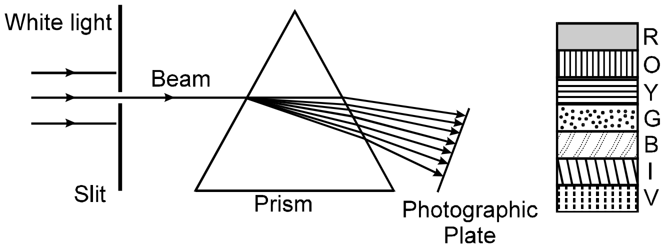


Figure-14

(b) Discrete spectra : It is of two type

(i) Band spectrum

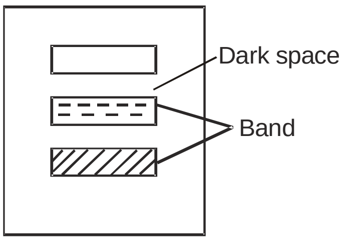


Figure-15

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

(ii) Line Spectrum :

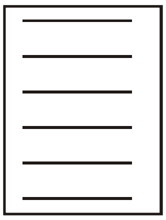


Figure-16

D25 This is the ordered arrangement of lines of particular wavelength seperated 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.

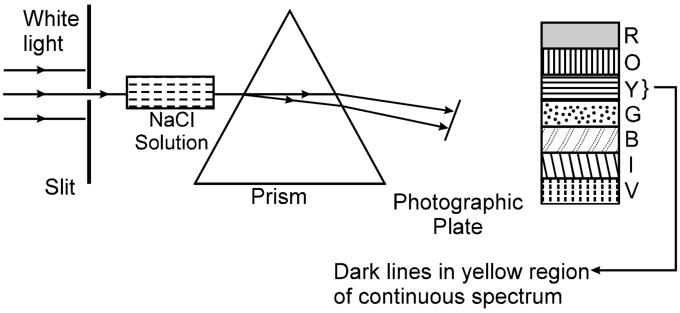


Figure-17

D27 EMISSION SPECTRUM OF HYDROGEN :

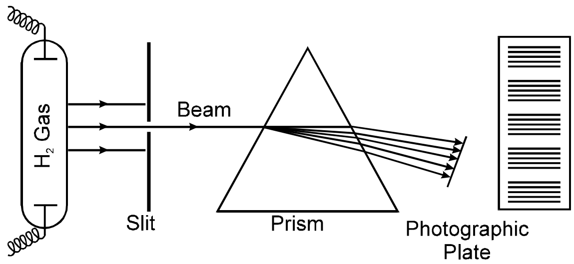


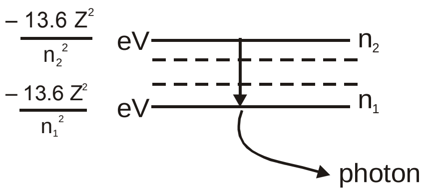
Figure-18

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 $= (\Delta E)_{n2 \to n1} = \dfrac{-13.6Z^2}{n_2^2} - \left(\dfrac{-13.6Z^2}{n_1^2}\right) = 13.6Z^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

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

R = Rydberg constant = $1.09678 \times 10^7 m^{-1}$; $R \simeq 1.1 \times 10^7\ m^{-1}$; $R = \frac{13.6eV}{hc}$; R ch = 13.6 eV

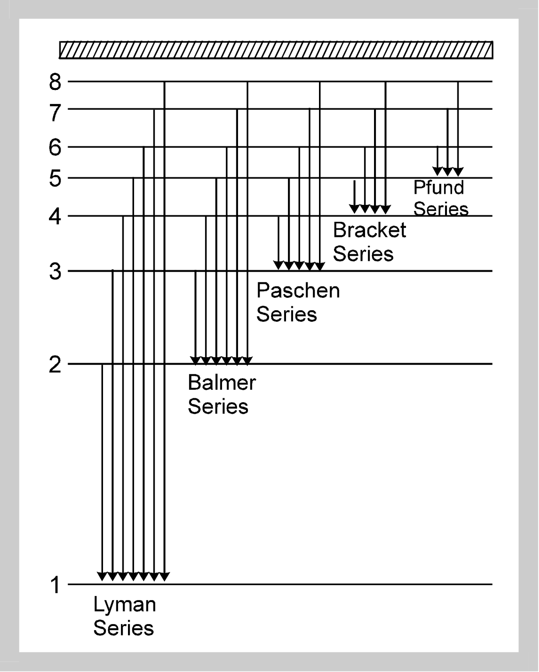


Figure-19

Solved Examples

Ex-7 Calculate the wavelength of a photon emitted when an electron in H- atom maker a transition from n = 2 to n = 1

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

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

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

* I^{st} line of lyman series $\Rightarrow 2 \rightarrow 1$
  II^{nd} line of lyman series = $3 \rightarrow 1$
  Last line of lyman series = $\infty \rightarrow 1$
  [10.2 eV $\leq (\Delta E)_{lyman} \leq$ 13.6 eV]

$$\frac{12400}{13.6} \leq \lambda_{lyman} \leq \frac{12400}{10.2} \text{ A}^o$$

* **Longest line :** longest wavelength line $\lambda_{longest}$ or $\lambda_{max.} = \dfrac{12400}{(\Delta E)_{min}}$

* **Shortest line :** shortest wavelength line $\lambda_{shortest}$ or $\lambda_{min} = \dfrac{12400}{(\Delta E)_{max}}$

* 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 I^{st} line of Lyman series = $\dfrac{1}{\lambda} = \bar{\nu} = R \times 1^2 \left(\dfrac{1}{1^2} - \dfrac{1}{2^2}\right)$

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

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

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

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,

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

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 = $\dfrac{n_1^2}{R_H} = \dfrac{2^2}{R_H} = \dfrac{4}{R_H}$

* $\dfrac{1}{\lambda} = R_H \left(\dfrac{1}{2^2} - \dfrac{1}{n_2^2}\right)$ where $n_2 > 2$ always.
  $1.9 \leq (\Delta E)_{balmer} \leq 3.4$ eV.
  All the lines of balmer series in H spectrum are not in the visible range. Infact only I^{st} 4 lines belongs to visible range.

$$\frac{12400}{3.4} \text{ A}^o \leq \lambda_{balmer} \leq \frac{12400}{1.9} \text{ Å}$$

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

Lines of balmer series (for H atom) lies in the visible range.
I[st] line of balmer series = 3 $\rightarrow$ 2
last line of balmer series = $\infty \rightarrow 2$

$(\bar{\nu})$ 1[st] 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 Examples

Ex-8 Calculate wavelength for 2nd line of Balmer series of He^+ ion

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

$n_1 = 2 \quad n_2 = 4$

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

$\frac{1}{\lambda} = \frac{3R}{4} \qquad \lambda = \frac{4}{3R}$ **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 is equal to $\frac{n \times (n-1)}{2}$.

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 is equal to $\frac{\Delta n(\Delta n + 1)}{2}$, 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 Examples

Ex-9 If electron make transition from 7th excited state to 2nd state in H atom sample find the max. number of spectral lines observed.

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

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

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

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

Equating both we get

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

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

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

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

$$m^2v^2 = 2emV$$

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

F29

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

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

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

From de-Broglie equation

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

$$\text{so, } mvr = \frac{nh}{2\pi}$$

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

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

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

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"

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

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

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

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

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

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

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

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

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

Solved Examples

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

Sol. According to de Broglie equation

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

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

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, $p = \frac{h}{\lambda} \Rightarrow p \to \infty$

So, to make $\Delta x \to 0$, $\lambda \to 0$ a photon of very high energy is used to locate it.
$\therefore$ When this photon will collide with the electron then momentum of electron will get changed by a large amount.

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

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

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

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

$\Delta E \longrightarrow$ 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 Examples

Ex-11 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.

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

Using the equation, $\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626\times10^{-34}}{4\times3.14\times40\times10^{-3}(0.9\,m\,s^{-1})} = 1.46 \times 10^{-33}$ 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.

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 nucles.

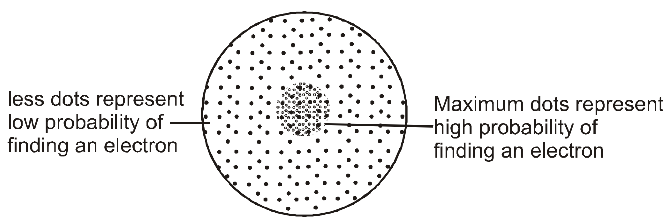


Figure-20

Difference between orbit and orbitals

Orbit	Orbitals
1. It is well defined circular path followed by revolving electrons around the nucleus	1. It is the region of space around the nucleus where electron is most likely to be found
2. It represents planar motion of electron	2. 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.	3. Orbitals can not accomodate more than 2 electrons.
4. Orbits are circular in shape.	4. 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	5. 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 uncentainty principle.	6. Concept of orbitals is in accordance with Heisenberg's principle

18. 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

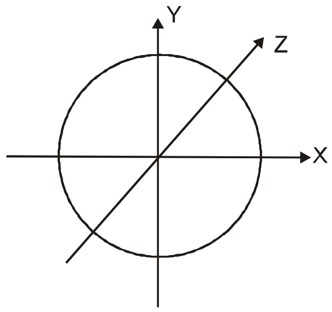


Figure-21

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

$\boxed{\uparrow\downarrow}$
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.

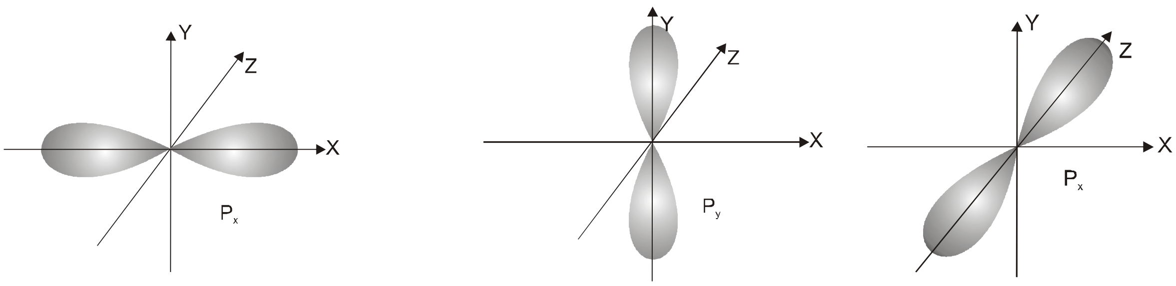


Figure-22

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

↑↓	↑↓	↑↓
p_x	p_y	p_z

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

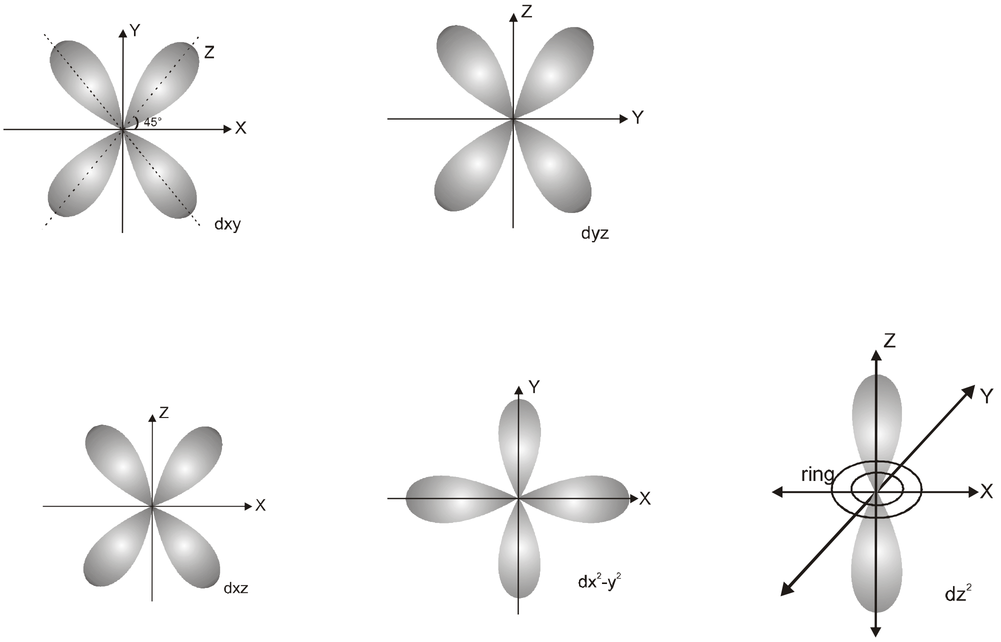


Figure-23

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

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

f-orbital : Shape $\rightarrow$ leaf like

↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

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

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.

F33 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

F34 Number of orbitals present in n^{th} shell = n^2 .

F35 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.

F36 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**

value of ℓ	subshell
0	s
1	p
2	d
3	f

F37 Number of orbitals in a subshell = $2\ell + 1$

F38 Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$

F39 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.

F40 The total number of orbitals present in a main energy level is 'n^2'.

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

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

Doublets & triplets are seen in multi electron system which made it evident that there must be some other energy level too than predicted by n, ℓ and m, it was later found to be *s.*

F41 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)

F42 It represents the value of spin angular momentum which is equal to $\frac{h}{2\pi}\sqrt{s(s+1)}$

F43 Maximum spin of atom $= \frac{1}{2}$ x 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 + ℓ Rule :

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

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

eg. 3d 4s

$(n + \ell) = 3 + 2 = 5$ $(n + \ell) = 4 + 0 = 4$

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

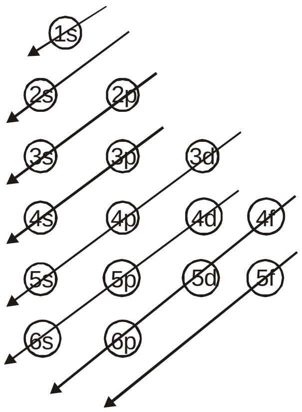
❖ If two sub-shell has same value of (n + ℓ) then the sub-shell with lower value of n has lower energy and it should be filled first.

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.

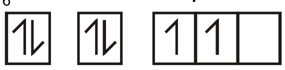
Solved Examples

Ex-12 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) $_{10}Ne$

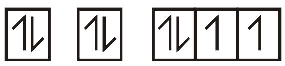
Sol. (i) $_6C \rightarrow 1s^2, 2s^2, 2p^2$



No. of unpaired electrons → 2.

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

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



1s 2s 2p

∴ No. of unpaired electrons = 2

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

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

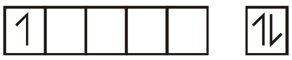
3s 3p

∴ 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] $4s^2\ 3d^1$



3d 4s

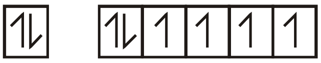
[Ar] $3d^1\ 4s^2$

∴ 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] $4s^2, 3d^6$



4s 3d

No. of unpaired electrons = 4

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

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

No. of unpaired electrons = 0

Total spin = 0

Ex-13 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-14 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 = $\sqrt{0}$

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).

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-44 $$\frac{\delta^2\psi}{\delta x^2}+\frac{\delta^2\psi}{\delta y^2}+\frac{\delta^2\psi}{\delta z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

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 meaninig 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.

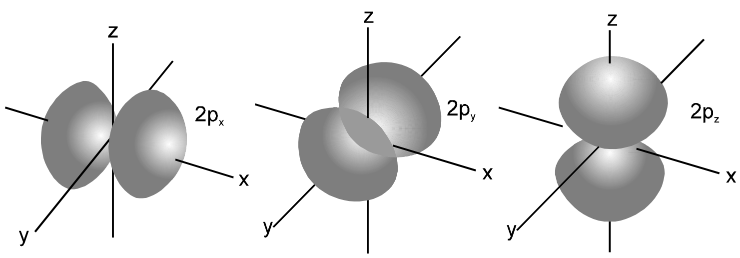
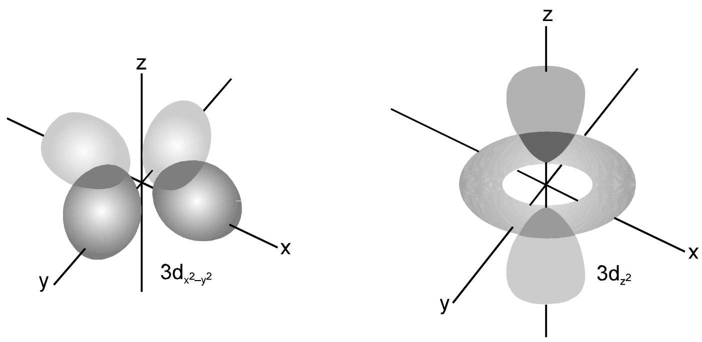
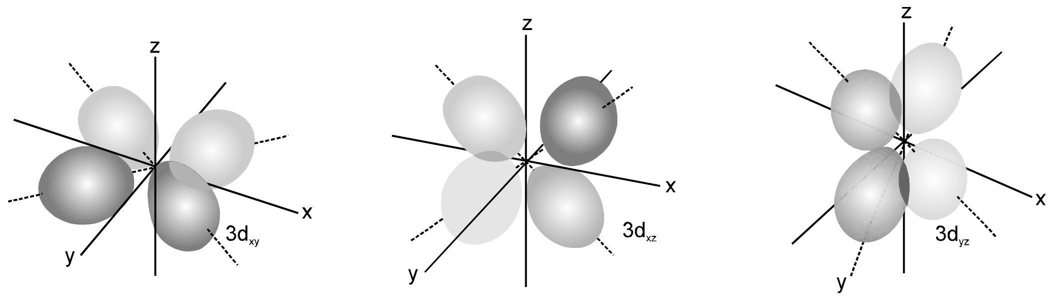


FIG. The 2p-orbitals of the hydrogen atom.





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 :

F45 Radial nodes = $n - \ell - 1$,

F46 Angular nodes = ℓ,

F47 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 (= $n - \ell - 1$)

Angular nodes = 1 (= ℓ)

Total nodes = 2 (one radial, one angular)

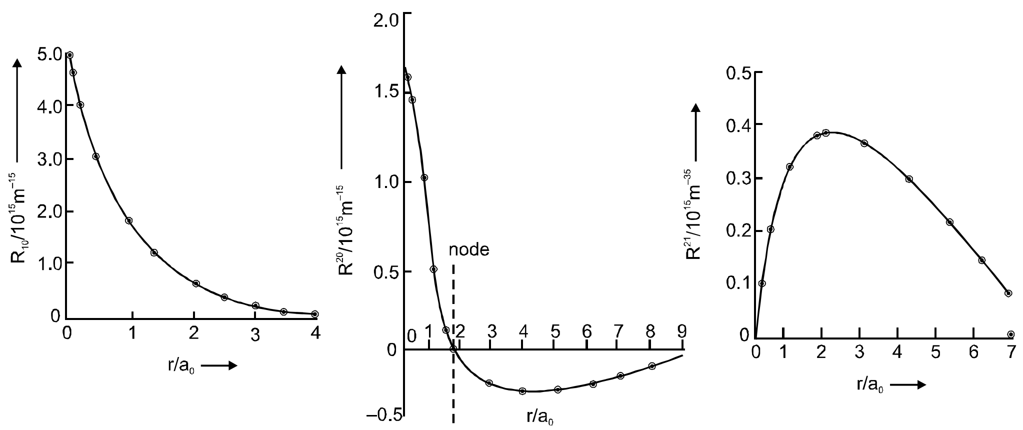
- $\psi_{(r)}$ i.e. radial part of wave function depends upon quantum number n and l and decides the size of an orbital.
- Angular part of wave function $\psi_{(\theta - \phi)}$, depends upon quantum numbers l and m and describes the shape of orbital.

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

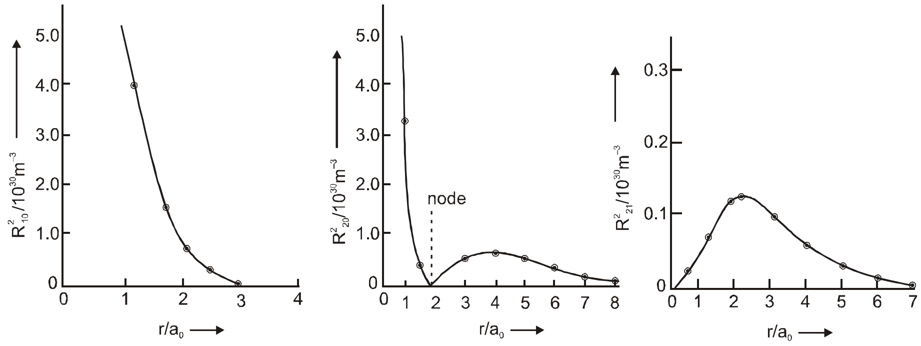
An atomic orbital is a one electron wave function Ψ (r, θ, ϕ) obtained from the solution of the Schrodinger equation. The orbital wave function Ψ has no physical significance but its square (Ψ^2) has a physical significance it measures the electron probability density at a point in an atom.

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

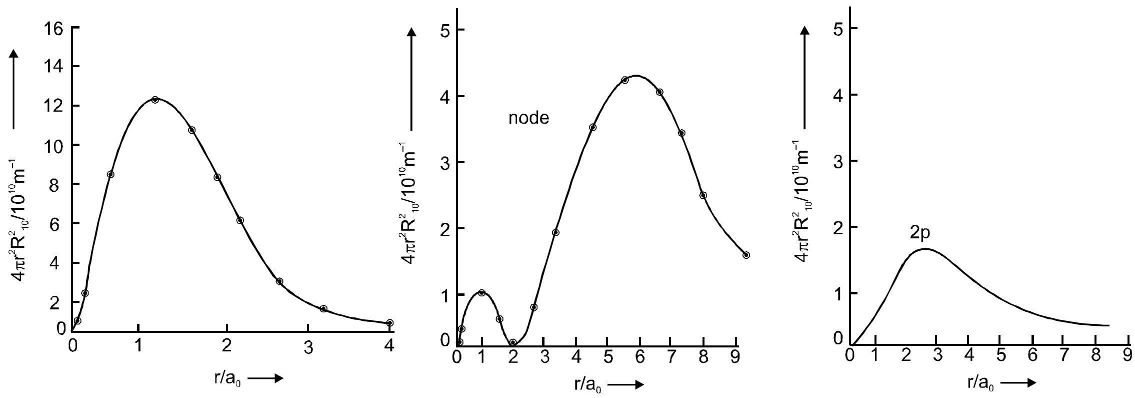
(i) Radial wave function (R) [Fig. (A)] : In all cases R approaches zero as r approaches infinity. We finds that there is a node in the 2s radial function. At the node the value of the radial function changes from positive to negative. In general, it has been found that ns-orbitals have (n–1) radial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

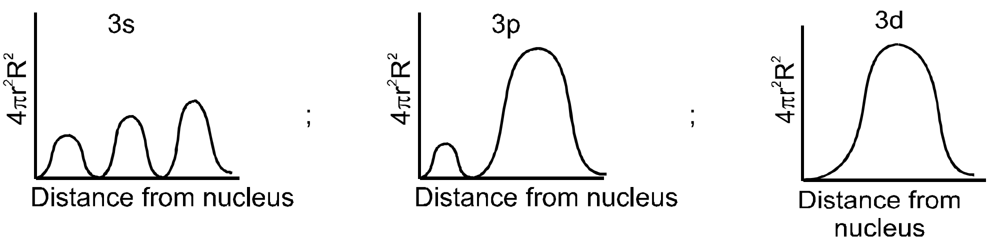


(ii) Radial Probability density (R^2) [Fig. (B)] : The radial density R^2 gives the probability density of finding the electron at a point along a particular radius line. Plots in fig. (B) give useful information about probability density or relative electron density at a point as a function of radius. 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.

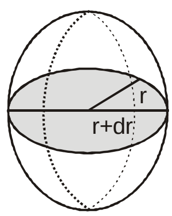


(iii) Radial probability function $4\pi r^2R^2$ [Fig.(C)] : Since the atoms have spherical symmetry, It is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radius (r + dr) and r. The volume of the shell is equal to $4/3\pi(r + dr)^3 - 4/3\pi r^3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





This probability which is independent of direction is called radial probibility 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.



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 $E = h\nu$.

2. According to Bohr model, the angular momentum of an electron is an integral multiple of $h/2\pi$.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, $\lambda = h/mv$.

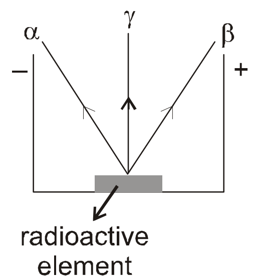
7. An orbital may be defined as a region in space around the nucleus where the probability of finding the electron is maximum.

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

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



Radiations :

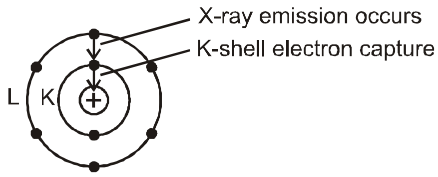
α : ${}_2He^4$ (${}^4_2He^{2+}$) (nucleus of He-atom)
β or β^- : ${}_{-1}e^0$ (fast moving electron emitted from nucleus)
γ : ${}_0\gamma^0$ (electromagnetic radiation (waves) of high frequency)

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

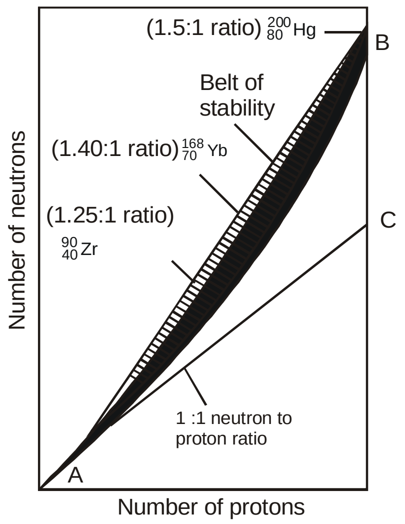
	Emission of rays	Usual condition	Effect	Process representation / example
1.	α	Z > 83	$\frac{n}{p}$ ratio increases	${}_{Z}X^{A} \rightarrow {}_{Z-2}X'^{A-4} + {}_{2}He^{4}$ ${}_{92}U^{238} \rightarrow {}_{90}Th^{234} + {}_{2}He^{4}$
2.	β	If $\frac{n}{p}$ ratio is high.	$\frac{n}{p}$ ratio decreases	${}_{Z}Y^{A} \rightarrow {}_{Z+1}Y'^{A-4} + {}_{-1}e^{0}$
	eg.	${}_{6}C^{12}$ (stable) $\frac{n}{p} = \frac{6}{6}$		${}_{6}C^{14} \rightarrow {}_{7}N^{14} + {}_{-1}e^{0}$
		${}_{6}C^{14}$ (radioactive) $\frac{n}{p} = \frac{8}{6}$ (high)		$\frac{n}{p} = \frac{8}{6}$ $\quad \frac{n}{p} = \frac{7}{7}$
	eg.	${}_{11}Na^{24}$ (radioactive) $\frac{n}{p} = \frac{13}{11}$ (high)		${}_{0}n^{1} \rightarrow {}_{1}p^{1} + {}_{-1}e^{0}$ (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 ($_{+1}e^{0}$)	If $\frac{n}{p}$ ratio is low	$\frac{n}{p}$ ratio increases	${}_{Z}Y^{A} \rightarrow {}_{Z-1}Y'^{A} + {}_{+1}e^{0}$ ${}_{11}Na^{22} \rightarrow {}_{10}Ne^{22} + {}_{+1}e^{0}$ ${}_{1}p^{1} \rightarrow {}_{0}n^{1} + {}_{+1}e^{0}$ (from nucleus)
	(b) Electron capture (EC) or K-shell	If $\frac{n}{p}$ ratio is low	$\frac{n}{p}$ ratio increases	${}_{Z}X'^{A} + \underset{\text{K-shell}}{{}_{-1}e^{0}} \rightarrow {}_{Z-1}X''^{A}$ ${}_{80}Hg^{197} + {}_{-1}e^{0} \rightarrow {}_{79}Au^{197}$

Electron capture

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



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 nuclie 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 nuclie
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 nuclie, new formed nuclie occupy two position left in periodic table.

* When 1β emission takes place from a nuclie, new formed nuclie 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 :

(α , p)
striking particle ← α ; p → emitted particle

* 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.

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 Examples

Ex.15 ^{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.16 The number of β-particle emitted during the change $^{c}_{a}X \longrightarrow {}^{b}_{d}Y$ is :

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

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

$\therefore$ c = b + 4m ......(i)

and a = d + 2m – n ......(ii)

by (i) & (ii)

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

Ex.17 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) $^{9}_{5}Be + {}^{4}_{2}He$

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

Ex.18 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.

Sol. 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)**

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’ Seperation 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	☐

Formule (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	Number of subshell present in n^{th} shell	☐
F34	Number of orbitals present in n^{th} shell	☐
F35	The maximum number of electrons in a principal energy shell	☐
F36	Angular momentum of any orbit	☐
F37	Number of orbitals in a subshell	☐
F38	Maximum number of electrons in particular subshell	☐
F39	Angular orbital momentum	☐
F40	Orbitals present in a main energy level is ‘n^2’.	☐
F41	Magnetic moment	☐
F42	Spin angular momentum	☐
F43	Maximum spin of atom	☐
F44	Schordinger’s equation	☐
F45	Radial nodes	☐
F46	Angular nodes	☐
F47	Total nodes	☐

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 ΔE & Δt	☐

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

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

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

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

Sol. $$\frac{13.6(Z)^2}{(3)^2} = 24$$
I.E. = $13.6(Z)^2 = (24 \times 9) = 216$ ev **Ans. (D)**

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

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

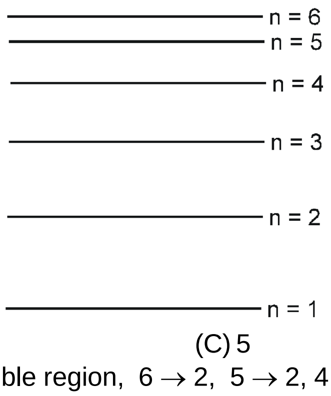
4. The wave number of the first line in the Balmer series of hydrogen is 15200cm^{-1}. What would be the wavenumber of the first line in the Lyman series of the Be^{3+} ion?
(A) $2.4 \times 10^5 cm^{-1}$ (B) $24.3 \times 10^5 cm^{-1}$ (C) $6.08 \times 10^5 cm^{-1}$ (D) 1.313×10^6 cm^{-1}

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. (D)**

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

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

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) $\frac{\lambda}{3\pi}$

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. (B)**

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

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

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

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

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 = – $\frac{1}{2}$

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

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

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

Ans. (C)