ATOMIC STRUCTURE

2.0 INTRODUCTION

Atom is a Greek work and its meaning Indivisible i.e. and ultimate particles which cannot be further subdivided. John Dalton considered that" all matter was composed of smallest indivisible particle called atom

Daltons Atomic Theory :

This theory is based on law of mass conservation and law of definite proportions., the salient feature's of this theory are :-

(1) Each element is composed of extremely small particles called atoms.

(2) Atoms of a particular element are like but differ from atom's of other element.

(3) Atom of each element is an ultimate particle and it has a characteristic mass but is structureless

(4) Atom's are indestructible i.e. they can neither be created nor be destroyed.

(5) Atom of element's take part in chemical reaction to form molecule.

GOLDEN KEY POINTS

- Particles carrying negative charge were called negatrons by Thomson. The name negtron was changed to 'electron' by Stoney.
  In cathode ray experiment particles (electron) forming the rays hve same specific charge (e/,) which is independent of the nature of gas and electrode used. It points out that electrons are present in all atoms.
- Mass of electron is $\frac{1}{1837}$ times that of proton.
- mass of moving e^- = $\frac{\text{rest mass of } e^-}{\sqrt{1-(v-c)^2}}$ (Where v is the velocity of the e^- and c is the velocity of light.)
- In anode ray experiment the particles forming rays have e/m value, dependent on the nature of ht gas taken in the discharge tube, i.e. +ve particles are different in different gases. Therefore, the mass of the proton can be calculated.
- Mass of the proton = $\frac{e}{e/m} = \frac{1.602\times10^{-19}}{9.579\times10^{4}}$ = 1.672×10^{-24} g = 1.672×10^{-27} kg

  Mass of proton in amu = $\frac{1.672\times10^{-24}}{1.66\times10^{-24}}$ = 1.0072 amu.

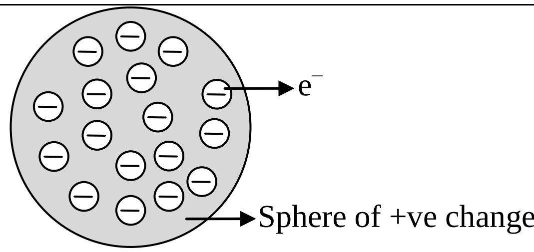
2.1 ATOMIC MODELS

(A) Thomson's Model of Atom [1904]

γ Thomson was the first to propose a detailed model of the atom.

γ Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are distributed more or less uniformly.

γ This model of atom is known as " Plum-Pudding model" or "Raisin Pudding Model" or "Water Melon Model".



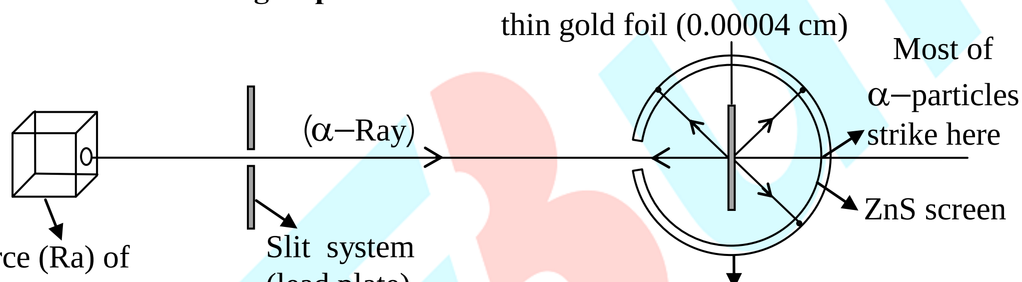
Drawbacks :

γ An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.

γ It is a static model. It does not reflect the movement of electron.

γ If couldn't explain the stability of an atom.

(B) Rutherford's Scattering Experiment



$\alpha = [{}_2He^4]^{+2}$

[doubly ionised He particle]

Rutherford observed that-

(i) Most of the α- particles (nearly 99.9%) went straight without suffering any deflection.

(ii) A few of them got deflected through small angles.

(iii) A very few (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even came back in the direction from which they have come i.e. a deflection of 180°.

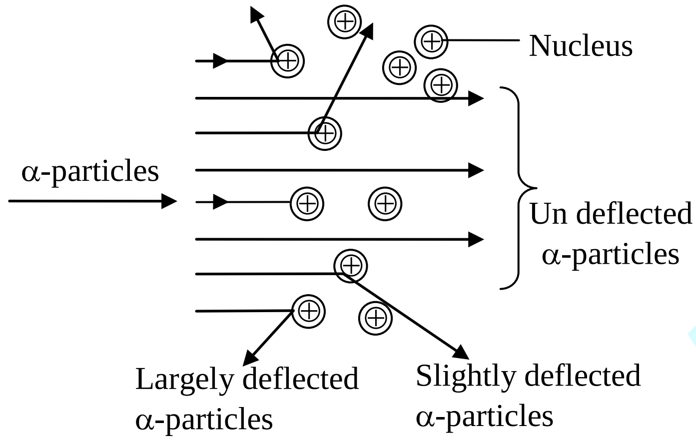
Following conclusions were drawn from the above observation-

(i) Since most of the α-particle went straight through the metal foil undeflected. It means that there must be very large empty space within the atom.

(ii) Since few of ht α-particles were deflected from their original paths through moderate angles; it was concluded that whole of the +ve charge is concentrated and the space occupied by this positive charge is very small in the atom.

γ When α-particles come closer to this point, they suffer a force of repulsion an d deviate from their paths.

γ The positively charged heavy mass which occupies only a small volume in an atom is called nucleus. It is supposed to be present at the centre of the atom.



(iii) A very few of the α-particles suffered strong deflections on even returned on their path indicating that the nucleus is rigid and α-particles recoil due to direct collision with the heavy positively charged mass.

(C) RUTHERFORD'S ATOMIC MODEL

On the basis of scattering experiments, Rutherford proposed model of the atom, which is known as nuclear atomic model. According to this model-

(i) An atom consists of a heavy positively charged nucleus where all the protons and neutrons are present. Protons & neutrons are collectively reffered to as nucleons. Almost whole of the mass of the atom is contributed by these nucleon. The magnitude of the + ve charge on the nucleus is different for different atoms.

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

$$\frac{D_A}{D_N} = \frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5 \text{ , } D_A = 10^5\, D_N$$

Thus diameter (size) of the atom is 10^5 times the diameter of the nucleus.

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

$$R \propto A^{1/3} \quad \Rightarrow \quad R = R_0 A^{1/3} \text{ cm}$$

Where $R_0 = 1.33\times10^{-13}$ (a constant) and A = mass number (p + n) and R = radius of the nucleus.

$$\boxed{R = 1.33\times10^{-13}\times A^{1/3} \text{ cm}}$$

(iii) There is an empty space around the nucleus called extra nuclear part. In this part electrons are present. The number of electrons in an atom is always equal to number of protons present in the nucleus. As the nuclear part of atom is responsible for the mass of the atom, the extra nuclear part is responsible for its volume.

The volume of the atom is about 10^{15} times the volume of the nucleus.

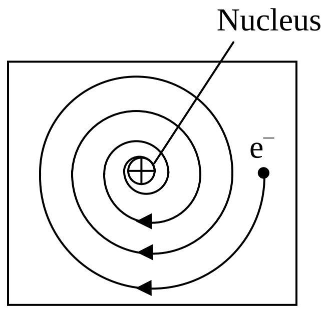
$$\frac{\text{volume of the atom}}{\text{volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = 10^{15}$$

(iv) Electrons revolve around the nucleus in closed orbits with high speed. The centrifugal force acting on the revolving e^- is being counter balanced by the force of attraction between the electrons and the nucleus.

γ This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets.

Drawbacks of Rutherford model -

(i) This theory could not explain stability of atom. According to Maxwell electron loose its energy continuously in the form of electromagnetic radiations. As a result of this, the e^- should loose energy at every turn and move closer and closer to the nucleus following a spiral path. The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable.



(ii) If the electrons loose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies. Hence, the loss of energy by electron is not continuous in an atom.

2.2 ATOMIC NUMBER AND MASS NUMBER

(a) Atomic Number :

It is represented by A. The number of protons present in the nucleus is cllled atomic number of an element. It is also known as nuclear charge.

For neutral atom : Number of proton = Number of electron

For charged atom : Number of e^- = Z – (charge on atom)

Z = number of protons only

(b) Mass Number (A)

It is represented by capital A the sum of number of Neutrons and protons is called the mass number of the element; it is also known as number of nucleons because neutron & proton are present in nucleus.

Formula A = number of protons + number of Neutrons

Note : It is always a whole number.

Atom

Inside the nucleus [n,p^+] | Outside the nucleus [e^-]

An atom of the element is represented by $_ZX^A$

Where, X = Symbol of element

Z = Atomic number = no. of proton = no. of e^- (If atom is neutral)

A = Mass number = no. of neutron + Atomic no.

eg.

$_{11}Na^+$	$_9F^-$	$_6C^{12}$	$_8O^{16}$
($p^+ \to 11$)	($p^+ \to 9$)	($p^+ \to 6$)	($p^+ \to 8$)
($e^- \to 10$)	($e^- \to 9+1=10$)	($e^- \to 6$)	($e^- \to 8$)

eg.

$_6C^{12}$	$_8O^{16}$
$p^+ \to 6$	$p^+ \to 8$
$n^0 \to 12 - 6 = 6$	$n^0 \to 16 - 8 = 8$
$e^- \to 6$	$e^- \to 8$

Mass Number [A] and **atomic weight** (amu = atomic mass unit)

Mass of Proton (m_p)	Mass of Neutron (m_n)	Mass of electron (m_e)
1.673×10^{-27} kg 1.673×10^{-24} grams 1.00750 a.m.u. [$m_p \propto m_n$]	1.675×10^{-27} kg 1.675×10^{-24} grams 1.00850 a.m.u. [$m_n > m_p$]	9.1×10^{-31} kg 9.1×10^{-28} grams 0.000549 a.m.u.

Method for Analysis of atomic weight →

eg $\quad {}_6C^{12}$

$p^+ \to 6$ Weight of Proton = 6×1.00750

$n^0 \to 6$ Weight of Neutron = 6×1.00850

$$e^- \to 6 \quad \frac{\text{Weight of electron} = 6\times0.000549}{\text{Weight of C atom} = 12.011\,\text{a.m.u.}}$$

Mass no. of C atom = 12[p^+ and n]

Note : Mass no. of atom is always a whole no, but atomic weight may be in decimal.

2.3 SOME IMPOTANT DEFINITIONS

(a) Isotopes : They are atoms of a given element which have the same atomic number but differ in the mass number.

eg. γ ${}_6C^{12}$, ${}_6C^{13}$, ${}_6C^{14}$

γ ${}_8C^{16}$, ${}_8C^{17}$, ${}_8C^{18}$

γ ${}_1C^{1}$, ${}_1C^{2}$, ${}_1H^{3}$

Explanation 1 :

${}_6C^{12}$	${}_6C^{13}$	${}_6C^{14}$
$p^+ \to 6$	6	6
$e^- \to 6$	6	6
$n^0 \to 6$	7	8

[**Note :** Isotopes have the same nuclear charge but differ in the number of neutrons in the nucleus]

Explanation 2 :

${}_1H^1$ Protium (H)	**${}_1H^2$** Deuterium (D)	**${}_1H^3$** (Radioactive element) Tritium (T)
$p^+ \to 1$	1	1
$e^- \to 1$	1	1
$n^0 \to 0$	1	2

γ Neutron is not available in Protium

γ No. of Neucleon = No. of Neutron + No. of Proton = n + p^+

Atomic Weight : The atomic weight of an element is the average of mass of all the isotopes of that element.

γ An element have three isotopes y_1, y_2 and y_3 and their isotopic weights are w_1, w_2, w_3 and their percentage/ possibility/probability/ ratio of occurance in nature are x_1, x_2, x_3 respectively, then the average atomic weight of element is

$$\text{Average atomic weight} = \frac{w_1x_1 + w_2x_2 + w_3x_3}{x_1 + x_2 + x_3}$$

eg.	Cl^{35}		Cl^{37}
Probability	75%		25%
Ratio	3	:	1

$$\text{Average atomic weight} = \frac{35\times3+37\times1}{3+1} = \frac{142}{4} = 35.5$$

(b) Isobars

Given by Aston, Isobars are the atoms of difference element which have the same mass number but different Atomic number i.e. they have different number of electrons, protons & neutrons but sum of number of neutrons & protons remains same.

Ex. 1 $\left.\begin{matrix} {}_1H^3 \\ p=1 \\ e=1 \\ n=2 \end{matrix}\right]$ $\left.\begin{matrix} {}_2He^3 \\ p=2 \\ e=2 \\ n=1 \end{matrix}\right]$ **Ex. 2** $\left.\begin{matrix} {}_{19}K^{40} \\ p=19 \\ e=19 \\ n=21 \end{matrix}\right]$ $\left.\begin{matrix} {}_{20}Ca^{40} \\ p=20 \\ e=20 \\ n=20 \end{matrix}\right]$

$p + n = 3$ $p + n = 3$ $p + n = 40$ $p + n = 40$

(c) Isodiapheres

They are the atoms of different element which have the same difference of the number of Neutorns & protons.

Ex.1	${}_5B^{11}$	${}_6C^{12}$	**Ex.2**	${}_7N^{15}$	${}_9F^{19}$
	p = 5	p = 6		p = 7	p = 9
	e = 5	e = 6		e = 7	e = 9
	n = 6	n = 7		n = 8	n = 10
	n – p = 1	n – p = 1		n – p = 1	n – p = 1

(d) Isotones/ Isonutronic Species/Isotonic

They are the atoms of different element which have the same number of neutrons.

Ex.1	${}_1H^3$	${}_2He^4$	**Ex.2**	${}_{19}K^{39}$	${}_{20}Ca^{40}$
	p = 1	p = 2		p = 19	p = 20
	e = 1	e = 2		e = 19	e = 20
	n = 2	n = 2		n = 20	n = 20

(e) Isosters

They ar the molecules which have the same number of atoms & electrons.

Ex.1 CO_2	N_2O	**Ex.2**	CaO	KF
Atoms = 1+2 = 3	Atoms 2 + 1 = 3	Atoms	2	2
Electrons = 6+9×2 = $22e^-$	Electrons 7×2+8 = $22e^-$	Electrons	22+8 $28e^-$	19+9 $28e^-$

(f) Isoelectronic Species

They are the atoms, molecules or ions which have the same number of electrons.

Ex.1	Cl^-	Ar
	18 e^-	18 e^-
Ex.2	H_2O	NH_3

$(2+8) = 10\ e^-$ $(7+3) = 10e^-$

Ex.3 $\mathbf{BF_3}$ $\mathbf{SO_2}$

$(5+9\times3) = 32\ e^-$ $(16+8\times2) = 32\ e^-$

GOLDEN KEY POINTS

- Isotopes have same chemical property but different physical property.
- Isotopes do not have the same value of e/m.
- Isobars do not have the same chemical & physical property.
- Isotopes do not have ht same value of e/m.
- For isotones, $A_1 - Z_1 = A_2 - Z_2$
- For isodiaphers, $A_1 - 2Z_1 = A_1 - 2Z_2$

Illustrations

Illustration. 1 If the mass of neutrons is doubled & mass of electron is halved the fond out the new atomic mass of ${}_6C^{12}$ and the percent by which it is increased.

Solution **Step-1** ${}_6C^{12} \rightarrow e = 6$

$$\left.\begin{array}{l} p = 6 = 6\,\text{amu} \\ n = 6 = 6\,\text{amu} \end{array}\right] = 12\ \text{amu}$$

If the mass of neutrons id doubled and mass of e^- is halved then.

Note : mass of e^- is negligible, so it is not considered in atomic mass

Step-2 % Increment = $\dfrac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 = \dfrac{18-12}{12} \times 100 = 50\%$

Illustration. 2 If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled the find out the new atomic weight of ${}_6C^{12}$.

Solution Step-1 ${}_6C^{12} \rightarrow \left.\begin{array}{l} p = 6 \\ n = 6 \end{array}\right]$ 12 amu

If mass of neutron is doubled, mass of proton is halved and mass of electron is doubled,

then new atomic mass will be : $\left.\begin{array}{l} n = 12\,\text{amu} \\ p = 3\,\text{amu} \end{array}\right]$ 15 amu

Step-2 % Increment = $\dfrac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \times 100 = \dfrac{15-12}{12} \times 100 = 25\ \%$

Illustration. 3 If no. of protons in X^{-2} is 16, then no. of e^- in X^{+2} will be-

(1) 14 (2) 16 (3) 18 (4) None

Solution $\because$ No. of proton in X^{-2} is 16

$\therefore$ No. of electron in X^{-2} is = 14

Illustration. 4 In C^{12} atom if mass of e^- is doubled and mass of proton is halved, the calculate the percentage change in mass number of C^{12}.

Solution

	${}_6C^{12}$		
e^-	p^+	n°	
6	6	6	$A \rightarrow 12$
12	3	6	$A \rightarrow 9$

% change = $\frac{3}{12}\times 100$ = 25%

Illustration. 5 Assuming that atomic weight of C^{12} is 150 unit form atomic table, then according to this assumption the weight of O^{16} will be :-

Solution $\because$ 12 amu = 150

$\therefore$ 1 amu = $\frac{150}{12}$

$\therefore$ 16 amu = $\frac{150}{12}\times 16$ = 200 Unit

Illustration. 6 An element have three isotopes and their isotopic weight are 11, 12, 13 unit and their percentage of occurance in nature is 85, 10, 5 respectively then calculate the average atomic weight of element.

Solution Average Atomic weight = $\frac{11\times 85+12\times 10+13\times 5}{85+10+5} = \frac{935+120+65}{100}$

Average weight = $\frac{1120}{100}$

Illustration. 7 Average atomic weight of an element M is 51.7. If two isotopes of M, M^{50} and M^{52} are present then calculate the percentage of occurance of M^{50} in nature.

Solution M^{50} M^{52}

$x_1 = (100 - x_1)$

Average atomic weight = $\frac{w_1x_1 + w_2x_2}{x_1 + x_2} = 51.7 = \frac{50\times x_1 + 52\times x_2}{x_1 + x_2}$

$51.7 = \frac{50x_1 + 52(100 - x_1)}{x_1 + (100 - x_1)}$

$5170 = 50x_1 + 5200 - 52x_1$

$5170 = -2x_1 + 5200$

$2x_1 = 30$

$x_1 = 15$

M^{50} = 15% M^{52} = 85%

BEGINNER'S BOX-1

1. Which of ht following statements is incorrect for anode rays?

(1) The are deflected by electric and magnetic fields.

(2) Their e/m ratio depends on the gas in the discharge tube used to produce the anode rays.

(3) The e/m ratio of anode ray is constant.

(4) They are produced by the ionization of ht gas in the discharge tube.

2. Which of the following pairs have identical value of e/m ?

(1) A protons and a neutron (2) A proton and deuterium

(3) Deuterium and an α- particle (4) An electron and γ-rays

3. Rutherford's α- particle scattering experiments led to the conclusion that

(1) Mass and energy are related together

(2) The mass and the positive charge of an atom are concentrated in the nucleus
(3) Neutrons re present in the nucleus
(4) Atoms are electrically neutral

4. The radius of $_{13}Al^{27}$ will be
(1) 1.2×10^{-15} m (2) $.7\times10^{-15}$ m
(3) 10.8×10^{-15} m (4) 4×10^{-15} m

5. Which of the following elements has maximum density of nucleus.
(1) $_{14}Si^{30}$ (2) $_{15}P^{31}$ (3) $_{8}O^{16}$ (4) All have same density

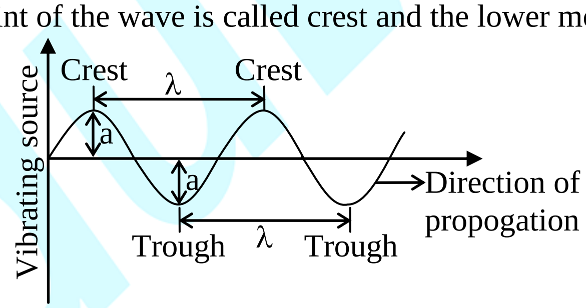
6. Select iso electronic set:-
(a) Na^+, H_3O^+, NH_4^+ (b) CO_3^{-2}, NO_3^-, H_2CO_3
(c) P^{-3}, HCl, $C_2H_5^-$, PH_3 (d) F^-, Ne, Na^+
(1) a, b, d (2) b, c, d (3) b, c, d (4) a, b, c, d

7. If the table of atomic masses were established with the oxygen atom and assigned value of 100, then the mass of Carbon atom would be, approximately :-
(1) 24 (2) 75 (3) 50 (4) 112

2.4 ELECTROMAGNETIC WAVES (EM WAVES) OR RADIANT ENERGY

According to this theory the energy transmitted form one body to another in the form of waves and these waves travel in the space with the same speed as light (3×10^8 m/s). These waves are known as Electro magnetic waves or radiant energy. Ex : Radio waves, micro waves, Infra red rays, visible rays, ultraviolet rays x-rays, gama rays.

γ The radiant Energy do not need any medium for propogation.
γ The radiant Energy have electric and magnetic fields and travel at right angle to these fields.
γ The upper most point of the wave is called crest and the lower most portion is called trough.



Some of the terms employed in dealing with the waves are described below.

(1) Wavelength (λ) (Lambda) : It is defined as the distance between two nearest crest or trough.
It is measured in terms of a Å (Angstrom), pm (Picometre), nm (nanometer), cm(centimeter), m(metre).
1 Å = 10^{-10} m, 1 pm = 10^{-12} m, 1nm = 10^{-9} m , 1 cm = 10^{-2} m

(2) Wave number ($\bar{\nu}$) (nu bar) : It is the reciprocal of the wavelength that is number of waves present in 1 cm $\bar{\nu} = \dfrac{1}{\lambda}$
It is measured in terms of cm^{-1}, m^{-1} etc.

(3) **Frequency (ν) (nu) :** Frequency of a wave is defined as the number of waves which pass through a point in 1 s. It is measured in terms of Hertz (Hz), s^{-1}, or cycle/s (cps) (1 Hertz = 1 s^{-1})

(4) **Time period (T) :** Time taken by a wave to pass through one point. $T = \frac{1}{\nu}$ second

(5) **Velocity (c) :** Velocity of a wave is defined as distance covered by a wave in 1 second

$c = \lambda/T = \lambda\nu$ or $\nu = c/\lambda$ or $c = \nu(s^{-1})\times\lambda(m)$ or $c = \nu\lambda(ms^{-1})$

Since c is constants i.e. frequency is inversely propotional to λ.

(6) **Amplitude (a) :** the amplitude of a wave is defined as the height of crust or depth of trough.

Important note : $\nu = \frac{c}{\nu} = c\bar{\nu}$ $\left(\bar{\nu} = \frac{1}{\lambda}\right)$

Electromagnetic spectrum of EM spectrum :

The arrangement obtained by arranging various types of EM waves in orders of their increasing frequency or decreasing wavelength is called as EM SPECTRUM

low (ν) low (E) longer (λ)	RW	MW	IR	Visible Rays	U.V	Xray	γ	high (ν) high (E) shorter (λ)
Boundaries	3×10^{14} Å – 3×10^{9} Å	3×10^{9} Å – 6×10^{6} Å	6×10^{6} Å – 7600 Å	7600 Å – 3800 Å	3800 Å – 150 Å	150 Å – 0.1 Å	0.1 Å – 0.01 Å	

Illustrations

Illustration 8. The vividh Bharti station of All India Radio broadcast on a frequency of 1368 Kilo Hertz Calculate the wavelength of the Electromagnetic waves emitted by the transmitter.

Solution As we know velocity of light (c) = 3×10^{8} m/s

Given n (frequency) = 1368 kHz = 1368×10^{3} Hz = $1368\times10^{3}\ s^{-1}$

$\Theta\ \lambda = \frac{c}{\nu}$ $\therefore \lambda = \frac{3\times10^{8}ms^{-1}}{1368\times10^{3}s^{-1}} = 219.3$ m

Illustration 9. Calculate $\bar{\nu}$ in cm^{-1} and ν of yellow radiations have wavelength of 5800 Å

Solution As we known $\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800\times10^{-8}cm} = \frac{10^{8}}{5800}cm^{-1} = 17241.37\ cm^{-1}$

$\nu = c\bar{\nu} = 3\times10^{10}\ cm\ s^{-1} \times 1.7\times10^{4}\ cm^{-1} = 3\times1.7\times10^{14} = 5.1\times10^{14}\ s^{-1}$

Illustration 10. A Particular radiostation broadcast at a frequency of 1120 Kilo Hertz another radio station broadcast at a frequency of 98.7 mega Hertz. What are the wavelength of radiations from each station.

Solution Station 1st $\lambda = \frac{c}{\nu} = \frac{3\times10^{8}\,ms^{-1}}{1120\times10^{3}s^{-1}} = 267.86$ m

Station 2nd $\lambda = \frac{c}{\nu} = \frac{3\times10^{8}\,ms^{-1}}{98.7\times10^{6}s^{-1}} = 3.0395$ m

Illustration 11. How long would it take a radio wave of frequency $6\times10^{3}\ s^{-1}$ to travel from mars to the earth, a distance of 8×10^{7} km?

Solution Distance to be travelled from mars to earth = 8×10^{7} km = 8×10^{10} m

Θ Velocity of EM waves = 3×10^{8} m/s

$\therefore$ Time = $\frac{\text{Distance}}{\text{Velocity}} = \frac{8\times10^{10}\,m}{3\times10^{8}\,m/s} = 2.66\times10^{2}$ s = 4 min 26 s

2.5 PLANCK'S QUANTUM THEORY

According to planck's quantum theory :

(1) The radiant energy emitted or absorbed by a body not continuously but discontinuously in the form of small discrete plackets of energy and these packets are called quantum.

(2) In case of light, the smallest packet of energy is called as 'photon' but in general case the smallest packet of energy called as quantum.

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

$E \propto \nu \quad \Rightarrow e = h\nu \quad$ or $\quad E = \frac{hc}{\lambda}\left\{Q\ \nu\frac{c}{\lambda}\right\}$

h is proportionality constant or Planck's constant

h = 6.626×10^{-34} kJs or 6.626×10^{-34} Js or 6.626×10^{-27} erg s

(4) Total amount of energy transmitted from one body to another will be some integral multiple of energy of q quantum. E = nhν ;

Where n is an integer and it is principle quantum number $\boxed{E\ nh\nu = \frac{nhc}{\lambda} = nhc\,\bar{\nu}}$

Illustrations

Illustration 12. Calculate the energy of a photon of sodium light of wave length 5.862×10^{-16} m in Joules.

Solution $\lambda = 5.886\times10^{-16}$ m, $c = 3\times10^{8}\ ms^{-1}$

$E = nh\nu$ or $\frac{nhc}{\lambda}$ (Θ n = 1)

$\therefore$ $E = \frac{hc}{\lambda} = \frac{1\times6.6\times10^{-34}Js\times3\times10^{8}ms^{-1}}{5.862\times10^{-16}m} = \frac{6.6\times3}{5.862}\times10^{-10}$ J = 3.38×10^{-10} J

Illustration 13. Calculate the frequency & energy of a photon of wavelength 4000Å.

Solution (a) Calculation of frequency : λ = 4000Å = 4000×10^{-10} m

$\Theta\ \nu = \frac{c}{\lambda} = \frac{3\times10^{8}m/s}{4\times10^{-7}m} = 0.75\times10^{15-}\ s^{-1} = 7.5\times10^{14}\ s^{-1}$

(b) Calculation of energy

E = hν = 6.626×10^{-34} joule second $\times7.5\times10^{14}\ s^{-1} = 4.96\times10^{-19}$ joule

Illustration 14. Calculate the λ and frequency of a photon having an energy of 2 electron volt.

Solution $\because$ 1 eV = 1.602×10^{-19} J $\therefore$ 2eV = 3.204×10^{-19} J = E

(a) Calculation of wavelength (λ) : $E = \frac{hc}{\lambda}$ or $\lambda = \frac{hc}{E} = \frac{6.626\times10^{-34}\,Js\times2\times10^{8}\,ms^{-1}}{3.204\times10^{-19}\,J}$

$= 6.204\times10^{-7}$m

(b) Calculation of frequency (ν): $\nu = \frac{c}{\lambda} = \frac{3\times10^{8}\,ms^{-1}}{6.204\times10^{-7}\,m} = 0.49\times10^{15}\ s^{-1} = 4.9\times10^{14}\ s^{-1}$

Illustration 15. Which has a higher energy?

(a) A photon of violet light with wavelength 4000Å

(b) A photon of red light with wavelength 7000Å

Solution (a) Violet light : $E_{violet} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}}{4000\times10^{-10}\,m} = 4.97\times10^{-19}$ joule

(b) Red light : $E_{red} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}}{7000\times10^{-10}\,m} = 2.8\times10^{-19}$ joule

2.6 BOHR'S ATOMIC MODEL

Some Important formulae :

γ This model was based on quantum theory of radiation and Classical laws of phiysics.

γ Bohr model is applicable only for single electron species like H, He^{+}, Li^{2+} etc.

γ Bohr model is based on particle nature of electron.

Coulombic force = $\frac{kq_1q_2}{r^2}$

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

Angular momentum = mvr

Important postulates :

1st Postulate :

γ Atom has a nucleus where all protons and neutrons are present.

γ The size of nucleus is very small and it is present at the centre of the atom.

2nd Postulate :

γ Negatively charged electron revolve around the nucleus in the same ways as the planets revolve around the sun.

γ The path of electron is circular.

γ The attraction force (Coulombic or electrostatic force) between nucleus and electron is equal to the centrifugal force on electron.

i.e. Attraction force towards nucleus = centrifugal force away from nucleus.

3rd Postulate :

γ Electrons can revolve only in those orbits in which angular momentum (mvr) of electron is integral multiple of $\frac{h}{2\pi}$ i.e. $mvr = \frac{nh}{2\pi} = n\hbar$ $\hbar = \frac{h}{2\pi}$

where : n = +ve Integer number (n = 1, 2, 3, 4,……..) or ($n \in I^{+}$)

h = Planck's constant

π = Constant

γ Angular momentum can have values such as $\frac{h}{2\pi}$, $2\frac{h}{2\pi}$, 3, $4\frac{h}{2\pi}$, $5\frac{h}{2\pi}$ …… but can not have fractional values such as $1.5\frac{h}{2\pi}$, $1.2\frac{h}{2\pi}$, $0.5\frac{h}{2\pi}$ ……

4th Postulate :

γ The orbits in which electron can revolve are known as stationary orbits because in these orbits energy of electron is always constant.

5th Postulate :

γ Each stationary orbit is associated with definite amount of energy therefore these orbits are also called as energy levels and are numbered as 1, 2, 3, 4, 5,….. or K, L, M, N, O, ….. from the nucleus outwards.

6th Postulate :

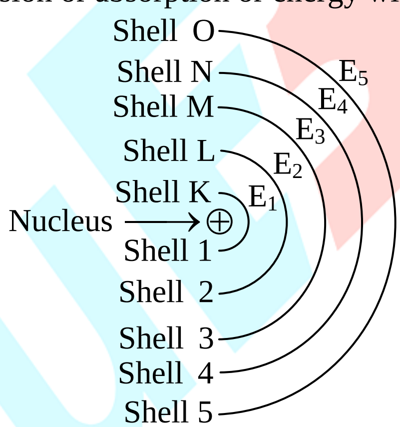
γ The emission or absorption of energy in the form of photon can only occur when electron jumps from one stationary state to another & it is

$\boxed{\Delta E = E_{higher} - E_{lower}}\boxed{= E_{n_2} - E_{n_1}}$ = Energy of a quantum

= hν = Bohr's frequency condition

γ Energy is absorbed when electron Jumps from inner to outer orbit and is emitted when electron moves from outer to inner orbit.

γ $n_2 > n_1$ whether emission or absorption or energy will occur.



BEGINNER'S BOX-2

1. Electromagnetic radiation travels through vaccum at a speed of

(1) 186000 m/s (2) 125 m/s

(3) 3.00×10^8 m/s (4) Id depends upon wavelength

2. Select incorrect statements.

(1) Every object emits radiation s whose predominant frequency depends on its temperature

(2) The quntum energy of a wave is proportional to its frequency.

(3) Photons are quanta of light

(4) the value of the planck's constant depends on energy.

3. What is the wavelength (Å) of a photon that has an energy of 4.38×10^{-18} J

(1) 454 Å (2) 2.3×10^7 Å (3) 6.89×10^{15} Å (4) 1.45×10^{-15} Å

4. A 1kw radio transmitter operates at a frequency of 800 Hz. How many photons per second does it emit.

(1) 1.71×10^{21} (2) 1.88×10^{33} (3) 6.02×10^{23} (4) 2.85×10^{20}

5. Bohr's theory is not applicable to

(1) He (2) Li^{+2} (3) He^{+} (4) H atom

2.7 APPLICATION OF BOHR'S MODEL

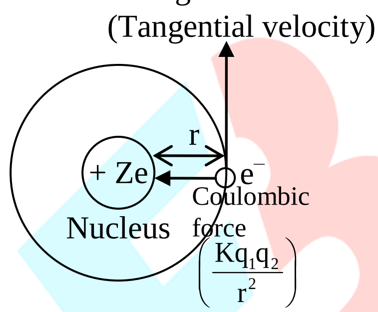
(A) Radius of Various Orbits (Shell)

Columbic force $= \dfrac{Kq_1q_2}{r^2}$

$$= \frac{K.Ze.e}{r^2} = \frac{K.Ze^2}{r^2}$$

Where $K = 9\times10^9\ Nm^2/coulomb^2$

As we know- Coulumbic force = Centrifugal force



$$\frac{K.Ze^2}{r^2} = \frac{mv^2}{r} \quad \text{or} \quad v^2 = \frac{K.Ze^2}{mr} \qquad \text{……(1)}$$

As we know- $mvr = \dfrac{nh}{2\pi}$ or $v = \dfrac{nh}{2\pi mr}$ …….(2)

Putting the value of c form equation (2) to equation (1)

$$\left(\frac{nh}{2\pi mr}\right)^2 = \frac{KZe^2}{mr} \quad \text{or} \quad \frac{n^2h^2}{2\pi^2m^2r^2} = \frac{KZe^2}{mr}$$

$$r = \frac{n^2h^2}{4\pi^2 mKZe^2} \qquad \text{…….(3)}$$

Putting the value of p, h, m, K, & e (constants) in the above equation (3)

$$r = 0.529\times10^{-8}\times\frac{n^2}{Z}\,\text{cm} \qquad (1\text{Å} = 10^{-10}\text{m} = 10^{-8}\text{cm})$$

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

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

(B) Velocity of an electron

Since coulombic force = Centrifugal force

$$\frac{KZe^2}{r^2} = \frac{mv^2}{r} \quad \text{or} \quad v^2 = \frac{KZe^2}{mr} \qquad \text{.....(1)}$$

Putting the value of Angular momentum

$$Mvr = \frac{nh}{2\pi} \quad \text{or} \quad KZe^2 = \frac{nh}{2\pi}(v)$$

$$\boxed{v = \frac{2\pi KZe^2}{nh}}$$

Putting the value of π, k, e & h $\boxed{v = 2.188\times10^6 \frac{Z}{n} \text{ m/s}}$

Illustrations

Illustration 16. Calculate t he radius of 1^{st}, 2^{nd}, 3^{rd}, 4^{th}, Bohr's Orbit of hydrogen.

Solution Radius of Bohr's orbit $r = 0.529\times\frac{n^2}{Z}$ Å

(a) Radius of 1^{st} orbit : $r = 0.529\times\frac{1^2}{1}$ Å = 0.529 Å

(b) Radius of 2^{nd} orbit : $r = 0.529\times\frac{2^2}{1}$ = 0.529Å×4 = 2.116 Å

(c) Radius of 3^{rd} orbit : $r = 0.529\times\frac{3^2}{1}$ = 0.529Å×9 = 4.761 Å

(b) Radius of 4^{th} orbit : $r = 0.529\times\frac{4^2}{1}$ = 0.529Å×16 = 8.464 Å

Illustration 17. Calculate the radius of 3^{rd} & 5^{th} orbit of He^+.

Solution Θ $r = 0.529\times\frac{n^2}{Z}$ Å and Atomic Number of He = 2

$\therefore$ $r_3 = 0.529\times\frac{(3)^2}{2} = 0.529\times\frac{9^2}{2}$ and $r_5 = 0.529\times\frac{(5)^2}{2} = 0.529\times\frac{25}{2}$

Therefore $\frac{r_3}{r_5} = \dfrac{0.529\times\frac{(3)^2}{2}}{0.529\times\frac{(5)^2}{2}} = \frac{9}{25}$ or $r_3 : r_5 = 9 : 25$

Illustration 18. Calculate the radius ratio of 2^{nd} orbit of hydrogen and 3ed orbit of Li^{+2}.

Solution Atomic number of H = 1, Atomic number of Li = 3,

2^{nd} orbit radius of Hydrogen $(r_2)_H = 0.529\times\frac{2^2}{1}$

3^{rd} orbit radius of Li^{+2} $(r_3)_{Li^+} = 0.529\times\frac{3^2}{3}$

Θ $\quad \dfrac{(r_2)_H}{(r_3)_{Li^+}} = \dfrac{0.529 \times \dfrac{2^2}{1}}{0.529 \times \dfrac{3^2}{3}} = \dfrac{4}{3}$

∴ $\quad (r_2)_H : (r_3)_{Li^{+2}} = 4 : 3$

Illustration 19. Calculate the radius ratio of 2^{nd} excited state of H & 1^{st} excited state of Li^{+2}

Solution $\quad 2^{nd}$ excited state, means e^- is present in 3^{rd} shell of hydrogen $r_3 = 0.529 \times \dfrac{(3)^2}{1} = 0.529 \times 9$

1^{st} excited state, means e^- exist in 2^{nd} shell of Li^{+2} $r_2 = 0.529 \times \dfrac{(2)^2}{3} = 0.529 \times \dfrac{4}{3}$

$$\frac{\text{radius of } 2^{nd} \text{ excited state of hydrogen}}{\text{radius of } 1^{st} \text{ excited state of } Li^{+2}} = \frac{(r_3)_H}{(r_2)_{Li^{+2}}} = \frac{0.529 \times \dfrac{9}{1}}{0.529 \times \dfrac{4}{3}} = \frac{7}{4}$$

Illustration 20. Calculate velocity of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second tat this electron makes around the nucleus.

Solution $\quad$ Velocity of electron in 3^{rd} orbit :

Θ $\quad V_n = 2.182 \times 10^6 \dfrac{Z}{n} ms^{-1}$

∴ $\quad V_3 = 2.182 \times 10^6 \dfrac{1}{3} ms^{-1} = 7.27 \times 10^5\ ms^{-1}$

Number of revolution per second

$$= \frac{v_n}{2\pi r_3} = \frac{v_n}{2\pi\left(\dfrac{n^2 a_0}{z}\right)} = \frac{7.27 \times 10^5}{2 \times 3.14 \times 9 \times 0.529 \times 10^{-10}} = 2.43 \times 10^{14} \text{ r.p.s.}$$

Illustration 21. How much time an e^-g will take for one complete revolution in 2^{nd} orbit of He^+?

Solution $\quad$ time taken $= \dfrac{\text{distance}}{\text{velocity}} = \dfrac{2\pi r}{v} = \dfrac{2 \times 3.14 \times 0.529 \times \dfrac{4}{2} \times 10^{-10} m}{2.18 \times 10^6 \times \dfrac{2}{2} ms^{-1}} = 3.05 \times 10^{-16}$ s

(C) Energy of an electron

Let the total energy of an electron be E. It is the sum of kinetic and potential Energy.

i.e. $\quad E = K.E. + P.E.$

$$E = \left(\frac{1}{2}mv^2\right) + \left(\frac{Kq_1q_2}{r}\right) \qquad \left[P.E. = -\frac{KZe^2}{r}\right]$$

$$E = \frac{1}{2}mv^2 + \frac{K.Ze.(-e)}{r} = \frac{1}{2}mv^2 - \frac{K.Ze^2}{r} \qquad \left[K.E. = \frac{1}{2}mv^2 = \frac{K.Ze^2}{2r}\right]$$

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

Putting the value of r from eq. (3)

$$E_n = \frac{KZe^2 \times 4\pi^2 mKZ^2}{2n^2h^2} \quad \text{or} \quad \boxed{E_n = -\frac{2\pi^2 mK^2Z^2e^4}{n^2h^2}}$$

Putting the value of p, K, e, m, h, we get :

$$\boxed{E_n = -\frac{21.69\times10^{-19}\times Z^2}{n^2}\ \text{J/atom}} \quad \text{or} \quad \boxed{E_n = -13.6\times\frac{Z^2}{n^2}\ \text{eV/atom}}$$

This formula is applicable for hydrogen atom & hydrogen like species i.e. single electron species. Since n can have only integral values, it follows that total energy of the e^- is quantized. The –ve sign indicats that the e^- is bonded towards nucleus.

Some extra points :

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

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

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

Conclusion : $\boxed{P.E. = (-)2KE}$ $\boxed{KE = (-)E}$ $\boxed{P.E. = 2E}$

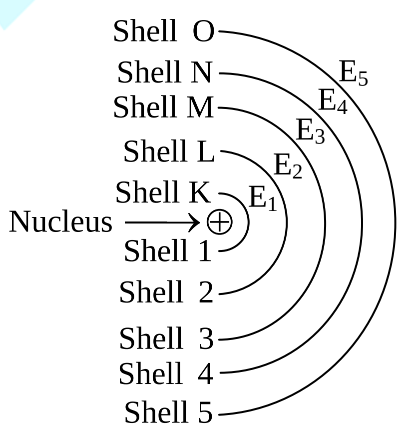
Energy difference between two energy levels :

$$E_{n_2} - E_{n_1} = -13.6\times Z^2\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$

Energy level for H atom can be represented as follows :

n = 6 or P	$E_6 = -0.38$ eV	
n = 5 or O	$E_5 = -0.54$ eV	
n = 4 or N	$E_4 = -0.85$ eV	$E_5 - E_4 = 0.31$ eV
n = 3 or M	$E_3 = -1.51$ eV	$E_4 - E_3 = 0.66$ eV
n = 2 or L	$E_2 = -3.4$ eV	$E_3 - E_2 = 1.89$ eV
n = 1 or K	$E_1 = -13.6$ eV	$E_2 - E_1 = 10.2$ eV

i.e. $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > (E_5 - E_4)$.....



Important Definitions :-

(i) **Ionization energy :** Minimum amount of energy required to electron from the ground state of an isolated atom is called as ionization energy.
$n_1 = 1, n_2 = \infty$

(ii) **Separation energy :** Minimum energy required to remove an electron from its excited state is called as separation energy.

(iii) **Excitation energy :** Amount of energy required to shift an electron from ground state to any excited state is called as excitation energy.
$n_1 = 1 \qquad n_2 = 2, 3, 4, 5, \ldots\ldots.$

Note : All these kinds of energy are always positive.

Illustrations

Illustration 22. If the total energy of an electron is –1.51 eV in hydrogen atom then find out K.E., P.E. orbit, radius and velocity of the electron in that orbit.

Solution
(i) K.E. = –E = 1.51 eV
(ii) PE = 2×E = –2×1.51 = –2.02 eV

(iii) Θ $E = -13.6 \times \frac{Z^2}{n^2}$ eV or $-1.51 = -13.6 \times \frac{1^2}{n^2}$

$\Rightarrow \quad n^2 = \frac{-13.6}{-1.51} = 9 \qquad \therefore n = 3 \qquad$ i.e $\quad 3^{rd}$ orbit

(iv) $r = 0.529 \times \frac{n^2}{Z^2} = 0.529 \times \frac{3 \times 3}{1} = 0.529 \times 9 = 4.761 Å$

(v) $v = 2.188 \times 10^8 \times \frac{Z}{n} = 2.188 \times 10^8 \times \frac{1}{3}$ cm/s $= 0.729 \times 10^8$ cm/s

Illustration 23. Calculate the nergy of Li^{+2} ion for 2^{nd} excited state

Solution $E = -13.6 \times \frac{Z^2}{n^2}$ $\quad\Theta$ Z = 3 and e^- exist in 2^{nd} excited state, means e^- present in 3^{rd} shell i.e.
n = 3

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

Illustration 24. Calculate the ratio of energies of He^+ for 1^{st} & 2^{nd} excited state.

Solution
$$\frac{\text{Energy of }(He^+)1^{st}\text{ Excited state}}{\text{Energy of }(He^+)2^{nd}\text{ Excited state}} = \frac{\text{Energy of }(He^+)2^{nd}\text{ shell}}{\text{Energy of }(He^+)3^{rd}\text{ shell}} = \frac{-13.6 \times \frac{(2)^2}{(2)^2}}{-13.6 \times \frac{(2)^2}{(3)^2}} = \frac{9}{4}$$

Illustration 25. The ionization energy for the hydrogen atom is 13.6 eV then the required energy in eV to excite it from the ground state to 1^{st} excited state

Solution
Ionization energy = 13.6 eV i.e. Energy in ground state = –13.6 eV
Energy of 1^{st} excited state i.e. 2^{nd} orbit = –3.4 eV
So, $E_2 - E_1 = -3.4 + 13.6 = 10.2$ eV

GOLDEN KEY POINTS

- Bohr's atomic model is applicable only for monoelectronic species like H, He^{+}, Li^{+2}, Na^{10+}, U^{91+}, etc.

$$E_{z,n} = E_H \times \frac{z^2}{n^2}$$

If z is same
$E_n = E_H \times$

If n is same
$E_z = E_H \times z^2$

BEGINNER'S BOX-3

1. In which of the following is the radius of the first orbit minimum?
(1) A hydrogen atom (2) A tritium atom
(3) Triply ionized (4) Double ionized helium

2. The energy needed to excite a hydrogen atom from its ground to its third excited state is
(1) 12.1 eV (2) 10.2 eV (3) 0.85 eV (4) 12.75 eV

3. The ionization energy of a hydrogen atom is 13.6 eV. The energy of the ground level in doubly ionized lithium is.
(1) –28.7 eV (2) –54.4 eV (3) –122.4 eV (4) –13.6 eV

4. What would be the radius of 2^{nd} excited state in Li^{+2} ion?
(1) 0.529 Å (2) 1.51 Å (3) 0.2645 Å (4) 0.5299Å

5. 2^{nd} separation energy of an electron in H atom
(1) 27.2 eV (2) 1.57 eV (3) 3.4 eV (4) 13.6 eV

6. How many much energy would be required by an electron while moving from ground stateto 3^{rd} excited state of He^{+} ion.
(1) 40.8 eV (2) 10.2 eV (3) 51 eV (4) 48.35 eV

2.8 SPECTRUM

When a radiation is passed through a spectroscope (prism)for the dispersion of the radiation, the pattern (photograph) obtained on the screen (photographic plate) is called as spectrum of the give radiation.

Classification of Spectrum

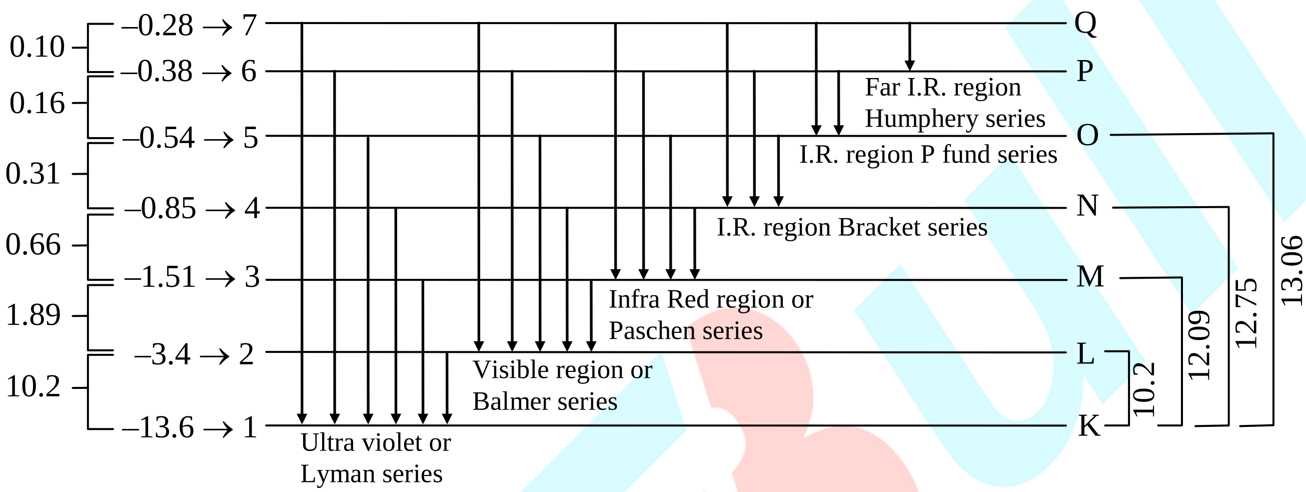
(1) Emission (2) Absorption

HYDROGEN SPECTRUM

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

Series	Discovered by	Regions	$n_2 \rightarrow n_1$	No. of lines

Lyman	Lyman	U.V. region	$n_2 = 2, 3, 4, \ldots./n_1 = 1$	$n_2 - 1$
Balmer	Balmer	Visible region	$n_2 = 3, 4, 5, \ldots./n_1 = 2$	$n_2 - 2$
Paschen	Paschen	Infra red (I.R.)	$n_2 = 4, 5, 6, \ldots./n_1 = 3$	$n_2 - 3$
Brackett	Brackett	I.R. region	$n_2 = 5, 6, 7, \ldots./n_1 = 4$	$n_2 - 4$
Pfund	Pfund	I.R. region	$n_2 = 6, 7, 8, \ldots./n_1 = 5$	$n_2 - 5$
Humphery	Humphery	Far I.R. region	$n_2 = 7, 8, 9, \ldots./n_1 = 6$	$n_2 - 6$



Similar words

- γ First line/Starting line/ Initial line (λ_{max} and ν_{min})
- γ Last line/limiting line/marginal line (λ_{min} and ν_{max})
- γ First line of any series = α line

  Second line of any series = β line

  Third line of any series = γ line

Calculation of number of spectral lines

(a) Total number of spectral lines = 1 + 2 + …….($n_2 - n_1$) = $\dfrac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$ if $n_1 = 1$ (ground state)

Total number of spectral lines = $\dfrac{(n_2 - 1)n_2}{2} = \dfrac{n(n-1)}{2}$

(b) Number of spectral lines which falls in a particular series ($n_2 - n_1$)
where n_2 = higher energy series, n_1 = lower energy series.

RYDBERG FORMULA

In 1890, Rydberg gave a very simplest theoretical Equation for the calculation of the wavelength various lines of hydrogen like spectrum

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

Where R = Rydberg constant = 109678 c,m^{-1} = 109700 cm^{-1} = 10970000 m^{-1} = 1.1×10^{7} m^{-1}

$$\frac{1}{R} = 9.12\times10^{-6} \text{ cm} = 912\text{Å}$$

Derivation of Rydberg formula :

$$\Delta E = E_{n_2} - E_{n_1}$$

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

$$= \frac{2\pi^2 mK^2Z^2e^4}{n_1^2h^2} - \frac{2\pi^2 mK^2Z^2e^4}{n_2^2h^2} \qquad \left(\because \Delta E = h = \frac{hc}{\lambda}\right)$$

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

where $\frac{2\pi^2 mK^2e^4}{ch^3}$ is a constant which is equal to rydberg constant (R).

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

Illustrations

Illustration 26. Calculate the wavelength of 1st line of Balmer series in Hydrogen spectrum.

Solution For first line of Balmer series $n_1 = 2, n_2 = 3$

$$\frac{1}{\lambda} = R(1)^2\left[\frac{1}{4} - \frac{1}{9}\right] = R\left[\frac{9-4}{36}\right] = R\left[\frac{5}{36}\right]$$

$$\Rightarrow \quad \lambda = \frac{36}{5R} = \frac{36}{5} \times \frac{1}{R} = \frac{36}{5} \times 9.12\times10^{-6} \text{ cm} = 65.66\times10^{-6} \text{ cm} = 6566\text{Å}$$

Illustration 27. Calculate the frequency of the last line of the lyman series in hydrogen spectrum

Solution For last line of Lyman series $n_1 = 1, n_2 = \infty$

$$\frac{1}{\lambda} = Rz^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{1} - 0\right) = R$$

$$\Rightarrow \quad \upsilon = \frac{c}{\lambda} = c\times\frac{1}{\lambda} = c\times R = 3\times10^{10} \text{ cm s}^{-1} = 3.29\times10^{15} \text{ s}^{-1}$$

Illustration 28. Calculate Wavelength of 3rd line of Bracket series in hydrogen spectrum.

Solution For 3rd line of bracket series $n_1 = 4, n_2 = 7$

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{(4)^2} - \frac{1}{(7)^2}\right] = R\left[\frac{1}{16} - \frac{1}{49}\right] = R\left[\frac{49-16}{16\times49}\right] = R\frac{33}{784}$$

Therefore, $\lambda = \frac{784}{33R} = \frac{784}{33} \times 912\text{Å} = 2166\text{Å}$

Illustration 29. The wave number of 1st line of Balmer series of hydrogen spectrum is 15200 cm^{-1}. The wave number of 1st line of Balmer series of Li^{+2} spectrum will be ?

Solution Wave number of 1st line of Balmer series of hydrogen spectrum $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

(for H, Z = 1) $\bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ = 15200 cm^{-1}

Wave number of 1st line of Balmer series of Li^{+2} ion is.

$$\bar{\nu} = Z^2 \times R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \{\because Z = 3 \text{ for } Li^{+2}\}$$

$\therefore$ $\bar{\nu}$ = $3^2 \times 15200 = 9 \times 15200 = 136800$ cm^{-1}

Illustration 30. Calculate the ratio of maximum λ of Lyman & Balmer series ?

Solution $E \propto \nu \propto \frac{1}{\lambda}$

$$\frac{\text{Maximum } \lambda \text{ of Lyman series}}{\text{Maximum } \lambda \text{ of Balmer series}} = \frac{1^{st} \text{ line of Lyman series}}{1^{st} \text{ line of Balmer series}}$$

$$\frac{\lambda_{Lyman}}{\lambda_{Balmer}} = \frac{\frac{1}{\lambda_B}}{\frac{1}{\lambda_L}} = \frac{R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]}{R\left[\frac{1}{1^2} - \frac{1}{2^2}\right]} = \frac{\frac{1}{4} - \frac{1}{9}}{\frac{1}{1} - \frac{1}{4}} = \frac{\frac{5}{36}}{\frac{3}{4}} = \frac{5}{36} \times \frac{4}{3} = \frac{5}{27}$$

Illustration 31. In a hydrogen spectrum if electron moves from 7 to 1 orbit by transition in multi steps then find out the total number of lines in the spectrum.

Solution

Lyman	=	$(n_2 - 1) = 7 - 1 = 6$
Balmer	=	$(n_2 - 1) = 7 - 1 = 6$
Paschen	=	$(n_2 - 1) = 7 - 1 = 6$
Bracket	=	$(n_2 - 1) = 7 - 1 = 6$
Pfund	=	$(n_2 - 1) = 7 - 1 = 6$
Humphrey	=	$(n_2 - 1) = 7 - 1 = 6$
Total	=	21

Total number of lines can be calculated as follows :

$$\text{Total number of lines} = \frac{(n_2 - n_1)\left[(n_2 - n_1) + 1\right]}{2} = \frac{(7-1)(6+1)}{2} = \frac{42}{2} = 21$$

Illustration 32. In a hydrogen spectrum if electron moves from 6th to 2nd orbit by transition in multi steps then find out the number of lines in spectrum.

Solution Total number of line = 4 + 3 + 2 + 1 = 10

or Total number of lines = $\frac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2} = \frac{(6-2)(4+1)}{2} = \frac{4 \times 5}{2} = 10$

Illustration 33. A certain electronic transition from an excited state to Ground state of the Hydrogen atom in one or more steps gives rise of 5 lines in the ultra violet region of the spectrum. How many lines does this transition produce in the Infra red region of the spectrum?

Solution (Lyman Series) ultra violet region : 5 lines i.e. e^- is coming from 6th to 1st Orbit Infrared region line

(i) Paschen series = (6–3) = 3 (ii) Bracket = (6–4) = 2 (iii) Pfund = (6–5) = 1

Total Number of lines are = 6

Illustration 34. In H atom if e^- moves, from n^{th} orbit by transition in multi steps, if there are total number of lines in spectrum are 10 then find out the value of n

Solution Total number of lines = $\dfrac{(n_2 - n_1)[(n_2 - n_1) + 1]}{2}$

So, $10 = \dfrac{(n-1)(n-1+1)}{2}$

or $20 = (n - 1)(n)$

$n^2 - n - 20 = 0$

$n^2 - 5n + 4n - 20 = 0$

$n(n - 5) + 4(n - 5) = 0$

$(n + 4)(n - 5) = 0 \quad \Rightarrow \quad n = 5$

Limitation of the Bohr's model :

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

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

(3) Bohr inter related quantum theory of radiation and classical law of physics without any theoretical explanation.

(4) Bohr's theory does not explain the fine structure of the spectral lines. Fine structure of the spectral line is obtained when spectrum is viewed by spectroscope of more resolution power.

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

BEGINNER'S BOX-4

1. The line spectra of two elements are not indentical because

(1) The elements don't have the same number of neutrons.

(2) They have different mass numbers

(3) Their outermost electrons are at different energy levels

(4) They have different valecies

2. In which of the following transition will the wavelength be minimum.

(1) n = 6 to n = 4 (2) n = 4 to n = 2

(3) n = 3 to n = 1 (4) n = 2 to n = 1

3. The wavelength of third line of the Balmer series for a H atom is

(1) $\dfrac{21}{100R}$ (2) $\dfrac{100}{21R}$ (3) $\dfrac{21R}{100}$ (4) $\dfrac{100R}{21}$

4. When the electron of hydrogen atom jumps from the n = 4 to the n= 1 state, the number of spectral lines emitted is

(1) 15 (2) 6 (3) 3 (4) 4

2.9 WAVE MECHNIAL MODEL OF AN ATOM

The model consists of following

(A) de-Brogle concept (Dual nature of Matter)

(B) Heisenberg's Uncertainty principle.

(A) THE DUAL NATURE OF MATTER (THE WAVE NATURE OF ELECTRON)

In 1924, a French physicist, Louis de-Broglie suggested that if the nature of light is both that of a particle and of a wave, then this dual behavior should be true for the matter also.

(1) The wave nature of light rays and X-rays is proved on the basis of their interference and diffraction and many facts related to radiations can only be explained when the beam of light rays is regarded as composed of energy corpuscles or photons whose velocity is 3×10^{10} cm/s.

(2) According to de-Broglie, the wavelength λ of an electron is inversely proportional to its momentum p.

$\lambda \propto \frac{1}{p}$ or $\lambda = \frac{h}{p}$ (Here h = Planck's constant, p = momentum of electron)

Θ Momentum (p) = Mass (m)×Velocity (v) $\therefore$ $\lambda = \frac{h}{mv}$

(3) The above relation can be confined as follows by using Einstein's equation. Planck's quantum theory and wave theory of light.

Einstein's equation, $E = mc^2$ where E is energy, m is mass of a body and c is its velocity.

Θ $E = h\nu = h\times\frac{c}{\lambda}$ (According to Planck's quantum theory) …..(i)

And $c = \nu\lambda$ (According to wave theory of light) $\therefore$ $\nu = \frac{c}{\lambda}$

But according to Einstein's equation $E = mc^2$ …….(ii)

From equation (i) & (ii) : $mc^2 = h\times\frac{c}{\lambda}$ or $mc = \frac{h}{\lambda}$ or $p = \frac{h}{\lambda}$ or $\boxed{\lambda = \frac{h}{p}}$

(4) It is clear from the above equation that the value of λ decreases on increasing either m or v or both. The wavelength of many fast moving objects like an aeroplane or a cricket ball, is very low because of their high mass.

Bohr's theory and de-broglie concept :

(1) According to de-Broglie, the nature of an electron moving around the nucleus is like a wave that flows in circular orbits around the nucleus.

(2) If an electron is regarded as a wave, the quantum condition as given by Bohr in his theory is readily fulfilled.

(3) If the radius of circular orbit is r, then its circumference will be $2\pi r$.

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

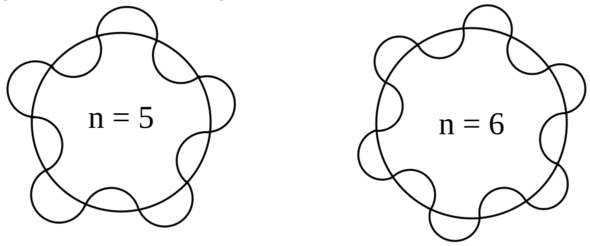
or $2\pi r = \frac{nh}{mv}$ (Θ mv = p momentum) or $2\pi r = \frac{nh}{p}$ $\left(Q\ \frac{h}{p} = \lambda\ \text{de} - \text{Broglie equation}\right)$

$\therefore$ $2\pi r = n\lambda$ (where n = total number of waves 1, 2, 3, 4, 5, …..∞ and λ = Wavelength

(5) Θ $2pr = \frac{nh}{mv}$ or $mvr = \frac{nh}{2\pi}$ Θ mvr = Angular momentum

Thus mvr = Angular momentum, which is a integral multiple of $\frac{h}{2\pi}$.

(6) It is clear from the above description that according to de-Broglie there is similarity between wave theory and Bohr theory.



Similarity between de-Broglie waves and Bohr's orbit

(B) HEISENBERG UNCERTAINITY PRINCIPLE

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

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

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

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

Where h is Planck's constant. $F \times \Delta t \times \Delta x \geq \dfrac{h}{4\pi}$ $\quad \boxed{\Delta E \times \Delta t \geq \dfrac{h}{4\pi}}$

(i) when $\Delta x = 0$, $\Delta v = \infty$

(ii) When $\Delta v = 0$, $\Delta x = \infty$ So, if the position is known quite accurately, i.e., Δx is very small, Δv becomes large and vice-versa.

GOLDEN KEY POINTS

- de-Broglie wavelength in term s of kinetic energy.

  Kinetic Energy (K.E.) = $\frac{1}{2} mv^{-2}$ or $m \times$K.E. = $\frac{1}{2} m^2v^2$ or m^2v^2 = 2m K.E. or mv = $\sqrt{2m\text{K.E.}}$

  But $\lambda = \dfrac{h}{mv}$ $\quad \therefore \quad \lambda = \dfrac{h}{\sqrt{2m\text{K.E.}}}$ $\quad \left(\text{Q } mv = \sqrt{2m\text{K.E.}}\right)$

- When a charged particle carrying Q coulomb is accelerated by applying potential difference V then K.E. = Q×V Joule

  But $\lambda = \dfrac{1}{\sqrt{2m\text{K.E.}}}$ $\quad \therefore \quad \lambda = \dfrac{h}{\sqrt{2mQV}}$ $\quad \boxed{\text{For electron } \left(\lambda = \sqrt{\dfrac{150}{V}}\,\text{Å}\right)} = \dfrac{12.25}{\sqrt{V}}\,\text{Å}$

- The wave nature of electron was verified experimentally by Davisson and Germer.
- de-Broglie hypothesis is applicable to macroscopie as well as microscopic objects but it has no physical significance for macroscopic objects.

- Remember $\boxed{\frac{h}{4\pi} = 0.527\times10^{-34} \text{ J sec}}$

Illustrations

Illustration 35. The mass of a particle is 1 mg and its velocity is 4.5×10^{5} cm per second. What should be the wavelength of this particle if h = 6.652×10^{-27} erg second.
(1) 1.4722×10^{-24} cm (2) 1.4722×10^{-29} cm (3) 1.4722×10^{-32} cm **(4)** 1.4722×10^{-34} cm

Solution Given that m = 1 mg = 1 $\times10^{-3}$ g, v = 4.5×10^{5} cm/s, h = 6.652×10^{-27} erg s.

$$\therefore \quad \lambda = \frac{h}{mv} = \frac{6.625\times10^{-27}\,\text{erg s}}{1\times10^{-3}\text{g}\times4.5\times10^{5}\text{cm/s}} = 1.4722\times10^{-29} \text{ cm}$$

Illustration 36. Which of the flowing should be the wavelength of an electron if its mass 9is 9.1×10^{-31} kg and its velocity is 1/10 of that of light and the value of h is 6.6252×10^{-34} joule second?
(1) 2.446×10^{-7} metre (2) 2.246×10^{-9} metre
(3) 2.246×10^{-11} metre (4) 2.246×10^{-13} metre

Solution Given that m = 9.1×10^{-31} kg, v = $\frac{1}{10}$ of velocity of light

or v = $\frac{1}{10}\times3\times10^{8}$ metre/second i.e. 3×10^{7} metre/second,

h = 6.6525×10^{-34} joule second

$$\lambda = \frac{h}{mc} = \frac{6.6252\times10^{-34}\,\text{J.s}}{9.1\times10^{-31}\text{kg}\times3\times10^{7}\,\text{m/s}} = \frac{6.6252\times10^{-34}}{27.3\times10^{-24}}$$

= 0.2426×10^{-10} metre = 2.426×10^{-11} metre

Illustration 37. A ball weight 25 g moves with a velocity of 6.6×10^{4} cm/s then find out the de-Broglie λ associated with it.

Solution $\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}\times10^{7}\,\text{erg}}{25\times6.6\times10^{4}\text{cm/s}}$ s = 0.04×10^{-31} cm = 4×10^{-33} cm

Illustration 38. If the uncertainity in position of a moving particle is 0 then find out Δp -

Solution $\Delta x\Delta p \geq \frac{h}{4\pi}$ or $\Delta p \geq \frac{h}{4\pi\Delta x}$ or $\Delta p \geq \frac{h}{4\pi\times0}$ or $\Delta p \geq \infty$

Illustration 39. Calculate the uncertainity in the position of a particle when the uncertainity in momentum is
(a) 1×10^{-3} g cm s^{-1} (b) zero

Solution (a) Given Δp = 1×10^{-3} g cm s^{-1}, h = 6.62×10^{-27} erg s, π = 3.142
According to uncertainity principle

$$\Delta x.\Delta p \geq \frac{h}{4\pi} \quad \text{or } \Delta x \geq \frac{h}{4\pi}.\frac{1}{\Delta p} \geq \frac{6.62\times10^{-27}}{4\times3.142}\times\frac{1}{10^{-3}} \geq 0.527\times10^{-24} \text{ cm}$$

(b) When the value of Δp = 0, the value of Δx will be infinity.

Illustration 40. The uncertainity in position and velocity of a particle are 10^{-10} m and 5.27×10^{-24} ms^{-1} respectively. Calculate the mass of the particle (h = 6.625×10^{-34} joule second)

Solution According to Heisenberg's uncertainity principle,

$$\Delta x.m\,\Delta v = \frac{h}{4\pi} \quad \text{or} \quad m = \frac{h}{4\pi\Delta x.\Delta v} = \frac{6.625\times10^{-34}}{4\times3.143\times10^{-10}\times5.27\times10^{-24}} = 0.099 \text{ kg}$$

Illustration 41. Calculate the uncertainity in velocity of a cricket ball of mass 150 g if the uncertainity in its position is of the order of 1Å ($h = 6.6\times10^{-34}$ kg m^2 s^{-1}).

Solution $$\Delta x.\,m\Delta v = \frac{h}{4\pi} \quad \text{or} \quad \Delta v = \frac{h}{4\pi\Delta x.m} = \frac{6.6\times10^{-34}}{4\times3.143\times10^{-10}\times0.150}$$

$= 3.499 \times 10^{-24}\ s^{-1}$

2.10 QUNATUM NUMBERS

To obtain complete information about an electron in an atom 4 identification numbers are required and these identification numbers are called as quantum numbers.

(a) Principal quantum number (n) $\rightarrow$ Shell (Orbit)

(b) Azimuthal quantum number (λ) $\rightarrow$ Sub shell

(c) Magnetic quantum number (m) $\rightarrow$ Orbital

(d) Spin quantum number (s) $\rightarrow$ Spin of e^-

(a) Principal Quantum Number (n)

Given By $\rightarrow$ Bohr

- It represents the name, size and energy of the shell to which e^- belongs
- The value of n lies between 1 to ∞

  i.e. n = 1, 2, 3, 4……∞ corresponding name of shells are K, L, M, N, O,…….
- Greater the value of n, greater is the distance from the nucleus.

  $r = 0.529\times\frac{n^2}{z}$ Å

  $r_1 < r_2 < r_3 < r_4 < r_5$ ………
- Greater the value of n, greater is the energy of shell

  $E = -13.6\times\frac{z^2}{n^2}$ eV/atom

  $E_1 < E_2 < E_3 < E_4$………
- Velocity of electron $v = 2.18\times10^6\,\frac{z}{n}$ m/s
- The angular momentum of a revolving electron is $mvr = \frac{nh}{2\pi}$

  Where n = Principal quantum number
- The number of electrons in a particular shell is equal to $2\,n^2$

(b) Azimuthal quantum number / Angular quantum number/ secondary quantum number/Subsidiary quantum number (λ)

Given by – Somerfield

- It represents the shape of the subshell and orbital and orbital angular momentum
- Value of λ between 0 to (n – 1)

  i.e. λ = 0, 1, 2……(n–1)

  λ = 0 (s Subshell)

  λ = 1 (p Subshell)

λ = 2 (d Subshell)

λ = 3 (f Subshell)

Ex. If n = 1 then $\lambda = 0 \Rightarrow$ 1s i.e. in n = 1 shell, only one subshell 's' is present.

If n = 2 then $\lambda = 0, 1 \Rightarrow$ 2s, 2p i.e. in n = 2 shell, only two subshell 's' & 'p' are present.

If n = 3 then $\lambda = 0, 1, 2 \Rightarrow$ 3s, 3p, 3d i.e. in n = 3 shell, only three subshell 's' & 'p' are present.

If n = 4 then $\lambda = 0, 1, 2, 3 \Rightarrow$ 4s, 4p, 4d, 4f i.e. in n = 4 shell, only four subshell 's' & 'p' are present.

- If the value of n is same then the order of energy of the various subshell will be
  s < p < d < f
  Ex. 4s < 4p < 4d < 4f, 3s < 3p < 3d, 2s < 2p
- If value of λ is same but value of n is different then the order of energy will be.
  Ex. 1s < 2s < 3s< 4s < 5s < 6s
  3d < 4d < 5d < 6d
  4p < 5p < 6p
- The orbital angular momentum = $\sqrt{l(l+1)}\frac{h}{2\pi}$ or $\sqrt{l(l+1)}\hbar$ $\left\{\because \hbar = \frac{h}{2\pi}\right\}$ {h is called 'hash'}
  Orbital angular momentum : For s subshell = 0
  For p subshell = $\sqrt{2}\frac{h}{2\pi}$ or $\sqrt{2}\hbar$
- The number of electron in a particular subhsell is equal to $2(2\lambda + 1)$
  For s subshell number of electrons = $2e^-$
  For p subshell number of electrons = $6\ e^-$
  For d subshell number of electrons = $10e^-$
  For f subshell number of electrons = $14\ e^-$
- Shape of the subshell : s $\rightarrow$ spherical
  p $\rightarrow$ dumb bell shape
  d $\rightarrow$ double dumb bell shape
  f $\rightarrow$ complex shape

BEGINNER'S BOX-5

1. de-Broglie wavelength is related to applied voltage is

(1) $\lambda = \frac{12.3}{\sqrt{h}}$ Å
(2) $\lambda = \frac{12.3}{\sqrt{V}}$ Å
(3) $\lambda = \frac{12.3}{\sqrt{r}}$ Å
(4) $\lambda = \frac{12.3}{\sqrt{m}}$ Å

2. Select the incorrect statements among the following.

(1) $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$
(2) $\Delta x \cdot \Delta p \geq \frac{h}{4\pi m}$
(3) $\Delta x \cdot \Delta V \geq \frac{h}{4\pi m}$
(4) $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$

3. If the kinetic energy of an electron is increased 4 times, the wavelength of the de-Broglie wave associated with it would become

(1) four times (2) two times (3) half times (4) one fourth times

4. Velocity of de-Broglie wave in given by

(1) $\frac{c^2}{\nu}$ (2) $\frac{h\nu}{mc}$ (3) $\frac{mc^2}{h}$ (4) $\nu\lambda$

5. The representation of an orbital with n= 4 and λ = 1 :

(1) 4d (2) 4s (3) 4f (4) 4p

6. Maximum number of electrons present in M shell is :

(1) 8 (2) 18 (3) 32 (4) 10

(c) Magnetic Quantum Number / Orientation Quantum Number (m) :

Given by linde

- It represents the shape of different orbitals and the orientation of electron cloud (orbital)
- Under the influence of magnetic field each subshell is further subdivided into orbitals (the electron cloud is known as orbital)
- Value of m = all integral value from – λ to + λ including zero.
  i.e. Value of m = –λ to +λ

Orbital : 3D space around the nucleus in which probability of finding electron is maximum is called an orbital. An orbital can be represented by 3 set of quantum numbers

= $\Psi_{n,\lambda,m}$ (classical representation) = nλx*

Ex. 1 : $2p_x$; n = 2, λ = 1, m = –1 or m = +1

Ex. 2 : $3d_{z^2}$; n = 3, λ = 2, m = 0

Ex. 3 : $\Psi_{(3,2,0)}$; n = 3, λ = 2, m = 0 ; $3d_{z^2}$

Node : It is point / line / plane / surface in which probability of finding electron is zero.

Total numbers of nodes = n – 1

They are of 2 types.

(i) Radial nodes / spherical nodes $\boxed{\text{number of radial nodes = n-}\lambda\text{-1}}$

(ii) Angular nodes / number of nodal planes $\boxed{\text{number of angular nodes/nodal planes = }\lambda}$

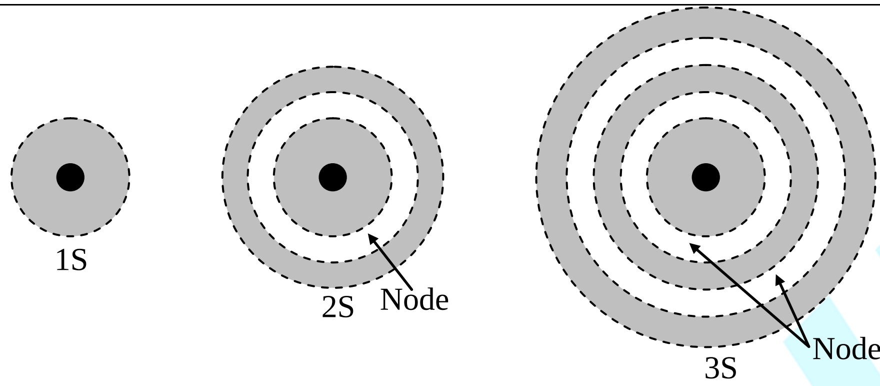
* Nucleus and ∞ are not considered as node.

Types of orbitals :

Case-I : If λ = 0 then m = 0 it implies that s subshall has only one orbital called as s orbital.

Shapes of s-orbitals :

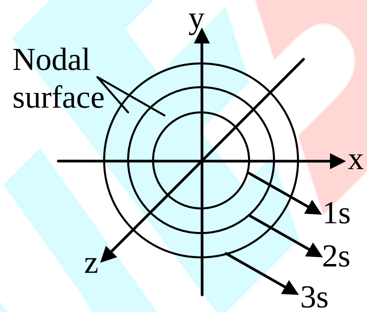
The s-orbitals are spherically symmetrical about the nucleus, i.e., the probability of finding s electron is same in all direction s from the nucleus. The size of the orbital depends on the value of principal quantum number, there is one spherically symmetrical orbital. The 1s orbital is smaller than 2s-orbital and 2s-orbital is smaller than 2s-orbital and 2s- orbital is smaller than 3s, but all are spherical in shape as shown in figure.



Although the s-orbitals belonging to different shells are spherically symmetrical, yet they differ in certain respects as explained below :

(i) The probability of 1s electron is found to be maximum near the nucleus and decreases as the distance from the nucleus increases. In case of 2s electrons, the probability is again maximum near the nucleus and then decreases to zero as the distance from the nucleus increases. The intermediate region (a spherical shell) where the probability is zero is called a nodal durface of simple node. Thus, 2s-orbital differs from 1s-orbital in having one node within it. Similarly, 3s has two nodes in general, any ns orbital has (n–1) nodes.

(ii) The size and energy of the s-orbital increases as the principal quantum number increases, i.e., the size and energy of s-orbital increases in the order 1s < 2s < 3s…..



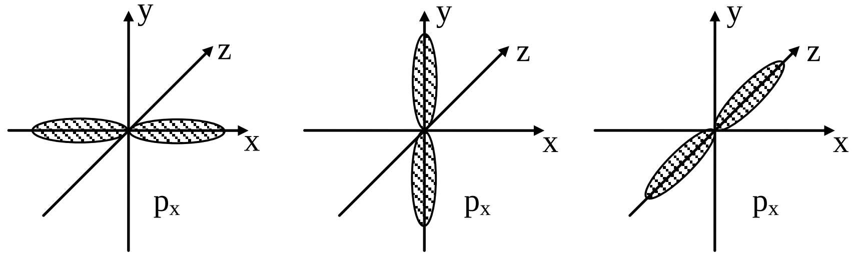
The s orbital of higher energy levels are also symmetrically spherical and can be represented as above

Case-II : If l = 1 (p-sbshell) then m = $\begin{array}{c|c|c} -1 & 0 & +1 \\ \hline p_x & p_z & p_y \end{array}$

It implies that, p subshell have three orbitals called as p_x, p_y and p_z.

Shape of p-orbitals :

There are three-orbitals, commonly referred to as p_x, p_y, and p_z. these three p-orbitals, possess equivalent energy and therefore, have same relation with the nucleus. They, however, differ in their direction & distribution of the charge.



These three p-orbitals ar situated at right angle to one another and are directed along x, y, and z axis (figure)

γ Each p orbital has dumb bell shape (2 lobes which are separated from each other by a point of zero probability called nodal point or node or nucleus.

γ The two lobes of each orbital are separated by a plane of zero electron density called nodal plane.

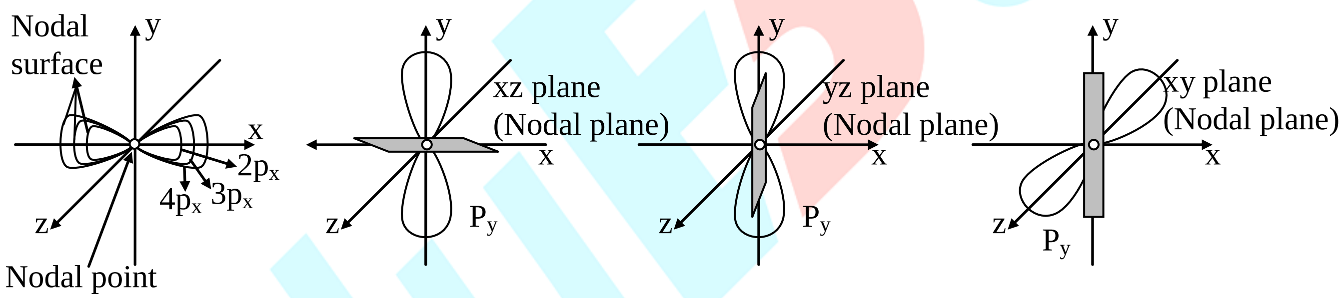
γ Each p orbital of higher energy level are also dumb bell shape but they have nodal surface.

Nodal surface :

Orbital	Nodal surface
$3p_x$	1
$4p_x$	2
np_x	(n – 2)

Nodal plane :

Orbital	Nodal plane
p_x	yz plane
p_y	xz plane
p_z	xy plane

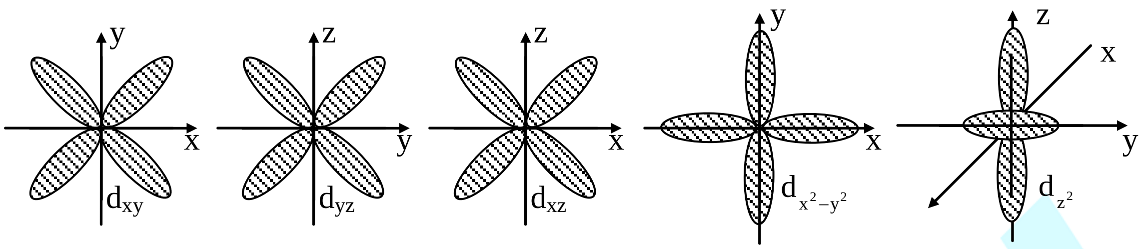


Case-III When λ = 2, ‘m’ has five values –2, –1, 0, +1, +2. It implies that d subshell of any energy shell has five orbitals. All the five orbitals are not identical in shape. Four of the d orbitals d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ contain four lobes while fifth orbital d_{z^2} consists of only two lobes, the lobes d_{xy} orbital lie between x and y axes. Similar is the case for d_{yz} and d_{xz}. Four lobes of $d_{x^2-y^2}$ orbital are lying along x and y axes while the two lobes of d_{z^2} orbital ar lying along z axes and contain a ring of negative charge surrounding the nucleus in xy plane. Geometry of d orbital is Double Dumb bell.

–2	–1	0	+1	+2
d_{xy}	d_{yz}	d_{z^2}	d_{zx}	$d_{x^2-y^2}$

Shape of d-orbitals :

It implies that d subshell has 5 orbitals i.e. five electron cloud and be represented as follows.



Each d- orbital of higher energy level are also double dumbled shape but they have nodal surface.

In d-orbitals :

(i) Nodal Point $\rightarrow$ 1

(ii) Nodal Surface $\rightarrow$ 1

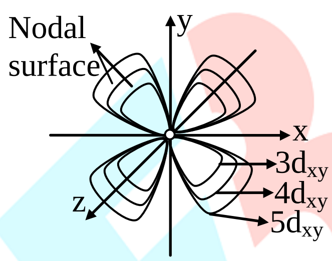
$3d_{xy} \rightarrow 0$ Nodal surface

$4d_{xy} \rightarrow 1$ Nodal surface

$5d_{xy} \rightarrow 2$ Nodal surface

$nd_{xy} \rightarrow (n-3)$

Number of nodal surface = $n - \lambda - 1$



(iii) Nodal plane :

$d_{xy} \rightarrow$ xz & yz nodal plane :

$d_{xz} \rightarrow$ xy & zy nodal plane :

$d_{zy} \rightarrow$ zx & yx nodal plane :

$d_{x^2-y^2} \rightarrow$ 2, nodal plane :

$d_{xy} \rightarrow$ 0, nodal plane :

Note : Orbital of d subshell are Equivalent in energy.

(d) Spin Quantum number (s) :

Given by Goudsmit and Uhlenback

- It represents the direction of electron Spin around its own axis
- For clock wise spin/spin up ($\uparrow$) electron $\rightarrow \pm$ ½
- For anticlock wise spin/spin down ($\downarrow$) electron $\rightarrow$ μ½

Spin angular momentum of an e^- = $\sqrt{s(s+1)}.\dfrac{h}{2\pi}$ or $\sqrt{s(s+1)}.h$

- Each orbital can accommodate 2 electrons with opposite spin or spin paired.

Correct $\boxed{\uparrow\downarrow}$ Spin paired e^- Wrong $\boxed{\uparrow\uparrow}$ Spin parallel e^-

Illustrations

Illustration 42. For 7 p_y, calculate the value of n, λ, m and s

Solution $n = 7, \lambda = 1, m = +1$ or -1, $s = +\dfrac{1}{2}$ or $-\dfrac{1}{2}$

Illustration 43. For 3s, calculate the value of n, λ, m and s.

Solution $n = 3, \lambda = 0, m = 0, s = +\frac{1}{2} \text{ or } -\frac{1}{2}$

Illustration 44. For $5dz^2$, calculate the value of n, λ, m and s

Solution $n = 5, \lambda = 2, m = 0, s = +\frac{1}{2} \text{ or } -\frac{1}{2}$

Illustration 45. Which of the following set of Quantum number is not possible ?

(a) $n = 2, \lambda = 0, m = -1, s = \frac{1}{2}$ **(b)** $n = 3, \lambda = 2, m = 0, s = \pm\frac{1}{2}$

(c) $n = 2, \lambda = 3, m = -2, s = \pm\frac{1}{2}$

Solution (a) not possible (b) possible (c) not possible

2.11 RULES FOR FILLING OF ELECTRONS

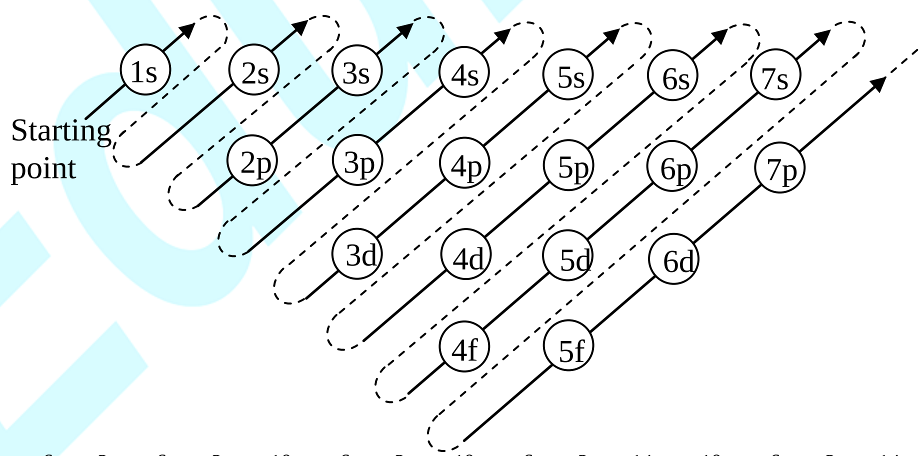
(a) Aufbau Principle (b) (n + λ) rule

(c) Hund's Maximum multiplicity principle (d) Pauli's exclusion principle

(a) Aufbau Principle

Aufbau is a German word and its meaning 'Building up'

- Aufbau principle gives sequence in which various subshell are filled up depending on the relative order of the Energies of various subshell.
- Principle : The subshell with minimum energy is filled up first when this subshell obtained maximum quota of electrons then the next subshell of higher energy starts filling.
- The sequence in which various subshell are filled are as follows.



$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, \ldots\ldots$

For Example

$_1H \rightarrow 1s^1$

$_2He \rightarrow 1s^2$

$_3Li \rightarrow 1s^2, 2s^1$

$_4Be \rightarrow 1s^2, 2s^2$

${}_{5}B \rightarrow 1s^2, 2s^2, 2p^1$
${}_{6}C \rightarrow 1s^2, 2s^2, 2p^2$
${}_{7}N \rightarrow 1s^2, 2s^2, 2p^3$
${}_{8}O \rightarrow 1s^2, 2s^2, 2p^4$
${}_{9}F \rightarrow 1s^2, 2s^2, 2p^5$
${}_{10}Ne \rightarrow 1s^2, 2s^2, 2p^6$
${}_{11}Na \rightarrow 1s^2, 2s^2, 2p^6, 3s^1$
${}_{12}Mg \rightarrow 1s^2, 2s^2, 2p^6, 3s^2$
${}_{13}Al \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
${}_{14}Si \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
${}_{15}P \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
${}_{16}S \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
${}_{17}Cl \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
${}_{18}Ar \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
${}_{19}K \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
${}_{20}Ca \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
${}_{21}Sc \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
${}_{22}Ti \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
${}_{23}V \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
${}_{24}Cr \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$ [Exception]
${}_{25}Mn \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
${}_{26}Fe \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
${}_{27}Co \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$
${}_{28}Ni \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$
${}_{29}Cu \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$ [Exception]
${}_{30}Zn \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

Electronic configuration can be written by following different methods :

- 26Fe $\rightarrow$ (1) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
  (2) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4d^6, 4s^2$
  (3) $\underset{2}{1s^2}, \underset{8}{2s^2p^6}, \underset{14}{3s^2p^6d^6}, \underset{2}{4s^2}$
  (4) [Ar] $4s^2\ 3d^6$
- 26Fe $\rightarrow$ $1s^2\ \underbrace{2s^2 2p^6}_{(n-2)}\ \underbrace{3s^2 3p^6 2d^6}_{(n-1)}\ \underbrace{4s^2}_{n}$

n $\rightarrow$ outer most shell or Ultimate shell or Valence shell
In this shell e^- are Called as Valence electron or this is called core charge
(n – 1) $\rightarrow$ Penultimate shell or core or pre valence shell
(n – 2) $\rightarrow$ Pre Penultimate Shell

- If we remove the last n shell (ultimate shell) then the remaining shell are collectively called as Kernel.

Ex. $\underbrace{1s^2 2s^2 2p^6 3d^6 3p^6}_{\text{Kernel}}\ 4s^2$

(b) **(n + λ) Rule (For multi electron species)**

According to it the sequence in which various subshell are filled up can also be determined with the help of (n + λ) value for a given subshell.

Principle of (n + λ) rule :

The subshell with lowest (n + λ) value is filled up first, when two or more subshell have same (n + λ) value then the subshell with lowest value of n is filled up first.

In case of H-atom :

Energy only depends on principle quantum number

1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < ……….

Sub Shell	**n**	**λ**	**n + λ**
1s	1	0	1
2s	2	0	2
2p	2	1	3 (1)
3s	3	0	3 (2)
3p	3	1	4 (1)
4s	4	0	4 (2)
3d	3	2	5 (1)
4p	4	1	5 (2)
5s	5	0	5 (3)
4d	4	2	6 (1)
5p	5	1	6 (2)
6s	6	0	6 (3)

Order : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4s^6, 5s^2, 4d^{10}, 5p^6, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}$,…..

(c) **Hund's Maximum Multiplicity Rule** (Multiplicity : Many of the same kind)

- According to Hund's rule electrons are distributed among the Orbitals of subshell in such a way as to give maximum number of unpaired electron with parallel spin.
- Thus the Orbital available in the subshell are first filled singly with parallel spin electron before they begin to pair this means that pairing of electrons occurs with the introduction of second electron in 's' subshell, fourth electron in 'p' subshell, 6^{th} electron in 'd' subshell & 8^{th} e^- in 'f' subshell.

Ex. $_5B \rightarrow 1s^2 \quad 2s^2 \quad 2p^1$

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

$_6C \rightarrow 1s^2 \quad 2s^2 \quad 2p^2$

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

$_7N \rightarrow 1s^2 \quad 2s^2 \quad 2p^3$

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

$_8O \rightarrow 1s^2 \quad 2s^2 \quad 2p^4$

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

$_9F \rightarrow 1s^2 \quad 2s^2 \quad 2p^5$

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

${}_{10}Ne \rightarrow 1s^2 \quad 2s^2 \quad 2p^6$

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

(d) Pauli Exclusion Principle

In 1925 Pauli stated that no two electron in an atom can have same values of all four quantum numbers i.e., A n orbital can accommodates maximum 2 electrons with opposite spin.

Ex. 1 ${}_6C^{12} \rightarrow$

	$1s^2$	$2s^2$	$2p^2$
	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{}$
			P_x P_z P_y
n	1	2	2
λ	0	0	1
m	0	0	+1, 0, –1
s	+½, –½	+½, –½	+½, +½

Ex. 2 ${}_{17}Cl \rightarrow$

	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$
	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$
n	1	2	2	3	3
λ	0	0	1	3	3
m	0	0	+1, –1, 0	0	+1, –1, 0
	+½, –½	+½, –½	+½, –½ +½, –½ +½, –½	+½,–½	+½,–½+½,–½+½

Exception of Aufbau principle :

In some cases it is seen that the electronic configuration is slightly different from the arrangement given by Aufbau principle. A simple region behind this is that half filled & full filled subshell have got extra stability.

Ex. 1 ${}_{24}Cr \rightarrow 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 4s^2 \quad 3d^4$ (wrong configuration)

$4s$: $\boxed{\uparrow\downarrow}$ $3d$: $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

${}_{24}Cr \rightarrow 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 4s^1 \quad 3d^5$ (right configuration)

$4s$: $\boxed{\uparrow}$ $3d$: $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

Ex. 2 ${}_{29}Cu \rightarrow 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 4s^2 \quad 3d^9$ (wrong configuration)

$4s$: $\boxed{\uparrow\downarrow}$ $3d$: $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

${}_{29}Cu \rightarrow 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 4s^1 \quad 3d^{10}$ (right configuration)

$4s$: $\boxed{\uparrow}$ $3d$: $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

Illustrations

Illustration 46. Calculate the number of unpaired e^- in Cr

Solution ${}_{24}Cr \rightarrow 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 4s^1 \quad 3d^5$

in ${}_{24}Cr$, $6e^-$ s are unpaired.

Illustration 47. The number of unpaired e^- in Cr^{+3}

Solution $Cr^{+3} \rightarrow 1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^0$ $3d^3$

in Cr^{+3}, $3e^-$ s are unpaired.

Illustration 48. The number of unpaired e^- in 3d subshell of Cr^{+3}

Solution 3

Illustration 49. The number of unpaired e^- in Fe^{+2} & Fe^{+3}

Solution $Fe^{+2} \rightarrow$ $1s^22s^22p^63s^23p^64s^03d^6$ = 4 unpaired e^-

$Fe^{+3} \rightarrow$ $1s^22s^22p^63s^23p^64s^03d^5$ = 5 unpaired e^-

BEGINNER'S BOX-6

1. A neutral atom of an element has 2K, 8L, 11 M and 2N electron. The number p-electron in the atom are

(1) 2 (2) 12 (3) 10 (4) 6

2. An atom has 2 electron in K-shell, 8 electrons in L-shell & 8 electrons in M-shell. The number of p-electrons presents in the element is:-

(1) 10 (2) 7 (3) 12 (4) 4

3. The maximum number of such electrons in an atom with quantum number n = 3, λ = 2 is

(1) 2 (2) 6 (3) 10 (4) 14

4. The number of orbitals in n = 3 are

(1) 1 (2) 4 (3) 9 (4) 16

5. In the potassium the probable order of energy level for 19[th] electron is

(1) 3s > 3d (2) 4s < 3d (3) 4s > 4p (4) 4s = 3d

ANSWER KEY

BEGINNER'S BOX-1

1.	(3)	**2.**	(3)	**3.**	(2)	**4.**	(4)	**5.**	(4)	**6.**	(4)	**7.**	(2)

BEGINNER'S BOX-2

1.	(3)	**2.**	(4)	**3.**	(1)	**4.**	(2)	**5.**	(1)

BEGINNER'S BOX-3

1.	(3)	**2.**	(4)	**3.**	(3)	**4.**	(2)	**5.**	(2)	**6.**	(3)

BEGINNER'S BOX-4

1.	(3)	**2.**	(3)	**3.**	(2)	**4.**	(2)

BEGINNER'S BOX-5

1.	(2)	**2.**	(3)	**3.**	(3)	**4.**	(3)	**5.**	(2)