ATOMIC STRUCTURE

INTRODUCTION

Atom is a Greek word and its meaning is indivisible i.e. an ultimate particle which cannot be further subdivided. John Dalton considered that " all matter are 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 atoms of other element.

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

(4) Atoms are indestructible i.e. they can neither be created nor be destroyed.

(5) Atoms of different elements take part in chemical reaction to form molecule.

POINTS TO REVISE

- Particles carrying negative charge were called negatrons by Thomson.The name negatron was changed to 'electron' by Stoney.

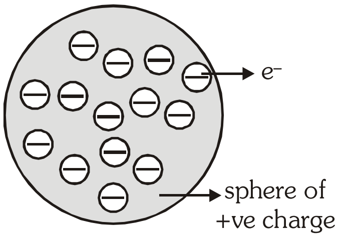
  In cathode ray experiment, particles (electron) forming the rays have same specific charge (e/m) which is independent of the nature of gas and electrode used. It points out that electrons are present in all atoms.
- Mass of electron is $\frac{1}{1837}$ times that of proton.
- Mass of moving electron = $\frac{\text{rest mass of electron}}{\sqrt{1-(v/c)^2}}$

  (Where v is the velocity of the electron and c is the velocity of light.)

  When $v = c \Rightarrow$ mass of electron = ∞ and if $v > c \Rightarrow$ mass of electron = imaginary
- In anode ray experiment, the particles forming rays have e/m value that is dependent on the nature of the gas taken in the discharge tube, i.e. +ve particles are different in different gases. Therefore, the mass of the proton can be calculated.

ATOMIC MODELS

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

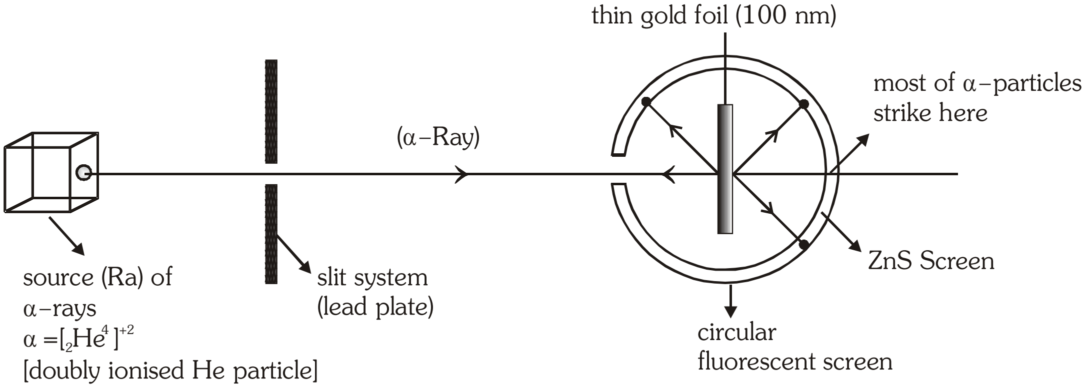


- Thomson was the first to propose a detailed model of the atom.
- Thomson proposed that an atom consists of a uniform sphere of positive charge in which the electrons are distributed more or less uniformly.
- This model of atom is known as "Plum-Pudding model" or "Raisin Pudding Model" or "Water Melon Model".

Drawbacks :

- An important drawback of this model is that the mass of the atoms is considered to be evenly spread over that atom.
- It is a static model. It does not reflect the movement of electron.
- It couldn't explain the stability of an atom.

(B) Rutherford's Scattering Experiment



Rutherford observed that -

(i) Most of the α-particles passed through the gold foil undeflected.

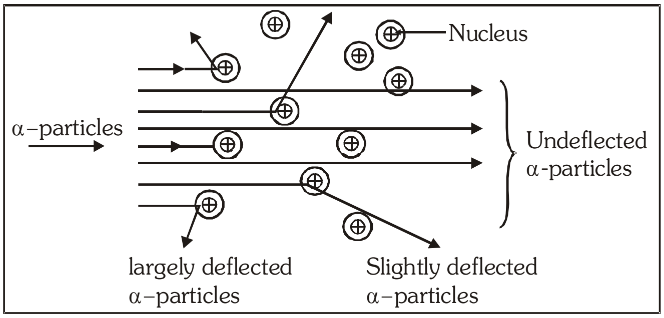
(ii) A small fraction of the α-particles were deflected by small angles.

(iii) A very few α-particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

Following conclusions were drawn from the above observations -

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

(ii) Since few of the 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.



- When α-particles come closer to this point, they suffer a force of repulsion and deviate from their paths.
- 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 or 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 referred to as nucleons. Almost whole of the mass of the atom is contributed by these nucleons. 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^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.

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

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

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

$$R \propto A^{1/3} \qquad \Rightarrow \qquad R = R_0 A^{1/3}$$

Where $R_0 = 1.33 \times 10^{-13}$ cm (a constant) and A = mass number (p + n) and R = radius of the nucleus.

$$\boxed{R = 1.33 \times 10^{-13} \times A^{1/3} \text{ cm}}$$

(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.

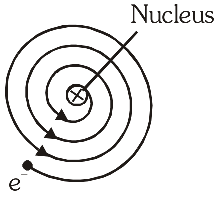
The volume of the atom is about 10^{15} times the volume of the nucleus.

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

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

- 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 the 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.

ATOMIC NUMBER AND MASS NUMBER

(a) Atomic Number

It is represented by Z. The number of protons present in the nucleus is called atomic number of an element.

For neutral atom : Number of electrons = Number of protons

For an ion : Number of electrons = Z – (charge on ion)

Z= number of protons only

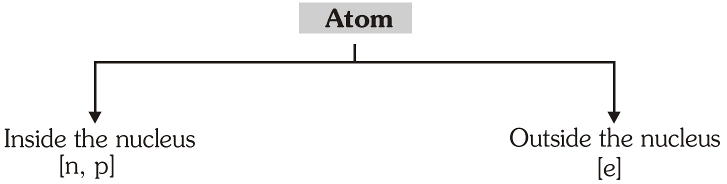
(b) Mass Number

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 neutrons & protons are present in nucleus.

Formula : A = number of protons + number of neutrons

Number of neutrons = A-Z

Note : A is always a whole number.



An atom of the element is represented by $^{A}_{Z}X$

Where, X = Symbol of element

Z = Atomic number = no. of protons = no. of electrons (If atom is neutral)

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

eg. $_{11}Na^+$ ($p \rightarrow 11$) ($e \rightarrow 10$)

$_9F^-$ ($p \rightarrow 9$) ($e \rightarrow 9 + 1 = 10$)

eg. $^{12}_{6}C$
$p \rightarrow 6$
$n \rightarrow 12 - 6 = 6$
$e \rightarrow 6$

$^{16}_{8}O$
$p \rightarrow 8$
$n \rightarrow 16 - 8 = 8$
$e \rightarrow 8$

Mass no. [A] and **atomic weight** (amu= atomic mass unit)

Mass of Proton (m_p)	**Mass of Neutron (m_n)**	**Mass of Electron (m_e)**
1.672×10^{-27} kg	1.675×10^{-27} kg	9.1×10^{-31} kg
1.672×10^{-24} g	1.675×10^{-24} g	9.1×10^{-28} g
1.00727 amu	1.00866 amu	0.000549 amu

Method for Analysis of atomic weight →

eg. $^{12}_{6}C$

$p \rightarrow 6$ Weight of proton = 6×1.00727

$n \rightarrow 6$ Weight of neutron = 6×1.00866

$e \rightarrow 6$ $\dfrac{\text{Weight of electron} = 6 \times 0.000549}{\text{Weight of } ^{12}_{6}C \text{ atom} = 12.099 \text{ amu}}$

Mass no. of $^{12}_{6}C$ atom = 12 [p and n]

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

SOME IMPORTANT DEFINITIONS

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

eg.
- $^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$
- $^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{8}O$
- $^{1}_{1}H$, $^{2}_{1}H$, $^{3}_{1}H$

Explanation 1:

	$^{12}_{6}C$	$^{13}_{6}C$	$^{14}_{6}C$
$p \rightarrow$	6	6	6
$e \rightarrow$	6	6	6
$n \rightarrow$	6	7	8

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

Explanation 2:

	$^{1}_{1}H$ Protium (H)	$^{2}_{1}H$ Deuterium (D)	$^{3}_{1}H$ (Radioactive element) Tritium (T)
$p \rightarrow$	1	1	1
$e \rightarrow$	1	1	1
$n \rightarrow$	0	1	2

- Neutron is not available in Protium
- No. of Nucleons = No. of Neutrons + No. of Protons
  = n + p

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

- If 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 occurence 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.	**^{35}Cl**		**^{37}Cl**
Probability	75%		25%
ratio	3	:	1

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

(b) Isobars

Isobars are the atoms of different 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 $^{3}_{1}H$	$^{3}_{2}He$	**Ex.2** $^{40}_{19}K$	$^{40}_{20}Ca$
p = 1	p = 2	p = 19	p = 20
e = 1	e = 2	e = 19	e = 20
n = 2	n = 1	n = 21	n = 20
p + n = 3	p + n = 3	n + p = 40	n + p = 40

(c) Isodiaphers

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

Ex.1 $^{11}_{5}B$	$^{13}_{6}C$	**Ex.2** $^{15}_{7}N$	$^{19}_{9}F$
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/Isoneutronic Species/Isotonic

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

Ex.1 $^{3}_{1}H$	$^{4}_{2}He$	**Ex. 2** $^{39}_{19}K$	$^{40}_{20}Ca$
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 are the molecules which have the same number of atoms & electrons.

Ex.1	CO_2		N_2O	**Ex.2**	CaO		KF
Atoms	= 1 + 2	Atoms	= 2 + 1	Atoms	= 2	Atoms	= 2
	= 3		= 3	Electrons	= 20 + 8	Electrons	= 19 +9
Electrons	= 6 + 8 × 2	Electrons	= 7 × 2 + 8		= 28 *e*		= 28 *e*
	= 22 *e*		= 22*e*				

(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) = 10 *e*
Ex.3	**BF_3**	**SO_2**
	(5 +9 ×3)=32 *e*	(16 +8 ×2)=32 *e*

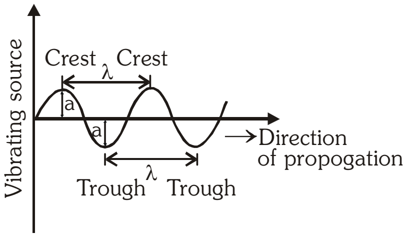
POINTS TO REVISE

- 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.
- Isobars do not have the same value of e/m
- For isotones, $A_1 - Z_1 = A_2 - Z_2$
- For isodiaphers, $A_1 - 2Z_1 = A_2 - 2Z_2$

ELECTROMAGNETIC WAVES (EM WAVES) OR RADIANT ENERGY

According to this theory, the energy is transmitted from 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, gamma rays.

- The radiant energy do not need any medium for propogation.
- The radiant energy have electric and magnetic fields and travel at right angle to these fields.
- The upper most point of the wave is called crest and the lower most point 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 Å (Angstrom), pm (picometre), nm (nanometer), cm(centimetre), m (metre)

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

(2) **Wave number** ($\bar{\nu}$) (nu bar) : It is the reciprocal of the wavelength, that is number of waves present in unit length $\boxed{\bar{\nu} = \frac{1}{\lambda}}$

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. $\boxed{T = \frac{1}{\nu}\text{second}}$

(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 $c = \nu\lambda\,(m\,s^{-1})$

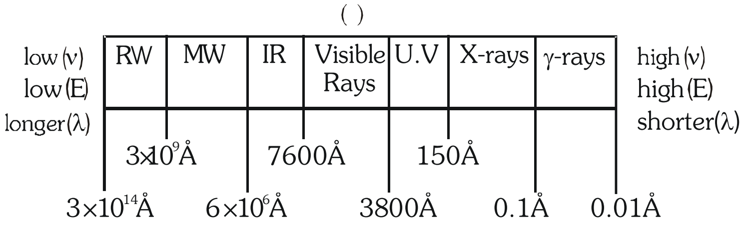
Since c is constants i.e. frequency is inversely propotional to λ

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

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

Electromagnetic spectrum or EM spectrum :

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



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 packets 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 is called as quantum.

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

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

h is proportionality constant or Planck's constant

$h = 6.626 \times 10^{-37}$ kJ s or 6.626×10^{-34} J s 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 a quantum. $\boxed{E = nh\nu = \frac{nhc}{\lambda} = nhc\bar{\nu}}$

where n = Positive integer
= Number of quanta

PHOTOELECTRIC EFFECT :

Hertz in ***1887*** observed that when a light of certain frequency strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is known as **photoelectric effect** and the ejected **electrons** are called **photoelectrons**.

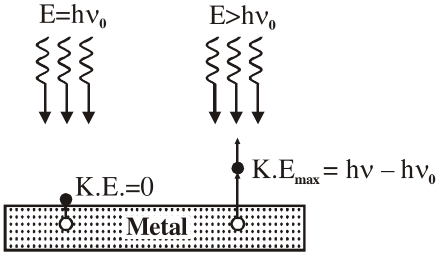
A few metals, which are having low ionisation energy like Cesium, show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light.

The experimental findings are summarized as below :

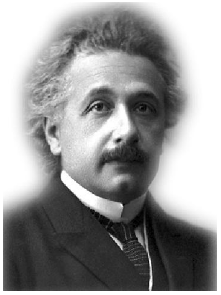
- Electrons come out as soon as the light (of sufficient energy) strikes the metal surface. There is no time lag between the two events.
- The light of any frequency will not be able to cause ejection of electrons from a metal surface. There is a minimum frequency, called the **threshold (or critical)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

Einstein's explanation :

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



This energy enables the electron to break away from the surface by overcoming the attractive influence of the nucleus. Thus each photon can eject one electron. If the frequency of light is less than ν_0 , there is no ejection of electron. If the frequency of light is higher than ν_0 (let it be ν), the photon of this light having higher energy ($h\nu$), will impart some energy to the electron that is needed to remove it away from the atom.



Albert Einstein (1879 - 1955)

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

Einstein proposed that light consisted of quanta, which we call photons with a frequency over a certain threshold would have sufficient energy to eject a single electron, producing the photoelectric effect.

Einstein's Equation for the Photoelectric Effect :

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

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

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

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

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

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

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

v = max. speed of photoelectron.

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

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

Important conclusions from photoelectric effect :

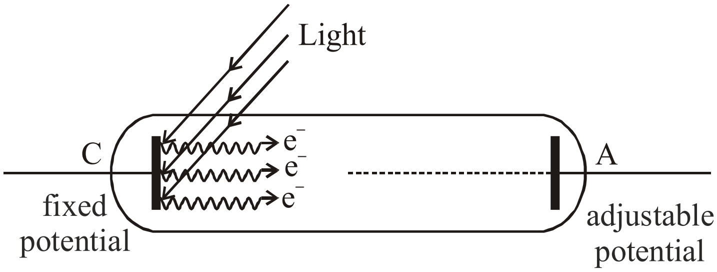
(i) Photoelectric effect demonstrates particle nature of radiation.

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

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

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

SATURATION CURRENT & STOPPING POTENTIAL



Case-I : $V_C = V_A$

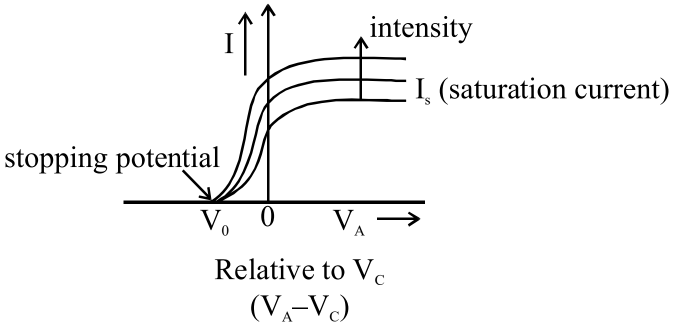
Some of the ejected electrons reach at electrode A resulting photocurrent.

Case-II : $V_C < V_A$

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

Case-III : $V_C > V_A$

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



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

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

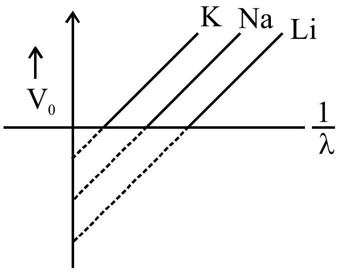
$$(KE)_{max} = eV_0$$

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

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

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

y x



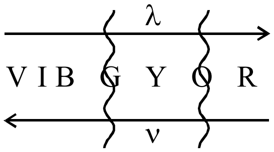
Ex. ***From a metal surface, photoelectron never comes out by orange light but comes from green light. Predict about the injection of photoelectron from the same metal by***

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

Sol: *(i) Red light = No*

(ii) Blue light = Yes

(iii) Yellow light = Can't say



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

Sol: $E = \frac{1240}{200} = 6.2\text{eV}$

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

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

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

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

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

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

$2E_1 = E_2$

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

Ex. ***A photon of wavelength 3000 Å strikes a metal surface, the work function of the metal being 2.20 eV. Calculate (i) the energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and (iii) the velocity of the photo electron.***

Sol. (i) Energy of the photon

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

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

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

(ii) Kinetic energy of the emitted photo electron

Work function $= 2.20$ eV

Therefore, KE $= 2.475 - 2.20$

$= 1.925\text{ eV} = 3.08 \times 10^{-19}\text{ J}$

(iii) Velocity of the photo electron

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

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

BOHR'S ATOMIC MODEL

Some Important formulae :

- This model was based on quantum theory of radiation and classical laws of physics.
- Bohr model is applicable only for single electron species like H, He^+, Li^{2+} etc.
- Bohr model is based on particle nature of electron.

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

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

Angular momentum = mvr

Important postulates :

1st Postulate :

- Atom has a nucleus where all protons and neutrons are present.
- The size of nucleus is very small and it is present at the centre of the atom.

2nd Postulate :

- Negatively charged electron revolve around the nucleus in the same way as the planets revolve around the sun.
- The path of electron is circular.
- 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 :

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

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

h = Planck's constant

π = Constant

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

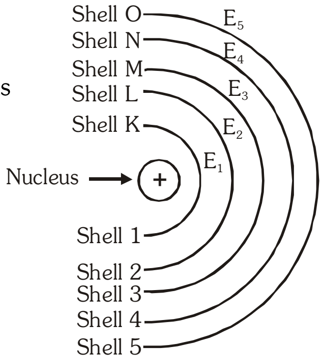
4th Postulate :

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

5th Postulate :

- 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



- 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

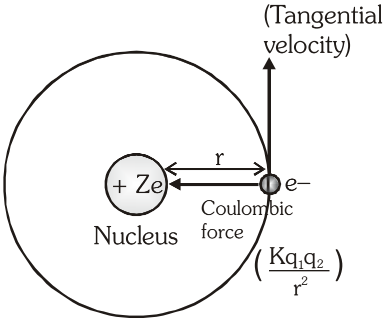
$$\boxed{\Delta E = E_{higher} - E_{lower} = E_{n_2} - E_{n_1}} = \text{Energy of a quantum}$$

$$= h\nu = \text{Bohr's frequency condition}$$

- Energy is absorbed when electron jumps from inner to outer orbit and is emitted when electron moves from outer to inner orbit.
- $n_2 > n_1$ whether emission or absorption of energy will occur.

APPLICATION OF BOHR'S MODEL

(A) Radius of Various Orbits (Shell)



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

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

Where K = $9 \times 10^9\ \text{Nm}^2/\text{coulomb}^2$

As we know – Coulombic force = Centrifugal force

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

As we know –

$$mvr = \frac{nh}{2\pi} \quad \text{or} \quad v = \frac{nh}{2\pi mr} \quad ....(2)$$

Putting the value of v from eq^n.(2) to eq^n.(1)

$$\left(\frac{nh}{2\pi mr}\right)^2 = \frac{KZe^2}{mr} \quad \text{or} \quad \frac{n^2h^2}{4\pi^2m^2r^2} = \frac{KZe^2}{mr}$$

$$\boxed{r = \frac{n^2h^2}{4\pi^2 mKZe^2}} \quad ....(3)$$

Putting the value of π, h, m, K, & e (Constants) in the above eq^n. (3)

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

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

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

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

Putting the value of Angular momentum

$$mvr = \frac{nh}{2\pi} \qquad \text{or,} \qquad KZe^2 = \frac{nh}{2\pi}(v)$$

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

Putting the value of π, k, e & h $\boxed{v = 2.188 \times 10^6 \frac{Z}{n} \text{m/s}}$

(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. E = K.E.+ P.E.

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

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

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

Putting the value of r from eq. (3)

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

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

$$\boxed{E_n = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} \text{ J/atom}} \qquad \text{or} \qquad \boxed{E_n = -13.6 \times \frac{Z^2}{n^2} \text{ eV/atom}}$$

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 quantised.

The –ve sign indicates that the electron 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.

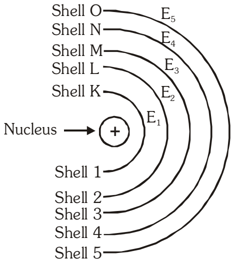
Conclusion : $\boxed{P.E = (-)2KE}$ $\boxed{KE = (-)E}$ $\boxed{P.E = 2E}$

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 Definations :-

(i) Ionization energy : Minimum amount of energy required to liberate an 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.
$n_1 = 2, 3, 4, 5, ...$; $n_2 = \infty$

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

Note : All these kinds of energy are always positive.

POINTS TO REVISE

- 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: $E_n = E_H \times \frac{1}{n^2}$

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

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 given radiation

Classification of Spectrum

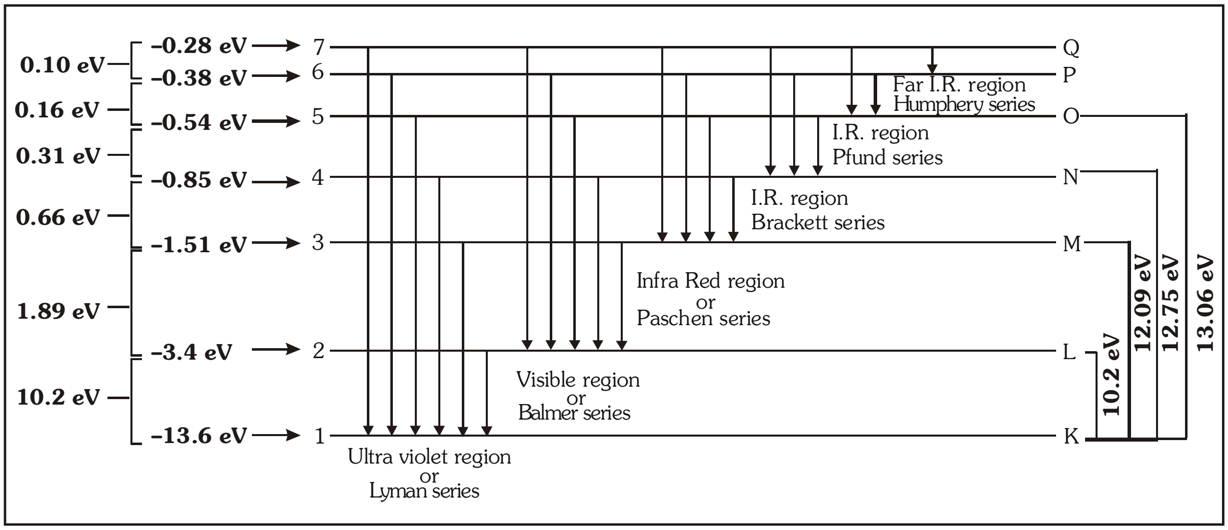
(1) Emission

(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 lines is obtained.The wavelength of various lines show that spectrum lines lie in Visible, Ultraviolet and Infra red region. These lines are grouped into different series.

Series	**Discovered by**	**regions**	$n_2 \to n_1$	**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

- First line / Starting line / Initial line ($\lambda_{max.}$ and ν_{min})
- Last line / limiting line / marginal line (λ_{min} and $\nu_{max.}$)
- First line of any series = α line

  Second line of any series = β line

  Third line of any series = γ line

Calculation of number of spectral lines

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

Where : n_2 = higher energy level; n_1 = lower energy level

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 level, n_1 = Fixed lower energy level of each series.

RYDBERG FORMULA

In 1890, Rydberg gave a very simple theoretical equation for the calculation of the wavelength of 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 cm^{-1} = 109700 cm^{-1} = 10970000 m^{-1} = 1.1×10^7 m^{-1}

$$\frac{1}{R} = 9.12 \times 10^{-6} \text{ cm} = 912 \text{ Å}$$

Derivation of Rydberg formula :

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

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

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

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

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

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

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 $\frac{nh}{2\pi}$, has not been explained by Bohr's theory.

(3) Bohr inter related quantum theory of radiation and classical laws of physics without any theoritical 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)

WAVE MECHANICAL MODEL OF AN ATOM

This model consists of following

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

(B) Heisenberg's Uncertainity 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 also for the matter.

(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.

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

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

(3) The above relation can be proved 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.

$\because$ $E = h\nu = h \times \frac{c}{\lambda}$ (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 a 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 $2\pi r = \frac{nh}{mv}$ ($\because$ mv = p momentum)

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

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

(5) $\because$ $2\pi r = \frac{nh}{mv}$ or $mvr = \frac{nh}{2\pi}$ $\because$ 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.

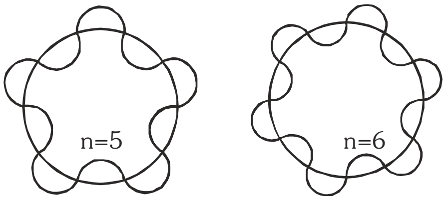


figure : Similarity between de-Broglie waves and Bohr's orbit

(B) HEISENBERG UNCERTAINITY PRINCIPLE

Bohr's theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de-Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electon 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 uncertainity 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 uncertainity in measurement of position, (Δx), and the uncertainity in momentum (Δp) are related by Heisenberg's relationship as

$$F \times \Delta t \times \Delta x \geq \frac{h}{4\pi} \quad \text{or} \quad \boxed{\Delta E \times \Delta t \geq \frac{h}{4\pi}}$$

where h is Planck's constant.

(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.

POINTS TO REVISE

- **de-Broglie wavelength in terms of kinetic energy.**

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

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

- **When a charged particle carrying Q coulomb charge is accelerated by applying potential difference of V volts, then :-**

K.E. = $Q \times V$ Joule

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

- The wave nature of electron was verified experimentally by Davisson and Germer.
- de-Broglie hypothesis is applicable to macroscopic as well as microscopic objects but it has no physical significance for macroscopic objects.
- Remember $\boxed{\frac{h}{4\pi} = 0.527 \times 10^{-34}\ \text{J sec}}$

QUANTUM 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) → Shell (Orbit)
(b) Azimuthal quantum number (ℓ) → Sub shell
(c) Magnetic quantum number (m) → Orbital
(d) Spin quantum number (s) → Spin of electron

(a) Principal Quantum Number (n)

Given By → Bohr

- It represents the name and energy of the shell to which electron belongs and size of orbital.
- 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.

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

$$r_1 < r_2 < r_3 < r_4 < r_5 - - - - - - - - -$$

- Greater the value of n, greater is the energy of shell

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

$$E_1 < E_2 < E_3 < E_4 - - - - - - - -$$

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

$$v_1 > v_2 > v_3 \ldots\ldots\ldots\ldots$$

- 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 $2n^2$

(b) Azimuthal quantum number / Angular quantum number / Secondary quantum number / Subsidiary quantum number (ℓ)

Given by – Sommerfeld

- It represents the name of the subshell, shape of orbital and orbital angular momentum
- Possible values of 'ℓ' are :-

  i.e ℓ = 0,1,2 – – – – – – – – – (n–1)

  ℓ = 0(s Subshell)

  ℓ = 1(p Subshell)

  ℓ = 2(d Subshell)

  ℓ = 3(f Subshell)
- Value of ℓ lies between 0 to (n – 1) in a particular n^{th} shell :-

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

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

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

  If n = 4 then ℓ = 0,1,2,3 $\Rightarrow$4s,4p, 4d, 4f i.e. in n =4 shell, four subshell 's' , 'p' , 'd' & 'f' are present.
- If the value of n is same then the order of energy of the various subshell will be

  s < p < d < f [valid only for multi-electron species]

  Ex. 4s < 4p < 4d < 4 f, 3s < 3p< 3d, 2s < 2p
- If Value of ℓ 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 = $\sqrt{\ell(\ell+1)}\ \frac{h}{2\pi}$ or $\sqrt{\ell(\ell+1)\hbar}$ $\left\{\because \hbar = \frac{h}{2\pi}\right\}$ { $\hbar$ is called as 'hash' }

  Orbital angular momentum : For s subshell = 0

  For p subshell = $\sqrt{2}\frac{h}{2\pi}$ or $\sqrt{2}\ \hbar$
- The number of electrons in a particular subshell is equal to $2(2\ell+1)$

  for s subshell number of electrons = 2 e^-

  for p subshell number of electrons = 6 e^-

  for d subshell number of electrons = 10 e^-

  for f subshell number of electrons = 14 e^-
- Shape of the orbital : s → spherical

  p → dumb bell shape

  d → double dumb bell shape

  f → complex shape

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

Given by linde

- It represents 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)

  Magnetic quantum number describe these different distributions of electron cloud.
- Value of m = all integral value from – ℓ to + ℓ including zero.

  i.e. Value of m = – ℓ to + ℓ

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

$= \Psi_{n,\ell,m}$

Ex. 1 : $2p_x$; $n=2$, $\ell=1$, $m=-1$ or $m=+1$

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

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

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

Total numbers of nodes = $\boxed{n-1}$

They are of 2 types.

(i) Radial nodes / Spherical nodes / Nodal surface $\boxed{\text{number of radial nodes} = n-\ell-1}$

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

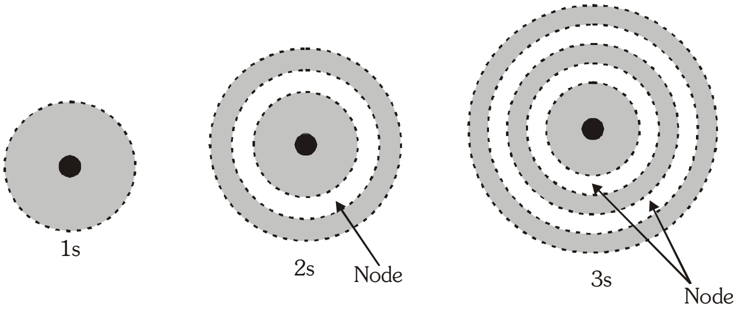
* Nucleus and ∞ (infinite) are not considered as node.

Types of orbitals :

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

Shapes of s-orbitals :

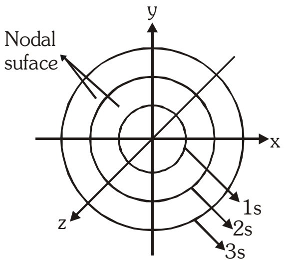
The s-orbitals are spherically symmetrical about the nucleus, i.e., the probability of finding electron is same in all directions from the nucleus. The size of the orbital depends on the value of principal quantum number. The 1s orbital is smaller than 2s-orbital and 2s-orbital is smaller than 3s, but 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 finding 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 surface or simply 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 inreases, i.e., the size and energy of s-orbital increases in the order $1s < 2s < 3s$ ....



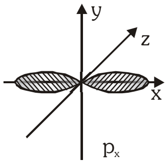
The s orbital of higher energy levels are also symmetrically spherical and can be represented as above

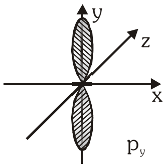
Case-II : If $\ell = 1$ (p - subshell) then $m = \begin{array}{c|c|c} -1 & 0 & +1 \\ \hline p_x & p_z & p_y \end{array}$

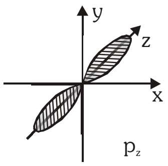
It implies that, p subshell have three orbitals called as p_x, p_y and p_z.

Shape of p-orbitals :

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

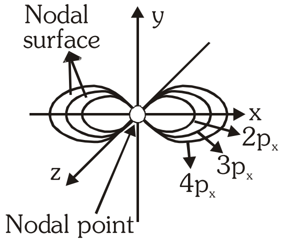
- Each p orbital has dumb bell shape (2 lobes which are separated from each other by a point of zero probability called nodal point or node or nucleus).
- The two lobes of each orbital are separated by a plane of zero electron density called nodal plane.
- Each p orbital of higher energy level are also dumb bell shape but they have nodal surface.

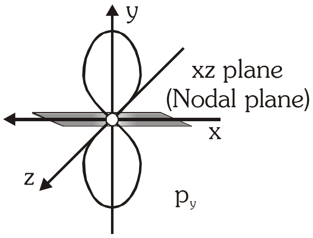
Nodal surface :

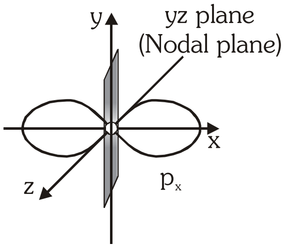
Orbital	Nodal surface
3 p_x	1
4 p_x	2
np_x	(n – 2)

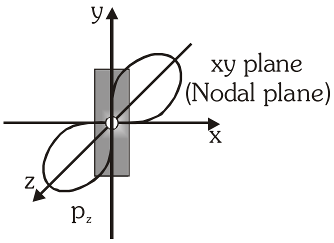
Nodal Plane :

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







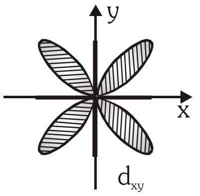


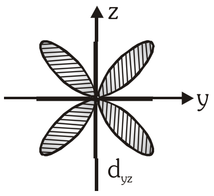
Case III When $\ell = 2$, 'm' has five values – 2, –1, 0, +1, +2. It implies that d subshell of any energy shell has five orbitals. All the five orbitals are not identical in shape. Four of the d orbitals d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ contain four lobes while fifth orbital d_{Z^2} consists of only two lobes. The lobes of 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 are lying along z axis and contain a ring of negative charge surrounding the nucleus in xy plane. Geometry of d orbital is double dumbbell

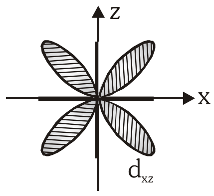
$$m = \left|\begin{array}{c|c|c|c|c} -2 & -1 & 0 & +1 & +2 \\ d_{xy} & d_{yz} & d_{z^2} & d_{zx} & d_{x^2-y^2} \end{array}\right|$$

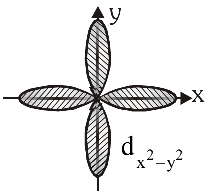
Shape of d–orbitals :

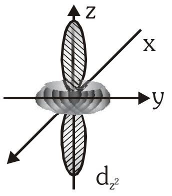
It implies that d subshell has 5 orbitals i.e. five electron cloud and can be represented as follows





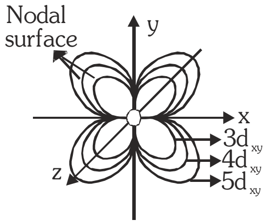






Each d-orbital of higher energy level also have double dumbbell shape but they have nodal surface.

In d-orbitals :



(i) Nodal Point → 1

(ii) Nodal Surface → $3\ d_{xy} \rightarrow 0$ Nodal surface
$4\ d_{xy} \rightarrow 1$ Nodal surface
$5\ d_{xy} \rightarrow 2$ Nodal surface
$n\ d_{xy} \rightarrow (n-3)$

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

(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 :
$d_{z^2} \rightarrow 0$, nodal plane :

Note: Orbitals of d subshell are equivalent in energy.

(d) Spin Quantum number (s) :

Given by **Goudsmit** and **Uhlenbeck**

- It represents the direction of electron spin around its own axis
- For clockwise spin/spin up(↑) electron → $\pm\frac{1}{2}$
- For anti-clockwise spin/spin down(↓) electron → $\mp\frac{1}{2}$

Spin angular momentum of an electron = $\sqrt{s(s+1)}.\dfrac{h}{2\pi}$ or $\sqrt{s(s+1)}\,\hbar$

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

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

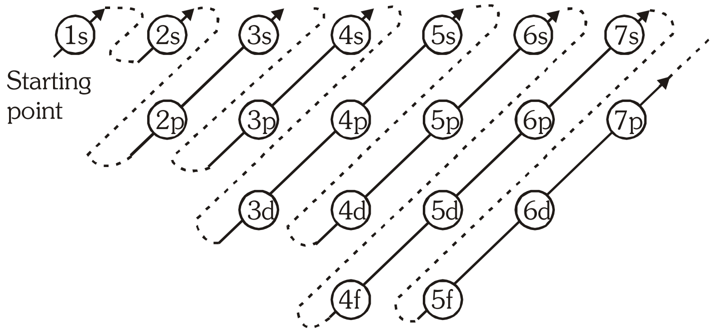
RULES FOR FILLING OF ELECTRONS

(a) Aufbau Principle
(b) ($n+\ell$) rule
(c) Hund's maximum multiplicity principle
(d) Pauli's exclusion principle

(a) Aufbau Principle

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

- Aufbau principle gives a 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.



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

For Example

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

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

- $_{26}Fe \rightarrow 1s^2\ \underbrace{2s^2 2p^6}_{(n-2)}\ \underbrace{3s^2 3p^6 3d^6}_{(n-1)}\ \underbrace{4s^2}_{n}$

n → Outer most Shell or Ultimate Shell or Valence Shell

In this Shell electrons are called as Valence electrons or this is called core charge

(n–1) → Penultimate Shell or core or pre valence Shell
(n–2) → Pre Penultimate Shell

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

Ex. $_{26}Fe \rightarrow \underbrace{1s^2 2s^2 2p^6 3s^2 3d^6 3p^6}_{\text{Kernel}}\ 4s^2$

(b) (n + ℓ) 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 +ℓ) value for a given subshell.

Principle of (n+ℓ) rule :

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

In case of H-atom :

Energy only depends on principal quantum number

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

Sub Shell	n	ℓ	n +ℓ	
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 : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}$, ...

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

- This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called degenerate orbitals).
- It states : pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.
- Since there are three p, five d and seven *f* orbitals, therefore, the pairing of electrons will start in the p, d and *f* orbitals with the entry of 4th, 6th and 8th electron, respectively.

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

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

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

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

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

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

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

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

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

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

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

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

(d) Pauli's Exclusion Principle

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

Ex.1. $^{12}_{6}C \rightarrow$

	$1s^2$	$2s^2$	$2p^2$
	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow}\boxed{\uparrow}\boxed{}$
n =	1	2	2
ℓ =	0	0	1
m =	0	0	+ 1, 0, –1
s =	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, +\frac{1}{2}$

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

	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$
	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}$	$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$
n =	1	2	2	3	3
ℓ =	0	0	1	0	1
m =	0	0	+1,–1, 0	0	+1,–1, 0
s =	$+\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},-\frac{1}{2}\ +\frac{1}{2},-\frac{1}{2}\ +\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},-\frac{1}{2}$	$+\frac{1}{2},-\frac{1}{2}\ +\frac{1}{2},-\frac{1}{2}\ +\frac{1}{2}$

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 reason behind this is that half filled & full filled subshell have got extra stability.

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

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

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

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

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

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

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

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