CHAPTER 2

ATOMIC STRUCTURE

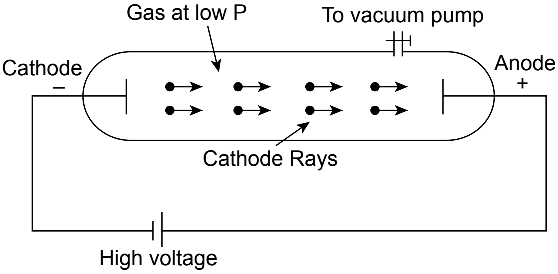
2.1 DALTON'S ATOMIC THEORY

This theory was proposed by **John Dalton** in **1803**. The important features are listed below:

(i) Atom is the basic unit of all the elements and molecules.
(ii) Atom is indivisible.
(iii) It can neither be created nor be destroyed.
(iv) Atoms of different elements differ in terms of their atomic masses due to which their properties differ from each other.

2.2 DISCOVERY OF CATHODE AND ANODE RAYS

Cathode rays were discovered by William Crookes with the help of a discharge tube, which was invented by Julius Plucker.



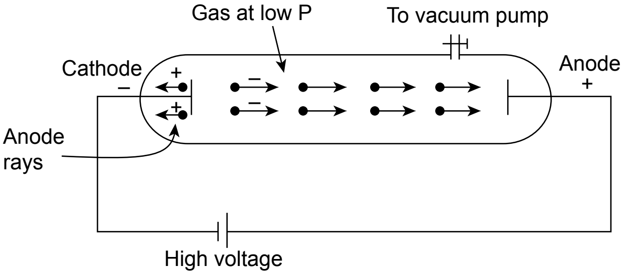
Discharge tube

- Colour of light depends upon the nature of a gas in the discharge tube.
- The value of **e/m** for cathode rays = 1.76×10^8 coulombs/gm.
- The fluorescence was caused due to the bombardment of the walls of the tube by rays emanating from cathode. So, they are called as **cathode rays**.

Properties of cathode rays:

(i) They travel in a straight line.
(ii) They have heating effect.
(iii) They consist of material particles because they can rotate light paddle wheel.
(iv) They are deflected towards +ve plate when an electric field is applied. It shows that they are –vely charged.
(v) When a magnetic field is applied perpendicular to the path of cathode rays, they get deflected in the direction expected for –ve particles.
(vi) They can ionise the gas through which they pass.
(vii) They can produce X-rays.
(viii) They can penetrate through thin metal foils.
(ix) The e/m ratio for the particles in the cathode is independent of the nature of the gas taken in the discharge or the nature of the cathode.

Anode or cathode rays: Anode rays were discovered by **Goldstein** in **1886**. He used a perforated cathode in the discharge tube.



Discharge Tube

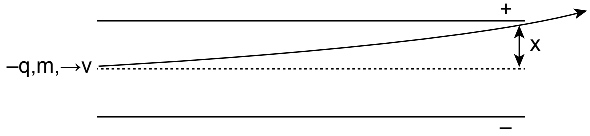
For anode rays, **e/m** = 9.58×10^4 coulombs/g.

Properties of anode rays:

(i) They travel in a straight line.
(ii) They show heating effect.
(iii) They consist of material particles.
(iv) In an electric field, they are deflected towards –ve charged plate. Hence, they are positively charged.
(v) In a magnetic field, they are deflected in the direction expected for +ve particles.
(vi) They can ionize the gas through which they pass.
(vii) They can produce X-rays.
(viii) They can penetrate through thin metal foils.
(ix) e/m ratio of anode rays is independent from the nature of anode but it depends upon the nature of gas taken in the discharge tube.

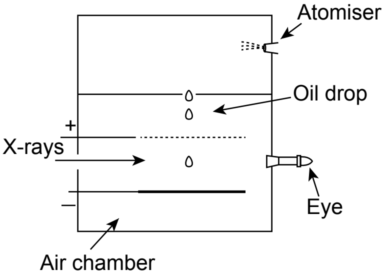
2.2.1 Determination of the Ratio of Charge to Mass (e/m) of Electron

When a charge particle of charge (q) and mass (m) moves through an electric field region of intensity (E), then specific charge of particle $\frac{q}{m} = \frac{2 \times v^2}{E\ell^2}$, where v is velocity of particles, x is vertical deflection between electrical plate and l is length of electrical region with intensity (E) velocity of particle $(V)=\frac{E}{B}$. Where B is magnetic field intensity and specific charge $\left(\frac{q}{m}\right)=\frac{2\times E}{B^2\ell^2}$.



2.3 MILLIKAN'S OIL DROP EXPERIMENT

This experiment was performed by **R. E. Millikan** in **1909** for the determination of charge on a particle. If a spherical oil drop is moving with constant velocity (v) through air with coefficient of viscosity (η), then radius of oil droplet $r=\sqrt{\frac{9\eta v}{2(\rho-\rho_0)}}$. However, when thin oil droplet is passed through an electric field, then charge on oil drop $q=\frac{18\pi}{E}\sqrt{\frac{\eta^3v^3}{2(\rho-\rho_0)g}}$



$$e=\frac{18\pi}{nE}\sqrt{\frac{\eta^3v^3}{2(\rho-\rho_0)g}}\quad \because q=ne$$

S. No.	Fundamental Particles	Mass	Charge	Discoverer
1.	Electron (e^-)	9.1×10^{-31} kg	-1.6×10^{-19}C	J. J. Thomson
2.	Proton (P)	1.672×10^{-27} kg	$+1.6\times10^{-19}$C	Goldstein
3.	Neutron (n)	1.675×10^{-27} kg	0	Chadwick

Note:

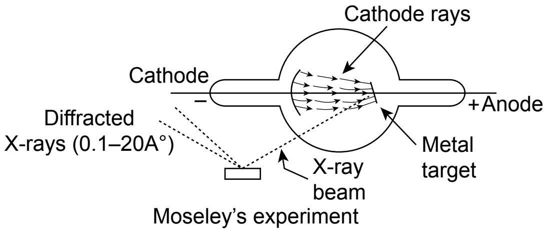
In this experiment X-rays are used to ionize the molecule of air so that electrons freed from air molecule may stick to oil droplets to make droplets electrically sensible.

2.4 DISCOVERY OF ATOMIC NUMBER

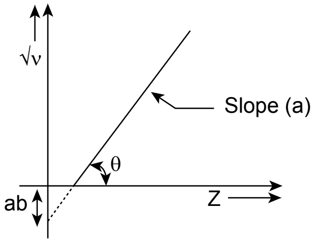
He observed that the frequency of a particular spectral line gradually increased with the increase of atomic mass of the element. But it was soon realized that the frequency of the particular spectral line was more precisely related with serial number of the element in the periodic table which he termed as **atomic number** (**z**).

$\sqrt{\nu}$ = **a(z – b);** where ν is frequency of spectral line, a is slope of line in plot between $\sqrt{\nu}$ and **z** and ab is intercept made by line on $\sqrt{\nu}$ axis.

The term **atomic number** was given by **H. G. J. Moseley** in **1912–1913**. To perform this, he considered gas discharge tube in which he took variety of **metal targets** (**anode**) starting from aluminium metal and ending with gold.



Moseley's experiment

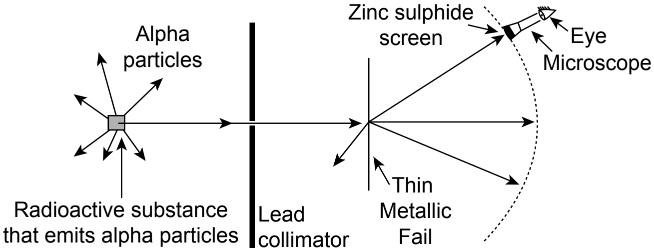


2.5 RUTHERFORD'S ATOMIC MODEL

2.5.1 Rutherford's Experiment (1908–1909)

Observation:

(i) Most of the α particles passed through the metal foil straight without any deflection.
(ii) Some of them (1 per cent) got deflected at different angles.
(iii) About 1 out of 8000 α particles got deflected at 180°.



2.5.2 Rutherford's Nuclear Atomic Model (1911)

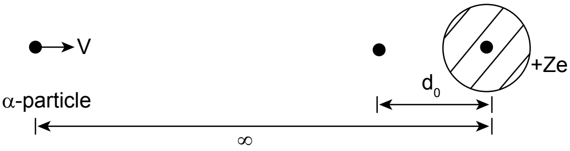
(i) Most of the inner part of an atom is empty.
(ii) All protons are accumulated at the centre of the atom in a very small volume called **nucleus**. Nucleus is a highly charged body which contains almost entire mass of the atom.
(iii) The electron are present in the **extra-nuclear space** and are not stationary but move with high velocity under the influence of the centripetal force (CPF). Due to this motion, the centrifugal force (CFF) is also developed which according to Rutherford counter balances the CPF. Therefore, electron follows a circular path called **orbit**.

2.5.3 Significances of Rutherford's Atomic Model

2.5.3.1 Calculation of distance of closest approach or effective nuclear radius

Effective nuclear radius or **distance of closest approach** is defined as that radius of the sphere or spherical region around the nucleus from where the α-particles gets deflected.

$\therefore$ Distance of closest approach, $d_0 = \dfrac{4ze^2}{4\pi\varepsilon_0 mv^2} = \dfrac{ze^2}{\pi\varepsilon_0 mv^2} = \dfrac{1}{4\pi\varepsilon_0}\dfrac{2ze^2}{KE}$



2.5.3.2 Calculation of radius of nucleus

In an atom, the radius of nucleus is proportional to the cube root of the number of nucleons within it.

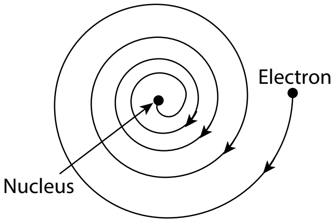
$R = R_0 A^{1/3}$cm; where $R_0 = 1.33 \times 10^{-13}$cm,
A = number of nucleons or mass number, and
R = radius of the nucleus.

2.5.3.3 Number of a particles striking at an angle θ

$N(\theta) \propto \dfrac{z^2}{\sin^4(\theta/2)}$; $N(\theta)$ = Number of α-particles per unit area that reach the screen at a scattering angle of θ.

2.5.4 Demerits of Rutherford's Atomic Model

Clark Maxwell's Theory: According to **Clark Maxwell,** when a moving charged particle is subjected to acceleration, it always loses energy in the form of electromagnetic radiations.



1. In Rutherford's model, an electron moves in circular orbits. Being a charged particle, it should lose energy as it is continuously subjected to acceleration. If this happens, e^- should start moving in smaller orbits and should finally hit the nucleus. This will make an atom unstable. However, an atom is stable suggesting that the Clark Maxwell law is not valid.
2. The spectrum was found to be discontinuous.
3. What is the cause of origin of spectrum?

2.6 QUANTUM THEORY

Quantum theory was given by **Max Planck** in **1901**. He developed this theory to explain the mode of **absorption** and **emission** of energy by black bodies. Later on, Einstein said that this theory is of general applicability. The important points are summarized hereunder.

Note:

*Einstein gave another name **photon** for quanta. One photon is equal to $h\nu$.*

(i) The absorption or emission of energy is a discontinuous process.

(ii) The energy is absorbed or emitted in the form of massless bundles. The energy associated with each bundle is known as one quanta and is given by $E = h\nu$; where h = Planck's constant; ν = frequency of radiation absorbed or emitted.

(iii) The energy can never be absorbed or emitted in fractions. It is absorbed or emitted either as $h\nu$ or its +ve integral multiples, $E = nh\nu$; (where n = 1, 2, 3,......).

2.7 BOHR'S ATOMIC MODEL

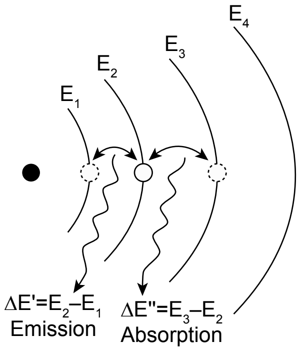
2.7.1 Bohr's Atomic Model

In **1913**, **Bohr** applied **quantum theory** on atoms and gave the following postulates.

1. Electrons follow a circular path called **orbit**.
2. An atom may contain many circular orbits. Each orbit is associated with **quantized** (i.e., fixed) amount of energy. Some orbits are of special kind and are known as '**stationary states**'. An electron prefers to be in the stationary state because then its energy does not change.
3. The angular momentum of an electron moving in a circular orbit is quantized and is given by

   $mvr = n\frac{h}{2\pi}$; where h = Planck constant, n = Principal quantum number.

   The angular momentum generates orbital energy of an electron. Since mvr is quantized the orbital energy of an electron will also be quantized (i.e., fixed) and different for different orbits.
4. An electron may change its energy by changing its original circular orbit. This electron may achieve by **absorbing** or **emitting** a quantized amount of energy.



2.7.2 Significances or (Merits) of Bohr's Atomic Model

2.7.2.1 The radius of the orbits or the size of the atom

$$r = \left[\frac{(4\pi\varepsilon_0)h^2}{4\pi^2 me^2}\right]\frac{n^2}{z} = \frac{n^2}{z} x a_0 \text{ ; where n = 1, 2, 3, ...}$$

where a_0 is Bohr radius having the value 0.529 Å.

2.7.2.2 Velocity of the electron

$$V_n = \left[\frac{2\pi e^2}{4\pi\varepsilon_0 h}\right]\frac{z}{n} = V_0\frac{z}{n} \text{ ; where } V_0 \text{ is Bohr velocity having the value } 2.18 \times 10^6 \text{ m/second.}$$

2.7.2.3 Frequency of revolution

$$f = \left(\frac{me^4}{4\varepsilon_0{}^2 h^3}\right)\frac{z^2}{n^3} = f_0 = \frac{z^2}{n^3} = 6.56\times10^{15}\frac{z^2}{n^3} \text{ revolution/second}$$

2.7.2.4 Energy of the electron

Let E_k and E_p be the kinetic energy and the potential energy respectively of the electron in the nth orbit. Then, the total energy is equal to the sum of E_k and E_p,

$$\text{i.e., } E_n = E_k + E_p - \left[\frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 h^2}\right]\frac{z^2}{n^2} = -2.18\times10^{-18}\left(\frac{z^2}{n^2}\right)\frac{J}{\text{atom}} = -13.6\left(\frac{z^2}{n^2}\right)\frac{eV}{\text{atom}}.$$

3.827×10^{-20} cal = 1eV = 1.602×10^{-19}J
1 cal = 4.184 J = 2.61×10^{19} eV
1 ev/atom = 96.485 kj/mol

2.8 ELECTRONIC SPECTRUM

(i) **Emission spectra**: When the light emitted from some source is directly passed on to a prism and then observed on a photographic film after dispersion, the resultant spectrum is called emission spectrum.

(ii) **Types of emission spectra:** If the source of light emits white light, e.g., sun or bulb, the spectrum consists of seven bands of colours (VIBGYOR) lying continuously and the specturm is called continous spectrum. If some volatile salt is placed in a Bunsen flame or electric discharge is passed through a gas at low pressure and the light emitted is resolved through a prism, the spectrum consists of a number of bright lines against a dark background and is called line spectra or atomic spectra.

(iii) **Absorption spectra:** When white light is passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, some dark lines are observed in the otherwise continuous spectrum at the background. The spectrum thus observed is called absorption spectrum. These dark lines are observed at the same wavelengths where coloured lines were obtained in the emission spectrum of the same substance.

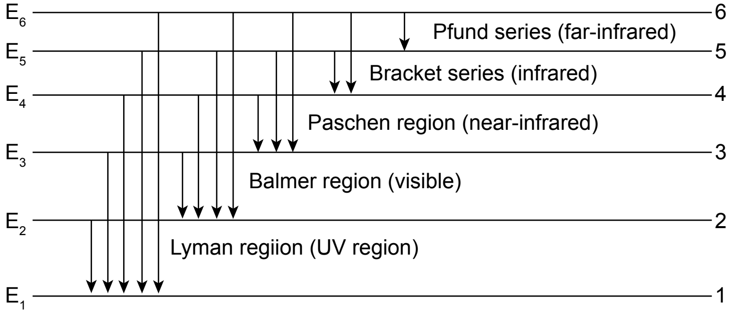
(iv) Every element gives a characteristic line spectrum differing from line spectra of all other elements. Hence, it is like a finger print of the element.

(v) In case of atoms, the energies are emitted or absorbed during electronic transition only thereby giving lines in the spectrum. Hence, their spectrum is called line spectrum or atomic spectrum. In case of molecules energies are absorbed for rotational, vibrational and electronic transition thereby producing groups of lines called bands and their spectrum is called band spectrum.

2.8.1 Line Spectrum of Hydrogen

(i) The line spectrum of hydrogen consists of Lyman, Balmar, Parchen, Bracpet, Pfund and Humphrey series. The first series lies in the ultraviolet region, the second in the visible region, the next two in the infrared region and the last two in the far-infrared region.

(ii) Rydberg's formula for calculation of wave number of lines in the hydrogen spectrum is R and is called Rydberg constant and its value is 109677 cm^{-1}.



Note:

1. *Total number of spectral lines obtained from any energy laval n to ground state = n(n – 1)/2.*
2. *Total number of spectral line between any two energy state* $n_1 \text{ and } n_2 = (n_2 - n_1)\frac{(n_2 - n_1 + 1)}{2}$.
3. *In any series, first line = transition from* $(n_1 + 1) \rightarrow n_1$, *also called* α*-line, second line = transition from* $(n_1 + 2) \rightarrow n_1$, *also called* β*-line and so on. e.g., In Lyman series a-line = 2 ⟶ 1; b-line = 3 ⟶ 1; g-line = 4 ⟶ 1.*

Determination of wavelength of transition:

When the electron in the initial stationary orbit of PQN (n_1) jumps to the another stationary orbit of PQN(n_2), then the difference in energy

$$\Delta E = E_{n_2} - E_{n_1} = -\frac{2\pi^2 me^4 z^2}{(4\pi\varepsilon_0)^2 h^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$\Delta E = \frac{2\pi^2 me^4 z^2}{(4\pi\varepsilon_0)^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{hc}{\lambda} = hc\bar{\nu}$$; where $\bar{\nu}$, is wave number.

$$\Rightarrow \quad \bar{\nu} = \frac{1}{\lambda} = R_H z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$ is **Rydberg's equation**.

where $\frac{me}{8\ \ ^2h^3c}$ = 1.097373 × 10^7 m^{-1}, is known as **Rydberg's constant**.

Experimental value of **$R = 1.096768 \times 10^7$ m^{-1}**, is known as **Ritz constant**.

Thus, there is very good agreement between the Rydberg and Ritz constants and this also support the postulates of Bohr.

2.8.2 Determination of Ionization Potential (IP) or Ionization Energy (IE)

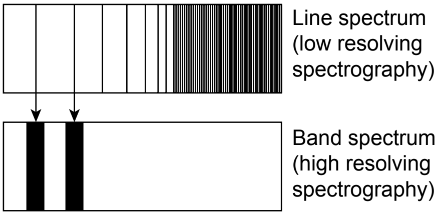
Ionization energy (IE) or ionization potential is defined as the amount of energy required to remove the **most loosely bound electron** from an **isolated gaseous atom** of an element. The lesser the ionization energy, the greater is the ease of the formation of a cation.

In an atom there are **infinite number of orbits**. To remove an electron from an atom means to send electron in infinite number of orbits i.e., $\mathbf{n_2} = \infty$.

$$\Rightarrow \quad \textbf{IP or IE} = \mathbf{E} = \frac{R_H hcz^2}{n_1^2} = \frac{2.18\times10^{-18} z^2}{n_1^2}\frac{\text{J}}{\text{atom}} = \frac{13.6z^2}{n_1^2}\frac{\text{eV}}{\text{atom}}$$

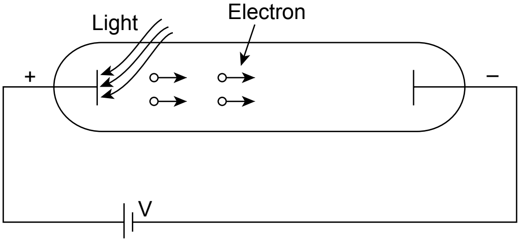
2.9 DEMERITS OF BOHR'S ATOMIC MODEL

1. When the energy of electron present in a **multielectron system** was determined with the help of Bohr's postulate, it was found to be not in agreement with experimental values. It means that **Bohr theory is applicable only for the system containing only one electron. e.g., H, He^+, Li^{++}, etc**.
2. According to Bohr, an electron follows a fixed path, i.e., a circular orbit. If this is true, then position and velocity both can be determined simultaneously with high degree of accuracy. This is against the **Heisenberg's uncertainty principle**, according to which an electron never follows a fixed path.
3. Bohr's theory failed to explain the **directional nature of a covalent bond** and hence the shape of the covalent molecules.
4. Bohr's theory failed to explain the **band** (or **fine**) **spectrum** of hydrogen.
5. Bohr's theory could not explain the splitting of lines of (**Zeeman effect**) and influence of an electric field **(Stark effect**).



2.10 PHOTOELECTRIC EFFECT

Emission of an electron from a metal surface when exposed to light radiations of appropriate wavelength is called **photoelectric effect**. The emitted electrons are called **photoelectrons**.



According to Einstein: Theroy of photoelectric an effect maximum KE of ejected electron = absorbed energy – work function.

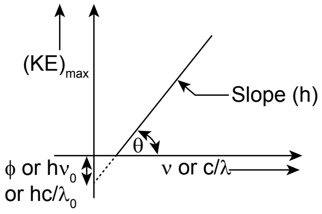
$\Rightarrow \quad (KE)_{max} = h\nu - \phi$

$$KE_{max} = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right];$$

where ν_0 and λ_0 are threshold frequency and threshold wavelength respectively.

2.10.1 Work Function or Threshold Energy

It may be defined as the **minimum amount of energy** required to eject electrons from a metal surface. It is represented by ϕ. The energies of electrons liberated by light depend on the frequency of the light.



2.10.2 Stopping Potential

The minimum potential at which the plate photoelectric current becomes zero is called **stopping potential**. If V_0 is the stopping potential, then $\mathbf{eV_0} = \mathbf{h}(\nu - \nu_0)$.

2.10.3 Laws of Photoelectric Effect

(i) Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.

(ii) The maximum KE of photoelectrons is directly proportional to the frequency of incident radiation; moreover, it is independent of the intensity of light used.

(iii) There is no time lag between incident of light and emission of photoelectrons.

(iv) For emission of photoelectrons, the frequency of incident light must be equal to or greater than the threshold frequency.

(v) The greater the work function of a metal, the more the energy is needed for an electron to leave the surface and the higher the critical frequency for photoelectric emission to occur.

Note:

$$\lambda_{\min} = \frac{hc}{eV} = \frac{1.240 \times 10^{-6}}{V} m = \lambda_{\min} \propto \frac{1}{V}$$

*The X-rays produced at a given accelerating potential V vary in wavelength but none has wavelength shorter than a certain minimum value λ_{min}. **Increasing V decreases** λ_{min}.*

2.11 DUALITY OF MATTER

Photoelectric effect phenomenon can be explained on the basis of particle nature of electron but it is not possible to explain the **interference and the diffraction phenomenon which are properties of wave**.

In **1905, Einstein** suggested that **light has dual nature**. By **1920**, it has been suggested that the **matter has dual nature**.

In **1924, De Broglie** postulated that the electron also has dual nature, i.e., **particle as well as wave**. He succeeded in deriving an expression which showed relationship between the wave and particle nature of a moving electron.

De Broglie wavelength: $\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2eVm}} = \frac{h}{\sqrt{2mKE}}$

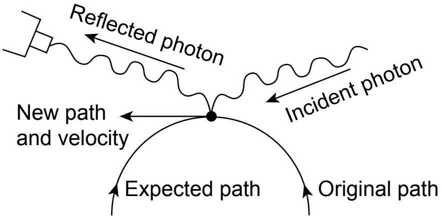
2.12 HEISENBERG'S UNCERTAINTY PRINCIPLE

The position and velocity of a big particle can be determined simultaneously with high degree of accuracy. However, this is not true for the tiny particles like electron, proton, neutron, etc. This principle states that:

'If we try to determine the position of a tiny particle accurately then there will be some uncertainty associated with the determination of its velocity and if the velocity is known accurately then its position will have some uncertainty'.

According to principle of optics, the accuracy with which the position of a particle can be measured depends upon the wavelength of light used. The uncertainity in position is $\pm\lambda$. The shorter the wavelength means higher the frequency and higher the energy. This high-energy photon on striking the electron changes its speed as well as direction.

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \text{ and } \Delta x \times \Delta \upsilon \geq \frac{h}{4\pi m}$$



Orbital: The small volume around the nucleus where the probability of finding an electron is maximum, i.e., 90 to 95 per cent is known as orbital.

2.13 WAVE MECHANICAL MODEL

The wave mechanical model is based on quantum mechanics which is developed independently by Schrödinger and Heisenberg. In quantum mechanics, duality of matter is taken into consideration.

Important features of wave mechanical model:

(i) The exact position and velocity of e^- cannot be determined simultaneously with high degree of accuracy. However, electron is present in a 3-dimensional space around the nucleus where probability of finding the e^- is maximum. This space is called an orbital.
(ii) Each orbital possess an unique orbital wave function value, these values; are outcome of solution of Schrödinger wave equation.
(iii) Many orbital wave functions are possible for an e^-, therefore there exist many quantized energy orbitals.
(iv) The wave function ψ is simply a function of coordinate of e^- and has no physical significance as such. However, ψ^2 gives us the probability of finding e^- at a point inside an atom.
(v) By finding ψ^2 at different points around the nucleus in an atom we can predict the region of space around the nucleus called orbital.
(vi) All the information about an electron is stored in its orbital wave function value and Schrödinger wave equation makes it possible to extract this information out of ψ.

Schrödinger wave equation: For an e^- moving in 3-dimensional space around the nucleus.

$H\psi = E\psi$; where H is a mathematical operator called Hamiltonian operator.

$H = T + V$; where T is kinetic energy operator and V is potential energy operator.

$T = -\frac{\hbar^2}{2m}\nabla^2$ where $\bar{V}^2$ = Laplacian operator

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

2.14 SHAPE OF ORBITAL

The position and energy of an electron may be determined with the help of certain numbers called **quantum numbers**. An electron is said to be identified or described or characterized when its position and energy is known. For the complete description of an electron, we need help of the following four quantum numbers.

(i) Principal quantum number (PQN) (**Bohr**).
(ii) Azimuthal quantum number or subsidiary quantum number or secondary quantum number or angular momentum quantum number or orbital quantum number (**Somerfield**).
(iii) Magnetic quantum number (MQN) (**Lande**).
(iv) Spin quantum number (**Uhlenbeck and Goudsmith**).

Principal quantum number represents the main shell, **azimuthal quantum number** represents the number of subshells present in the main shell, **magnetic quantum number** represents the number of orbitals present in the subshell and **spin quantum number** tells the direction of spin of the electron, i.e., clockwise or anticlockwise. Further, **principal quantum number tells about the size, azimuthal quantum number about the shape and magnetic quantum about the orientation of the orbital**. Also, principal quantum number tells about the energy of the electron, whereas azimuthal quantum number tells about the angular momentum of the electron.

The values of quantum number are related to each other as follows:

$n = 1, 2, 3, 4, ...$

For a given value of n, $l = 0$ to $n - 1$

For a given value of l, $m = -1$ to $+1$ including ‘0’

For a given value of m, $s = + 1/2, -1/2$

Designation of the subshells:

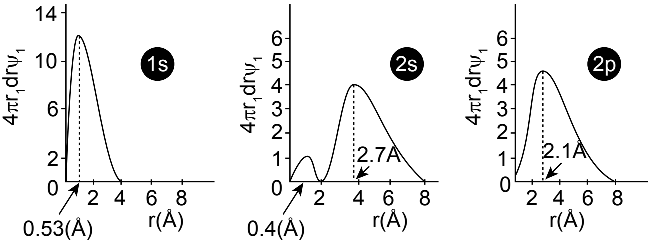
Value of l	Sub-shell
0	s
1	p
2	d
3	f

Thus, number of subshells in the nth shell = n

Number of orbitals in a subshell = $2l + 1$

Number of orbitals in nth shell = n^2

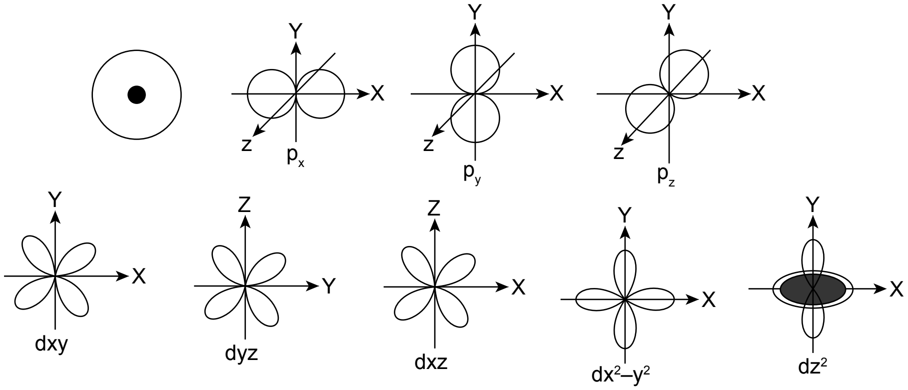
Radial probability distribution curves: Radial probability is $R = 4\pi r^2 dr\psi^2$. The plots of R versus distance from nucleus are as follows:



In the plots of radial probability versus distance from the nucleus, number of peaks i.e., region of maximum probability = n – l.

For example, 2s has two peaks, 3s will have 3 peaks, 2p has one peak, 3p has two peaks and so on.

Shapes of s, p and d-orbitals



Spherical (radial) nodes and nodal planes

A spherical surface within an orbital on which the probability of finding the electron is zero is called a **spherical or radial node.** The number of spherical or radial nodes in an orbital = (n – l – 1).

For example, 1s orbital (n =1, l = 0) has no spherical node
2s orbital (n =2, l = 0) has one spherical node
2p orbital (n =2, l = 1) has no spherical node
3p orbital (n =3, l = 1) has one spherical node and so on.

A plane passing through the nucleus on which the probability of finding the electron is zero is called a nodal plane. The number of nodal planes in an orbital = l for example

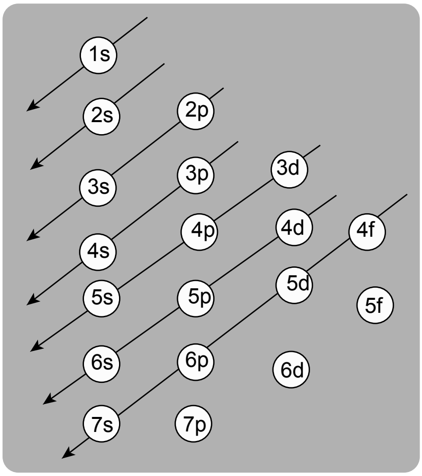
s orbital (l = 0) no nodal plane
p orbital (l = 1) one nodal plane
d orbital (l = 2) two nodal planes and so on.

Pauli's exclusion principle: Pauli exclusion principle states that 'No two electrons in an atom can have the same set of four quantum number' or 'an orbital can have maximum two electrons and they must have opposite spin.'

Aufbau principle

Aufbau principle states that 'in the ground state of the atom, the orbitals are filled in order of their increasing energies, starting with the orbital of lowest energy.' The word aufbau is a German word which means building up. The increasing order of energy and hence that of filling of orbitals is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5p, 6s, 4f, 5d, 6p...

This can be remembered from the adjoining diagram in which starting from the top, the direction of arrows give the order of filling.



Note:

In case of H-atom, the energies of atomic orbitals increase as follows:
1s < 2s = 2p < 3s =3p = 3d < 4s = 4p = 4d = 4f and so on.
i.e., subshells of the same main shell have equal energies.

The order of energies and hence that of filling of orbitals can be calculated by (n + l) rule which states as follows:

(i) Orbitals are filled in order of increasing (n + l) values.

(ii) If two orbitals have the same (n + l) values, the orbital with lower value of n is filled first.

2.14.1 Hund's Rule

Hund's rule of maximum multiplicity states that 'pairing of electrons in the orbitals belonging to the same sub-shell (degenerate orbitals) does not take place till each orbital of that sub-shell has got one electron each, i.e., is singly occupied Orbitals must have their electron with spin in the same direction (so that repulsion is minimum and stability is maximum).

Half-filled and fully-filled electronic configurations are more stable because of (i) greater symmetry and (ii) greater exchange energy.

2.15 ELECTRONIC CONFIGURATION OF ION

First write the electronic configuration of a neutral atom. For cation, remove the number of electrons equal to the units of +ve charge on the cation, starting from the outermost shell. For anion, add number of electrons equal to the units of –ve charge on the anion.

2.16 DIAMAGNETIC AND PARAMAGNETIC SUBSTANCES

2.16.1 Diamagnetic Substances ⇅ (Paired Spin)

Substances having all electrons paired are known as diamagnetic substances and their magnetism as diamagnetism.

The magnitude of diamagnetism is very small because of **cancellation of magnetic moment due to spin motion and also due to quenching of orbital motion** (nullified due to other atom's orbitals molecule).

2.16.2 Paramagnetic Substances ↑ (Parallel Spin)

All substances having one or more unpaired electrons are called **paramagnetic substances** and their magnetism **paramagnetism**. The **magnitude of paramagnetism is much higher than diamagnetism** because of full contribution of spin motion of the electron.

The **magnitude of paramagnetism increases with increase of number of unpaired electrons**. In general, **paramagnetic substances are more reactive than diamagnetic substances**.

Magnetic moment of paramagnetic substances

$\mu = \sqrt{N(N+2)}$ **BM (1 BM = 9.27×10^{-24} J/T);** where **N** is the number of unpaired electrons.

(i) All paramagnetic substances except hydrogen also have some diamagnetism but converse is not true.

(ii) **Ion with unpaired electron in d or f orbitals will be coloured.** For example Cu^+ with electronic configuration [Ar] $3d^{10}$ is colourless and Cu^{2+} with electronic configuration [Ar] $3d^9$ (one unpaired electron in 3d) is coloured (blue).