

ATOMIC STRUCTURE**Different models of atom****(1) Dalton's atomic model.**

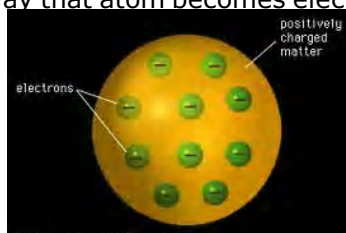
Dalton's atomic model is one of the fundamentals of physics and chemistry. This theory of atomic composition was hypothesized and partially confirmed by the English chemist and Physicist John Dalton. Dalton came with his Atomic theory as a result of his research into gases. He discovered that certain gases only could be combined in certain proportions even if two different compounds shared the same common element or group of elements. Through deductive reasoning and experimentation, he made an interesting discovery. His findings led him to hypothesize that elements combine at the atomic level in fixed ratios. This ratio would naturally differ in compounds due to the unique atomic weights of the elements being combined.

This was a revolutionary idea but further experimentation by himself and others confirmed his theory. The findings became the basis of Dalton's Atomic Laws or Model. These laws focus on five basic theorems.

- (1) Pure Elements consist of particles called atoms.
- (2) Atoms of an element are all the same for that element. That means gold is gold and oxygen is oxygen down to the last atom.
- (3) Atoms of different elements can be told apart by their atomic weights.
- (4) Atoms of elements unite to form chemical compounds.
- (5) Atoms can neither be created or destroyed in chemical reaction. The grouping only changes.

(2) Thomson's model or Plum Pudding model or Raisin Pudding model or water melon model.

Thomson stated that atom is uniform sphere of positive charge with negatively charged electron embedded in it in such a way that atom becomes electrically neutral.



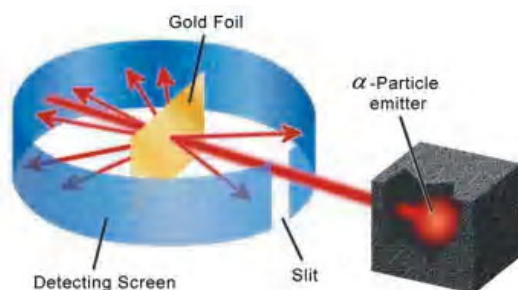
- **Important features :**

- It shows electrical neutrality of atom.
- The mass of the atom is assumed to be uniformly distributed over the atom.

The model was rejected as it was not consistent with the results of alpha scattering experiment.

(3) Rutherford's Nuclear Model of Atom :

α -particle scattering experiment :-



A beam of α -particle was projected towards this gold foil. The foil was surrounded by circular fluorescent ZnS screen which produces flash when α -particle collide with it.

- **Observations of experiment :**

- Most of α -particles passed through the foil un deflected or deflected by very small angles [less than 1°].
- Few particles were deflected through angles as large as 90° .
- Very few particles [1 in 20 thousand] bounce back or rejected through an angle almost equal to 180° .
- Angle of deflection increases with increase in atomic number.

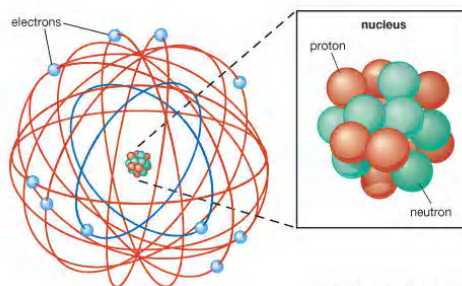
- **Conclusions**

- Since, most of the α -particles passed through the foil un deflected, therefore there must be large empty space present in the atom.
- α -particles are positively charged and having considerable mass could be deflected by only some heavy positively charged centre by repulsion.[Rutherford named this positively charged heavy centre as nucleus]
- Since, very few α -particles were thrown back therefore the size of nucleus should be very small and is should be rigid because α -particle can recoil back only if it undergo direct collision with the heavy positively charged centre.

- **Rutherford's model**

On the basis of scattering experiment, Rutherford proposed an atomic model or nuclear atomic model or

nuclear model of atoms.



- The electrons are revolving around the nucleus in circular path and electrostatics force of attraction between the electrons and nucleus is balanced by the centrifugal force acting on revolving electron.
- The -ve charge on electrons are equal to the total positive charge on the nucleus and therefore as a whole atom is electrically neutral.
- Size of the nucleus is extremely small as compared to size of the atom.

Radius of nucleus

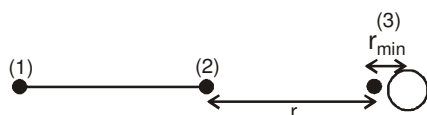
Radius of nucleus is of the order of 10^{-15} m and radius of atom is order of 10^{-10} m.

$$r = r_0 A^{1/3}$$

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

r_0 = constant = 1.2×10^{-13} cm.

• **Distance of closest approach :**



If the α -particle is projected with some velocity $-v$ from very large distance then at point (1), energy

of the α -particle $E = \frac{1}{2}mv^2 + 0$
(K.E.) (P.E.)

As the particle is moving closer to the nucleus of other particle, repulsive coulombic force increase (P.E. increases) and velocity of the particle decrease \therefore kinetic energy is converted into P.E.

\therefore At point (2) $E = \text{K.E.} + \text{P.E.} = \frac{1}{2}mv^2 + \frac{kq_1q_2}{r}$

[As no ext. force is acting, \therefore Total energy of system remains constant]

velocity becomes zero at r_{\min} distance where coulombic potential energy of repulsion becomes equal to the initial kinetic energy.

At point (3),

$$E = \text{P.E.} + 0 = \frac{kq_1q_2}{r_{\min}}$$

$$\Rightarrow \frac{1}{2}mv^2 = \frac{kq_1q_2}{r_{\min}}$$

$$r_{\min} = \frac{2kq_1q_2}{mv^2} = \frac{2kz_1z_2e^2}{mv^2}$$

$$q_1 = z_1e ; q_2 = z_2e$$

$$e = \text{electronic charge} = 1.6 \times 10^{-19} \text{ C}$$

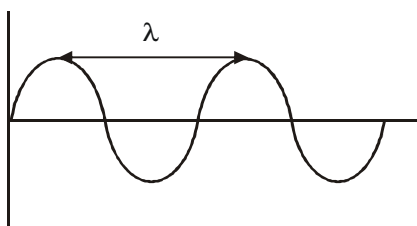
$$z_1 = z_2 = \text{Atomic number}$$

• **Failures of Rutherford's Model :**

- (1) According to maxwell's wave theory, an accelerated charged particles (like electron) revolving in the field of another charged particle like nucleus loses energy in the form of electromagnetic radiation and if this happen then orbit of the revolving electron should keep on decreasing and ultimately electron should fall into the nucleus and atom should collapse but this doesn't happen actually.
- (2) Rutherford's model didn't give any idea about electronic arrangement of an atom and since he didn't mention specific energy levels he couldn't explain the discontinuous atomic hydrogen spectrum.

WAVES AND ITS CHARACTERISTICS

It is a periodical disturbance causing transfer of energy without transfer of matter.



- Characteristics of waves :**

Amplitude : Maximum displacement from mean position it remains constant with distance except stationary or standing waves.

Wavelength : It is the distance between two adjacent crest or troughs.

Frequency (μ or ν) : The no of waves passing through a point in 1second, unit-sec⁻¹ or Hz

Wave number ($\bar{\mu}$ or $\bar{\nu}$) : No. of waves present in unit distance.

$$\bar{\mu} = \frac{1}{\lambda} = \text{metre}^{-1}, \text{cm}^{-1} \text{ etc.}$$

Velocity : linear distance travelled by wave in one second.

$$v = \mu\lambda$$

NATURE OF LIGHT

- Maxwell electromagnetic wave theory (wave nature of light) :**

An accelerated electrically charged particle produces and transmits electrical and magnetic field. These are transmitted in the form of waves known as electromagnetic waves or electromagnetic radiations.

He stated that light also possess electrical and magnetic field and \therefore it is also known as electromagnetic radiations or e.m.w.

- Characteristics of Electromagnetic Radiations :**

1. In these electromagnetic radiation electrical and magnetic field oscillates \perp er to each other and it also propagates \perp er to both field.

2. All these electromagnetic radiation do not require any medium and can travel in vacuum.

3. Velocity of all electromagnetic radiation is 3×10^8 m/s in vacuum.

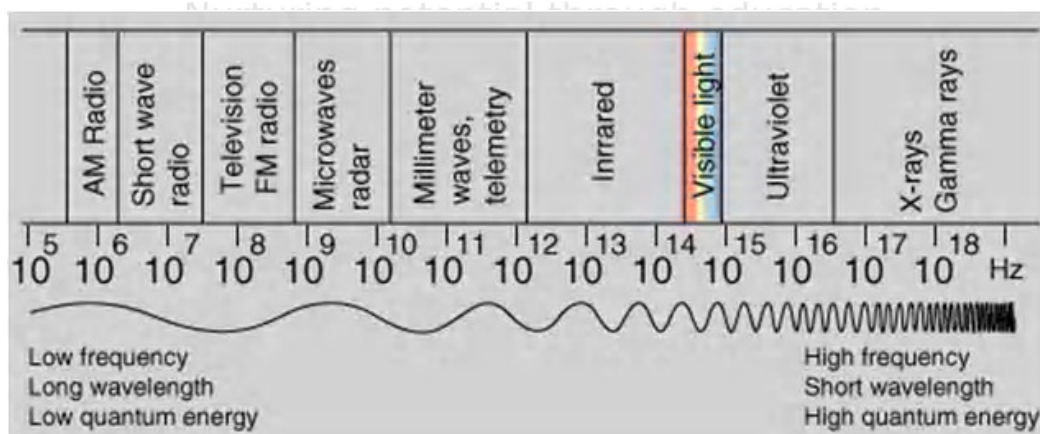
4. Energy of an electromagnetic wave is directly proportional to intensity and it is independent of frequency.

5. There are also showing diffraction and interference

And therefore. Maxwell concluded light to be wave nature.

But Maxwell theory couldn't explain the results of photoelectric effect and black body radiations.

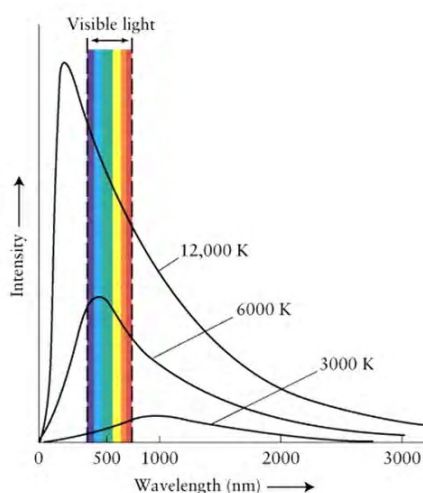
Photon Energies for EM Spectrum



A Blackbody

A blackbody is an object that emits a well defined spectrum of radiation solely based on its temperature. We see from figure at right that the hotter the blackbody, the more intense it is, and the shorter the peak wavelength.

The picture does not say anything about what the object is made of, or how heavy it is, etc. It doesn't matter! The only property that determines the spectrum of a blackbody is its temperature. Brick, iron or a dense gas will emit the same spectrum as long as they are at the same temperature. That spectrum will have a peak that lies at a particular wavelength.



- **Planck's Quantum Theory : [Particle nature of light] :**

He stated that a body radiates energy in the form of discontinuous energy packets or bundles. Each bundle of energy is known as quantum and quantum of light is known as photons.

Energy of each quantum is directly proportional to frequency of radiation.

$$E \propto \nu$$

$$E = h\nu$$

↓

Plank's constant

Total energy absorbed or emitted by a body will be whole no. integral multiple of energy of quantum

$$E_{\text{abs}} \text{ or } E_{\text{emitted}} = nh\nu$$

Ex. Calculate the no. of photons emitted by 60 watt bulb in 10 hrs. When light of wavelength 6000 Å is emitted by it.

Sol. $E = \frac{nhc}{\lambda} = 6.5 \times 10^{24}$

Energies in Electron Volts

- Room temperature thermal energy of a molecule.....0.04 eV
- Visible light photons.....1.5-3.5 eV
- Energy for the dissociation of an NaCl molecule into Na⁺ and Cl⁻ ions:.....4.2 eV
- Ionization energy of atomic hydrogen13.6 eV
- Approximate energy of an electron striking a color television screen (CRT display)20,000 eV
- High energy diagnostic medical x-ray photons.....200,000 eV (=0.2 MeV)
- Typical energies from nuclear decay:
 - (1) gamma.....0-3 MeV
 - (2) beta.....0-3 MeV
 - (3) alpha.....2-10 MeV
- Cosmic ray energies1 MeV - 1000 TeV
- 1 MeV = 10⁶ eV, 1 GeV = 10⁹ eV, 1 TeV = 10¹² eV

• Explanation of black body radiations using Planck’s quantum theory :

When a solid substance like iron piece is heated it emits radiations. As heating is continued, more and more energy is being absorbed by the atom and hence, more energy will be emitted and therefore energy of e.m.w. increases and frequency of e.m.w. increases and therefore body first becomes red then yellow and finally white.

Therefore, it can be concluded that light posses particle nature and energy of electromagnetic radiation depends upon frequency.

• Explanation of Photo electric Effect using Planck’s Quantum Theory :

When a metal sheet is subjected to electromagnetic radiation of suitable frequency then some electrons are ejected from metal surface and these electrons are known as photoelectron and the effect is known as photoelectric effect.

If electromagnetic radiation of low frequency are used then there is no ejection of electron inspite of continuous increasing intensity. This observation was contradicting to maxwell theory according to which energy electrom agnetic radiation $\propto I$ but can be explained using Planck’s quantum theory i.e.

$E \propto \nu.$

DUAL NATURE OF LIGHT

Since, wave nature of light explains diffraction interference phenomenon while particle nature explains black body radiation and photo electric effect \therefore light was considered to have dual nature particle nature as well as wave nature.

• Electromagnetic spectrum :

The arrangement of all the electromagnetic radiation in a definite order (decreasing or increasing of wavelength or frequency is known as electron magnetic spectrum

SPECTRUM

When light coming from a source is passed through a prism, the radiation of different wavelength deviated through different angles and get separated.

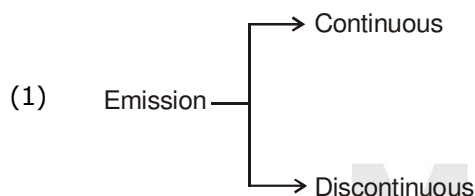
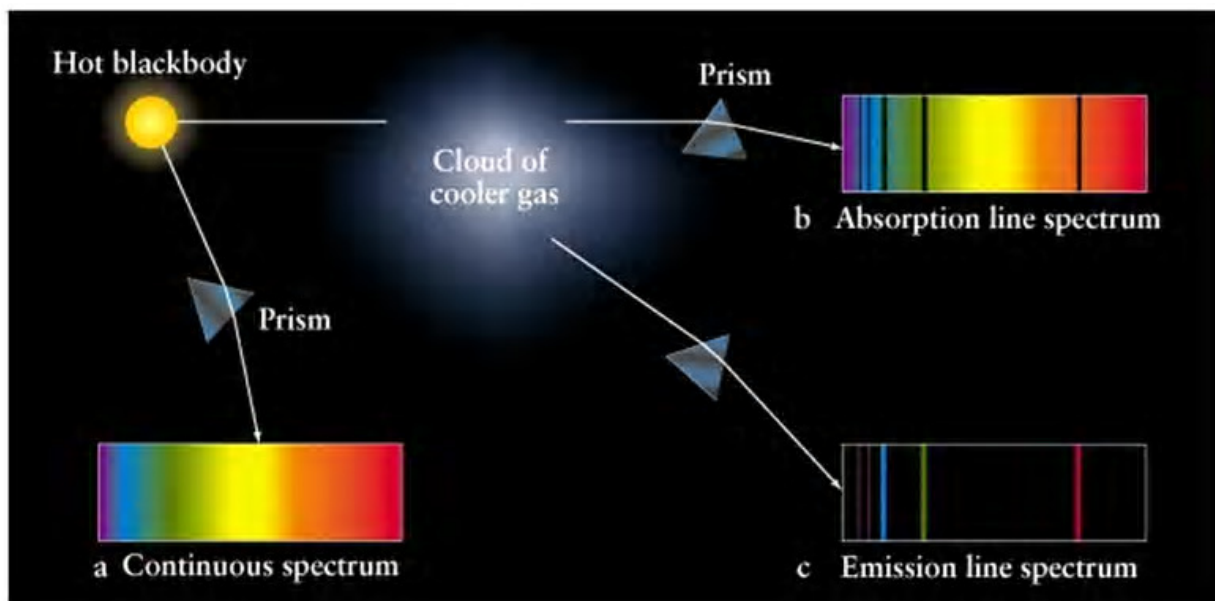
$$\text{Angle of deviation} \propto v \propto \frac{1}{\lambda}$$



this process is called dispersion.

And such a collection or dispersed light giving its wavelength composition is known as spectrum.

• **Spectrum are of two types.**



(2) Absorption :

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EMISSION SPECTRUM

This is the spectrum of radiations emitted by any source or atom or molecule of any substance (Which is excited by heating or electric discharge).

(i) Continuous Spectrum :

When white light from a source is dispersed, a bright spectrum continuously distributed on the dark background is obtained. The colours are continuously changing from violet to red and there is no Sharp boundaries between various colour. These colours appear to be merge into each other and therefore spectrum is known as continuous spectrum.

(ii) Discontinuous Spectrum :

When a atom is subjected to electromagnetic radiation, it cause excitation of electron to higher

energy level. When electrons return back to lower energy level, it emits certain radiations corresponding to difference in energy level and therefore spectrum obtained in case of atom is discontinuous spectrum having specific wavelength is known as Atomic spectrum or line spectrum.

● **Absorption Spectrum :**

When an atom is subjected to white light it absorbs some specific radiation corresponding to the difference in energy level \therefore the remaining radiations (transmitted radiations) are devoid of certain specific frequencies which is observed in the form of missing line and this spectrum is known as absorption spectrum.

It is photographic negative of emission spectrum i.e. those bright lines which are present in emission spectrum of an atom are missing.

In the absorption spectrum and observed in the form of dark lines.

(4) Bohr's Model

It was the first model based on Planck's quantum theory and the model explained stability of atom and line spectrum of hydrogen.

● **Postulates of Bohr's model**

1. An atom consist of centrally located small, dense, positively charged nucleus and electrons are revolving around the nucleus in circular paths known as circular orbits and coulombic force of attraction between nucleus and electron is balanced by centrifugal force of the revolving electron.

2. Out of the infinite circular orbits only those circular orbits are possible in which angular momentum of electron is integral multiple of $h/2\pi$ i.e. angular momentum of an electron can have fixed values like

$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$ etc. i.e., angular momentum of electron is quantised.

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

m and v are mass and velocities of electron respectively and r is radius of orbit and n is integer which is later related with orbit number and shell number and h is Plank's constant.

3. The energy of these circular orbits have fixed values and hence electron in an atom can have only certain values of energy. It is characteristic of an orbit and it cannot have any orbit value of its own. And therefore energy of an electron is also quantised.
4. As long as electrons remains in these fixed orbits, it dosen't lose energy i.e. energy of an electron is stationary (not changing with time) and therefore these orbits are known as allowed energy levels or stationary states and this explains the stability of atom.
5. The energy levels are designated as K, L, M, N and numbered as 1, 2, 3, 4 etc from nucleus outwards and as the distance of the shell's or energy level from the nucleus increases the energy of the energy level also increases i.e., $E_N > E_M > E_L > E_K$
6. The emission or absorption of energy in the form of radiations can only occur when an electron jump from one stationary states to other.

$$\Delta E = E_{\text{higher}} - E_{\text{lower}}$$

$\Delta E = h\nu$ where $h\nu$ is the energy of absorbed photon or emitted photon which corresponds to the difference in energy levels. Energy is absorbed when electron jumps from lower energy level (normal state)

to higher energy level (excited, unstable state) and energy is emitted when electrons jumps from higher energy level to lower energy level.

- **Bohr's model is applicable for a one electron species only, like H, He^+ , Li^{+2} , Be^{+3} etc.**
- **Derivation of Radius of different orbits in one electron species (using Bohr's model) :**

$$mvr = \frac{nh}{2\pi} \quad \dots(1)$$

$$q_1 = e, \quad q_2 = Ze$$

$$\frac{mv^2}{r} = \frac{kq_1q_2}{r^2} = \frac{kZe^2}{r^2} \quad \dots(2)$$

$$\Rightarrow \frac{mn^2h^2}{4\pi^2m^2r^2 \cdot r} = \frac{kZe^2}{r^2}$$

$$\Rightarrow r = \frac{mn^2h^2}{4\pi^2m^2kZe^2}$$

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

$$\Rightarrow \frac{h^2}{4\pi^2mke^2} \times \frac{n^2}{Z} = \frac{(6.625 \times 10^{-34})^2}{4\pi^2 \times 9.1 \times 10^{-31} \times 9 \times 10^9 \times (1.6 \times 10^{-19})^2} \times \frac{n^2}{Z}$$

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

$$r \propto \frac{n^2}{Z}$$

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for a particular atom $r \propto n^2$

Radius of 1st orbit of H atom

$$r = 0.529 \text{ \AA}$$

Ex. Calculate ratio of radius of 1st orbit of H atom to Li^{+2} ion :

$$\text{Sol.} = \frac{\text{Radius of 2nd orbit of H atom}}{\text{Radius of 3rd orbit of } \text{Li}^{+2} \text{ atom}} = \frac{n^2}{Z} \times \frac{Z_1}{n_1^2} = \frac{4}{3}$$

• **Derivation of Velocity of electron in Bohr's orbit :**

$$v = \frac{nh}{2\pi mr}, \text{ putting value of } r.$$

$$v = \frac{nh \times 4\pi^2 m k Z e^2}{2\pi m n^2 h^2}$$

$$v = \frac{2\pi k Z e^2}{h \cdot n} = \frac{2\pi k e^2}{h} \times \frac{Z}{n}$$

$$v = 2.18 \times 10^6 \frac{Z}{n} \text{ m/s}$$

$$v \propto \frac{Z}{n}$$

• **Derivation of total energy of electron / system :**

T.E. of system = K.E. of e^- + P.E. of system (nucleus and e^-)

$$\text{kinetic energy of electron} = \frac{1}{2}mv^2 = \frac{1}{2} \frac{kze^2}{r}$$

$$\text{PE} = - \frac{kze^2}{r}$$

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

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

$$\text{T.E.} = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom}$$

As shell no. or distance increases, the value of T.E. and P.E. increases (however magnitude decreases) and becomes maximum at infinity i.e., zero.

negative sign indicates that electron is under the influence of attractive forces of nucleus.

$$\text{K.E.} = - \frac{\text{P.E.}}{2}$$

$$\text{T.E.} = \frac{\text{P.E.}}{2}$$

$$\text{T.E} = - \text{K.E.}$$

Calculation of energy of energy level in H atom

(i) When $n = 1$ (ground level)

$$\text{K.E.} = 13.6 \text{ eV (atom)}$$

$$\text{P.E.} = -27.2 \text{ eV / atom}$$

$$\text{T.E.} = -13.6 \text{ eV/atom}$$

(ii) When $n = 2/2^{\text{nd}}$ energy level / 1^{st} excited state

$$\text{K.E.} = \frac{13.6}{4} \text{ eV/atom} = 3.4 \text{ eV / atom}$$

$$\text{P.E.} = -6.8 \text{ eV/atom}$$

$$\text{T.E.} = -3.4 \text{ eV/atom}$$

$$E_2 - E_1 = -3.4 + 13.6 \text{ eV/atom} = 10.2 \text{ eV/atom}$$

(iii) When $n = 3 / 3^{\text{rd}}$ energy level/ 2^{nd} excited state.

$$\text{K.E.} = \frac{13.6}{9} \text{ eV/atom} = 1.51 \text{ eV/atom}$$

$$\text{P.E.} = -3.02 \text{ eV/atom}$$

$$\text{T.E.} = -1.51 \text{ eV/atom}$$

$$\begin{aligned} -E_3 - E_2 &= -1.51 \text{ eV/atom} + 3.4 \text{ eV/atom} \\ &= 1.89 \text{ eV atom.} \end{aligned}$$

(iv) when $n = 4 / 3^{\text{rd}}$ excited state

$$\text{K.E.} = \frac{13.6}{4^2} \Rightarrow \frac{13.6}{16 \times 10} = 0.85 \text{ eV/atom}$$

$$\text{P.E.} = -1.70 \text{ eV/atom} \quad \text{T.E.} = -0.85 \text{ eV/atom}$$

$$E_4 - E_3 = 0.66$$

As distance increases (n increases) energy of the energy level increases but energy difference between consecutive energy level keeps on increasing i.e., maximum energy difference between 2 to 1 (consecutive)

If reference value (P.E at ∞) is assigned value other than zero. – (i) All K.E. data remains same.

(ii) P.E./T.E. of each shell will be changed however difference in P.E./T.E. between 2 shell will remain unchanged.

• Hydrogen spectrum (Before Bohr's Model)

The spectrum of H atom is observed as discontinuous line spectra. The line spectra of different in 3 region UV, visible and IR. The different lines observed H spectrum were classified in to different series and named after their discoverers.

Rydberg gave an empirical formula to calculate wavelength, which is applicable to all series.

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad R_H = 109677 \text{ cm}^{-1} \text{ Rydberg's constant.}$$

n_1 and n_2 are integers.

• **Explanation of Hydrogen spectrum using Bohr's model**

When electron in an excited atom comes back from higher energy level (n_2) to lower energy level (n_1) then it emits a photon, having energy equal to difference in energy levels.

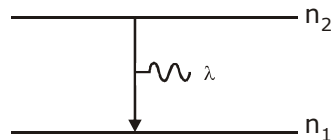
$$h\nu = \Delta E = E_{n_2} - E_{n_1}$$

$$h\nu = \frac{-2\pi^2mk^2e^4z^2}{n_2^2h^2} - \left(\frac{-2\pi^2mk^2e^4z^2}{n_1^2h^2} \right)$$

$$h\nu = \frac{2\pi mk^2e^4z^2}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\frac{1}{\lambda} = \frac{2\pi mk^2e^4z^2}{h^3c} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

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



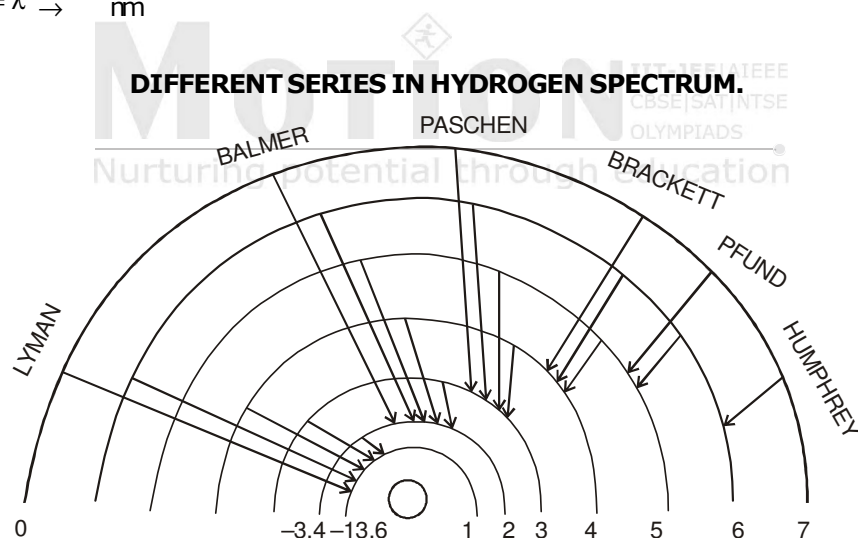
The theoretical value is very closed to observed value

∴ Bohr's model provides theoretical explanation of H spectrum.

Wavelength or wave no. of any line of any one electron species can be calculated as

$$\frac{1}{\lambda} = R_H Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right], \quad \frac{hc}{\lambda} = \Delta E$$

$$\frac{1240}{\Delta E(\text{ev})} = \lambda \rightarrow \text{nm}$$



☞ LYMAN SERIES : $n_f = 1,$ $n_i = 2, 3, 4, 5, - - - - -$
ULTRAVIOLET

☞ BALMER SERIES : $n_f = 2,$ $n_i = 3, 4, 5, 6, - - - - -$
VISIBLE

☞ PASCHEN SERIES : $n_f = 3,$ $n_i = 4, 5, 6, 7, - - - - -$
INFRARED

☞ BRACKETT SERIES : $n_f = 4,$ $n_i = 5, 6, 7, - - - - -$
INFRARED

☞ PFUND SERIES : $n_f = 5,$ $n_i = 6, 7, - - - - -$
FARINFRARED

☞ HUMPHREY SERIES : $n_f = 6,$ $n_i = 7, 8, - - - - -$
FARINFRARED

Ex. Calculation of different types of maximum possible radiations which can be observed in (from higher energy level to lower energy level)

Sol. $n_2 = n,$ $n_1 = 1$
Total no. of radiation obtained having difference wave lengths = Transition ending at 1st level +
Transite
ending at 2nd level Transition
ending at (n – 1) energy levels.
= Total no. of radiation in lyman series + total no. of radiation in Balmer series + Total no.
of radiation in (n – 1) series.

= (n – 1) + (n – 2) + (n – 3) + 2 + 1

$\Rightarrow \frac{(n-1)(n-1+1)}{2} \Rightarrow \frac{n(n-1)}{2}$

$\Rightarrow (n_1 - n_1) + n_2 - (n_1 + 1) + 2 + 1$

Total no. of different radiation

$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2} = \frac{N(N+1)}{2}$

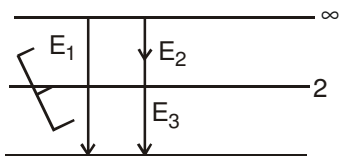
N = difference in higher energy level and lower energy level

Ex. The energy level of an atom for 1st, 2nd and third levels are E , $4E$, $2E$ respectively. If photon of wavelength λ is emitted for a transition 3 to 1. Calculate the wavelength for transition 2 to 1 in terms of λ .

Sol. $2E - E = E = \frac{hc}{\lambda_1}$ $\frac{4E}{3} - E = \frac{E}{3} = \frac{hc}{\lambda_2} \Rightarrow 3\lambda = \lambda_2$

Ex. Let ν_1 be the frequency of series limit of lyman series, ν_2 be the frequency of 1st line of lyman series, ν_3 be the frequency of series limit of Balmer series. Then find relation between ν_1 , ν_2 and ν_3

Sol.



$$E_1 = E_2 + E_3$$

$$\Rightarrow h\nu_1 = h\nu_2 + h\nu_3 \Rightarrow \nu_1 = \nu_2 + \nu_3$$

Ex. Hydrogen like species is observed to emit 6 wavelengths originating from all possible transitions between a group of levels these energy levels have energy between -0.85 eV and -0.544 eV (including both these energy levels) calculate

(i) The quantum number of levels between which transition is taking place.

(ii) Find the atomic number of species.

Sol. $(n_2 - n_1)(n_2 - n_1 + 1) = 12$

$$n_2 - n_1 = x \times (x + 1) = 12$$

$$n_2 = n_1 + 3$$

$$-13.6 \times \frac{Z^2}{n_1^2} \quad -13.6 \times \frac{Z^2}{n_1^2} = -0.85$$

$$-13.6 \times \frac{Z^2}{(n_1 + 3)^2} \quad n_1 = 12 ; \quad n_2 = 15$$

● **Failures of Bohr's Model :**

- It is applicable only for one electron species.
- He couldn't explain the fine spectrum of hydrogen when a powerful spectroscopy is used then several lines which are very closely placed are observed in addition to the expected lines later this problem was solved by Sommerfeld who introduced the concept of sub shell.
- He couldn't explain splitting of spectral lines into a group of finer lines under the influence of external magnetic field (Zeeman effect) or under the influence of external electric field (stark effect).
- He couldn't give theoretical reason for most of his assumption, for example he couldn't justify why angular momentum of electron should be quantised.
- Spectrum of isotopes of hydrogen were expected to be same according to the Bohr's model but found different experimentally.

(5) Sommerfeld model of Atom

Three refinements of the Bohr model were worked out by Arnold. Sommerfeld and are jointly responsible for giving rise to small deviations in the allowed energies from the values E_n . These refinements brought the calculated frequencies into even better agreement with observation (from four to five significant digits). The refinements were:

- the introduction of elliptical orbits;
- allowance for an orbiting motion of the nucleus; and
- the consideration of relativistic mass effects.

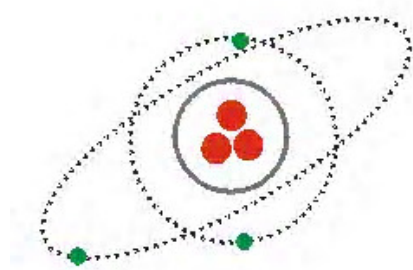
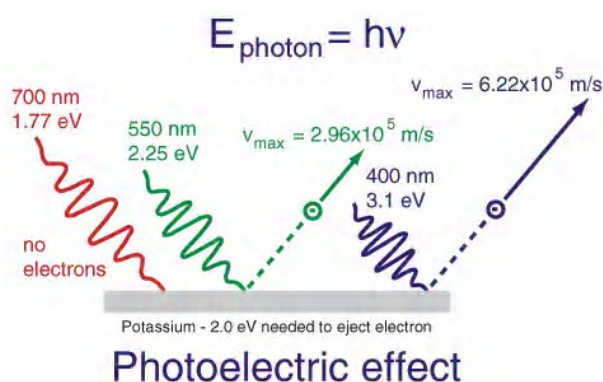
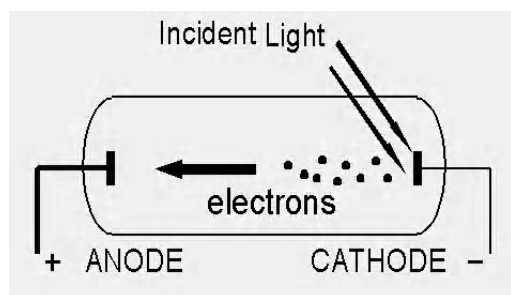


PHOTO ELECTRIC EFFECT

Emission of electron from the metal surface when the light of suitable frequency is subjected to the metal surface. The effect is known as photoelectric effect and the ejected electrons are known as photoelectrons.



• Terms used in photo electric effect

- Work function (w)** : It is the minimum amount of energy required to cause a photo emission from the metal surface. It is also known as threshold energy or Binding energy. [Work function depends upon ionisation energy and therefore w is minimum for alkali metals].
- Threshold frequency (ν_0)** : The minimum value of frequency that can cause photo emissions. If $\nu < \nu_0$, then there is no photo emission.

$$w = h \nu_0 \Rightarrow w = \frac{hc}{\lambda_0}$$

- Threshold wavelength : (λ_0)** The maximum value of wavelength that can cause photo emission. If $\lambda > \lambda_0$, then photo emission is not possible.

- Intensity (I)** : Energy falling on metal surface of unit area of unit time

$$I = \frac{E}{At} = \frac{nh\nu}{At}$$

(5) **Photo intensity (I_p)** : It is number of photons falling per unit area per unit time.

$$I_p = \frac{n}{At}$$

Relation between I and I_p :

$$I = I_p h\nu$$

Photo intensity is independent of frequency while intensity depends on frequency.

Power : Total energy radiated per unit time.

$$P = \frac{E}{t} = \frac{nh\nu}{t}$$

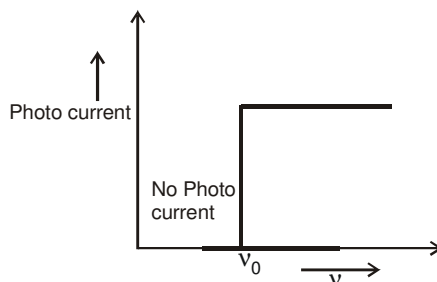
EFFECT OF VARIATION OF FREQUENCY

(a) **Effect of Photo Emission** :

$$I = I_p h\nu$$

If frequency of subjected photon increases (intensity increases keeping photo intensity constant) then there is no change in no of ejected photo electrons as well as no

change in photo current.



(b) **Effect on kinetic Energy** :

Average k. E. as well as k. E. max increases with increases in frequency.

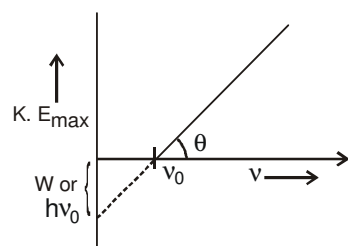
$$h\nu - W = K E_{\max}$$

$$K E_{\max} = h\nu - h\nu_0$$

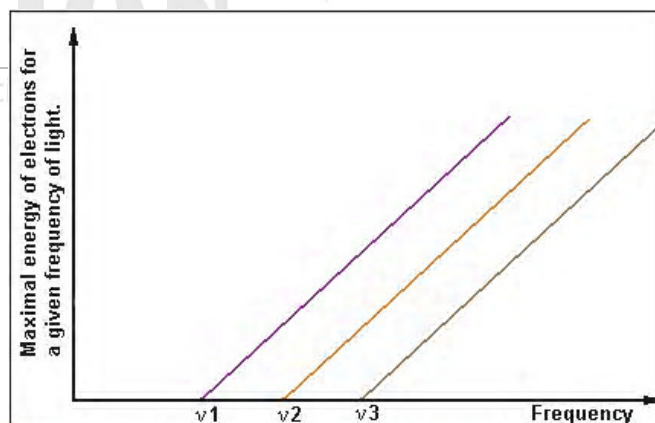
$$y = mx + c$$

$$K E_{\max} = h\nu - \frac{hc}{\lambda_0}$$

$$K_{\max} = h\nu - w$$



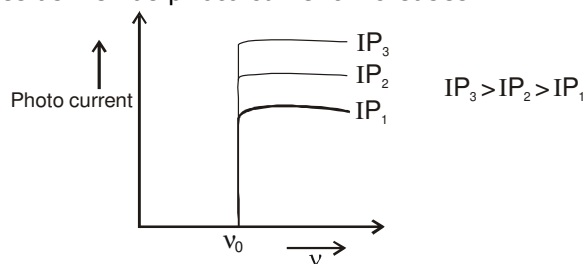
$$\tan \theta = \text{slope} = h$$



The diagram shows the interdependence between light frequency and the maximal energy of electrons emitted from metal. It shows the interdependence for three different metals. See that it clearly shows the limiting frequencies - different for different metals

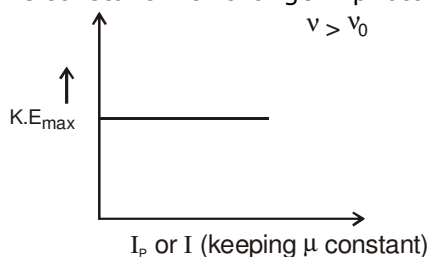
EFFECT OF VARIATION OF PHOTO INTENSITY

On increasing intensity, keeping frequency constant (i.e. increasing photo intensity) no of ejected photo electrons increases as well as photo current increases.



- Effect on Kinetic Energy**

Average K.E. and $K.E_{\max}$ remains constant with change in photo intensity



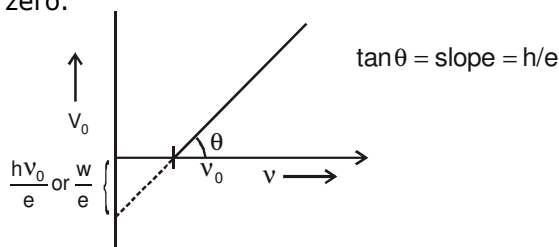
- Stopping Potential or Retarding Potential (V_0)**

It is the minimum potential require to stop the fastest moving electrons completely or it is the minimum potential at which photo current becomes zero.

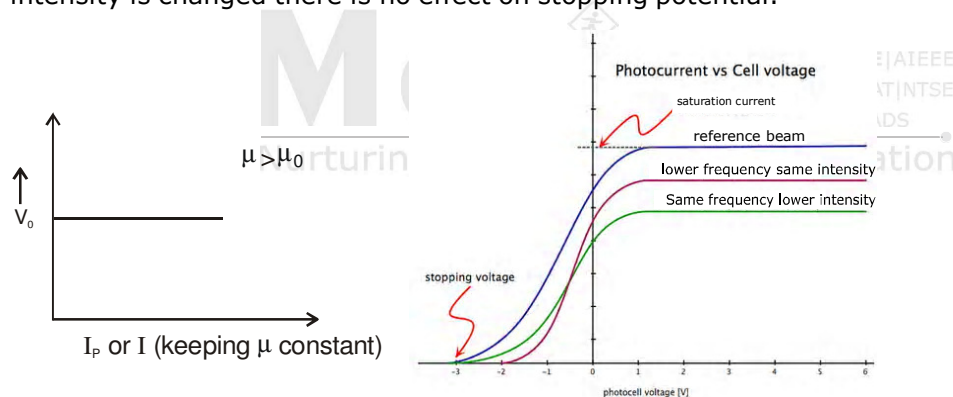
$$eV_0 = h\nu - w$$

$$eV_0 = h\nu - h\nu_0$$

$$\Rightarrow V_0 = \frac{h\nu}{e} - \frac{h\nu_0}{e}$$



It can be commented that stopping potential increase with increase in frequency how ever if photo intensity is changed there is no effect on stopping potential.



Ex. In ultraviolet light of wavelength 200 nm is used in an experiment of photoelectric effect with lithium cathode ($w = 2.5 \text{ eV}$). Then calculate

- (i) $K.E_{\max}$ (ii) Stopping potential

Sol. $K.E_{\max} = h\nu - w$

$$\Rightarrow \frac{hc}{\lambda} - 2.5$$

$$\Rightarrow \frac{1240}{2400} - 2.5$$

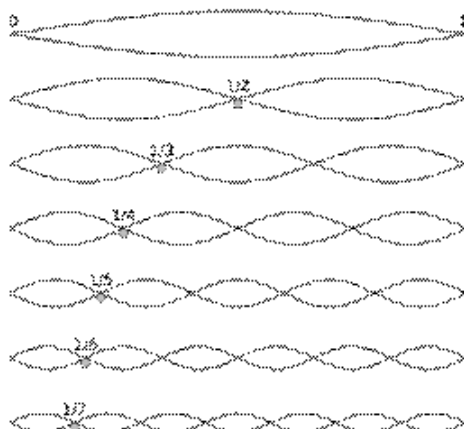
$$\Rightarrow 6.2 - 2.5$$

$$\Rightarrow 3.7 \text{ eV}$$

Stopping Potential = 3.7 V

DeBroglie's hypothesis (dual nature of matter) :

deBroglie proposed that like light, electron possess dual nature i.e. behave like both as material particle and as wave. The concept of dual character of metal evolved a wave mechanical theory of atom according to which electrons, protons and even atoms possess wave properties when moving.



Derivation of deBroglie Relation ship :

For a photon,

$$E = \frac{hc}{\lambda} \quad \dots(i)$$

$$E = mc^2 \quad \dots(ii)$$

$$mc^2 = \frac{hc}{\lambda}$$

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

He concluded that as electromagnetic radiation have some associated mass or associated momentum, in the same way every moving particle of mass 'm' and velocity 'v' is associated with waves and these associated waves are known as matter waves or deBroglie's waves.

$$\lambda = h/mv = h/p$$

• **Experimentation verification of deBroglie's hypothesis : Given by Davission and Germer.**

They observed that a beam of electrons are diffracted by nickel crystal just like the x-rays. More over it wavelength of the electrons determined by the diffraction experiments are equal to the values calculated from deBroglie's relations ship.

DERIVATION OF BOHR'S POSTULATE OF QUANTISATION OF ANGULAR MOMENTUM FROM DEBROGLIE'S EQUATIONS-

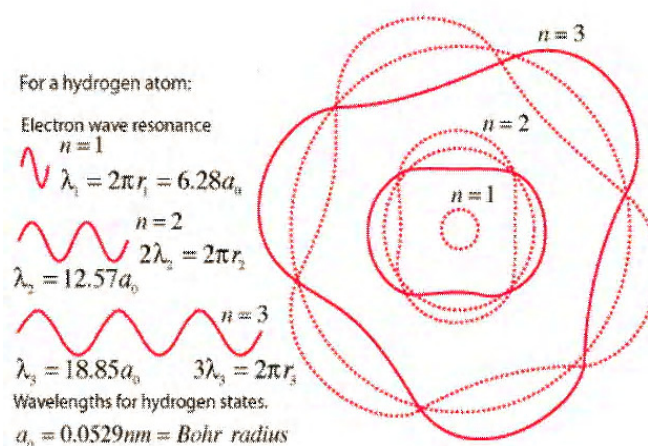
According to deBroglie moving electron is associated with waves must be completely in phase and there fore only those orbits are possible where circumference of the orbit is integral multiple of λ i.e.

$$2\pi r = n\lambda, \text{ where } n \text{ is the no. of waves}$$

$$2\pi r = \frac{nh}{mv} \Rightarrow mvr = \frac{nh}{2\pi}$$

From the above expression it can be commented that

no of waves in a shell waves = shell no.



• **Calculation of deBroglie wavelength if K.E. of the particle is E :**

$$E = \frac{1}{2}mv^2 \quad 2E = mv^2 \quad 2mE = m^2 v^2 = p^2$$

$$p = \sqrt{2mE}$$

$$\frac{h}{\lambda_{dB}} = \sqrt{2mE}$$

$$\lambda_{dB} = \frac{h}{\sqrt{2mE}}$$

If a charge particle at rest (having charge 'q') is accelerated by potential difference 'V' volt then

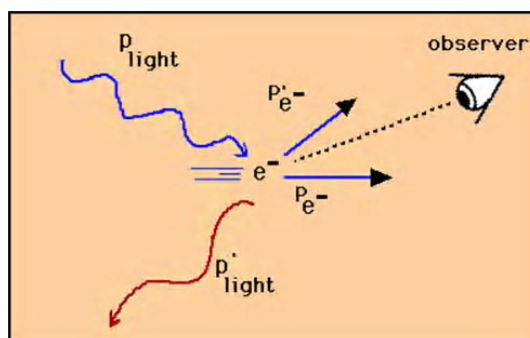
$$\lambda_{dB} = \frac{h}{\sqrt{2mqv}},$$

$$\lambda_{dB} = \sqrt{\frac{150}{V}} \text{ \AA} \quad (\text{Only for electron})$$

Ex. Calculate λ_{dB} of electron have K.E. 3eV

Sol. $\lambda_{dB} = \sqrt{\frac{150}{3}} = \sqrt{50} \text{ \AA}$

The Uncertainty Principle



The position and momentum of a particle cannot be simultaneously measured with arbitrarily high precision. There is a minimum for the product of the uncertainties of these two measurements. There is likewise a minimum for the product of the uncertainties of the energy and time.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

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

The uncertainty principle contains implications about the energy that would be required to contain a particle within a given volume. The energy required to contain particles comes from the fundamental forces, and in particular the electromagnetic force provides the attraction necessary to contain electrons within the atom, and the strong nuclear force provides the attraction necessary to contain particles within the nucleus. But Planck's constant, appearing in the uncertainty principle, determines the size of the confinement that can be produced by these forces. Another way of saying it is that the strengths of the nuclear and electromagnetic forces along with the constraint embodied in the value of Planck's constant determine the scales of the atom and the nucleus.

Q. Does uncertainty principle violates energy conservation principle?

(6) Wave mechanical model of Atom

Schrodinger equation :

The Schrodinger equation plays the role of Newton's laws and conservation of energy in classical mechanics - i.e., it predicts the future behavior of a dynamic system. It is a wave equation in terms of the wave function which predicts analytically and precisely the probability of events or outcome. The detailed outcome is not strictly determined, but given a large number of events, the Schrodinger equation will predict the distribution of results.

$$\mathbf{H}\Psi = \mathbf{E}\Psi$$

The kinetic and potential energies are transformed into the Hamiltonian which acts upon the wave function to generate the evolution of the wave function in time and space. The Schrodinger equation gives the quantized energies of the system and gives the form of the wave function so that other properties may be calculated.

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - U) \Psi = 0$$

Where, E = total energy of electron

U = potential energy of electron

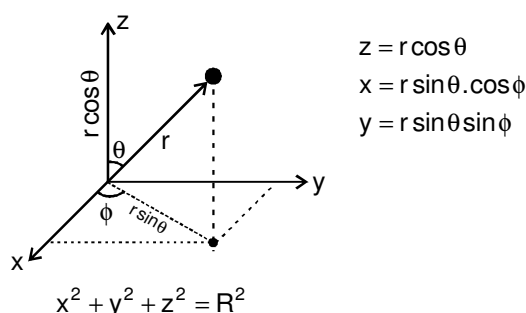
$$\nabla^2 = \text{Laplacian operator} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and ψ = wave function of electron = amplitude of matter wave.

Schrodinger equation can be solved completely for hydrogen atom and hydrogen-like species like He^+ , Li^{2+} .

The Schrodinger equation can also be written in terms of spherical polar coordinates (r, θ, ϕ) in addition to Cartesian coordinate x, y, z .

Since, H-atom possesses spherical symmetry, \therefore it is easier to solve Schrodinger equation if it is represented in polar coordinate.



When Schrodinger equation in polar coordinate is solved for H-atom then the solution obtained can be expressed as

$$\Psi = \Psi_r \cdot \Psi_{\theta, \phi}$$

Ψ_r represents radial wave function which depends on n, ℓ .

$\Psi_{\theta, \phi} \rightarrow$ Angular wave function which depends on m, ℓ .

Ψ (Psi) : [Wave function or Amplitude of Electron Wave]

It is also known as atomic orbitals. It is a mathematical function whose value depends on coordinates of electron in an atom. It may be +ve or -ve depending upon value of coordinates and it has no physical significance.

Ψ^2 [Probability Density] :

According to electromagnetic wave theory, intensity of light is proportional to square of amplitude. In the same way Ψ^2 gives an idea of intensity of electron wave i.e. probability of finding electron at that point.

Q. What is the significance of $\Psi^2(x).dx$?

Q. What is the significance of $\Psi^2.dV$?

ORBITALS

Orbitals are defined as that region or zone in the space where probability of finding electrons is possible (more than 90%). In an atom large no. of permissible orbitals are present.

These orbitals are designated by a set of 3 quantum number (n, ℓ, m) which arise as a natural consequence in the solution of Schrodinger equation i.e. the values of 3 quantum numbers are restricted by the solution of Schrodinger equation.

The Postulates of Quantum Mechanics

1. Associated with any particle moving in a conservative field of force is a wave function which determines everything that can be known about the system.
2. With every physical observable q there is associated an operator Q , which when operating upon the wave function associated with a definite value of that observable will yield that value times the wave function.
3. Any operator Q associated with a physically measurable property q will be Hermitian.
4. The set of eigen functions of operator Q will form a complete set of linearly independent functions.
5. For a system described by a given wave function, the expectation value of any property q can be found by performing the expectation value integral with respect to that wave function.
6. The time evolution of the wave function is given by the time dependent Schrodinger equation.

The Wave function Postulate

It is one of the postulates of quantum mechanics that for a physical system consisting of a particle there is an associated wave function. This wave function determines everything that can be known about the system. The wave function is assumed here to be a single-valued function of position and time, since that is sufficient to guarantee an unambiguous value of probability of finding the particle at a particular position and time. The wave function may be a complex function, since it is its product with its complex conjugate which specifies the real physical probability of finding the particle in a particular state.

$\psi(x, t)$ = single-valued probability amplitude at (x, t)

$\psi^*(x, t)\psi(x, t)$ = probability of finding particle at x at time t provided the wave function is normalized.

Q. How can a continuous description such as wave lead to discrete energy levels ?

Constraints on Wave function

In order to represent a physically observable system, the wave function must satisfy certain constraints:

1. Must be a solution of the Schrodinger equation.
2. Must be normalizable. This implies that the wave function approaches zero as x approaches infinity.
3. Must be a continuous function of x .

4. The slope of the function in x must be continuous.

Specifically $\frac{\partial \psi(x)}{\partial x}$ must be continuous.

These constraints are applied to the boundary conditions on the solutions, and in the process help determine the energy eigenvalues.

Few Radial Functions $R_{n,\ell}$

$$n = 1, \ell = 0 \quad R_{10}(r) = 2 \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

$$n = 2, \ell = 0 \quad R_{20}(r) = \frac{1}{\sqrt{8}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$n = 2, \ell = 1 \quad R_{21}(r) = \frac{1}{\sqrt{24}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0}$$

$$n = 3, \ell = 0 \quad R_{30}(r) = \frac{2}{81\sqrt{3}} \left(\frac{1}{a_0} \right)^{3/2} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2} \right) e^{-r/3a_0}$$

$$n = 3, \ell = 1 \quad R_{31}(r) = \frac{2}{9\sqrt{6}} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - 2 \frac{r^2}{a_0^2} \right) e^{-r/3a_0}$$

$$n = 3, \ell = 2 \quad R_{32}(r) = \frac{4}{81\sqrt{30}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}$$

$\Psi(r, \theta, \phi)$ for Hydrogen Atom

$$n = 1, \ell = 0, m_\ell = 0 \quad \Psi_{100}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

$$n = 2, \ell = 0, m_\ell = 0 \quad \Psi_{200}(r) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$n = 2, \ell = 1, m_\ell = 0 \quad \Psi_{210}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$$

$$n = 2, \ell = 1, m_\ell = \pm 1 \quad \Psi_{21\pm 1}(r, \theta, \phi) = \frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$$

$$n = 3, \ell = 0, m_\ell = 0 \quad \Psi_{300}(r) = \frac{1}{81\sqrt{3\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2} \right) e^{-r/3a_0}$$

$$n = 3, \ell = 1, m_\ell = 0 \quad \psi_{310}(r, \theta, \phi) = \frac{1}{81} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \cos \theta$$

$$n = 3, \ell = 1, m_\ell = \pm 1 \quad \psi_{31\pm 1}(r, \theta, \phi) = \frac{1}{81\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} + \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin \theta e^{\pm i\phi}$$

$$n = 3, \ell = 2, m_\ell = 0 \quad \psi_{320}(r, \theta, \phi) = \frac{1}{81\sqrt{6\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$$

$$n = 3, \ell = 2, m_\ell = \pm 1 \quad \psi_{32\pm 1}(r, \theta, \phi) = \frac{1}{81\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$$

$$n = 3, \ell = 2, m_\ell = \pm 2 \quad \psi_{32\pm 2}(r, \theta, \phi) = \frac{1}{162\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$$

Real Wave Functions For Hydrogen Atom

$$\psi_{2p_x}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta \cos \phi$$

$$\psi_{2p_y}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta \sin \phi$$

$$\psi_{2p_z}(r, \theta, \phi) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$$

$$\psi_{3p_x}(r, \theta, \phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin \theta \cos \phi$$

$$\psi_{3p_y}(r, \theta, \phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin \theta \sin \phi$$

$$\psi_{3p_z}(r, \theta, \phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \cos \theta$$

$$\psi_{3d_{z^2}}(r, \theta, \phi) = \frac{1}{81\sqrt{6\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$$

$$\psi_{3d_{xz}}(r, \theta, \phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta \cos \phi$$

$$\psi_{3d_{yz}}(r, \theta, \phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta \sin \phi$$

$$\psi_{3d_{x^2-y^2}}(r, \theta, \phi) = \frac{\sqrt{2}}{81\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta \cos 2\phi$$

$$\psi_{3d_{xy}}(r, \theta, \phi) = \frac{1}{81\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta \sin 2\phi$$

QUANTUM NUMBERS

In the solution to the Schrodinger equation for the hydrogen atom, three quantum numbers arise from the space geometry of the solution and a fourth arises from electron spin. No two electrons can have an identical set of quantum numbers according to the Pauli exclusion principle, so the quantum numbers set limits on the number of electrons which can occupy a given state and therefore give insight into the building up of the periodic table of the elements.

(1) Principal Quantum No. (n) :

The principal quantum number or total quantum number n arises from the solution of the radial part of the Schrodinger equation for the hydrogen atom. The bound state energies of the electron in the hydrogen atom are given by

$$E_n = \frac{-13.6\text{eV}}{n^2}$$

- (i) Permissible values of n : all integers from 1 to ∞ (infinity)
- (ii) This no. identifies shell in an atom.
- (iii) It gives an idea of average distance 'R' [size of any orbital from the nucleus higher the value of n , higher will be the average distance and hence greater will be the size].
- (iv) It gives idea of energy of electron upto some extent. Higher the value of n , higher will be the energy (if ' ℓ ' is constant).
for example order of energy $4s > 3s > 2s > 1s$
- (v) It gives value of total no. of orbitals present in any shell and that is equal to n^2 .
- (vi) It gives value of total no. of electrons which may be present in the given shell = $2n^2$.
- (vii) It gives value of angular momentum of electron i.e. $\frac{nh}{2\pi}$
- (viii) It gives variation of radial probability distribution.

(2) Azimuthal Quantum No. or Angular momentum Quantum no. (ℓ) :

Permissible values of ℓ is 0 to $(n-1)$. i.e. value of ℓ is restricted by n .

$$n = 1, \quad \ell = 0$$

$$n = 2, \quad \ell = 0, 1; \text{ i.e. 2 values of } \ell.$$

$$n = 3, \quad \ell = 0, 1, 2. \text{ i.e. 3 values of } \ell.$$

No. of values of ' ℓ ' is equal to ' n ' principal quantum number

It identifies sub shell in an atom

The value of ' ℓ ' gives name of sub-shell and shape of orbital.

ℓ	Notation	Name	Shape
0	s	Sharp	Spherical
1	p	Principal	dumbell shaped
2	d	diffuse	double dumbell
3	f	fundamental	complex

(3) magnetic quantum number (m)

The direct implication of this quantum number is that the z-component of angular momentum is quantized according to $L_z = m_l \hbar / 2\pi$

It is called the magnetic quantum number because the application of an external magnetic field causes a splitting of spectral lines called the Zeeman effect. The different orientations of orbital angular momentum represented by the magnetic quantum number can be visualized in terms of a vector model.

(4) Spin quantum number (s)

An electron, besides charge and mass, has also spin angular momentum commonly called **spin**. The spin angular momentum of the electron is constant and cannot be changed.

An electron spin $s = 1/2$ is an intrinsic property of electrons. Electrons have intrinsic angular momentum characterized by quantum number $1/2$. In the pattern of other quantized angular momenta, this gives total angular momentum

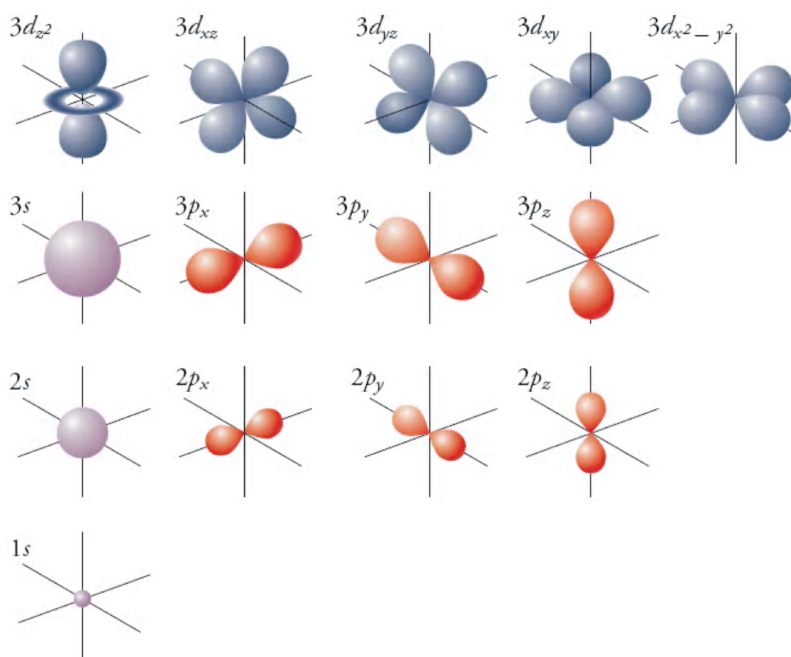
The resulting fine structure which is observed corresponds to two possibilities for the z-component of the angular momentum.

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)} \hbar = \frac{\sqrt{3}}{2} \hbar$$

This causes an energy splitting because of the magnetic moment of the electron

$$S_z = \pm \frac{1}{2} \hbar$$

Orbitals diagram



Filling of Orbitals in atoms :

The filling of electrons into the orbitals of different atoms take place on the basis of 3 principles :

AUFBAU's PRINCIPLE

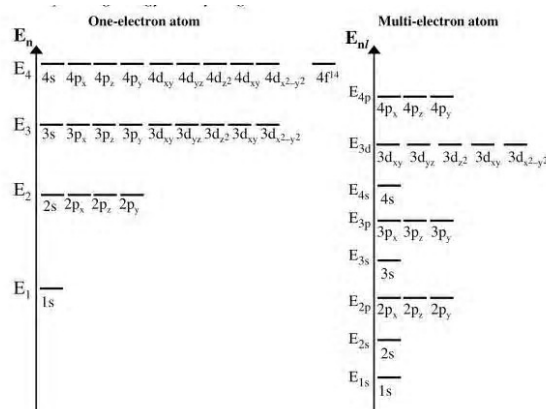
The electrons are added progressively to Various orbitals in the order of increasing energy, starting with the orbital of lowest energy, generally.

ENERGY OF ORBITALS

- (i) **Hydrogen atom :** In case of hydrogen atom, the orbital is mainly determined by principle quantum n
 $\therefore n \uparrow, E \uparrow$

For H atom

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

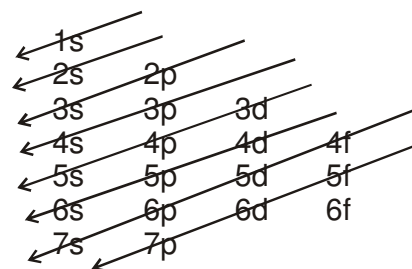


- (ii) **Multielectronic atoms :** In case of multielectronic atoms, energy of orbitals depends upon both n and l and hence energy of orbitals is compared on the basis of $(n + l)$ rules generally

$\Rightarrow n + l$ rule :

- (iii) As the value $(n + l)$ increases the total energy of orbitals also increases.
- (iv) If value of $(n + l)$ is same or different orbital then orbital with lower value of n , have lower energy.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$$

**PAULI'S EXCLUSIONS PRINCIPLE**

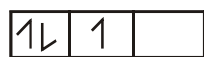
The principle states that no two electrons in an atom can have same set of all 4 quantum no.

Therefore spin quantum No. have only two values therefore it can also be commented that orbital can have maximum two electrons with opposite spin.

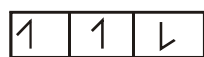
HUND'S RULE OF MAXIMUM MULTIPLICITY

While filling the orbitals of same energy (i.e. orbitals of same subshell) pairing of electron start only when each orbital have got 1 electron that too with same spin or parallel spin.

Multiplicity is expressed as $2|s| + 1$ where s represent total spin.



$$s = +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} = +\frac{1}{2} \quad 2|s| + 1 = 2$$



$$s = +\frac{1}{2} + \frac{1}{2} - \frac{1}{2} = +\frac{1}{2}, \quad 2|s| + 1 = 2$$



$$s = +\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = +\frac{3}{2}, \quad 2\left|\frac{3}{2}\right| + 1 = 4 \quad (\text{It has maximum multiplicity})$$

Q. Total spin resulting from d^7 configuration ?

ELECTRONIC CONFIGURATION OF ATOM

The distribution of electrons of an atom in its various shell, sub shells and orbitals is known as electron configuration.

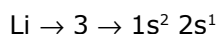
Valence shell or outer most shell $\rightarrow n^{\text{th}}$ shell

Penultimate shell-Inner to outermost shell $\rightarrow (n - 1)$ shell

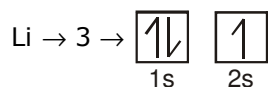
Anti Penultimate shell $\rightarrow (n - 2)$ shell

Electronic configuration can be expressed in the following ways :

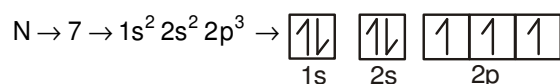
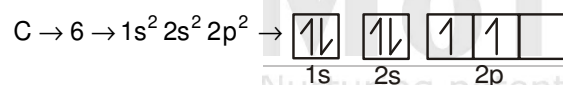
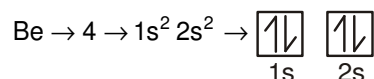
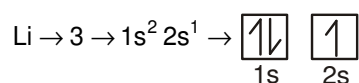
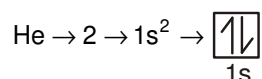
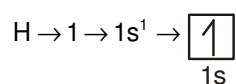
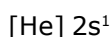
(i) Orbital notation method : $n \ell^x$



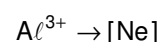
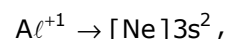
(ii) Orbital diagram method :



(iii) Condensed form :

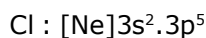
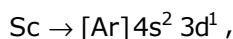


● **Electronic Configuration of ions :**

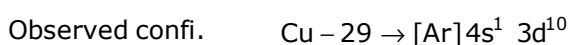


Similarly in case of transition elements electrons are removed from n^{th} shell for e.g. 4^{th} shell in case of

3d series.



Exceptional configuration



Above exceptional configuration can be explained on the basis of following factor.

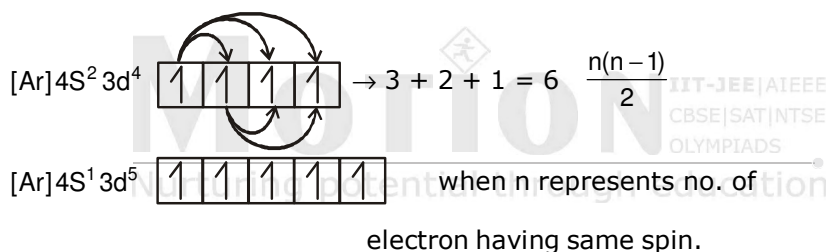
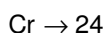
(i) Symmetrical Electronic Configuration :

It is well known fact that symmetry leads to stability, \therefore orbitals of a sub shell having half-filled or full-filled configuration (i.e. symmetrical distribution of electrons) are relatively more stable. This effect is dominating in d and f subshell.

$\therefore d^5, d^{10}, f^7, f^{14}$ configurations are relatively more stable.

(ii) Exchange Energy :

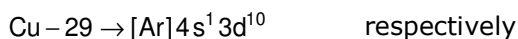
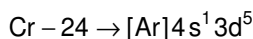
It is assumed that electrons in de-generate orbitals, do not remain confined to a particular orbital rather it keep on exchanging its position with electron having same spin and same energy (electrons present in orbitals having same energy). Energy is released in this process known as exchange energy which imparts stability to the atom. More the number of exchanges, more will be the energy released, more the energy released stability will be more.



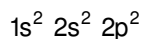
The relative value of exchange energy + (energy released during depairing) depairing energy and transfer energy [4s \rightarrow 3d]

decides the final configuration. For example, if magnitude of

Dep. energy + Ex. energy > transfer. energy as in cases of Cu and Cr then configuration is



In case of carbon magnitude of transfer energy > dep. energy + exch. energy and
 \therefore configuration of carbon is



Magnetic moment (μ) : It is the measure of the magnetic nature of substance

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

When $\mu = 0$, then there is no unpaired electron in the species and it is known as diamagnetic specie. These species are repelled by magnetic field.

When $\mu \neq 0$, for paramagnetic species. These species have unpaired electrons and are weakly attracted by the magnetic field.

Calculate magnetic moment of these species

(i) Cr (ii) N (iii) Cl (iv) Ar

(i) Cr : No. of unpaired electrons = 6.

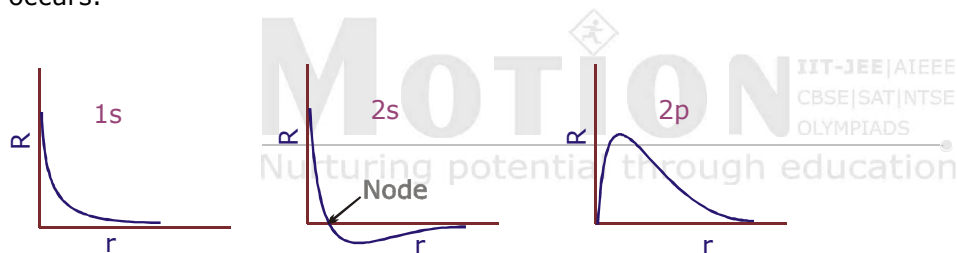
$$= \sqrt{6(6+2)} = \sqrt{48} \text{ BM}$$

Generally species having unpaired electrons are coloured or impart colour to the flame. Species having unpaired electrons can be easily excited by the wavelengths corresponding to visible lights and hence they emit radiations having characteristic colour.

(A) Radial wave function (R)

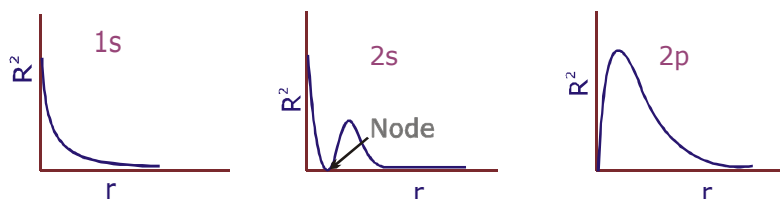
In all cases R approaches zero as r approaches infinity. One finds that there is a node in the 2s radial function. In general, it has been found that ns-orbitals have (n-1) nodes, np-orbitals have (n-2) nodes etc.

The importance of these plots lies in the fact that they give information about how the radial wave function changes with distance r and about the presence of nodes where the change of sign of R occurs.



(B) Radial Probability density (R^2)

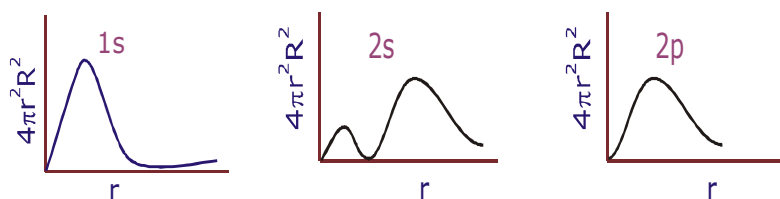
The square of the radial wave function R^2 for an orbital gives the radial density. The radial density gives the probability density of finding the electron at a point along a particular radius line. To get such a variation, the simplest procedure is to plot R^2 against r. These plots give useful information about probability density or relative electron density at a point as a function of radius. It may be noted that while for s-orbitals the maximum electron density is at the nucleus. all other orbitals have zero electron density at the nucleus.

**(C) Radial probability functions $4\pi r^2 R^2$**

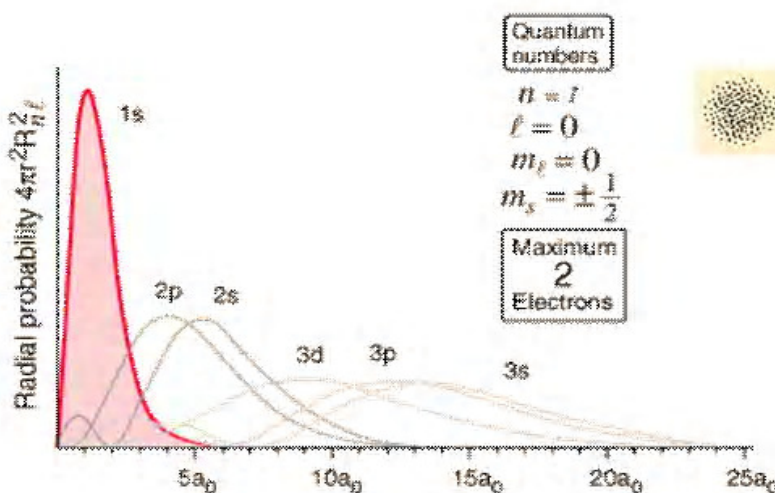
The radial density R^2 for an orbital, as discussed above, gives the probability density of finding the electron at a point at a distance r from the nucleus. Since the atoms have spherical symmetry, it is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radius $(r + dr)$ and r . The volume of the shell is equal to $\frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3 = 4\pi r^2 dr$.

This probability which is independent of direction is called radial probability and is equal to $4\pi r^2 dr R^2$.

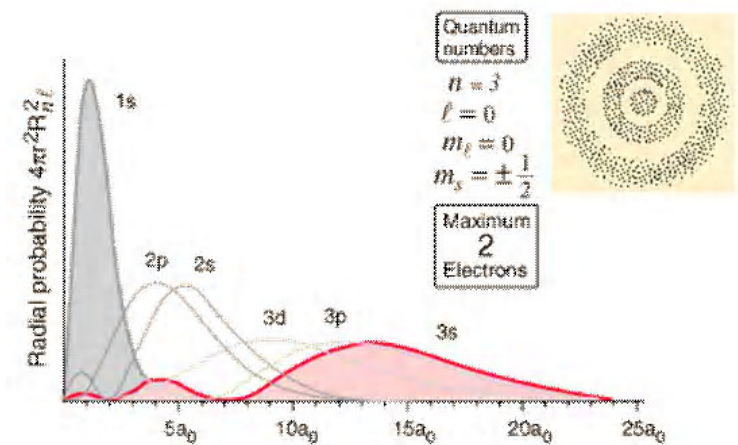
Radial probability function ($4\pi r^2 dr R^2$) gives the probability of finding the electron at a distance r from the nucleus regardless of direction.



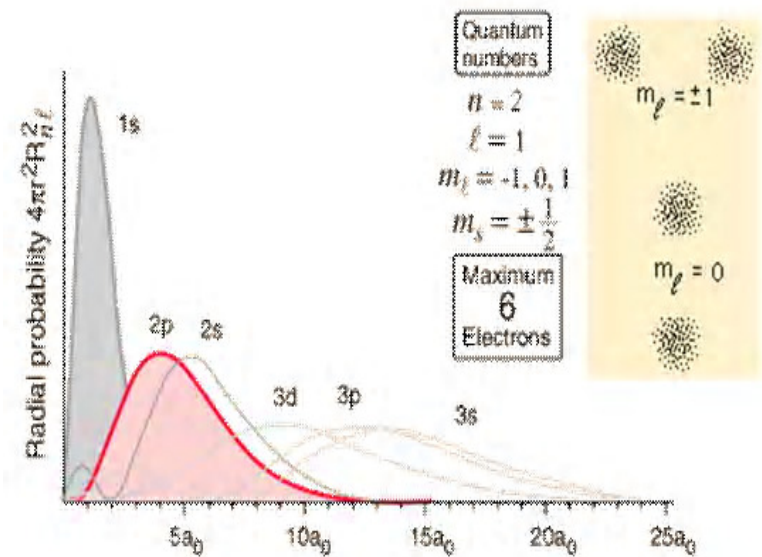
The radial probability distribution curves obtained by plotting radial probability functions versus distance r from the nucleus for 1s, 2s and 2p orbitals are shown in fig.

Hydrogen 1s Radial Probability

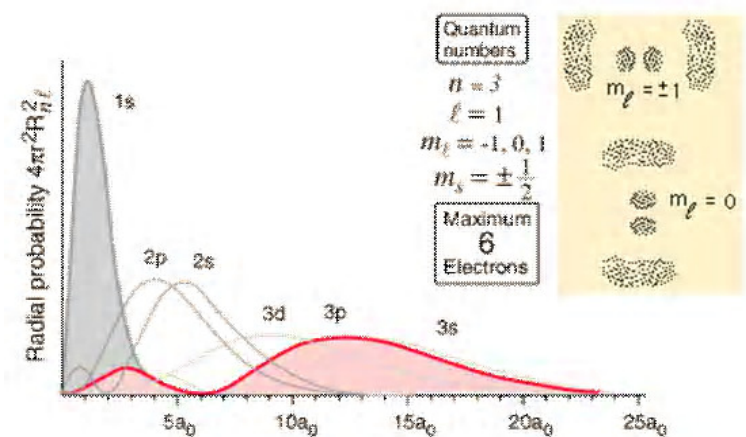
Hydrogen 3s Radial Probability



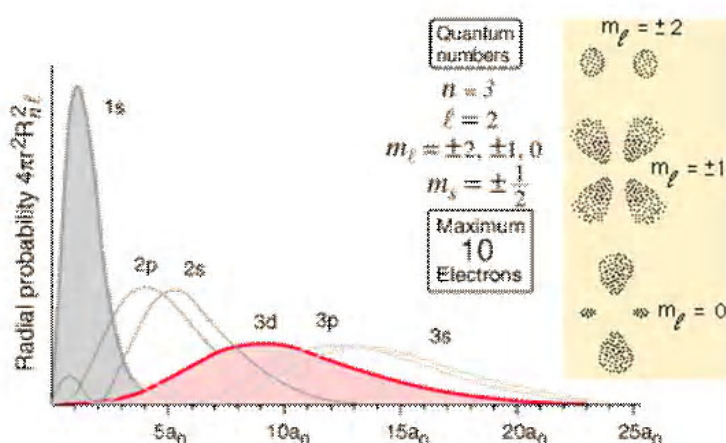
Hydrogen 2p Radial Probability



Hydrogen 3p Radial Probability



Hydrogen 3d Radial Probability



Angular wave Function $\Theta\Phi$.

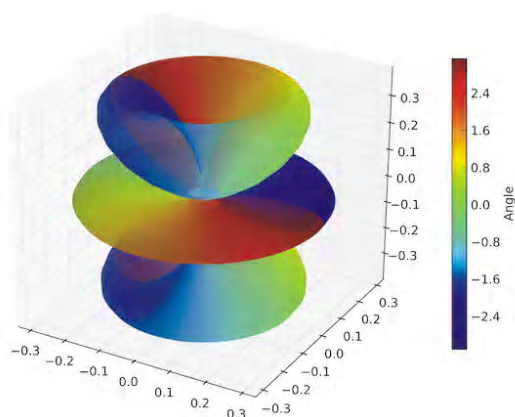
The angular wave function ' $\Theta\Phi$ ' depends only on the quantum number ℓ and m_l and is independent of the principal quantum number n for a given type of orbital. It therefore means that all s orbitals will have same angular wave function.

(A) Angular Wave Function, ' $\Theta\Phi$ '

For an s-orbital, the angular part is independent of angle and is, therefore, of constant value. Hence this graph is circular or, more properly, in three dimensions i.e., spherical. For the p_z orbital, we get two tangent spheres. The p_x and p_y orbitals are identical in shape but are oriented along the x and y axes respectively. The angular, wave function plots for d and f-orbitals are four lobed and six-lobed respectively. It is necessary to keep in mind that in the angular wave function plots, the distance from the center is proportional to the numerical values of ' $\Theta\Phi$ ' in that direction and is not the distance from the center of the nucleus.

(B) Angular Wave Function, $|\Theta\Phi|^2$

The angular probability density plots can be obtained by squaring the angular function plots shown in fig. On squaring, different orbitals change in different ways. For an s orbital, the squaring causes no change in shape since the function everywhere is the same: thus another sphere is obtained.



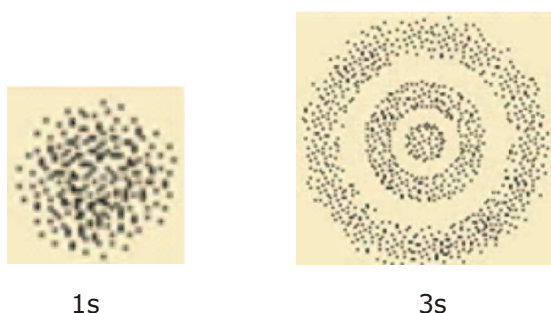
Plots of Total probability density: Shapes of Atomic Orbitals.

The problems associated with the representations of the variations of $|\Psi|^2$ in space have been circumvented by the following two approaches.

- (a) Charge cloud diagrams
- (b) Boundary surface diagrams

(A) Charge cloud diagrams

In this approach, the probability density $|\Psi|^2$ is shown as a collection of dots such that the density of dots in any region represents the electron probability density in that region. Fig. shows such plots for some orbitals. These give some ideal about the shapes of the orbitals.

**(B) Boundary surface diagrams**

In these diagrams, the shape of an orbital is defined as a surface of constant probability density that encloses some large fraction (say 90 %) of the probability of finding the electron. The probability density is $|\Psi|^2$. When $|\Psi|^2$ is constant, so is $|\Psi|$. Hence $|\Psi|$ is constant on the surface for an s orbital ($l = 0$) has the shape of a spherical shell centered on the nucleus, fig. For each value of n , there is one s orbital. As n increases, there are $(n-1)$ concentric spherical shells like the successive layers in an onion.

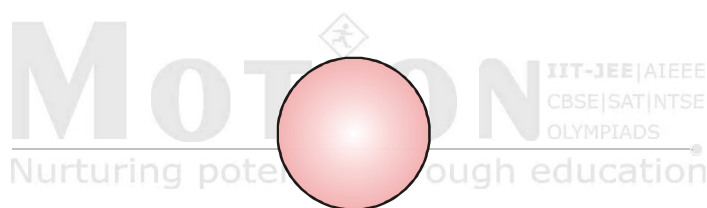
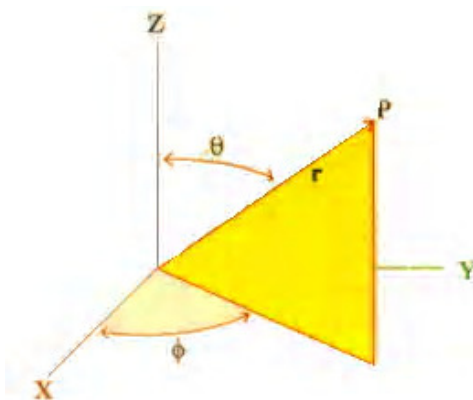
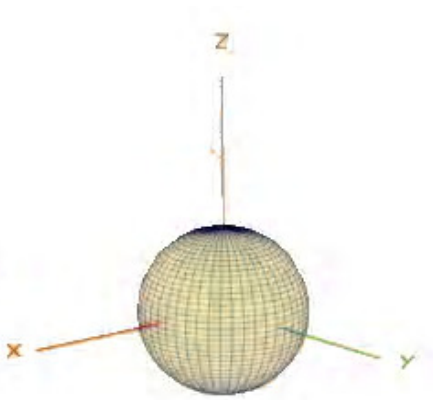


Fig. Boundary surface diagrams for the 1 s orbital.

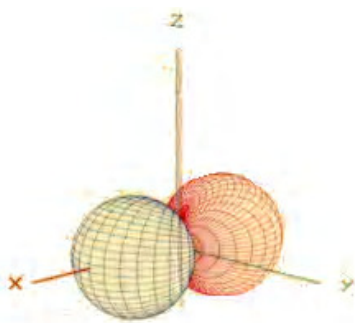
SHAPES OF ATOMIC ORBITALS



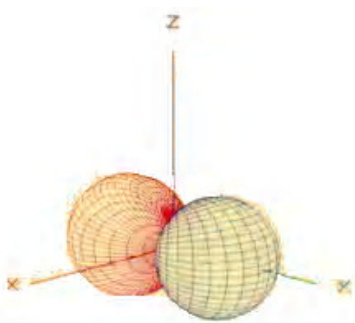
The spherical Polar Coordinates



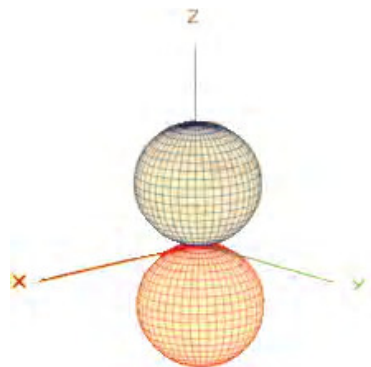
S



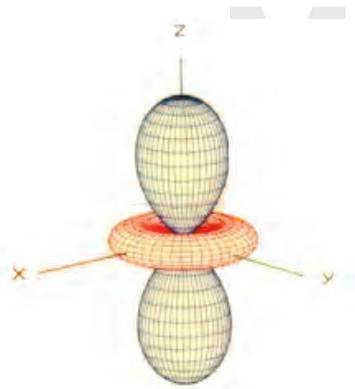
p_x



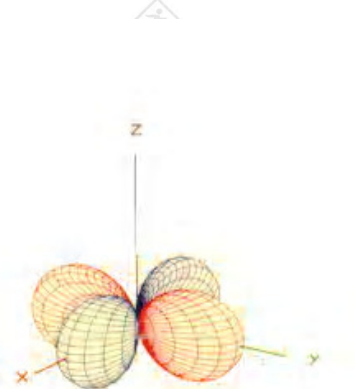
p_y



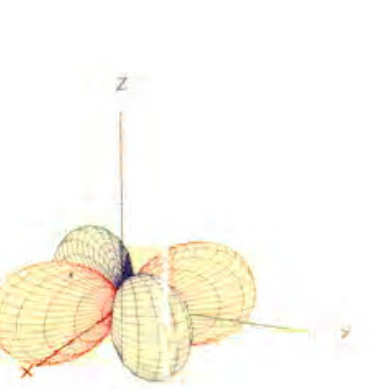
p_z



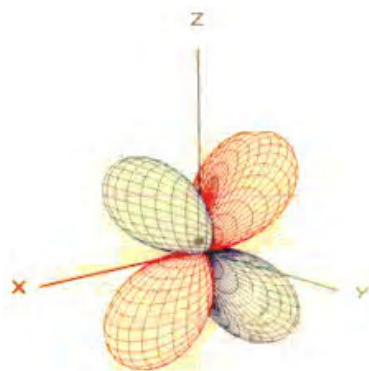
d_{z^2}



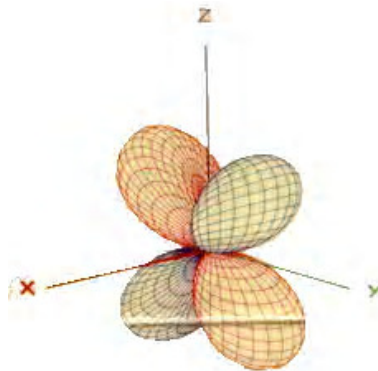
$d_{x^2-y^2}$



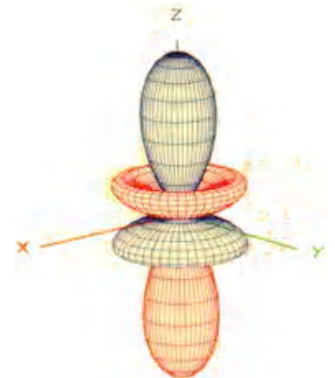
d_{xy}



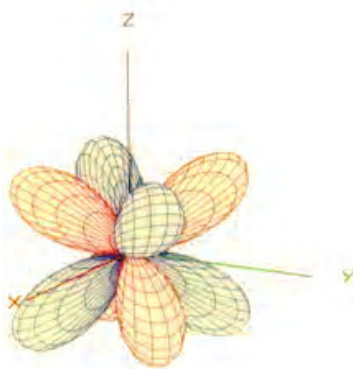
d_{xz}



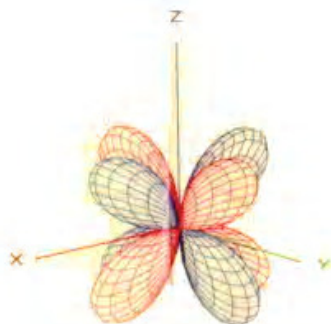
d_{yz}



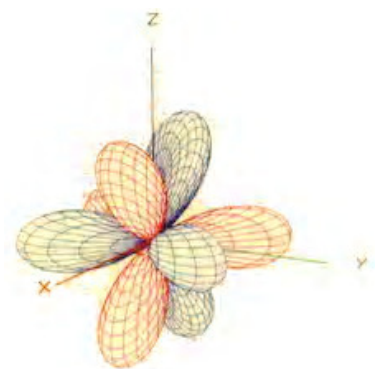
f_{z^3}



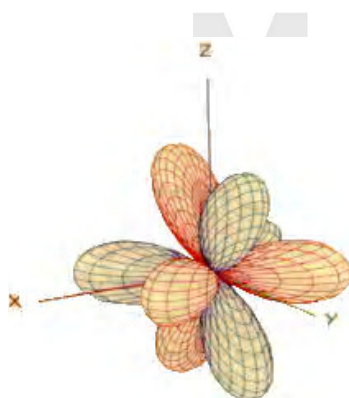
f_{xyz}



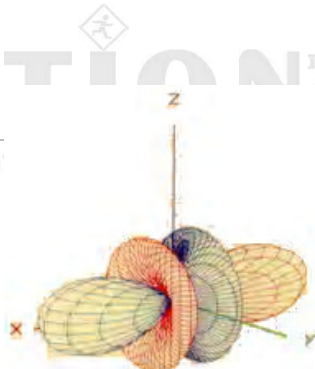
$f_{z(x^2-y^2)}$



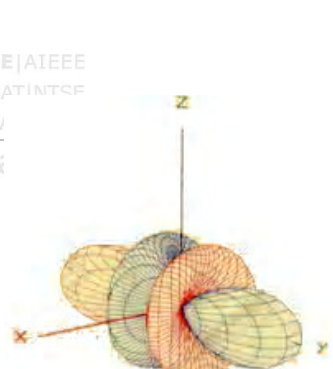
$f_{x(y^2-z^2)}$



$f_{y(z^2-x^2)}$



f_{x^3}



f_{y^3}