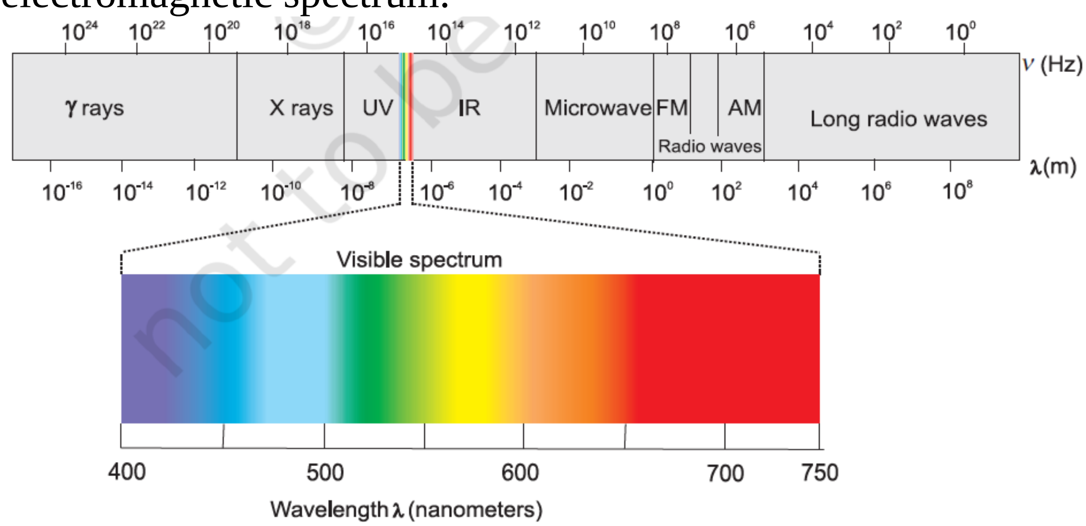
CHAPTER- STRUCTURE OF ATOM

<u>Electromagnetic radiation</u>: The energy is emitted from source continuously in the form of radiations and magnetic fields.
All electromagnetic waves travel with the velocity of light (3×10^8 m / s) and do not require any medium for their propagation.
An electromagnetic wave has the following characteristics:
(i) **Wavelength** It is the distance between two successive crests or troughs of a wave. It is denoted by the Greek letter λ (lambda).
(ii) **Frequency** It represents the number of waves which pass through a given point in one second. It is denoted by υ (nu).
(iii) **Velocity** (v) It is defined as the distance covered in one second by the waves. Velocity of light is 3×10^8 ms^{-1}.
(iv) **Wave number** It is the reciprocal of wavelength and has units cm^{-1}
It is denoted by $\bar{\upsilon}$ (nu bar).
(v) **Amplitude** (a) It is the height of the crest or depth of the trough of a wave. Wavelength (λ), frequency (v) and velocity (c) of any electromagnetic radiations are related to each other as $c = \upsilon\lambda$

Electromagnetic Spectrum

The different types of electromagnetic radiations differ only in their wavelengths and hence. frequencies. When these electromagnetic radiations are arranged in order to their increasing wavelengths or decreasing frequencies, the complete spectrum obtained is called electromagnetic spectrum.



Electromagnetic spectra may be emission or absorption spectrum on the basis of energy absorbed or emitted.

<u>Planks quantum theory</u> :

- The radiant energy is emitted or absorbed not continuously but discontinuously in form of small disecret packets of energy called 'quantum'. In case of light, the quantum of energy is called 'photon'.
- The energy of each quantum is directly proportional to the frequency of radiation i.e $E \propto \upsilon$ or $E = h\upsilon$ h = planks constant = 6.626×10^{-34} Js.
- Energy is always emitted or absorbed as integral multiple of this quantum $E = nh\upsilon$, where n = 1,2,3…

Black body: an ideal body, which emits and absorb all frequencies is called a black body. The radiation emitted by such body is called black body radiation.

Photoelectric effect: It is the phenomenon in which beam of light of certain frequency falls on the surface of metal and electrons are ejected from it.

This phenomenon is known as photoelectric effect. It was first observed by Hertz.

- The electrons are ejected from the metal surface as soon as the beam of light strikes the surface.
- The number of electrons ejected is proportional to the intensity or brightness of light.
- Threshold frequency (ν_o) = For each metal, there is a characteristic minimum frequency below which photoelectric effect is not observed.
- Photo electric work function (W_o) = the minimum energy required to eject the electron is called work function. $W_o = h\nu_o$
- Energy of the ejected electrons = $h(\nu - \nu_o) = \frac{1}{2} m_e v^2$, m_e = mass of electron v = velocity of ejected electron

<u>Dual behaviour of electromagnetic radiation</u> :

The particle possesses particle as well as wave like properties i.e light has dual behavior whenever radiation interact with matter it displays particle like properties. (black body radiation and photoelectric effect) wave like properties are exhibited when propagates (diffraction and interference).

<u>Spectrum</u> : when a ray of white light is spread out into a series of coloured bands called spectrum. Two types of spectrum

Continuous spectrum : the spectrum which consists of all the wavelengths.

Line spectrum : A spectrum in which only specific wavelengths are present.

Atomic spectrum is also classified as emission and absorption spectrum:

An **emission spectrum** is obtained when a substance emits radiation after absorbing energy.

An **absorption spectra** is obtained when a substance absorbs certain wavelengths and leave dark spaces in bright continuous spectrum.

The study of emission or absorption spectra is referred to as spectroscopy.

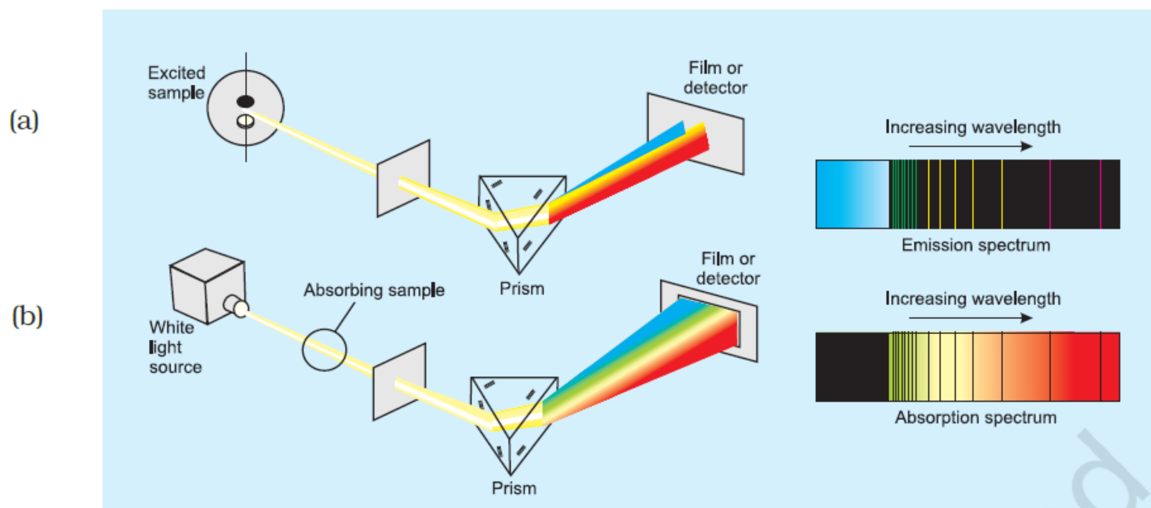


Fig. 2.10 (a) Atomic emission. *The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum.* ***(b) Atomic absorption.*** *When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.*

<u>Line spectrum of hydrogen</u> :

The spectral lines for atomic hydrogen :

Series	n_1	n_2	Spectral Region
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

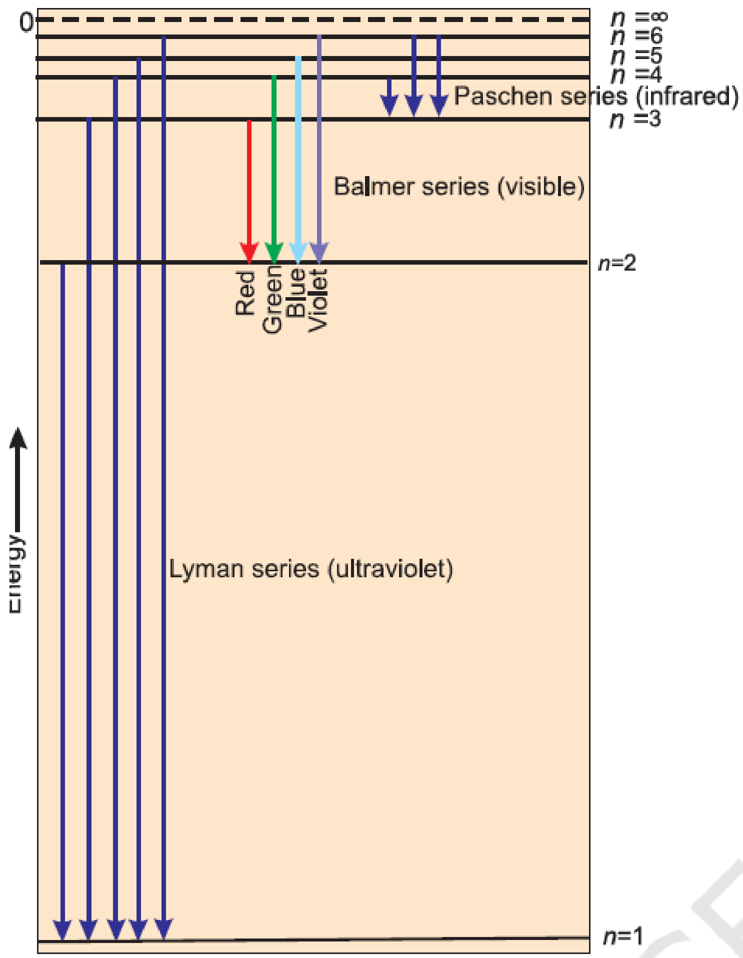


Fig. 2.11 *Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)*

<u>Bohr’s model of hydrogen atom</u>:

Neils Bohr proposed his model in 1931. Bohr‟s model is applicable only for one electron system like H, He^+, Li^{2+} etc.

Assumptions of Bohr‟s model are:

1. Electrons keep revolving around the nucleus in certain fixed permissible orbits where it doesn't gain or lose energy. These orbits are known as stationary orbits.
2. The electrons can move only in those orbits for which the angular momentum is an integral multiple of $h / 2\pi$, i.e., $mvr = nh / 2\pi$ where, m = mass of electron: v = velocity of electron; r = radius of orbit n = number of orbit in which electrons are present
3. Energy is emitted or absorbed only when an electron Jumps from higher energy level to lower energy level and vice-versa. $\Delta E = E2 – E1 = h\upsilon = hc / \lambda$
4. The most stable state of an atom is its ground state or normal state, From Bohr's model, energy, velocity and radius of an electron in nth Bohr orbit are :
   Radius of nth orbit is given by $r_n = 52.9\ n^2/ Z$ pm
   Energy of nth orbit is given by $E_n = 2.18\times10^{-18}\ Z^2/n^2$ J
   $\Delta E = 2.18\times10^{-18}\ (1/n_i^2 – 1/n_f^2)$

Limitations of bohr's model

1. It is unable to explain the spectrum of atom other than hydrogen like doublets or Multi electron atoms.
2. It could not explain the ability of atom to form molecules by chemical bonds. Hence. It could not predict the shape of molecules.
3. It is not in accordance with the Heisenberg uncertainty principle and could not explain the concept of dual character of matter.
4. It is unable to explain the splitting of spectral lines in the presence of magnetic field(Zeeman effect) and electric field (Stark effect)

De-Broglie Principle:

de-Broglie explains the dual nature of electron i.e.. both particle as well as wave nature.

$\lambda = h / mv$ or $\lambda = h /P$

where, λ = wavelength: v = velocity of particle; m = mass of particle, P = momentum

Heisenberg's Uncertainty Principle

According this principle, "it is impossible to specify at any give instant both the momentum and the position of subatomic particles like electron."

$\Delta x \cdot \Delta P \geq h / 4\pi$

where, Δx = uncertainty in position; Δp = uncertainty in momentum

Reason of failure of bohr's model :

- It ignore dual behavior of matter
- It contradicts Heisenberg's uncertainity principle

Classical mechanics is based on newton's law of motion. It successfully describes the motion of macroscopic particles but fail in the case of microscopic particles.

Quantum Mechanics is a theoretical science which deals with the study of the motions of microscopic objects that have both observable particle and wave like properties. It Is given by Werner Heisenberg and Erwin Schrodinger

Schrodinger wave equation is

$H\Psi = E\Psi$

where, H is the total energy operator, called Hamiltonian. E = total energy of the system (potential energy + kinetic energy)

ψ = wave function which is the amplitude of electron wave

The orbital wave function, Ψ has no significance, but ψ^2 has significance, it measures the electron probability density at a point in an atom. Ψ can he positive or negative but ψ^2 is always positive.

Orbital: The region of space around the nucleus where the probability of finding an electron is maximum.

Quantum numbers : there are a set of four quantum numbers which specify the energy ,shape, size and orientation of an orbital.

Principal quantum number (n) : it identifies the shell, size and energy of the orbitals.

n	1	2	3	4
Shell No. :	K	L	M	N
Total no. of orbitals in a shell = n^2	1	4	9	16
Maximum no. of electrons = $2n^2$	2	8	18	32

Azimuthal quantum number (*l*): azimuthal quantum number is also known as orbital angular quantum number or subsidiary quantum numbers. It identify sub shell, determine the shape of orbitals energy of electrons in multi- electron atoms along with principal quantum number and orbital angular momentum $\sqrt{l(l+1)}\frac{h}{2\pi}$. the number of orbitals in a shell = 2*l* + 1. For a given value of n,it can have n values ranging from 0 to n-1. Total number of subshells in main shell is equal to the value of n.

n	l	Subshell notation
1	0	$1s$
2	0	$2s$
2	1	$2p$
3	0	$3s$
3	1	$3p$
3	2	$3d$
4	0	$4s$
4	1	$4p$
4	2	$4d$
4	3	$4f$

<u>Magnetic quantum number or magnetic orbital quantum number</u> (m_l):

gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis. For any sub-shell (defined by '*l*' value) 2*l*+1 values of m*l* are possible and these values are given by :

$m_l = -l, -(l-1), -(l-2)... 0,1... (l-2), (l-1), l$

Subshell notation	**S**	**p**	**d**	**f**	**g**
Value of ' *l*'	0	1	2	3	4
No. of orbitals	1	3	5	7	9

<u>Spin quantum number</u> (s): It indicates the direction of spinning of electron, i.e., clockwise(+1/2)spin or anti- clockwise(-1/2) spin.

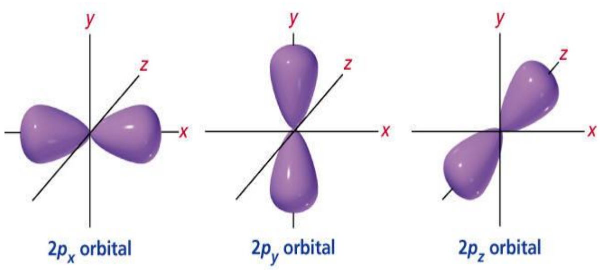
Node

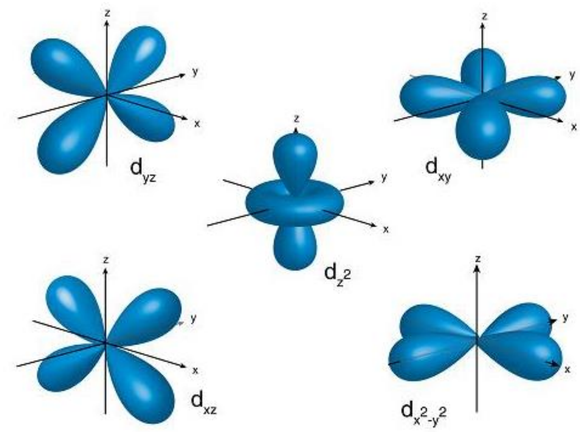
A region or space, where probability of finding an electron is maximum is called a peak, while zero probability space is called node. Nodes are of two types:

(a) Radial nodes occurs when the probability density of wave function of the electron is zero on a spherical surface of a particular radius.

(b) Angular nodes occur when the probability density wave function of the electron is zero along the directions specified by a particular angle.

(i) (n – l – 1) = no. of radial node
(ii) (l) = no. of angular node
(iii) (n – 1) = total no. of nodes
Degenerate orbitals : orbitals having the same energy is called degenerate orbitals.
Shape of p and d orbitals:





Sheilding effect or screening effect: Due to the presence of electrons in the inner shells, the electron in the outer shell will not experience the full positive charge of the nucleus .
The effect will be lowered due to the partial screening of positive charge on the
nucleus by the inner shell electrons. This is known as the shielding of the outer shell electrons from the nucleus by the inner shell electrons.
The net positive charge experienced by the outer electrons is known as effective nuclear charge ($Z_{eff}\, e$).

Aufbau Principle

According to this principle, in the ground state of an atom, the electrons occupy the lowest energy orbitals available to them, i.e., the orbitals are filled in order of increasing value of n + l.
For the orbitals having the same value of n + 1, the orbital having lower value of n is filled up first.
The general order of increasing energies of the orbital is

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

Half-filled and completely filled electronic configurations are more stable Hence. Outer configuration of Cr is $3d^5\ 4s^1$ and Cu is $3d^{10}\ 4s^1$.

Pauli Exclusion Principle:

It states, no two electrons in an atom can have identical set of four quantum numbers.

Only two electrons exist in a same orbital but will have different spin.

The maximum number of electrons in s subshell is 2, p subshell is 6 d subshell is 10 and f subshell is 14.

Hund's Rule of Maximum Multiplicity

It states that

(i) In an atom no electron pairing takes place in the p, d or (orbital. until each orbital of the given subshell contains one electron.

(ii) The unpaired electrons present in the various orbitals of the same subshell should have parallel spins.

Electronic Configuration

Arrangement of electrons in the space around nucleus in an atom known as electronic Configuration.

Methods of Writing Electronic Configuration:

1) **nl^x notation :** In this, the electrons present in respective main shells and orbitals are denoted. n = main shell (1,2,3…) , *l*= subshell/ orbital (s,p,d,f), x = no. of electron.

   e.g CI(17) = $1s^2,2s^2,2p^6,3s^2,3p^5$

2) **orbital digram method:**

	1s	2s	2p		
Li	↑↓	↑			
Be	↑↓	↑↓			
B	↑↓	↑↓	↑		
C	↑↓	↓↑	↑	↑	
N	↑↓	↑↓	↑	↑	↑
O	↑↓	↑↓	↑↓	↑	↑
F	↑↓	↑↓	↑↓	↑↓	↑
Ne	↑↓	↑↓	↑↓	↑↓	↑↓

Stability of completely filled and exactly half filled orbitals

1.Symmetrical distribution of electrons: The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable.
2.Exchange Energy: Two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled.