Class : Chemistry
Class : XI

Kannada

STRUCTURE OF ATOM

Importance of Chemistry :

- **Faraday** studied electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes.**

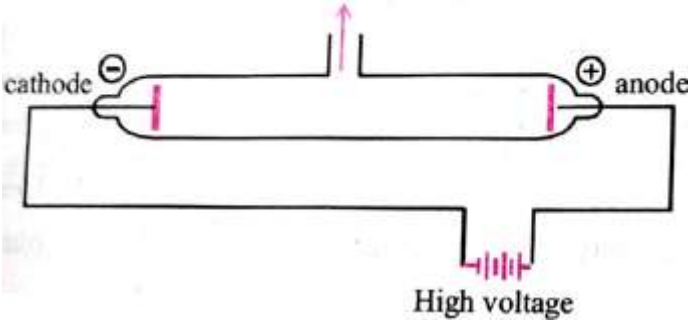


Fig. A cathode ray discharge tube

- The electrical discharge through the gases could be observed only at **very low pressures** and at **very high voltages.**
- At high voltage, current starts flowing through a stream of particles moving in the tube from the negative electrode **(cathode)** to the positive electrode **(anode)**. These were called **cathode rays or cathode ray particles.**
- In the absence of electrical or magnetic field, these rays travel in straight lines. But in its presence cathode rays get deviated which confirms that they are composed of negatively charged particles, called **electrons.**
- The characteristics of cathode rays do not depend upon the material of **electrodes** and the **nature of the gas** present in the cathode ray tube.
- J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons.
- Thomson argued that the amount of **deviation of the particles** from their nath in the presence of electrical or magnetic filed depends upon.
  - ❖ The **magnitude of the negative charge** on the particle, greater the magnitude of the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.
  - ❖ **The mass of the particle** lighter the particle, greater the deflection.
  - ❖ The **strength of the electrical or magnetic filed** the deflection of electrons f rom its original path increase with the increase in the voltage across the electrodes, or the strength of the magnetic field. Thomson determine the value of **e/m_e** as

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\ C\ kg^{-1}$$

Where me is the mass of the electron in kg. e is the magnitude of the charge on the electron in coulomb (C)

- **R.A. Millikan** (1868–1953) devised a method known as **oil drop experiment** (1906-14), to determine the charge on the electrons.
- Millikan concluded that the **magnitude of electrical charge**, q, on the droplets is always an integral multiple of the electrical charge, e, that is, q = n e, where n = 1, 2, 3...
- The charge on the electron was found to be 1.6 x 10^{-19} C. The present accepted value of electrical charge is - 1.602176 × 10^{-19} C.
- The **mass of the electron** (m_e) was determined by combining these results with **Thomson's** value of e/m ratio.

$$me = \frac{e}{e/m_e} = \frac{1.602176\times10^{-19}C}{1.758820\times10^{11}C\,kg^{-1}}$$

- Electrical discharge carried out in the modified cathode ray tube led to the discovery of **canal rays** carrying positively charged particles.
  The characteristics of these positively charged particles are

- ❖ Unlike cathode rays, mass of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.
- ❖ The e/m of the particles depends on the gas from which these originate.
- ❖ The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

- The smallest and lightest positive ion was obtained from hydrogen and was called **proton.**
- The **neutrons (electrically neutral particles)** were discovered by **Chadwick** (1932) by bombarding a thin sheet of **beryllium by α-particles.**
- Neutrons are electrically neutrals particles having a mass slightly greater than that of the protons.

Naem	Symbol	Absolute	Relative charge	Mass/ kg	Mass/ n	Approx mass/u
Electron	e	$-1.602176 \times 10^{-19}$	–1	9.109382×10^{-31}	0.00054	0
Proton	p	$+1.602176 \times 10^{-19}$	+1	$1.6726216 \times 10^{-27}$	1.00727	1
Neutron	n	0	0	1.674927×10^{-27}	1.00867	1

Atomic Models

- **J. J. Thomson model of an atom :** In atom possesses a spherical shape (radius approximately 10-10 m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement,
- The other name of this model is **plum pudding, raisin pudding or watermelon.**
- An important feature of this model is that the **mass of the atom** is assumed to be **uniformly distributed** over the atom.
- **Rutherford** found that α-rays consist of high energy particles carrying two units of positive charge and four unit of atomic mass.
- **α-rays** are **negatively charged** particles similar to electrons.
- **α-rays** are high energy radiations like **X-rays,** are **neutral in nature** and do not consist of particles.
- Penetrating power of rays are: **y-rays > X rays > β-rays > α-rays**
- **Rutherford's Nuclear model of an atom:** a-particle scattering experiments.
- A stream of **high energy** a-particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of **gold metal.**
- **Observation :**
  - ❖ most of the a-particles passed through the gold foil undeflected.
  - ❖ a small fraction of the a-particles was deflected by small angles.
  - ❖ a very few a-particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.
- **Conclusions :**
  - ❖ Most of the space in the atom is empty as most of the a-particles passed through the foil undeflected.
  - ❖ A few positively charged a-particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged a-particles.
  - ❖ Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The **radius of the atom** is about 10^{-10m}, while that of nucleus is 10^{-15m}

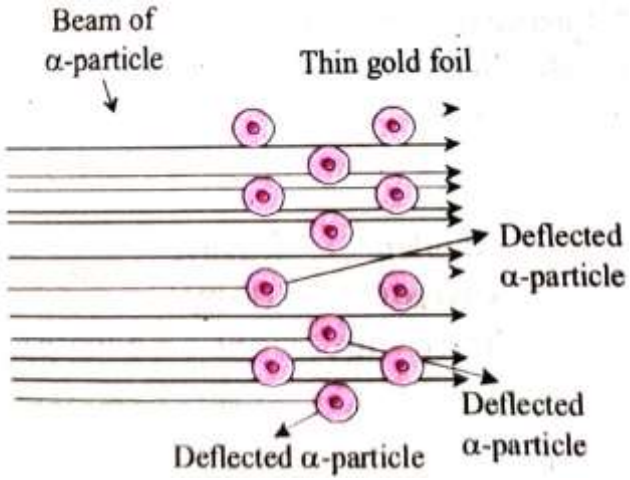


Fig. : Schematic molecular view of the gold foil

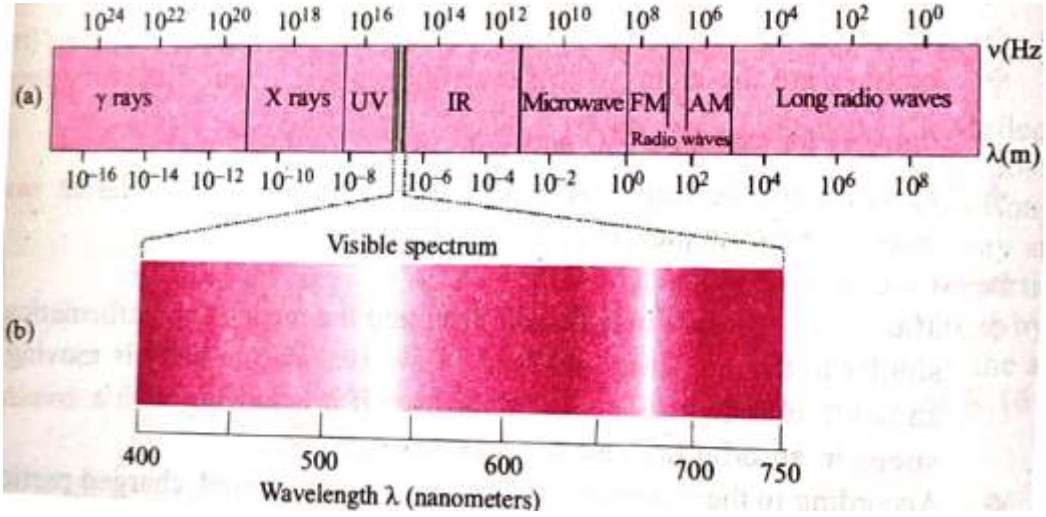
- On the basis of above **observations and conclusions,** Rutherford proposed the **nuclear model** of atom. According to this model:
  - ❖ The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus by Rutherford.
  - ❖ The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets.
  - ❖ **Electrons** and the **nucleus** are held together by **electrostatic forces of attraction.**
- **Wilhalm Röentgen discovered X-rays: X-rays** are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason these rays are **used** to study the **interior of the objects**.
  - ❖ **X-rays** are of very short wavelengths (~0.1 nm) and possess electro- magnetic character.
- **Henri Becqueral** (1852-1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as radioactivity and the elements known as **radioactive elements**

Atomic Number and Mass Number:

- ❖ Atomic number (Z) = number of protons in the nucleus of an atom number of electrons in a nuetral atom.
- ❖ Mass number (A) = number of protons (Z) + number of neutrons (n)
- ❖ Isobars are the atoms with same mass number but different atomic number for example, $^{14}_{6}C$ and $^{14}_{7}C$.
- ❖ Isotopes are the atoms with same atomic number but different mass number for example, $_1H^1$, $_1H^2$ and $_1H^3$

- **Drawbacks of Rutherford Model:**
  - ❖ The **coulomb force** between electron and the nucleus is mathematically similar to the **gravitational force**. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction.
  - ❖ According to the electromagnetic theory of Maxwell, charged particles when accelerated shoul amit electromagnetic radiation, Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink.
  - ❖ Calculations show that it should take an electron only 10–8 s to spiral into the nucleus. But this does not happen. Thus , th Rutherford model cannot explain the stability of and atom.
  - ❖ Another drawback of the Rutherford model is that it say nothing about distribution of the electrons around the nucleus and the energies of these electron.
- Two developments played a major role in the formulation of Bohr's model of atom. These were:
  - ❖ Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties.
  - ❖ Experimental results regarding atomic spectra.

- **Wave Nature of Electromagnetic Radiation:**
  - ❖ James Maxwell suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiation.
  - ❖ Electric and magnetic field components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.
  - ❖ Unlike sound waves or waves produced in water, electromagnetic waves do not require medium and can move in vacuum.
  - ❖ There are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called electromagnetic spectrum.



  - ❖ These radiations are characterised by the properties, namely, frequency (i), wavelength ($\overline{e}$), velocity (c) and wave number ($\overline{v}$).
  - ❖ Frequency is defined as the number of waves that pass a given point in one second. The SI unit of frequency is hertz (Hz, s^{-1}).
  - ❖ **Wavelength** is the distance between any two consecutive crests or troughs. The **SI unit** of wavelength is meter but is expressed in angstrom (10-10 m), picometer (10-12 m) and nanometer(10-9 m).
  - ❖ In vacuum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0×10^8 m s^{-1} (2.997925×10^8 m s^{-1}, to be precise). This is called speed of light (c). The frequency, wavelength and velocity of light are related by the equation, $c = 2\lambda$.
  - ❖ The wave number is defined as the number of wavelengths per unit length. Its SI unit is m^1. However commonly used unit is cm^{-1} (not SI 1 unit).

    The relation between wave number and wavelength is $\overline{v}=\frac{1}{\lambda}$

Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

- ❖ An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called **black body radiation.**
- ❖ The energy (E) of a quantum of radiation is proportional to its frequency (v) and is expressed by equation, E = hv The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} J s.
- ❖ With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures.
- ❖ The energy can take any one of the values from the following set, but cannot take on any values between them. E = 0, hv, 2hv, 3hv....nhv.....

- Photoelectric Effect: H. Hertz performed a, experiment in which electrons (or electric current) were ejected when certain metals (K, Rb, Cs etc.) were exposed to a beam of light. The phenomenon is called Photoelectric effect. The results observed in this experiment were:
  - ❖ 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.

- ❖ For each metal, there is a characteristic minimum frequency, vo (threshold frequency) below which photoelectric effect is not observed.
- ❖ At a frequency v > vo, the ejected electrons come out with certain 0 kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.
- ❖ The kinetic energy of the ejected electron is given by the following equation

$$hv = hv + \frac{1}{2}m_e v^2$$

where m = mass of the electron
v = velocity associated with the ejected electron.
hv = energy of the striking photons
hv_0 = minimum energy required to eject the electron (also called work function, wo).

- **Dual Behaviour of Electromagnetic Radiation**
  - ❖ When radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates.
  - ❖ Ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called spectrum.
  - ❖ The spectrum of white light, that we can see, ranges from violet at 7.50 x 1014 Hz to red at 4x1014 Hz. Such a spectrum is called continuous spectrum. Continuous because violet merges into blue, blue into green and so on.
  - ❖ The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum.
  - ❖ The emission spectra of atoms, in the gas phase, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra because the emitted radiation is identified by the appearance of bright lines in the spectra.
  - ❖ A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.
  - ❖ The study of emission or absorption spectra is referred to as spectroscopy.
  - ❖ When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. Balmer showed in 1885 on the basis of experimental observations that
  - ❖ if spectral lines are expressed in terms of wave number ($\overline{v}$), then the visible lines of the hydrogen spectrum obey the following formula:

$$\overline{v} = 109.677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\text{cm}^2$$

where n is an integer equal to or greater than 3 (i.e., n = 3,4,5,....)
The series of lines described by this formula are called the Balmer series.
Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression:

$$\overline{v} = 109.677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-1}$$

where n_1 =1,2..... and $n_2 = n_1 + 1, n_1 + 2$.....

  - ❖ The value 109,677 cm^{-1} is called the Rydberg constant for hydrogen. The first five series of lines that correspond to $n_1 = 1, 2, 3, 4, 5$ are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively. Following table shows these series of transitions in the hydrogen spectrum.

Series	n1	n2	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

- ❖ Of all the elements, hydrogen atom has the simplest line spectrum Line spectrum more and more and more complex for heavier atom.

Bohr.s Model for Hydrogen Atom

- ❖ When radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates.
- ❖ Ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called spectrum.

- Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy.
- Bohr's model for hydrogen atom is based on the following postulates:
  - ❖ The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.
  - ❖ The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.
  - ❖ The **frequency of radiation** absorbed or emitted when transition occurs between two stationary states that differ in energy by "E, is given by:

$$v=\frac{\Delta E}{h}=\frac{E_2-E_1}{h}$$

    This expression is commonly known as **Bohar's frequency rule.**
  - ❖ The **angular momentum** of an electron is quantised. In a given stationary state it can be expressed as

$$m_e vr=n\frac{h}{2\pi}\quad n=1,2,3.....$$

  - ❖ An electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$. That means angular momentum is quantised.
  - ❖ **Radiation is emitted or absorbed** only when transition of electron takes place from one quantised value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here that is why only certain fixed orbits are allowed.
- **According to Bohr's theory for hydrogen atom:**
  - ❖ The stationary states for electron are numbered n = 1,2,3..... These integral numbers are known as Principal quantum numbers.
  - ❖ The radii of the stationary states are expressed as: $r_n = n^2 a_0$ l
    where a_0 = 52.9 pm. Thus the radius of the first stationary state, called the Bohr orbit, is 52.9 pm.
  - ❖ The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n=R_H\left(\frac{1}{n^2}\right)\quad n = 1, 2, 3 .....$$

    where R is called Rydberg constant and its value is 2.18×10^{-18} J.
  - ❖ When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number n and is called as ionized hydrogen atom.
  - ❖ The energies of the stationary states associated with hydrogen like species (He^+, Li^{2+}, Be^{3+}) are given by the expression.

$E_n = 2.18 \times 10^{-18} l \left(\frac{Z^2}{n^2}\right)$ J and radii by the expression

$r_n = \frac{52.9(n^2)}{Z}$ pm

- ❖ Qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

- The energy (ΔE), frequency (ν) and wavenumbers ($\overline{\nu}$) associated with the absorption and emission of the photon can be evaluated by using following equation.

$$\Delta E = \left(-\frac{R_H}{n_1^2}\right) - \left(-\frac{R_H}{n_f^2}\right) = 2.18 \times 10^{-18} \text{J} \left(\frac{1}{n_1^2} - \frac{1}{n_f^2}\right)$$

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_1^2} - \frac{1}{n_f^2}\right) = 3.29 \times 10^{-15} \left(\frac{1}{n_1^2} - \frac{1}{n_f^2}\right) \text{Hz}$$

$$\overline{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_f^2}\right) = 1.09677 \times 10^{-7} \left(\frac{1}{n_1^2} - \frac{1}{n_f^2}\right) \text{m}^{-1}$$

(where n_i and n_f stand for initial orbit and final orbits)

- In case of absorption spectrum, $n_ı > n$, and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum nn "E is negative and energy is released.
- In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. T
- he brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.
- **Limitations of Bohr's Model:**

  Bohr's model was too simple to account for the following points.
  - ❖ This model fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques.
  - ❖ This model is unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons
  - ❖ Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).
  - ❖ It could not explain the ability of atoms to form molecules by chemical

Towards Quantum Mechanical Model of the Atom

- **Dual Behaviour of Matter:**
  - ❖ de Broglie proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particles and wave like properties.
  - ❖ de Broglie gave the following relation between wavelength (e) and momentum (p) of a material particle.

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

Where m is the mass of the particle, its velocity and p its momentum

- ❖ Heisenberg's Uncertainty Principle: According to Heisenberg's Uncertainty Principle "it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron". Mathematically, it can be given as

$$\Delta x \times \Delta px \geq \frac{h}{4\pi}$$

or $$\Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

or $\Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$

where Δx is the uncertainty in position and Δp_x (or Δv_x) is the uncertainty in momentum (or velocity) of the particle.

- ❖ Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects.
- ❖ **Bohr model** of the hydrogen atom not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.

Quantum Mechanical Model Atom

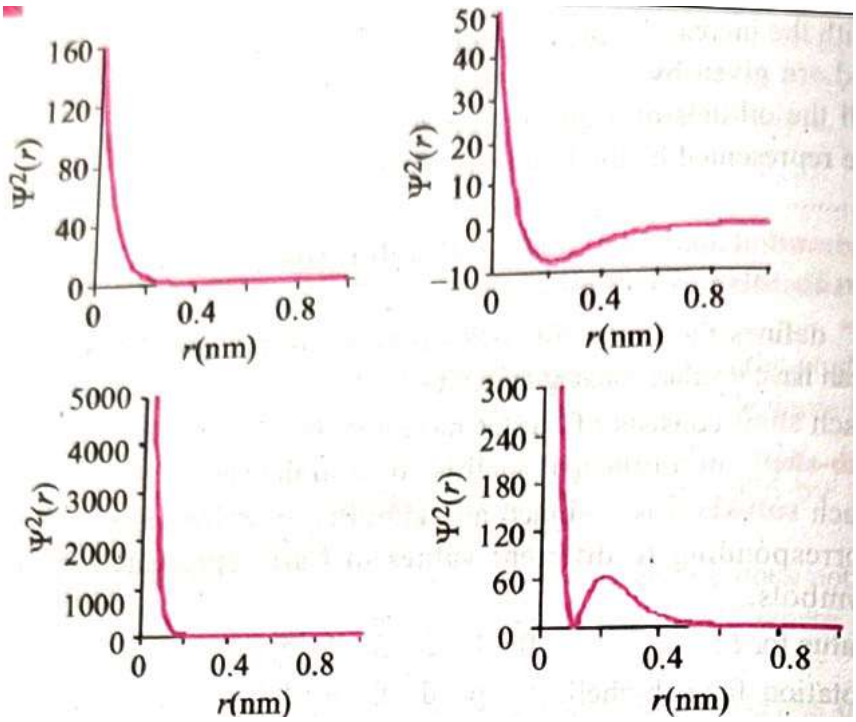
- The branch of science that takes into account dual behaviour of matter is called quantum mechanics.
- Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties.
- Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger.
- For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as HY = mathematical operator called Hamiltonian. EY where H is a
- The total energy of the system takes into account the kinetic energies of all the subatomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually.
- Solution of Schrödinger equation gives E and Ψ.
- When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (4) of the electron associated with each energy level.
- The quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum numbers n, azimuthal quantum numbers l and magnetic quantum numbers m) arise as a natural consequence in the solution of of Schrodinger equation.
- The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning.
- The wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals.l bas
- The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function $[\Psi]^2$ is known as probability density and is always positive.
- The Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods.
- Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, I and m_1.
- The principal quantum number 'n' is a positive integer with value of n = 1,2,3..... The principal quantum number determines the size and to large extent the energy of the orbital. It also identifies the shell.
- l
- With the increase in the value of 'n', the number of allowed orbital increases and are given by 'n^{2+}'
- All the orbitals of a given value of 'n' constitute a single shell of atom and are represented by the following letters = 1 2 3 4 Shell = K L M N .....
- **Azimuthal quantum number.** "I' is also known as orbital angular momentum or subsidiary quantum number.
- 'I' defines the three-dimensional shape of the orbital. For a given value of n I can haven values ranging from^0 ton^{-1}
- Each shell consists of one or more subshells or sub-levels. The number of sub-shells in a principal shell is equal to the value of n.
- Each sub-shell is assigned an azimuthal quantum number (1). Sub-shells corresponding to different values of / are represented by the following symbols.
  symbos.

Value for I :	0	1	2	3	4	5 .....
notation for sub-shell:	s	p	d	f	g	h .....

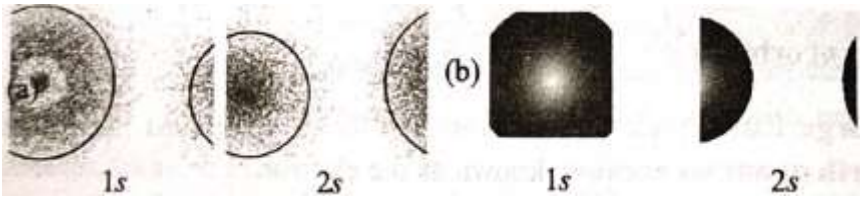
- **Magnetic orbital quantum number, 'm*l*'** gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis. For any sub-shell (defined by "I' value) 2 +1 values of m_1 are possible and these values are given by :
  m1 = l, – (1 – *l*), – (*l* – 2) ... 0, 1.... – (*l* – 2), – (*l* – 1), *l*
- The following chart give the relation between the **subshell** and the number of **orbitals** associated with it.

Value of I	0	1	2	3	4	5
Subshell notation	s	p	d	f	g	h
Number of orbitals	1	3	5	7	9	11

- George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the electron spin quantum number.
- Spin angular momentum of the electron, a vector quantity, can have two orientations relative to the chosen axis.
- The two orientations are distinguished by the spin quantum numbers m which can take the values of +½ or -2.
- Two electrons that have different m, values (one +½ and the other -½) are S said to have opposite spins.
- An orbital cannot hold more than two electrons and these two electrons should have opposite spins.
- According to the German physicist, Max Born, the square of the wave function (i.e.,ψ^2) at a point gives the probability density of the electron at that point. The variation of ψ as a function of r for 1s and 2s orbitals is given as



- The probability density variation can be visualised in terms of charge cloud diagrams.
- Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals.
  - ❖ s-orbitals: Boundary surface diagram for an s orbital is actually a sphere centred on the nucleus.



  - ❖ s-Orbitals, increases in size and energy with increase in the principal quantum number.

- **p-Orbitals:**
  - ❖ Each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus.
  - ❖ The probability density function is zero on the plane where the two lobes touch each other.
  - ❖ The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented.
  - ❖ Since the lobes may be considered to lie along the x, y or z axis, they are given the designations $2p_x$, $2p_y$, and $2p_z$.
  - ❖ Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number

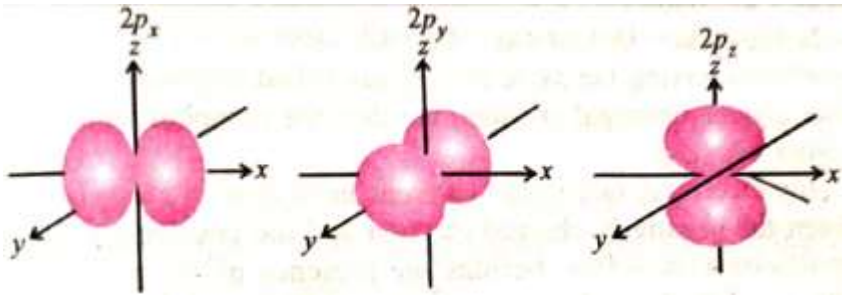
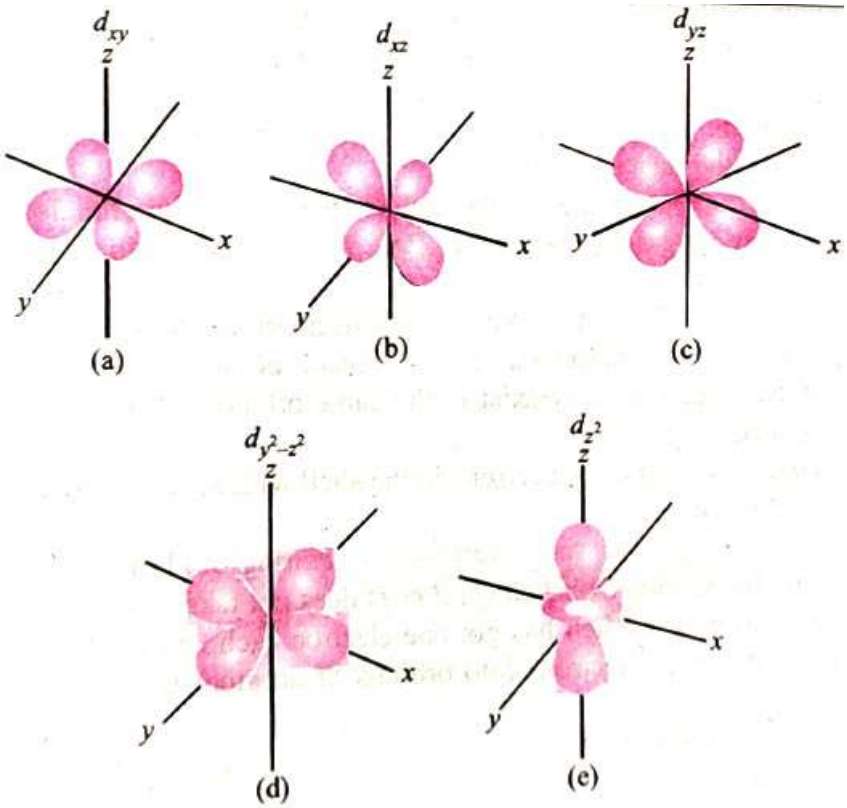


Fig. : Boundary surface diagrams of the three 2p orbitals.

- **d-Orbitals:**
  - ❖ Three are five m_1 values (–2, –2, 0, +1 and +2) for l = 2 and thus there are five d orbitals.
  - ❖ The boundary surface diagram of d orbitals are shown in in fig. The five d-orbitals are designated as d_{xy}, d_{yz}, dxz, d_{x2-y2} and d_{z2}



- The nodal plane are also called angular nodes and number of angular nodes are given by 'l', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals etc.
- The total number of nodes are given by (n-1). i.e., sum of / angular nodes and (n-1-1) radial nodes.
- The energy of an electron in a hydrogen atom is determined solely by the principal quantum number. Thus the energy of the orbitals in hydrogen atom increases as follows:
- 1s 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f <
- The orbitals having the same energy are called degenerate.
- Within a given principal quantum number, the energy of orbitals increases in the order s < p < d < f
- The only electrical interaction present in hydrogen atom is the attraction between the negatively charged electron and the positively charged nucleus. In multielectron atoms, besides the presence of attraction between the electron and nucleus, there are repulsion between every electron and other electrons present in the atom. Thus the stability of an electron in a multi-electron atom is because total attractive interactions are more than the repulsive interactions.
- k
- 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, and the net positive charge experienced by the outer electrons is known as effective nuclear charge (Zer).
- If two orbitals have the same value of (n + 1), the orbital with lower value of n will have the lower energy.
- Aufbau Principle: In the ground state of the atoms, the orbitals are filled in order of their increasing energies. 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...
- Pauli Exclusion Principle: No two electrons in an atom can have the same set of four quantum numbers. Pauli exclusion principle can also be stated as : "Only two electrons may exist in the same orbital and these electrons must have opposite spin."
- The maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.
- Hund's Rule of Maximum Multiplicity: Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.
- The distribution of electrons into orbitals of an atom is called its electronic configuration
  - ❖ spd ..... notation
  - ❖ Orbital diagram k



- The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy.
- Symmetrical distribution of electrons: The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable.
- The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell.
- The 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.
- Higher the exchange energy, higher will be the stability.
- The extra stability of half-filled and completely filled subshell is also due to:
  - ❖ relatively small shielding
  - ❖ smaller coulombic repulsion energy
  - ❖ larger exchange energy

Past Year ONE-LINERS NEET/JEE Main/Board :

- Number of values of m, possible for a given value of 1 = (2l + 1) Possible values of m_l = –l to +l.
- The frequency (v), wavelength (λ) and velocity of light are related by the equation, c = νλ.
- Lyman and Balmer series falls in UV and visible spectral region respectively whereas Paschen, Brackett and Pfund series falls in IR region.
- n + l rule is used to predict the correct energy order of orbitals.
- Linear speed (v) = angular speed (ω) x radius of the rotation (r)

  $\therefore v \propto \frac{1}{n}$ and $r \propto n$ so $\omega \propto \frac{1}{n^3}$
- Heisenberg's principle is mathematically represented as $\Delta E \times \Delta t \geq h/4\pi$

  $\Rightarrow$ Half filled or completely filled orbitals are more stable due to its greater symmetry, exchange energy and arrangement.

  $\Rightarrow$ The energy of the orbitals in hydrogen like atoms increases as 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f<

  $\Rightarrow$ de-Broglie proposed the relation between wavelength, momentum of a particle which is a $\lambda = \frac{h}{mv}$
- The quantum numbers, n, l, m, s are used to determine shell, subshell, orientation and spin of electrons (spin orientation) of orbitals respectively. Two electrons differs in its spin orientation if both occupy same orbitals.
- Anglar node = l, Radial node = n – l – 1
- Incident energy energy of photon (hv) = work function (hv_0) + kinetic energy (K.E.)

  de-Brogli wavelength = $\frac{h}{mv}$ or $\lambda = \frac{h}{\sqrt{2m\,K.E.}}$
- Number of orbitals in a shell = n^2. Where n is the principle quantum number.
- $r = 0.529 \times \frac{n^2}{Z}$ Å and for two different radii $r_{n2} - r_{n1} = \frac{0.529}{Z}\left[n_2^2 - n_1^2\right]$; where $n_2 > n_1$
- $\overline{v} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

  For Lyman series $\overline{v}_{(min)} = R\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$ Here $n_1 = 1$, $n_2 = s\ \infty$;

  $\overline{v}_{(min)} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$ Here $n_1 = 1$, $n_2 = 2$

  For Balmer series $\overline{v}_{(min)} = R\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right]$ Here $n_1 = 2$, $n_2 = s\ \infty$;

  $\overline{v}_{(min)} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$ Here $n_1 = 2$, $n_2 = 3$
- Radius of n^{th} Bohr orbit in H atom = $0.53n^2$ Å
- Wavelength of electron wave (λ) = $\frac{h}{\sqrt{2m}K.E.}$. Here K.E = eV
- Total energy = $\frac{-13.6 \times Z^2}{n^2}$ eV

Tips/ Tricks/ Techniques ONE-LINERs

- **(n + 1) rule**
- This rule states that electrons are filled in orbitals according to their increasing values of n + l. When (n + l) is same for sub energy levels, the electrons first occupy the sublevels with lowest "n" value. Thus, order of filling up of orbitals is as follows:

  1s < 2s < 2p < 3 < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d
- Orbital angular momentum = $\frac{h}{2\pi}\sqrt{l(l+1)}$

- Spin Angular Momentum = $\frac{h}{2\pi}\sqrt{s(s+1)}$
- Relation Between Potential energy (P.E) Kinetic energy (K.E) & Total energy

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

P.E. = $-\frac{Ze^2}{r}$, K.E. = $-\frac{1}{2}\frac{Ze^2}{r}$, T.E. = $-\frac{1}{2}\frac{Ze^2}{r}$

- **Total number of spectral lines**

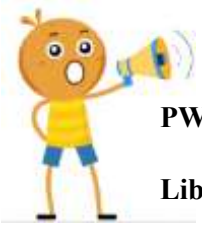
(i) $\frac{n(n-1)}{2}\rightarrow$ when electron jumps from n^{th} level to ground level

(ii) $\frac{(n_2-n_1)(n_2-n_1+1)}{2}\rightarrow$ when electron returns from n_2 to n_1.

- **Nodal Point :** The nucleus of an atom is called nodal point.
- **Isodiaphers :** The elements which have same value of (n -p) are called isodiaphers.
- **Isomorphous :** The two different types of compounds which contain same crystalline structure are called isomorphous and this property is called isomorphism.
- Substances which have same number of electrons and atoms called isosters.
- **Promotion :** The transfer of electrons between subshells in an orbit is called promotion, while the transfer of electrons from one energy level to another is called transition. After the completion of promotion, the transition process occurrs.

S.No.	Radius	Velocity	Energy
i.	$r=\frac{n^2h^2}{4\pi^2mZe^2}$	$V=\frac{2\pi Ze^2}{nh}$	$E=-\frac{Ze^2}{2r}$
ii.	$r=\frac{n^2}{Z}\times 0.529Å$	$V=\left(\frac{Ze^2}{rm}\right)^{1/2}$	$E=-\frac{2\pi^2mZ^2e^4}{n^2h^2}$
iii.	$r=\frac{n^2}{Z}\times 0.0529$ nm	$V=\frac{nh}{2\pi mr}$	$E=-Rch\times\frac{Z^2}{n^2}$
iv.	$r\propto n^2$ (Z const.)	$V\propto\frac{1}{n}$ (Z cosnt.)	$E=-\frac{Z^2}{n^2}\times 313.6$ k Cal
v.	$\frac{r^1}{r^2}=\frac{n_1^2}{n_2^2}$ (Z const.)	$\frac{V_1}{V_2}=\frac{n_2}{n_1}$ (Z const.)	$E\propto -Z^2$
vi.	$r\propto 1/Z$ (n const.)	Time period $T=\frac{2\pi r}{V}$	(n const.) $\frac{E_1}{E_2}=\frac{Z_1^2}{Z_2^2}$

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