

Structure of Atom



STRUCTURE OFATOM

Ļ	Ļ	ļ
Rutherford's	Bohr's	Wave mechanical
Model	Model	Model

Dalton's concept of the indivisibility of the atom was completely discredited by a series of experimental evidences obtained by scientists. A number of new phenomena were brought to light and man's idea about the natural world underwent a revolutionary change. the discovery of electricity and spectral phenomena opened the door for radical changes in approaches to experim entation. It was concluded that atoms are made of three particles : electrons, protons and neutrons. These particles are called the fundamental particles of matter.

EARLIER EFFORTS TO REVEAL STRUCTURE OF ATOM

CATHODE RAYS - DISCOVERY OF ELECTRON



In 1859 **Julius Plucker** started the study of conduction of electricity through gases at low pressure $(10^{-4}$ atm) in a discharge tube When a high voltage of the order of 10,000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrode these rays are called as cathode rays.

PROPERTIES OF CATHODE RAYS



Cathode rays have the following properties.

- (i) Path of travelling is straight from the cathode with a very high velocity as it produces shadow of an object placed in its path.
- (ii) Cathode rays produce mechanical effects. If small light paddle wheel is placed between the electrodes, it rotates. This indicates that the cathode rays consist of material particles.
- (iii) When electric and magnetic fields are applied to the cathode rays in the discharge tube. The rays are deflected thus establishing that they consist of charged particles. The direction of deflection showed that cathode rays consist of negatively charged particles called **electrons**.
- (iv) They produce a green glow when strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.
- (v) Cathode rays penetrate through thin sheets of aluminium and metals.
- (vi) They affect the photographic plates
- (vii) The ratio of charge(e) to mass(m) i.e. charge/mass is same for all cathode rays irrespective of the gas used in the tube. $e/m = 1.76 \times 10^{11} \text{ Ckg}^{-1}$

Thus, it can be concluded that electrons are basic constituent of all the atoms.

PRODUCTION OF AN ODE RAYS (DISCOVERY OF PROTON)

Goldstein (1886) repeated the experiment with a discharge tube filled with a perforated cathode and found that new type of rays came out through the hole in the cathode.



When this experiment is conducted, a faint red glow is observed on the wall behind the cathode. Since these rays originate from the anode, they are called anode rays.

PROPERTIES OF ANODE RAYS:

- Anode rays travel along straight paths and hence they cast shadows of object placed in their path.
- *They rotate a light paddle wheel placed in their path.* This shows that anode rays are made up of material particles.
- They are deflected towards the negative plate of an electric field. This shows that these rays are positively charged.
- For different gases used in the discharge tube, the charge to mass ratio (e/m) of the positive particles constituting the positive rays is different. When hydrogen gas is taken in the discharge tube, the e/m value obtained for the positive rays is found to be maximum. Since the value of charge (e) on the positive particle obtained from different gases is the same, the value of m must be minimum for the positive particles obtained from hydrogen gas. Thus, the positive particle obtained from hydrogen gas is the lightest among all the positive particles obtained from different gases. This particle is called the proton.

DISCOVERY OF NEUTRON :

Later, a need was felt for the presence of electrically neutral particles as one of the constituent of atom. These particles were discovered by Chadwick in 1932 by bombarding a thin sheet of Beryllium with α -particles, when electrically neutral particles having a mass slightly greater than that of the protons were emitted. He named these particles as neutrons.

 ${}^9_4\text{Be} + {}^4_2\text{He} \longrightarrow {}^{12}_6\text{C} + {}^1_0\text{n}$

THE NUCLEUS :

Electrons, protons & neutrons are the fundamental particles present in all atoms, (except hydrogen)

		18	ible:1	
Particles	Symbol	Mass	Charge	Discoverer
Electron	$_{-1}e^0$ or β	9.10939 x 10 ⁻³¹ kg	– 1.6022 x 10 ^{–19} Coulombs	J.J. Thomson Stoney Lorentz 1887
		0.00054 u	$-4.803 \times 10^{-10} \text{ esu}$	
Proton	$_1\mathrm{H}^1$	1.6722 x 10 ⁻²⁷ kg	+ 1.6022 x 10 ⁻¹⁹	Goldstein
			Coulombs	Rutherford1907
		1.00727 u	+ 4.803 x 10 ⁻¹⁰ esu	
Neutron	$_0 n^1$	1.67493 x 10 ⁻²⁷ kg	neutral	James Chadwick
		1.00867 u	0	1932
		1 amu $\approx 1.66 \times 10^{-27}$	kg	

ATOMIC MODELS :

(A) Thomson's Model of the Atom :

An atom is electrically neutral. It contains positive charges (due to the presence of protons) as well as negative charges (due to the presence of electrons). Hence, J.J. Thomson assumed that an atom is a uniform sphere of positive charges with electrons embedded in it.



(B) Rutherford's Experiment :



Observation :

- 1. Most of the α -particles passed straight through the gold foil without suffering any deflection from their original path.
- 2. A few of them were deflected through small angles, while a very few were deflected to a large extent.
- 3. A very small percentage (1 in 20000) was deflected through angles ranging from 90° to 180°.

Rutherford's nuclear concept of the atom.

- (i) The atom of an element consists of a small positively charged 'nucleus' which is situated at the centre of the atom and which carries almost the entire mass of the atom.
- (ii) The electrons are distributed in the empty space of the atom around the nucleus in different concentric circular paths, called orbits.
- (iii) The number of electrons in orbits is equal to the number of positive charges (protons) in the nucleus. Hence, the atom is electrically neutral.
- (iv) The volume of the nucleus is negligibly small as compared to the volume of the atom.
- (v) Most of the space in the atom is empty.

DRAWBACKS OF RUTHERFORD'S MODEL:

1. This was not according to the classical theory of electromagnetism proposed by maxwell. According to this theory, every accelerated charged particle must emit radiations in the form of electromagnetic waves and loses it total energy.

Since energy of electrons keep on decreasing, so radius of the circular orbits should also decrease and ultimately the electron should fall in nucleus.

2. It could not explain the line spectrum of H-atom.

PROPERTIES OF CHARGE :

- 1. Q = ne (charge is quantized)
- 2. Charge are of two types :

(i) positive charge (ii) Negative Charge $e = -1.6 \times 10^{-19}$

 $p = +1.6 \times 10^{-19}C$

This does not mean that a proton has a greater charge but it implies that the charge is equal and opposite. Same charge repel each other and opposite charges attract each other.

3. Charge is a SCALAR Qty. and the force between the charges always acts along the line joining the charges.

The magnitude of the force between the two charge placed at a distance 'r' is given by

$$F_{E} = \frac{1}{4\pi\varepsilon_{0}} \frac{q_{1}q_{2}}{r^{2}}$$
(electrical force)

4. If two charge q_1 and q_2 are sepreated by distance r

$$P.E. \qquad = \quad \frac{1}{4\pi\epsilon_0} \ \frac{q_1q_2}{r}$$

5. If a charged particle q is placed on a surface of potential V then the potential energy of the charge is q x V.

Estimation of closest distance of approach (derivation)

Ex. An α -particle is projected from infinity with the velocity V₀ towards the nucleus of an atom having atomic number equal to Z then find out (i) closest distance of approach (R) (ii) what is the velocity of the α -particle at the distance R₁ (R₁ > R) from the nucleus.



From energy conservation $P.E_1 + KE_1 = P.E_2 + KE_2$

$$\Rightarrow 0 + \frac{1}{2} m_{\alpha} V_{\alpha}^{2} = \frac{\mathsf{K}(\mathsf{Ze})(\mathsf{2e})}{\mathsf{R}} + 0$$

$$R = \frac{4KZe^2}{m_{\alpha}V_{\alpha}^2} \qquad (closest$$

(closest distance of approch)

Let velocity at R_1 is V_1 . From energy conservation $P.E_1 + KE_1 = P.E_3 + KE_3$

$$\Rightarrow 0 + \frac{1}{2} m_{\alpha} V_{\alpha}^{2} = \frac{K(Ze)(2e)}{R_{1}} + \frac{1}{2} m_{\alpha} V_{1}^{2}$$

SIZE OF THE NUCLEUS

The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.

Thus, diameter (size) of the atom is 100,000 times the diameter of the nucleus.

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

$$R = R_0 (A)^{1/3} cm$$

where R_0 can be 1.1×10^{-13} to 1.44×10^{-13} cm ; A = mass number ; R = Radius of the nucleus.

Nucleus contains protons & neutrons except hydrogen atoms which does not contain neutron in the nucleus.

ATOMIC NUMBER (Z) AND MASS NUMBER (A)

O Atomic number (Z) of an element

- =Total number of protons present in the nucleus
- = Total number of electrons present in the atom
- Atomic number is also known as proton number because the charge on the nucleus depends upon the number of protons.
- Since the electrons have negligible mass, the entire mass of the atom is mainly due to protons and neutrons only. Since these particles are present in the nucleus, therefore they are collectively called **nucleons**.
- As each of these particles has one unit mass on the atomic mass scale, therefore the sum of the number of protons and neutrons will be nearly equal to the mass of the atom.
- **O** Mass number of an element

= No. of protons (Z) + No. of neutrons (n).

• The mass number of an element is nearly equal to the atomic mass of that element. However, the main difference between the two is that mass number is always a whole number whereas atomic mass is usually not a whole number. The atomic number (Z) and mass number (A) of an element 'X' are usually represented along with the symbol of the element as

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e.g. $^{23}_{11}$ Na, $^{35}_{17}$ Cl and so on.

1. **Isotopes :** Such atoms of the same element having same atomic number but different mass numbers are called isotopes.

 ${}_{1}^{1}H$, ${}_{1}^{2}D$ and ${}_{1}^{3}T$ and named as protium, deuterium (D) and tritium (T) respectively. Ordinary hydrogen is protium.

2. Isobars : Such atoms of different elements which have same mass numbers (and of course different atomic numbers) are called isobars

e.g. ⁴⁰₁₈ Ar, ⁴⁰₁₉K, ⁴⁰₂₀Ca.

3. Isotones : Such atoms of different elements which contain the same number of neutrons are called isotones

4. Isoelectronic : The species (atoms or ions) containing the same number of electrons are called isoelectronic.

For example, O^{2-} , F^- , Na^+ , Mg^{2+} , Al^{3+} , Ne all contain 10 electrons each and hence they are isoelectronic.

Solved Examples

Ex-1. Complete the following table :

Particle	Mass No.	Atomic No.	Protons	Neutrons	Electrons
Nitrogen atom	-	-	-	7	7
Calcium ion	-	20	-	20	-
Oxygen atom	16	8	-	-	-
Bromide ion	-	_	_	45	36

Structure of Atom

Sol. For nitrogen atom.

No. of electron $= 7$	(given)
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No. of neutrons = 7 (given)

 \therefore No. of protons = Z = 7

 $(\therefore$ atom is electrically neutral)

Atomic number = Z = 7

Mass No. (A) = No. of protons + No. of neutrons

= 7 + 7 = 14

For calcium ion.

(Given)

Atomic No. (Z) = 20 (Given)

 \therefore No. of protons = Z = 20;

No. of electrons in calcium atom

= Z = 20

But in the formation of calcium ion, two electrons are lost from the extranuclear part according to the equation $Ca \rightarrow Ca^{2+} + 2e^{-}$ but the composition of the nucleus remains unchanged.

 \therefore No. of electrons in calcium ion

$$= 20 - 2 = 18$$

Mass number (A) = No. of protons + No. of neutrons

= 20 + 20 = 40.

For oxygen atom.

Mass number (A) = No. of protons + No. of neutrons

= 16 (Given

Atomic No. (Z) = 8 (Given)

No. of protons = Z = 8,

No. of electrons = Z = 8

No. of neutrons = A - Z = 16 - 8 = 8

For bromide ion.

No. of neutrons = 45 (given)

No. of electrons = 36 (given)

But in the formation of bromide ion, one electron is gained by extra nuclear part according to equation

 $Br + e^- \rightarrow Br^-$, But the composition of nucleus remains unchanged.

:. No. of protons in bromide ion = No. of electrons in bromine atom = 36 - 1 = 35

Atomic number (Z) = No. of protons = 35

Mass number (A) = No. of neutrons + No. of protons = 45 + 35 = 80.

ELECTROMAGNETIC WAVE

RADIATION



The oscillating electrical/magnetic field are electromagnetic radiations. Experimentally, the direction of oscillations of electrical and magnetic field are prependicular to each other.



 \vec{E} = Electric field, \vec{B} = Magnetic field



Direction of wave propogation.

SOME IMPORTANT CHARACTERISTICS OFAWAVE



Wavelength of a wave is defined as the distance between any two consecutive crests or troughs. It is represented by λ (lambda) and is expressed in Å or m or cm or nm (nanometer) or pm (picometer).

$$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

 $1 \text{ nm} = 10^{-9} \text{ m}, 1 \text{ pm} = 10^{-12} \text{ m}$

Frequency of a wave is defined as the number of waves passing through a point in one second. It is represented by v (nu) and is expressed in Hertz (Hz) or cycles/sec or simply sec⁻¹ or s⁻¹.

1 Hz = 1 cycle/sec

Velocity of a wave is defined as the linear distance travelled by the wave in one second. It is represented by v and is expressed in cm/sec or m/sec (ms^{-1}).

Amplitude of a wave is the height of the crest or the depth of the trough. It is represented by 'a' and is expressed in the units of length.

Wave number is defined as the number of waves present in 1 cm length. Evidently, it will be equal to the reciprocal of the wavelength. It is represented by \overline{v} (read as nu bar).

$$\overline{\nu}=\frac{1}{\lambda}$$

If λ is expressed in cm, $\overline{\nu}$ will have the units cm⁻¹.

Relationship between velocity, wavelength and frequency of a wave. As frequency is the number of waves passing through a point per second and λ is the length of each wave, hence their product will give the velocity of the wave. Thus

Order of wavelength in Electromagnetic spectrum

Cosmic rays $< \gamma$ - rays < X-rays < Ultraviolet rays < Visible < Infrared < Micro waves < Radio waves.

PARTICLE NATURE OF ELECTROMAGNETIC RADIATION

Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction and interference can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained

- (i) the nature of emission of radiation from hot bodies (black body radiation)
- (ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

BLACK BODY RADIATION

When solids are heated they emit radiation over a wide range of wavelengths.

The ideal body, which emits and absorbs all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature.



The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner.

QUANTUM THEORY OF LIGHT

The smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation is called as quantum of light.

According to Planck, the light energy coming out from any source is always an integral multiple of a smallest energy value called quantum of light.

Let quantum of light be = $E_0(J)$, then total energy coming out is = nE_0 (n = Integer)

Quantum of light = Photon

(Packet or bundle of energy)

Energy of one photon is given by

$$E_0 = h_v(v-Frequency of light)$$

 $h = 6.626 \text{ x } 10^{-34} \text{ J-Sec}$

(h - Planck const.)

$$E_0 = \frac{hc}{\lambda}$$
 (c - speed of light)

 $(\lambda$ - wavelength)

Order of magnitude of E₀ =
$$\frac{10^{-34} \times 10^8}{10^{-10}}$$

 $= 10^{-16} \text{ J}$

Solved Examples

Ex-2. Certain sun glasses having small of AgCl incorporated in the lenses, on expousure to light of appropriate wavelength turns to gray colour to reduce the glare following the reactions:

AgCl $hv \rightarrow Ag(Gray) + Cl$

If the heat of reaction for the decomposition of AgCl is 248 kJ mol⁻¹, what maximum wavelength is needed to induce the desired process?

Sol. Energy needed to change = 248×10^3 J/mol

If photon is used for this purpose, then according to Einstein law one molecule absorbs one photon.

Therefore,
$$\therefore$$
 $N_A \cdot \frac{hc}{\lambda} = 248 \times 10^3$
 $\lambda = \frac{6.626 \times 10^{-34} \times 3.0 \times 10^8 \times 6.023 \times 10^{23}}{248 \times 10^3}$
 $= 4.83 \times 10^{-7} \text{ m}$

ONE ELECTRON VOLT (e.v.) :

Energy gained by an electron when it is accelerated from rest through a potential difference of 1 volt.

Note : Positive charge always moves from high potential to low potential and –ve charge always. moves from low potential to high potential if set free.



$$P.E._{i} + K.E._{i} = P.E._{f} + K.E._{f}$$

$$(-e) 0 + 0 = (-e)(1V) + \frac{1}{2} mV_{f}^{2}$$

$$K.E. = \frac{1}{2} mV_f^2 = e(1 \text{ volt})$$

If a charge 'q' is accelerated through a potential dirrerence of 'V' volt then its kinetic energy will be increased by q.V.

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

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

PHOTOELECTRIC EFFECT

:..

When certain metals (for example Potassium, Rubidium, Caesium etc.) were exposed to a beam of light electrons were ejected as shown in Fig.



The phenomenon is called **Photoelectric effect**. The results observed in this experiment were :

- (i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.
- (ii) The number of electrons ejected is proportional to the intensity or brightness of light.
- (iii) For each metal, there is a characteristic minimum frequency, v_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $v > v_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to h_{v} and the minimum energy required to eject the electron is hv_0 (is also called work function, W_0) then the difference in energy $(hv - hv_0)$ is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation

 $h_{v} = h_{v_{0}} + \frac{1}{2}m_{e}v^{2}$

where m_{e} is the mass of the electron and v is the velocity associated with the ejected electron.

Solved Examples

Ex-3. The threshold frequency v_0 for a metal is $6 \times 10^{14} \, \text{s}^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $v = 1.1 \times 10^{15} \, \text{s}^{-1}$ hits the metal.

Sol. K.E. =
$$\frac{1}{2}$$
 m_eV² = h (v − v₀)
∴ K.E. = (6.626 × 10⁻³⁴) (1.1 × 10¹⁵ − 6 × 10¹⁴)
∴ K.E. = (6.626 × 10⁻³⁴) (5 × 10¹⁴)
= 3.313 × 10⁻¹⁹ J

BOHR'S ATOMIC MODEL

It is based on quantum theory of light.

Assumptions of Bohr's model :

• There are certain orbits around the nucleus such that if electron will be revolving in these orbit, then it not emit any electromagnetic radiation. These are called stationary orbit.

The neccessary centripetal force is produced by attraction forces of nucleus.

$$\frac{mv^2}{r} = \frac{Ke^2Z}{r^2}$$

Angular momentum of the electron in these stationary orbit is always an integral multiple of $\frac{h}{2\pi}$

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

• Electron can make jump from one stationary orbit to another stationary orbit by absorbing or emitting a photon of energy equal to difference in the energies of the stationary orbit.

$$\frac{hc}{\lambda} = \Delta E$$

 ΔE – difference in the energy of orbit

MATHEMATICAL FORMS OF BOHR'S POSTULATES

Calculation of the radius of the Bohr's orbit :

Suppose that an electron having mass 'm' and charge 'e' revolving around the nucleus of charge 'Ze' (Z is atomic number & e = charge) with a tangential/linear velocity of 'v'. Further consider that 'r' is the radius of the orbit in which electron is revolving.

According to Coulomb's law, the electrostatic force of attraction (F) between the moving electron and nucleus is -

$$F = \frac{KZe^2}{r^2} \text{ where : } K = \text{constant} = \frac{1}{4\pi\epsilon_0} = 9 \text{ x } 10^9$$
$$Nm^2/C^2$$

and the centrifugal force $F = \frac{mv^2}{r}$

For the stable orbit of an electron both the forces are balanced.

i.e
$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

then $v^2 = \frac{KZe^2}{mr}$ (i)
From the postulate of Bohr

From the postulate of Bonr,

$$mvr = \frac{nh}{2\pi} \implies v = \frac{nh}{2\pi mr}$$

On squaring
$$v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$$
 (ii)



From equation (i) and (ii)

 $\frac{\text{KZe}^2}{\text{mr}} = \frac{n^2 h^2}{4\pi^2 m^2 r^2}$

On solving, we will get

$$r = \frac{n^2 h^2}{4\pi^2 m K Z e^2}$$

On putting the value of e, h, m, the radius of nth Bohr orbit is given by :

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

Solved Examples

Calculate radius ratio for 2nd orbit of He⁺ ion & Ex.4 3rd orbit of Be⁺⁺⁺ ion.

Sol.
$$r_1$$
 (radius of 2nd orbit of He⁺ ion) = 0.529 $\left(\frac{2^2}{2}\right)$ Å
 r_2 (radius of 3rd orbit of Be⁺⁺⁺ ion) = 0.529 $\left(\frac{3^2}{4}\right)$ Å

Therefore
$$\frac{r_1}{r_2} = \frac{0.529 \times 2^2/2}{0.529 \times 3^2/4} = \frac{8}{9}$$

CALCULATION OF VELOCITY OF AN ELECTRON IN BOHR'S ORBIT

Angular momentum of the revolving electron in nth orbit is given by

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

$$v = \frac{nh}{2\pi mr} \qquad \dots \dots \dots (iii)$$

put the value of 'r' in the equation (iii)

then,
$$v = \frac{nh \times 4\pi^2 mZe^2 K}{2\pi mn^2 h^2}$$

$$v = \frac{2\pi Z e^2 K}{nh}$$

on putting the values of π , e⁻, h and K

velocity of electron in nth orbit $v_n = 2.18 \times 10^6$

$$x \frac{Z}{n} m/sec;$$
 $v \propto Z$; $v \propto \frac{1}{n}$

T, Time period of revolution of an electron in its orbit

$$=\frac{2\pi r}{v}$$

f, Frequency of revolution of an electron in its orbit

$$=\frac{v}{2\pi}$$

CALCULATION OF ENERGY OFAN ELECTRON

> The total energy of an electron revolving in a particular orbit is

$$T.E. = K.E. + P.E.$$

where :

P.E. = Potential energy, K.E. = Kinetic energy,

T.E. = Total energy

The K.E. of an electron = $\frac{1}{2}$ mv²

and the P.E. of an electron $= -\frac{KZe^2}{r}$

Hence, T.E. = $\frac{1}{2}mv^2 - \frac{KZe^2}{r}$ we know that, $\frac{mv^2}{r} = \frac{KZe^2}{r^2}$ or

 $mv^2 = \frac{KZe^2}{r}$

substituting the value of mv^2 in the above equation :

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

substituting the value of 'r' in the equation of T.E. Then

T.E. =
$$-\frac{KZe^2}{2} \times \frac{4\pi^2 Ze^2 m}{n^2 h^2} = -\frac{2\pi^2 Z^2 e^4 m K^2}{n^2 h^2}$$

Thus, the total energy of an electron in nth orbit is given by

T.E. =
$$E_n = -\frac{2\pi^2 me^4 k^2}{h^2} \left(\frac{z^2}{n^2}\right)$$
 ... (iv)

Putting the value of m,e,h and π we get the expression of total energy

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

$$n \uparrow \text{ T.E.} \uparrow \quad ; \quad Z \uparrow \text{ T.E.} \downarrow$$

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

$$\text{T.E.} = \frac{1}{2} \text{ P.E.}$$

$$\text{T.E.} = -\text{ K.E.}$$
Note : - The P.E. at the infinite = 0

Note : - The P.E. at the infinite = 0The K.E. at the infinite = 0

CONCLUSION FROM EQUATION OF ENERGY

- (a) The negative sign of energy indicates that there is attraction between the negatively charged electron and positively charged nucleus.
- (b) All the quantities on R.H.S. in the energy equation [Eq. iv] are constant for an element having atomic number Z except 'n' which is an integer such as 1,2,3, etc. i.e. the energy of an electron is constant as long as the value of 'n' is kept constant.
- (c) The energy of an electron is inversely proportional to the square of 'n' with negative sign.

Solved Examples

- **Ex-4** What are the frequency and wavelength of a photon emitted during a transition from n = 5 state to the n = 2 state in the hydrogen atom ?
- **Sol.** Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series.

$$\Delta E = 2.18 \times 10^{-18} \text{ J} \left[\frac{1}{5^2} - \frac{1}{2^2} \right]$$
$$= -4.58 \times 10^{-19} \text{ J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$v = \frac{\Delta E}{h} = \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}}$$
$$= 6.91 \times 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{v} = \frac{3.0 \times 10^8 \text{ms}^{-1}}{6.91 \times 10^{14} \text{Hz}} = 434 \text{ nm}$$

FAILURES / LIMITATIONS OF BOHR'S THEORY

- (a) He could not explain the line spectra of atoms containing more than one electron.
- (b) He also could not explain the presence of multiple spectral lines.
- (c) He was unable to explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect)
- (d) No conclusion was given for the principle of quantisation of angular momentum.
- (e) He was unable to explain the de-Broglie's concept of dual nature of matter.
- (f) He could not explain Heisenberg's uncertainty principle.

ENERGY LEVEL DIAGRAM

- (i) Orbit of lowest energy is placed at the bottom, and all other orbits are placed above this.
- (ii) The gap between two orbits is proportional to the energy difference of the orbits.



Energy level diagram of H-atom

DEFINITION VALID FOR SINGLE ELECTRON SYSTEM :

(i) Ground state :

Lowest energy state of any atom or ion is called ground state of the atom It is n = 1.

Ground state energy of H-atom = - 13.6 ev

Ground state energy of He^+ Ion = -54.4 ev

(ii) Excited State :

States of atom other than the ground state are called excited states :

n = 2	first excited state
n = 3	second excited state
n = 4	third excited state
n = n + 1	n th excited state

(iii) Ionisation energy (IE) :

Minimum energy required to move an electron from ground state to

 $n = \infty$ is called ionisation energy of the atom or ion. Ionisation energy of H-atom = 13.6 ev Ionisation energy of He⁺ ion = 54.4 ev Ionisation energy of Li⁺² ion = 122.4 ev

(iv) Ionisation Potential (I.P.) :

Potential difference through which a free electron must be accelerated from rest, such that its kinetic energy becomes equal to ionisation energy of the atom is called ionisation potential of the atom. I.P. of H atom = 13.6 V, I.P. of He⁺ Ion= 54.4 V

(v) Excitation Energy :

Energy required to move an electron from ground state of the atom to any other state of the atom is called excitation energy of that state.

Excitation energy of 2^{nd} state = excitation energy of 1^{st} excited state = 1^{st} excitation energy = 10.2 ev.

(vi) Excitation Potential :

Potential difference through which an electron must be accelerated from rest to so that its kinetic energy become equal to excitation energy of any state is called excitation potential of that state.

Excitation potential of third state = excitation potential of second excitation excitation potential = 12.09 V.

(vii) Binding Energy 'or' Seperation Energy :

Energy required to move an electron from any state to $n = \infty$ is called binding energy of that state.

Binding energy of ground state = I.E. of atom or Ion.

Solved Examples

Ex-5 A single electron system has ionization energy 11180 kJ mol⁻¹. Find the number of protons in the nucleus of the system.

Sol. I.E.
$$= \frac{Z^2}{n^2} \times 21.69 \times 10^{-19} \text{ J}$$

 $\frac{11180 \times 10^3}{6.023 \times 10^{23}} = \frac{Z^2}{1^2} \times 21.69 \times 10^{-19} \text{ Ans. } \mathbf{Z} = \mathbf{3}$

HYDROGEN SPECTRUM

Study of Emission and Absorption Spectra :

An instrument used to separate the radiation of different wavelengths (or frequencies) is called spectroscope or a spectrograph. Photograph (or the pattern) of the emergent radiation recorded on the film is called a spectrogram or simply a spectrum of the given radiation The branch or science dealing with the study of spectra is called **spectroscopy**.



Emission spectra :

When the radiation emitted from some source e.g. from the sun or by passing electric discharge through a gas at low pressure or by heating some substance to high temperature etc, is passed directly through the prism and then received on the photographic plate, the spectrum obtained is called 'Emission spectrum'.

Depending upon the source of radiation, the emission spectra are mainly of two type :

(a) Continuous spectra :

When white light from any source such as sun, a bulb or any hot glowing body is analysed by passing through a prism it is observed that it splits up into seven different wide band of colours from violet to red. These colours are so continuous that each of them merges into the next. Hence the spectrum is called continuous spectrum.



(b) Discrete spectra : It is of two type

(i) Band spectrum



Band spectrum contains colourful continuous bands sepearted by some dark space.

Generally molecular spectrum are band spectrum

(ii) Line Spectrum :



This is the ordered arrangement of lines of particular wavelength seperated by dark space eg. hydrogen spectrum.

Line spectrum can be obtained from atoms.

(b) Absorption spectra :

When white light from any source is first passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, it is observed that some dark lines are obtained in the continuous spectrum. These dark lines are supposed to result from the fact that when white light (containing radiations of many wavelengths) is passed through the chemical substance, radiations of certain wavelengths are absorbed, depending upon the nature of the element.





When hydrogen gas at low pressure is taken in the discharge tube and the light emitted on passing electric discharge is examined with a spectroscope, the spectrum obtained is called the emission spectrum of hydrogen.

LINE SPECTRUM OF HYDROGEN

Line spectrum of hydrogen is observed due to excitation or de-excitation of electron from one stationary orbit to another stationary orbit

Let electron make transition from n_2 to $n_1 (n_2 > n_1)$ in a H-like sample



Energy of emitted photon = $(\Delta E)_{n2 \rightarrow n1}$

$$=\frac{-13.6Z^2}{n_2^2}-\left(\frac{-13.6Z^2}{n_1^2}\right)$$

$$= 13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Wavelength of emitted photon

$$\lambda = \frac{hc}{\left(\Delta E\right)_{n_2 \to n_1}}$$

$$\lambda = \frac{hc}{13.6Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

$$\frac{1}{\lambda} = \frac{(13.6)z^2}{hc} \left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2} \right)$$

Wave number, $\frac{1}{\lambda} = \overline{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

R = Rydberg constant = $1.09678 \times 10^7 \text{m}^{-1}$;

 $R \simeq 1.1 \times 10^7 \text{ m}^{-1}$; $R = \frac{13.6 \text{eV}}{\text{hc}}$; R ch = 13.6 eV



Solved Examples

Ex-6 Calculate the wavelength of a photon emitted when an electron in H- atom maker a transition from n=2 to n=1

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

 $\therefore \frac{1}{\lambda} = R(1)^2 \left[\frac{1}{1^2} - \frac{1}{2^2} \right]$
 $\therefore \frac{1}{\lambda} = \frac{3R}{4} \text{ or } \lambda = \frac{4}{3R}$

SPECTRA LINES OF HYDROGEN ATOM-LYMAN SERIES

- * It is first spectral series of H.
- * It was found out in ultraviolet region in 1898 by Lyman.
- * It's value of $n_1 = 1$ and $n_2 = 2,3,4$ where ' n_1 ' is ground state and ' n_2 ' is called excited state of electron present in a H atom.

*
$$\frac{1}{\lambda} = R_{\text{H}} \left[\frac{1}{1^2} - \frac{1}{n_2^2} \right]$$
 where $n_2 > 1$ always.

- * The wavelength of marginal line = $\frac{n_1^2}{R_H}$ for all series.
 - So for lyman series $\lambda = \frac{1}{R_{H}}$.
- * Ist line of lyman series $\Rightarrow 2 \rightarrow 1$ IInd line of lyman series $= 3 \rightarrow 1$ Last line of lyman series $= \infty \rightarrow 1$ $[10.2 \text{ eV} \le (\Delta E)_{\text{lyman}} \le 13.6 \text{ eV}]$

 $\frac{12400}{13.6} \leq \lambda_{lyman} \leq \ \frac{12400}{10.2} \ A^o$

* **Longest line :** longest wavelength line λ_{longest} or

$$\lambda_{\text{max.}} = \frac{12400}{(\Delta E)_{\text{min}}}$$

* Shortest line : shortest wavelength line $\lambda_{shortest}$ or

$$\lambda_{\min} = \frac{12400}{(\Delta E)_{\max}}$$

- * First line of any spectral series is the longest (λ_{max}) line.
- * Last line of any spectral series is the shortest (λ_{min}) line.

Series limit :

It is the last line of any spectral series.

Wave no of Ist line of Lyman series

$$= \frac{1}{\lambda} = \frac{1}{\nu} = R \times 1^{2} \left(\frac{1}{1^{2}} - \frac{1}{2^{2}} \right)$$
$$\frac{1}{\nu} = R \times 1^{2} \left(\frac{4-1}{4} \right)$$
$$\frac{1}{\nu} = \frac{R \times 3}{4} = \frac{3R}{4}$$
$$\therefore \qquad \left[\lambda = \frac{4}{3R} \right]$$

Wave no of last line of Lyman series

$$\overline{\nu} = \mathbf{R} \times 1^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right)$$
$$\overline{\nu} = \mathbf{R}$$

For Lyman series,

$$\lambda_{\text{longest}} = \frac{12400}{(\Delta E)_{2-1}}, \ \lambda_{\text{shortest}} = \frac{12400}{(\Delta E)_{\infty \to 1}}$$

BALMER SERIES :

- * It is the second series of H-spectrum.
- * It was found out in 1892 in visible region by Balmer.
- * It's value of $n_1 = 2$ and $n_2 = 3, 4, 5, \dots$
- * The wavelength of marginal line of Balmer series

$$=rac{n_1^2}{R_H}=rac{2^2}{R_H}=rac{4}{R_H}$$

$$\frac{1}{\lambda} = R_{\rm H} \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right) \text{ where } n_2 > 2 \text{ always.}$$

$$1.9 \leq (\Delta E)_{\text{halmer}} \leq 3.4 \text{ eV}.$$

All the lines of balmer series in H spectrum are not in the visible range. Infact only Ist 4

lines belongs to visible range.

$$\frac{12400}{3.4} A^{o} \le \lambda_{balmer} \le \frac{12400}{1.9} Å$$

$$3648 \text{ Å} \le \lambda_{\text{balmer}} \le 6536 \text{ Å}$$

Lines of balmer series (for H atom) lies in the visible range.

Ist line of balmer series = $3 \rightarrow 2$

last line of balmer series = $\infty \rightarrow 2$

$$(\overline{v})$$
 1st line = R ×1 $\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R}{36}$
 (\overline{v}) last line = R $\left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) = \frac{R}{4}$

PASCHEN SERIES :

- (a) It is the third series of H spectrum.
- (b) It was found out in infrared region by Paschen.
- (c) It's value of $n_1 = 3$ and $n_2 = 4,5,6$
- (d) The wavelength of marginal line of Paschen series

$$=rac{n_1^2}{R_H}=rac{3^2}{R_H}=rac{9}{R_H}$$

(e)
$$\frac{1}{\lambda} = R_{\text{H}} \left[\frac{1}{3^2} - \frac{1}{n_2^2} \right]$$
 where $n_2 > 3$ always

BRACKETT SERIES :

(a) It is fourth series of H - spectrum.

.2

- (b) It was found out in infrared region by Brackett.
- (c) It's value of $n_1 = 4$ and $n_2 = 5,6,7$
- (d) The wavelength of marginal line of brackett series

$$= \frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$$
(e) $\frac{1}{\lambda} = R_H \left[\frac{1}{4^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 4$ always.

PFUND SERIES :

- (a) It is fifth series of H- spectrum.
- (b) It was found out in infrared region by Pfund.
- (c) It's value of $n_1 = 5$ and $n_2 = 6,7,8$ where n_1 is ground state and n_2 is excited state.
- (d) The wavelength of marginal line of Pfund series

$$= \frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$$
(e) $\frac{1}{\lambda} = R_H \left[\frac{1}{5^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 5$ always.

HUMPHRY SERIES :

- (a) It is the sixth series of H spectrum.
- (b) It was found out in infrared region by Humphry.
- (c) It's value of $n_1 = 6$ and $n_2 = 7$, 8, 9.....
- (d) The wavelength of marginal line of Humphry series

$$= \frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$$
(e) $\frac{1}{\lambda} = R_H \left[\frac{1}{6^2} - \frac{1}{n_2^2} \right]$ where $n_2 > 6$.

Solved Examples

Sol. $\frac{1}{\lambda} = R(2)^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ $n_1 = 2$ $n_2 = 4$ $\frac{1}{\lambda} = R(2^2) \left[\frac{1}{2^2} - \frac{1}{4^2} \right]$ $\frac{1}{\lambda} = \frac{3R}{4}$ $\lambda = \frac{4}{3R}$ Ans.

NO. OF PHOTONS EMITTED BY

A SAMPLE OF HATOM

If an electron is in any higher state n = n and makes a transition to ground state, then total no. of different photons emitted is equal to $\frac{n \times (n-1)}{2}$.

If an electron is in any higher state $n = n_2$ and makes a transition to another excited state $n = n_1$, then total no. of different photons emitted is equal to

$$\frac{\Delta n(\Delta n+1)}{2}$$
, where $\Delta n = n_2 - n_1$

Note : In case of single isolated atom if electron make transition from n^{th} state to the ground state then max. number of spectral lines observed = (n-1)

Solved Examples

Ex-8 If electron make transition from 7th excited state to 2nd state in H atom sample find the max. number of spectral lines observed.

Sol. $\Delta n = 8 - 2 = 6$

spectral lines =
$$6\left(\frac{6+1}{2}\right) = 6 \times \frac{7}{2} = 21$$

DUAL NATURE OF ELECTRON (DE-BROGLIE HYPOTHESIS)

- (a) Einstein had suggested that light can behave as a wave as well as like a particle i.e. it has dual character.
- (b) In 1924, de-Broglie proposed that an electron behaves both as a material particle and as a wave.
- (c) This proposed a new theory wave mechanical theory of matter. According to this theory, the electrons protons and even atom when in motion possess wave properties.
- (d) According to de-Broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation,

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

where h is Planck's constant

(e) This can be derived as follows according to Planck's equation.

$$E = h_{\nu} = \frac{h.c}{\lambda}$$

Energy of photon on the basis of Einstein's mass energy relationship

$$E = mc^2$$
 or $\lambda = \frac{h}{mc}$

Equating both we get

$$\frac{h.c}{\lambda} = mc^2$$
 or $\lambda = \frac{h}{mc}$

Which is same as de - Broglie relation.

This was experimentally verified by Davisson and Germer by observing diffraction effects with an electron beam.

Let the electron is accelerated with a potential of V then the K.E. is

$$\frac{1}{2} mv^{2} = eV$$

$$m^{2}v^{2} = 2emV$$

$$mv = \sqrt{2emV} = p \text{ (momentum)}$$

$$\lambda = \frac{h}{\sqrt{2emV}}$$

If we associate Bohr's theory with de - Broglie equation then

$$2\pi \mathbf{r} = \mathbf{n}\lambda$$
 or $\lambda = \frac{2\pi \mathbf{r}}{\mathbf{n}}$

From de-Broglie equation

$$\lambda = \frac{h}{mv}$$
 therefore $\frac{h}{mv} = \frac{2\pi r}{n}$

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

m = dynamic mass =
$$\frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

 $m_0 = rest mass of particle$ depended on velocity c = velocity of light If velocity of particle is zero then :

dynamic mass = rest mass

Rest mass of photon is zero that means photon is never at rest

* K.E. =
$$\frac{1}{2}$$
 mv²

m (K.E.) = $\frac{1}{2}$ m² v² multiplied by mass on both side

$$\Rightarrow$$
 m.v. = $\sqrt{2m(K.E.)}$

$$\lambda = \frac{h}{\sqrt{2m(K.E.)}}$$

If a charge q is accelerated through a potential difference of 'V' volt from rest then K.E. of the charge is equal to : "q.V"

$$\Rightarrow \quad \lambda = \frac{h}{\sqrt{2m(q.V)}}$$

* If an electron is accelerated through a potential difference of 'V' volt from rest then :

$$\Rightarrow \lambda = \frac{h}{\sqrt{2m_e(eV)}}$$

$$\Rightarrow \lambda = \left(\frac{150}{V}\right)^{\frac{1}{2}} \dot{A} \quad (\text{on putting values of h, m_e and e})$$

$$\Rightarrow \lambda = \frac{12.3}{\sqrt{V}} \dot{A} \qquad (V \text{ in volt})$$

$$* \quad \text{mvr} = n \times \frac{h}{2\pi}$$

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

$$mv = \frac{h}{\lambda} \text{ putting this in } mvr = \frac{nh}{2\pi}$$

$$\therefore \quad \frac{h}{\lambda}r = \frac{nh}{2\pi} \Rightarrow \left[\lambda = \frac{2\pi r}{n}\right] \text{ de Broglie wavelength}$$

Solved Examples

- **Ex-9** What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} (NCERT)
- Sol. According to de Broglie equation

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ Js})}{(0.1 \text{ kg})(10 \text{ ms}^{-1})}$$
$$= 6.626 \times 10^{-34} \text{ m (J} = \text{kg m}^2 \text{ s}^{-2}).$$

HEISENBERG'S UNCERTAINTY PRINCIPLE

The exact position and momentum of a fast moving particle cannot be calculated precisely at the same moment of time. If Δx is the error in the measurement of position of the particle and if Δp is the error in the measurement of momentum of the particle, then:

$$\Delta x \, . \, \Delta p \geq \frac{h}{4\pi} \quad \text{or} \qquad \Delta x \, . \, (m\Delta v) \geq \frac{h}{4\pi}$$

where, $\Delta x =$ uncertainty in position

 Δp = uncertainty in momentum

- h = Plank's constant
- m = mass of the particle

 $\Delta v =$ uncertainty in velocity

If the position of a particle is measured precisely, i.e. $\Delta x \rightarrow 0$ then $\Delta p \rightarrow \infty$.

If the momentum of the particle is measured precisely. i.e. $\Delta p \rightarrow 0$ then $\Delta x \rightarrow \infty$.

This is because of a principle of optics that if a light of wavelength ' λ ' is used to locate the position of a particle then maximum error in the position measurement will be $\pm \lambda$

i.e.
$$\Delta x = \pm \lambda$$

If $\Delta x \to 0$; $\lambda \to 0$

But,

 $p = \frac{h}{\lambda} \Rightarrow p \to \infty$

So, to make $\Delta x \to 0$, $\lambda \to 0$ a photon of very high energy is used to locate it.

:. When this photon will collide with the electron then momentum of electron will get changed by a large amount.

$$\Delta p.\Delta x \ge \frac{h}{4\pi}$$
 (multiplied & divided by Δt)

*

$$\begin{split} & \frac{\Delta P}{\Delta t} \Delta t.\Delta x \geq \frac{h}{4\pi} \\ & (\frac{\Delta P}{\Delta t} = \text{rate of change in momentum} = F) \\ & F.\Delta x.\Delta t \geq \frac{h}{4\pi} \\ & \Delta E \ . \ \Delta t \geq \frac{h}{4\pi} \end{split}$$

 $\Delta E \longrightarrow$ uncertainty in energy

 $\Delta t \longrightarrow$ uncertainty in time

 \checkmark In terms of uncertainty in energy ΔE , and uncertainty in time Δt , this principle is written as,

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

 Heisenberg replaced the concept of definite orbits by the concept of probability.

Solved Examples

Ex-10 A golf ball has a mass of 40 g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

(NCERT)

Sol. The uncertainty in the speed is 2%, i.e., $45 \times \frac{2}{100}$

$$= 0.9 \text{ m s}^{-1}$$
.

Using the equation

$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 40 \times 10^{-3} (0.9 \,\text{ms}^{-1})}$$
$$= 1.46 \times 10^{-33} \,\text{m}$$

This is nearly $\sim 10^{18}$ times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

ORBITAL

An orbital may be defined as the region of space around the nucleus where the probability of finding an electron is maximum (90% to 95%)

Orbitals do not define a definite path for the electron, rather they define only the probability of the electron being in various regions of space around the nucles.



Maximum dots represent high probability of finding an electron

Difference between orbit and orbitals

Orbit

- 1. It is well defined circular path followed by revolving electrons around the nucleus
- 2. It represents planar motion of electron
- The maximum no. of electron in an 3. orbits is $2n^2$ where n stands for no oforbit
- 4. Orbits are circular in shape.
- 5 Orbit are non directional in character. Hence, they cannot explain shape of molecules
- 6. Concept of well defined orbit is against Heisenberg's uncentainty principle.

Orbitals

- 1. It is the region of space around the nucleus where electron is most likely to be found
- 2. It represents 3 dimensional motion of an electron around the nucleus
- 3. Orbitals can not accomodate more than 2 electrons.
- 4. Orbitals have different shape e.g. s-orbital is spherical, p - orbital is dumb- bell shaped.
- 5. Orbitals (except s-orbital) have directional character. Hence, they can account for the shape of molecules.
- 6. Concept of orbitals is in accordance with Heisenberg's principle

18. SHAPE OF THE ORBITALS

Shape of the orbitals are related to the solutions of Schrodinger wave equation, and gives the space in which the probability of finding an electron is maximum.

s-orbital : Shape \rightarrow spherical

s- orbital is non directional and it is closest to the nucleus, having lowest energy.



s-orbital can accomodate maximum no. of two 1↓ electrons. n s

p-orbital : Shape \rightarrow **dumb bell**

Dumb bell shape consists of two lobes which are separated by a region of zero probability called node.



p - orbital can accomodate maximum no. of six electrons.



d - Orbital :

Shape \rightarrow double dumb bell





d - orbital can accomodate maximum no. of 10 electrons.

	↑↓	1 ↓	↑↓	↑↓	↑↓	
	dxy	dyz	dz^2	dx ² -y ²	dxz	
f	- orbi	tal :	Sh	ape →	leaf li	ke
r					A 1	

f - orbital can accomodate maximum no. of 14

QUANTUM NUMBERS

electrons.

The set of four numbers required to define an electron completely in an atom are called quantum numbers. The first three have been derived from Schrodinger wave equation.

(i) Principal quantum number (n) : (Proposed by Bohr)

It describes the size of the electron wave and the total energy of the electron. It has integral values 1, 2, 3, 4, etc., and is denoted by K, L, M, N. ..., etc.

* Number of subshell present in n^{th} shell = n

n	subshell
1	S
2	s, p
3	s, p, d
4	s, p, d, f

- Number of orbitals present in n^{th} shell = n^2 .
- The maximum number of electrons which can be present in a principal energy shell is equal to 2n².
 No energy shell in the atoms of known elements possesses more than 32 electrons.
- * Angular momentum of any orbit = $\frac{nh}{2\pi}$

(ii) Azimuthal quantum number (ℓ) :

(Proposed by Sommerfield)

It describes the shape of electron cloud and the number of subshells in a shell.

- * It can have values from 0 to (n-1)
- * value of ℓ subshell

S

f

- 0
- 1 p
- 2 d
- 3
- * Number of orbitals in a subshell = $2\ell + 1$
- * Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$
- * Orbital angular momentum $L = \frac{h}{2\pi} \sqrt{\ell(\ell+1)}$

$$=\hbar \sqrt{\ell(\ell+1)} \qquad \left[\hbar = \frac{h}{2\pi}\right]$$

i.e. Orbital angular momentum of s orbital =0, Orbital

angular momentum of p orbital = $\sqrt{2} \frac{h}{2\pi}$,

Orbital angular momentum of d orbital = $\sqrt{3} \frac{h}{2\pi}$

(iii) Magnetic quantum number (m) : (Proposed by Linde)

It describes the orientations of the subshells. It can have values from $-\ell$ to $+\ell$ including zero, i.e., total $(2\ell+1)$ values. Each value corresponds to an orbital. s-subshell has one orbital, p-subshell three orbitals $(p_x, p_y \text{ and } p_z)$, d-subshell five orbitals $(d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2})$ and f-subshell has seven orbitals. The total number of orbitals present in a main energy level is 'n²'.

(iv) Spin quantum number (s) :

(Proposed by Samuel Goldsmit & Uhlenbeck)

It describes the spin of the electron. It has values +1/2 and -1/2. signifies clockwise spinning and anticlockwise spinning.

* Spin magnetic moment $\mu_s = \frac{eh}{2\pi mc} \sqrt{s(s+1)}$ or μ

= $\sqrt{n(n+2)}$ B.M. (n = no. of unpaired electrons)

- * It represents the value of spin angular momentum which is equal to $\frac{h}{2\pi} \sqrt{s(s+1)}$
- * Maximum spin of atom = $\frac{1}{2}x$ No. of unpaired electron.

ELECTRONIC CONFIGURATION

Pauli's exclusion principle :

No two electrons in an atom can have the same set of all the four quantum numbers, i.e., an orbital cannot have more than 2 electrons because three quantum numbers (principal, azimuthal and magnetic) at the most may be same but the fourth must be different, i.e., spins must be in opposite directions.

Aufbau principle :

Aufbau is a German word meaning building up. The electrons are filled in various orbitals in order of their increasing energies. An orbital of lowest energy is filled first. The sequence of orbitals in order of their increasing energy is :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d,

The energy of the orbitals is governed by $(n + \ell)$ rule.

'n + e RULE

The relative order of energies of various sub-shell in a multi electron atom can be predicated with the help of 'n + ℓ ' rule

• The sub-shell with lower value of $(n + \ell)$ has lower energy and it should be filled first.

eg. 3d 4s

$$(n + \ell) = 3 + 2 (n + \ell) = 4 + 0$$

 $= 5 = 4$

Since, $(n + \ell)$ value of 3d is more than 4s therefore, 4s will be filled before 3d.

- If two sub-shell has same value of (n + ℓ) then the sub-shell with lower value of n has lower energy and it should be filled first.
 - eg. 3d 4p $(n + \ell) = 3 + 2 = 4 + 1$ = 5 = 5

3d is filled before 4p.

MEMORY MAP



HUND'S RULE

No electron pairing takes place in the orbitals in a sub - shell until each orbital is occupied by

one electron with parallel spin. Exactly half filled and fully filled orbitals make the atoms more stable,

i.e., p^3 , p^6 , d^5 , d^{10} , f^7 and f^{14} configuration are most stable.

Solved Examples

Ex-11 Write the electronic configuration and find the no. of unpaired electrons as well as total spin for the following atoms :

$(1)_{6}C$	(2)	O_8
$(3)_{15}P$	(4)	₂₁ Sc
$(5)_{26}$ Fe	(6)	₁₀ Ne

 $\textbf{Sol.}~(1)_6C~\rightarrow 1s^2,\,2s^2,2p^2$

		11	11	1	1		
--	--	----	----	---	---	--	--

No. of unpaired electrons $\rightarrow 2$.

Total spin =
$$\frac{+2}{2}$$
 or $\frac{-2}{2}$

$$(2)_8 O \rightarrow 1s^2, 2s^2, 2p^4$$

11	11	11	1	1
1s	2s		2p	

 \therefore No. of unpaired electrons = 2

Total spin = $\frac{+2}{2}$ or $\frac{-2}{2}$

(3)
$$_{15}P \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$$

11	1	1	1
3s		Зр	

 \therefore No. of unpaired electrons = 3

Total spin =
$$\frac{+3}{2}$$
 or $\frac{-3}{2}$

(4)
$$_{21}$$
Sc $\rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
or [Ar] 4s² 3d¹

 $[Ar] 3d^1 4s^2$

 \therefore No. of unpaired electrons = 1

$$\therefore \qquad \text{Total spin} = \frac{+1}{2} \text{ or } \frac{-1}{2}$$



Ex-12 Write down the four quantum numbers for fifth and sixth electrons of carbon atom.

```
Sol. {}_{6}C: 1s^{2}, 2s^{2} 2p^{2}
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fifth electron : n = 2 $\ell = 1$ m = -1 or +1 $s = +\frac{1}{2}$ or $-\frac{1}{2}$ sixth electron : n = 2 $\ell = 1$ m = 0 $s = +\frac{1}{2}$ or $-\frac{1}{2}$

- *Ex-13* Calculate total spin, magnetic moment for the atoms having at. no. 7, 24 and 36.
- Sol. The electronic configuration are

⁷N: 1s², 2s² 2p³ unpaired electron = 3 ²⁴Cr : 1s², 2s² 2p⁶, 3s² 3p⁶ 3d⁵, 4s¹ unpaired electron = 6 ³⁶Kr : 1s², 2s² 2p⁶, 3s² 3p⁶ 3d¹⁰, 4s² 4p⁶ unpaired electron = 0 ∴ Total spin for an atom = $\pm 1/2 \times \text{no. of unpaired}$ electron For ₇N, it is = $\pm 3/2$; For ₂₄Cr, it is = ± 3 ; For ₃₆Kr, it is = 0 Also magnetic moment = $\sqrt{n(n+2)}$ For ₇N, it is = $\sqrt{15}$; For ₂₄Cr, it is = $\sqrt{48}$; For ₃₆Kr, it is = $\sqrt{0}$

EXCEPTIONS

- (1) $_{24}Cr = [Ar] 4s^2$, $3d^4$ (Not correct) [Ar] $4s^1$, $3d^5$ (correct : as d^5 structure is more stable than d^4 structure)
- (2) $_{29}Cu = [Ar] 4s^1, 3d^{10}$

(correct : as d^{10} structure is more stable than d^9 structure).

THE SCHRODINGER EQUATION

The de Broglie wave relation is the basis for predicting the behavior of freely moving particles. Shortly after it was proposed, Erwin Schrodinger demonstrated that the de Broglie expression could be generalized so as to apply to bound particles such as electrons in atoms. The heart of Schrodinger's theory is that the allowed energies of physical systems can be found by solving an equation which so resembles the equations of classical wave theory that it is called the wave equation. For the motion of one particle in one (the x) direction, the Schrodinger wave equation is

$$- \frac{h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \ . \label{eq:phi}$$

The "knowns" in this equation are m, the mass of the particle, and V, its potential energy expressed as a function of x. The "unknowns" to be found by solving the equation are E, the quantized or allowed energies of the particle, and ψ , which is called the wave function. The quantity $d^2\psi/dx^2$ represents the rate of change of $d\psi/dx$, the rate of change of ψ . When this equation is applied to real systems such as the hydrogen atom, it is found that it cannot be solved unless E takes on certain values which are related by integers. Thus quantized energy and quantum numbers are an automatic consequence of the Schrodinger theory, and do not have to be tacked on to Newtonian mechanics as was done by Bohr. What is ψ ? By itself, it has no physical meaning. However, the square of the absolute value of ψ , $|\psi|^2$, does have an important physical interpretation.

It is a mathematical expression of how the probability of finding a particle varies from place to place. Thus the exact trajectories of Newtonian mechanics and the Bohr theory do not appear in the results of the Schrodinger quantum mechanics; this, according to the Uncertainty Principle, is as it should be.

A similar analysis is possible for the other 2pfunctions. The p_x function has the yz-plane as an angular node, since the function is proportional sin θ $\cos \phi$ and $\cos \phi = 0$ everywhere in the yz-plane. The maximum values of 1 for sin θ and $\cos \phi$ occur along the positive x-axis. The p_y function, proportional to the sin $\theta \sin \phi$, vanishes in the xz-plane, where $\sin \phi =$ 0, and has a maximum along the positive y-axis, where both sin θ and sin ϕ are unity.



FIG. The 2p-orbitals of the hydrogen atom. (Adapted from K. B. Harvey and G. B. Porter, An Introduction to Physical Inorganic Chemistry. Reading, Mass.: Addison-Wesley, 1963.)





The 3d-orbitals of the hydrogen atom. Note the relation between the labeling of the d-orbitals and their orientations in space. (Adapted from K. B. Harvey and G. B. Porter, An Introduction to Physical Inorganic Chemistry. Reading, Mass.: Addison-Wesley, 1963.)



Radial probability density for some orbitais of the hydrogen atom. Ordinate is proportional to $4\pi r^2 R^2$, and all distributions are to the same scale.

- (i) total nodes = n 1,
- (ii) angular nodes = ℓ ,
- (iii) radial nodes = $n \ell 1$.

Structure of Atom

