1. ATOMIC STRUCTURE

Synopsis :

Fundamental particles:

- According to Dalton atom is the smallest indivisible particle. But discharge tube experiments have proved that atom consists of some more smaller particles.
- Electrons, protons and neutrons are the fundamental particles of an atom.
- Electron was discovered in cathode ray experiment.
- Ideal conditions to produce cathode rays in the discharge tube are very low pressure (0.01 mmHg) and high electric discharge (10,000 V) potential.
- Cathode rays can be deflected in electric and magnetic field which shows that they are negatively charged particles.
- Particle nature of cathode rays was proved by (a) Their ability to cause mechanical motion (b) Photo-electric effect (c) Compton effect.
- Cathode rays are negatively charged consisting of electrons.
- Anode rays are positively charged ions.
- Protons and neutrons are present in the nucleus and are called as nucleons.
- Protium contains only electron and proton. Except protium all the atoms contain electron, proton and neutron.
- Electrons are the negatively charged particles with unit negative charge and negligible mass.
- Protons are the positively charged particles with unit mass.
- Proton was discovered in the anode ray experiment.
- Anode rays, also called as canal rays or positive rays, were discovered by E. Goldstein.
- Anode rays contain material particles obtained by the removal of one or more electrons from the gaseous atoms/ molecules present in the tube.
- The positively charged particles present in the anode rays produced when Hydrogen gas is present in the discharge tube were called protons by Rutherford (proton = first particle).
- The specific charge on the anode rays was found to be maximum when gas present in the discharge tube was hydrogen.
- Neutrons are neutral particles with unit mass

Fundamental particle	Charge	Mass	Specific Charge (e/m)
Electron	1.6022×10^{-19} coulomb (or) 4.802×10^{-10} e.s.u.	9.1095×10^{-31} kg (or) 0.000548 a.m.u. 1/1836 of H atom	1.76×10^{8} c/g
Proton	1.6022×10^{-19} coulomb (or) 4.802×10^{-10} e.s.u.	1.67252×10^{-27} kg (or) 1.007548 a.m.u.	9.58×10^{4} c/g
Neutron	'0'	1.6749×10^{-27} kg (or) 1.00898 a.m.u.	'0'

- The ratio of charge to mass is called specific charge.
- Electron has the highest specific charge because of its negligible mass.
- The mass of electron increases with increase in velocity. Thus e/m of electron decreases with increase in velocity.
- If electron moves with a velocity equal to that of light, then it's mass becomes infinity and e/m becomes zero.
- e/m of cathode rays is independent of nature of the gas in the discharge tube, because electrons are universal constituents.
- e/m of anode rays depends on the nature of the gas in the discharge tube.
- The number of electrons or protons present in an atom of an element is called its atomic number.
- A neutral atom contains equal number of electrons and protons.
- Atomic number is denoted by Z.
- Atomic number is equal to the nuclear charge of an element.
- Moseley proposed a simple relationship between frequencies of the characteristic x-rays of an element and its atomic number.

  $\sqrt{\upsilon} = a(Z - b)$
- υ is the frequency of characteristic x-rays.
- Z = atomic number
- 'a' and 'b' are constants having definite values for that element.
- The sum of number of protons and neutrons in the atom of an element is called its mass number and it is denoted by 'A'
- Number of neutrons = A – Z.
- Mass number is always a whole number.
- Atoms of elements having the same atomic number but different mass numbers are called isotopes.
- Isotopes of an element have the same number of protons and electrons but differ in the number of neutrons.
- Isotopes of an element have same chemical properties but different physical properties.

Rutherford's atomic model:

- This is called planetary model or nuclear model of atom.
- Rutherford's atomic model is based on the findings of α-ray scattering experiment.
- An atom is a hollow sphere and the entire mass and positive charge are concentrated at the centre of the atom in the smallest region called nucleus.
- Electrons revolve around the nucleus in circular path.
- This model failed to explain the stability of atoms and line spectra of atoms.
- As per the laws of electrodynamics an electron moving around the nucleus must radiate energy continuously and must spiral down into the nucleus.
- If an electron radiates energy continuously the atomic spectrum should be a continuous spectrum.
- The atom should collapse if it happens.
- But all the atoms give line spectra.

Nature of light:

- The two theories, which explain the nature of light are (i) wave theory, (ii) corpuscular theory.
- The wave theory of light could satisfactorily explain diffraction, refraction etc.

- Corpuscular theory could explain photoelectric effect and Compton effects.
- Wave theory is superior to corpuscular theory.
- Visible light is only a small portion of electromagnetic spectrum.
- All radiant energy is in the form of electromagnetic waves.
- These radiations are associated with electric and magnetic fields.
- The vertical component of the wave (E) indicates the variation of electric field strength.
- The horizontal component of the wave (H) indicates the variation of magnetic field strength.
- The distance between two successive crests or troughs is called the wavelength (λ).
- Wavelength is measured in Angstrom units or nanometres.
- 1 Å = 10^{-8} cm = 10^{-10} m; 1 nm = 10^{-9} m = 10 Å
- The number of waves passing through a given point in one second is called as frequency of the wave.

  $\upsilon = c / \lambda$

  Units of frequency is Hz.
- The velocity of light in air or in vacuum is $\times 10^8$ ms^{-1} or 3×10^{10} cms^{-1}.
- Frequency $\times$ wavelength = velocity; $\upsilon\lambda = c$
- The reciprocal of wavelength is called wave number.

  Wave number $\bar{\upsilon} = \frac{1}{\lambda}$
- The units of wave number is cm^{-1} or m^{-1}.

  $\bar{\upsilon} = \frac{1}{\lambda}$; $\upsilon = \frac{c}{\lambda}$;

  $\upsilon = c.\bar{\upsilon}$
- 'A' is the amplitude of the wave or intensity of the light.
- The intensity of color depends on amplitude and color of the light depends on frequency. ($I \propto A^2$)

Sources of different radiations:

- High-pressure hydrogen or deuterium discharge tube is the source of ultraviolet rays.
- The wavelength range of ultraviolet rays is 1850 Å to 3750 Å.
- To obtain high energetic U.V. xenon arc lamp or mercury vapour lamp can be used.
- The glass enclosed tungsten filament is the source of visible radiation. Incandescent lamp is the source of I.R. radiation.
- The best source of near infrared radiations is a black body.
- To produce far infrared radiations Nernst glower or globar source is used.
- The wavelength of these radiations is about 14,000 Å.
- A mixture of Zirconium and Yttrium oxides shaped into a small hollow rod is used in Nernst glower.
- The glower is heated to 1500 °C to 2000 °C.
- The globar source is a rod of sintered silicon carbide, which is heated to 1300 °C to 1700 °C.

Planck's Quantum theory:

- Planck's quantum theory explains black body radiation.
- A hollow sphere coated inside with platinum black and having a pinhole acts as a nearer black body.

- A black body is not only a prefect absorber but also a perfect emitter of radiant energy.
- Black body kept at high temperature give radiations in a wide range of different wavelengths.
- The curves are obtained at different temperatures when the intensity of radiations is plotted against wavelength.
- If the energy is emitted continuously the curve should be as shown by the dotted lines.
- The study of the curves shows that the nature of the radiation depends on temperature.
- At a given temperature, the intensity of radiation increases with wavelength reaches a maximum and then decrease.
- As the temperature increases the peak of the curve shifts to lower wavelengths. (ie. towards left)
- Based on the above observations of black body radiation, Planck proposed quantum theory of radiation. The salient features of the theory are
- The vibrating particle in the black body does not emit energy continuously.
- It is emitted in the form of small discrete packets called quanta.
- The emitted radiant energy is propagated in the form of waves.
- If the vibrating particles oscillates with a frequency v, then the energy associated with a quantum. $E \propto v$;

  $E = hv$ (h = Planck's constant. $h = 6.625 \times 10^{-27}$ ergs-sec, $h = 6.625 \text{ X } 10^{-34}$ J-sec)
- Energy is emitted or absorbed in some simple integral multiples of a quantum i.e. E = 1 hv (or) 2hv (or) 3hv but not fractional multiple of hv.
- This is called quantization of energy.
- Einstein's generalisation of Planck's quantum theory:
- Planck's quantum theory was extended to all types of electromagnetic radiations by Einstein.
- According to Einstein energy is released in the form of photons and they continue to exist as photons till they are absorbed by another body.
- According to Max Planck, energy is emitted in the form of packets and propagated in the form of waves.
- According to Einstein, both emission and propa-gation of energy take place in the form of photons.
- Einstein explained photoelectric effect with the help of his generalized quantum theory.
- Emission of electrons from the metal surface when it is exposed to light is called photoelectric effect.
- Such emitted electrons are called photoelectrons.
- According to Einstein electron is ejected from a metal when it is struck by a photon which has sufficient energy.
- If the photon has insufficient energy it cannot eject the electron and photo electric effect is not observed.
- Photon of violet light has higher energy than that of red light. It is observed that violet light is able to eject electrons from potassium but red light has no effect.
- When the photon having energy h*v*, strikes the metal surface, some part of it is utilised to eject electron and the remaining part is utilised to increase the K.E. of photo electron.
- If the frequency of incident radiation increased, K.E. of photoelectrons increase.
- If the intensity of incident radiation increases rate of photoelectric emission increases.

$$hv = W + K.E$$

hv = energy of striking photon; W = energy required to eject the electron (work function); K.E. = kinetic energy of the emitted electron.

Light spectra:

- Spectrum: It is the pattern of lines produced on the photographic plate, by the dispersion of a beam when it is passed through the prism.
- Spectrometer: It is the device used to record the spectrum.
- Spectrograph It consists of source of light, Prism and photographic plate.
- Spectra are of 2 types: 1. Emission spectrum 2. Absorption spectrum

Emission Spectrum:

- When the substances are in the excited state they emit light. Spectrum obtained with this emitted light is called emission spectrum.
- Emission spectrum is obtained by heating the substances on a flame or by passing electric discharge through the gases.
- Emission spectrum consists of bright lines on dark background.

Absorption spectrum:

- It is due to absorption of light.
- When the substances are in the ground state, they absorb radiation and go to excited state, the spectrum so obtained is called absorption spectrum.
- Absorption spectrum consists of dark lines on bright background.
- In the absorption spectrum lines are formed at same wavelengths as those of emission spectrum.
- Emission spectrum or absorption spectrum is of two types.

Continuous spectrum or band spectrum:

- In this spectrum formation of lines is continuous.
- Each color fades in to the next color as in rainbow.
- A beam of white light when passed through a prism, it gives a continuous spectrum of seven colors i.e. VIBGYOR.
- Incandescent lamp or hot solids at high temperatures will give continuous spectrum.

Discontinuous spectrum or line spectrum:

- Line spectrum consists of sharp, distinct and well defined lines.
- Gases or vapours of elements when heated in a flame or by passing electric discharge through them, line spectrum is obtained.
- Line spectrum is given by atoms and so it is called atomic spectrum.
- Each element has it's own characteristic line spectrum, by which the element can be identified.

Band spectrum:

- It consists of series of bands where each band is a group of lines merged together.
- Band spectrum is given by molecules and so it is called molecular spectrum.

Hydrogen spectrum:

- It consists of number of lines.
- They can be classified into various series.
- Only one such series is visible to the naked eye and is termed as the visible region of hydrogen spectrum i.e. Balmer series.
- The wavelength or wave number of various lines in the visible region can be expressed by an equation.
  (Reydberg – Ritz equation) :

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

Where $n_1 = 2$ which is constant for all the lines in Balmer series; $n_2 = 3, 4, 5.....$

Series in hydrogen spectrum:

Name of series	n_1(lower orbit)	n_2 (higher orbit)	Spectral region
Lyman series	1	2, 3, 4, 5...	ultraviolet
Balmer series	2	3,4,5,6...	visible
Paschen series	3	4,5,6,7...	near infrared
Brackett series	4	5,6,7...	infrared
Pfund series	5	6,7,8...	far infrared

- The other series in the hydrogen spectrum are invisible.
- The wavelength or wavenumber of all the lines in all the series can be calculated by using Rydberg's equation or Rydberg-Ritz equation.

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

- The value of R = 1,09,677 cm^{-1} is valid only for the lines in the hydrogen spectrum.
- For a spectral line of one electron species like He^+, Li^{2+} the value of R = 1,09,677 × Z^2 cm^{-1}.
- The first line in Balmer series is called Hα line and its wavelength is 6563 Å.
- The second line is called Hβ line and its wavelength is 4861 Å.
- The spectral lines get closer when the n_2 value is increased.

Bohr's atomic theory:

- Bohr recognized the relationship between the nature of the series of spectral lines and the arrangement of electrons in the atom.
- Bohr applied Planck's quantum theory to the electrons revolve around the nucleus. He retained the basic concept of Rutherford's model of atom that electrons revolve round the positively charged nucleus.
- Bohr proposed his theory to explain the structure of atom.

The important postulates of his theory are:

- Electrons revolve around the nucleus with definite velocities in concentric circular orbits. These orbits are called stationary orbits as the energy of the electron remains constant. As long as the electron revolves in the same circular orbit it neither radiates nor absorbs energy.
- The angular momentum of the electron is quantised. The electronic motion is restricted to those orbits where the angular momentum of an electron is an integral multiple of $h/2\pi$ or $mvr = nh/2\pi$. This is called Bohr's quantum condition or quantisation of angular momentum.
- Energy of the electron changes only when it moves from one orbit to another orbit.
- Energy is absorbed when an electron jumps from a lower orbit to a higher outer orbit.
- If electron is in 1s orbit, it can only absorb but cannot emit energy.
- Energy is released when an electron jumps from higher orbit to a lower orbit.

- The released or absorbed energy is equal to the difference between the energies of the two orbits.
- If E_2 is the energy of the electron in the outer orbit (n_2) and E_1 is the energy of the electron in the inner orbit (n_1), then $E_2 - E_1 = \Delta E = h\upsilon$.
- Where n is called principal quantum number and it represents the main energy level.
- It takes all positive and integral values 1, 2, 3, 4… etc.
- With the help of these postulates Bohr derived the expression for the radius of the circular orbit, energy of the electron in a circular orbit and velocity of the electron in a circular orbit.
- Bohr's theory could satisfactorily explain the formation of different series of lines in hydrogen spectrum.
- The wavelengths and the frequencies of the lines determined experimentally are in excellent agreement with those calculated by using Bohr's equation.

Radius of orbit:

- Hydrogen atom contains one proton in the nucleus and one electron revolving around the nucleus in a circular orbit of radius r.
- The electron maintains the same circular motion in given orbit as centripetal and centrifugal forces are equal in magnitude and opposite in direction.
- Centripetal force = centrifugal force (columbic forces of attraction provides necessary centripetal force)

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

  According to Bohr's quantum condition;

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

  $v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$; $\frac{e^2}{r} = \frac{m \cdot n^2h^2}{4\pi^2m^2r^2}$; $e^2 = \frac{n^2h^2}{4\pi^2mr}$; $r = \frac{n^2h^2}{4\pi^2me^2}$

  The radius of the nth orbit is given by

  $r_n = n^2\left(\frac{h^2}{4\pi^2me^2}\right)$

  $= 0.529 \times 10^{-8}\ n^2 cm$

  Where h = Planck's constant; m = mass of electron; e = charge of electron; r_n = radius of nth orbit
- The radius of the first orbit of hydrogen atom is called Bohr's radius which is denoted by r_0.

  $r_0 = 0.529 \times 10^{-8}$ cm = 0.529 Å

Energy of electron:

- The total energy of the electron in a stationary orbit is equal to sum of its kinetic and potential energies.

  Total energy of electron E = K.E + P.E.

  K.E. is always positive and P.E is always negative.

  K.E. is half to that of P.E. in magnitude.

  $\frac{1}{2}mv^2 - \frac{e}{r} = \frac{1}{2}\frac{e^2}{r} - \frac{e^2}{r} (\because mv^2 = \frac{e^2}{r}) = -\frac{1}{2}\frac{e^2}{r}$

  Energy of electron for single electron species is $E_n = -\frac{2\pi^2e^4m}{h^2} x \frac{z^2}{n^2}$.

By substituting the value of r.

$E_n = -\frac{1}{2}\frac{e^2 4\pi^2 me^2}{n^2h^2}$;

$E_n = -\frac{2\pi^2 e^4 m}{n^2h^2}$;

$E_n = -\frac{k}{n^2}$ (k is constant ; $k = \frac{2\pi^2 e^4 m}{h^2}$);

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

(or) $-\frac{2.18 \times 10^{-11}}{n^2}$ ergs/atom

(or) $-\frac{2.18 \times 10^{-18}}{n^2}$ J/atom

(or) $-\frac{313.6}{n^2}$ kcal/mole

$-\frac{1312}{n^2}$ kJ/mole

- The energy of electron is negative in the atom.
- As the value of n increases energy increases.
- When n is infinity the value of E is zero.
- When n value decreases the energy of electron also decreases.

Rydberg constant (R):

- When an electron jumps from outer energy level (n_2) to inner energy level (n_1), energy is released.

  i.e. $E_2 - E_1 = \Delta E = \Delta h\upsilon$

  E_2 = energy of electron in higher orbit (n_2)

  E_1 = energy of electron in lower orbit (n_1)

  $E_2 - E_1 = \frac{-2\pi^2 e^4 m}{n_2^2 h^2} + \frac{2\pi^2 e^4 m}{n_1^2 h^2}$;

  $\Delta E = \frac{2\pi^2 e^4 m}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$;

  $h\upsilon = \frac{2\pi^2 e^4 m}{h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$;

  $\upsilon = \frac{2\pi^2 e^4 m}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$;

  Wave number $\overline{\upsilon} = \frac{1}{\lambda} = \frac{v}{c}$

$$c\bar{\upsilon} = \frac{2\pi^2 e^4 m}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]; \qquad \bar{\upsilon} = \frac{2\pi^2 e^4 m}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right];$$

$\therefore \upsilon = c\bar{\upsilon}$;

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

$$R = \frac{2\pi^2 e^4 m}{ch^3} = 1{,}09{,}681 \text{ cm}^{-1}.$$

- This value Rydberg constant (R) calculated by Bohr as above is in good agreement with experimental value.

Velocity of element in the nth orbit:

- As per Bohr's quantum condition, $mvr = n\frac{h}{2\pi}$; $V_n = \frac{nh}{2\pi mr}$;

  Substituting 'r'; $V_n = \frac{2\pi e^2}{nh}$ (for 'H' atoms for any other single electron species; $V_n = \frac{2\pi e^2}{h} x \frac{z}{n}$
- Sub situating the values of constants,

  $V_n = \frac{2.188}{10^{-8}} x \frac{z}{n}$ cm/sec.
- Number of revolutions per second, made by electron in circular orbit is = $\frac{\text{velocity}}{\text{circumference}} = \frac{v}{2\pi r}$

Hydrogen spectrum – Bohr's explanation:

- When hydrogen gas is heated or exposed to light energy or subjected to electric discharge different atoms absorb different amounts of energy and electrons are excited to different higher energy levels.
- The bright light emitted when passed through a prism and received on a photographic plate and is recorded as the atomic spectrum of hydrogen.
- The hydrogen spectrum is the simplest of all the atomic spectra. It is line spectrum and emission spectrum.
- It contains a number of series of lines.
- The electrons in the excited atoms may be completely knocked out of the atom if the absorbed energy is greater than or equal to 13.58 eV which is the ionization potential of hydrogen atom.
- If the energy available is less than 13.58 eV the electron absorbs only a certain quantum of energy and the electron jumps to higher orbit.
- The electron in higher quantum state tends to emit energy and come back to the lower energy level.
- This may happen in a single step or in multiple steps.
- If electron jumps from any higher orbit to 1st orbit Lyman series is formed in u.v. region.

  Electron transitions: $\infty \rightarrow 1$

  $7 \rightarrow 1$

  $6 \rightarrow 1$

  $5 \rightarrow 1$ so on.
- If electron jumps back from any higher orbit to 2nd orbit Balmer series is formed in visible region.
- Electron transitions: $\infty \rightarrow 2$; $7 \rightarrow 2$, $6 \rightarrow 2$……
- If electron jumps back from any higher orbit to 3rd orbit Paschen series is formed in near I.R.

region.

- Electron transitions: $\infty \rightarrow 3$; $7 \rightarrow 3$, $6 \rightarrow 3$; and so on.
- If electron jumps back from any higher orbit to 4^{th} orbit, Bracket series is formed in the I.R. region.
- Electron transitions: $\infty \rightarrow 4$; $7 \rightarrow 4$, $6 \rightarrow 4$ and so on.
- If electron jumps back from any higher orbit to 5^{th} orbit.
- Electron transitions: $\infty \rightarrow 5$; $7 \rightarrow 5$, $6 \rightarrow 5$
- If electron jumps back from infinite state to corresponding lower orbit, spectral line is called limiting line or limiting series

Rydberg's equation for limiting line is $\bar{v} = R\left(\frac{1}{n_1^2} - \frac{1}{\infty^2}\right) = \frac{R}{n_1^2}$

n a given series the line of longest wavelength is 1^{st} line ($2 \rightarrow 1$) and the line of shortest wavelength is limiting line.

In all the five series of H - spectrum, the line of longest wavelength is 1^{st} line of Pfund series ($6 \rightarrow 5$) and the line of shortest wavelength is limiting line of Lyman series(∞ to 1)

No.of possible spectral lines $= \frac{n(n+1)}{2}$; $n = n_2 - n_1$

As the value of 'n' increases

i) the total energy of electron increases
ii) the energy difference between the successive orbits decreases
iii) P.E increases and K.E. decreases
iv) radius of orbits increases
v) velocity of electron decreases

Merits of Bohr's theory:

- He could explain the spectra of H - atom and other single electron species like He^+, Li^{2+} etc.
- He could determine frequency, wavelength, wave number of lines in H - spectrum.
- He could calculate the value of Rydberg constant (R).
- He could determine energy and velocity of electron and radius of orbits.
- He could explain the stability of atoms that is why, electrons are not falling into the nucleus and atoms are not collapsed.

Demerit's of Bohr's theory:

- Bohr failed to explain spectra of multi electron species.
- He failed to explain fine structure of the H-spectrum.
- He failed to consider the wave number of electron.
- Bohr's theory contradicts Hisenberg's uncertainty principle.

Quantum numbers:

- To fully explain the motion of electron and to locate it's correct address the following four quantum numbers are required.

Principal quantum number (n) :

- It is proposed by Bohr and denoted by 'n'.
- It represents the main energy level.
- It determines the size of the orbit and energy of the electron.
- It takes all positive and integral values from 1 to n.
- The maximum number of electrons in a main energy level is $2n^2$, and number of orbitals is n^2.

- If 'n' is the principal quantum number the energy of the electron in the principal quantum level is

  $E_n = -\frac{2\pi^2 e^4 m}{h^2}\frac{1}{n^2}$; $E_n = -\frac{13.6}{n^2}$ eV/atom
- As the value of 'n' increases, the energy of electron increases.
- The energy of electron in the ground state of hydrogen atom is – 13.6 eV/atom(or) -2.176×10^{-11} erg per atom(or) -2.176×10^{-18} joule per atom(or) –1312 kJ per mole (or) –313.6 kcal per mole.
- The energy of the electron in the second orbit of hydrogen atom is

  $= -\frac{13.6}{2^2} = -3.4$ eV/atom

Azimuthal quantum number (ℓ):

- It is also known as angular momentum quantum number or orbital quantum number (or) subsidiary quantum number.
- To express the quantised values of the orbital angular momentum, azimuthal quantum number was proposed.
- It is denoted by ℓ and takes values from 0 to n – 1.
- The number of values of 'ℓ' is equal to the value of n.
- It explains fine structure in H-spectrum.
- It determines the shape of orbitals.
- More fine lines in each main spectral line are seen.

  If n = 1, ℓ = 0 (s - sub-shell)

  If n = 2, ℓ = 0, 1 (s, p sub-shells)

  If n = 3, ℓ = 0, 1, 2 (s, p, d sub-shells)

  If n = 4, ℓ = 0,1, 2, 3 (s, p, d, f - sub-shells)
- The orbital angular momentum of electron = $\frac{h}{2\pi}\sqrt{\ell(\ell+1)}$
- Azimuthal quantum number determines the shape of the orbital.
- The number of orbitals in a sub shell is $(2\ell + 1)$.
- The maximum number of electrons in a sub shell is $2(2\ell + 1)$.

Magnetic quantum number:

- To explain Zeeman and Stark effects Lande proposed magnetic quantum number.
- It is denoted by m.
- It represents the sub-sub energy level or atomic orbital.
- It determines the orientation of orbital in space.
- When the atom is placed in an external magnetic field, the orbit changes its orientation.
- The number of orientations is given by the values of the magnetic quantum number m.
- m takes the values form $-\ell$ to $+\ell$ through 0. Total values of m for a given value of $\ell = (2\ell + 1)$ values.
- A sub shell having azimuthal quantum number ℓ, can have $(2\ell + 1)$ space orientations.
- The number of orbitals in a subsheII = $(2\ell + 1)$.
- If the changes in the axis in one direction are indicated by + m values, the changes in the axis in the opposite direction are indicated by – m.

Spin quantum number (s):

- In the fine spectrum of alkali metals pairs of widely separated lines are observed which are different from duplet, triplet, and quadruplets observed in the hydrogen spectrum.
- To recognise and identify these pairs of lines Goudsmit and Uhlenbeck proposed that an electron rotates or spins about its own axis.
- This results in the electron having spin angular momentum, which is also quantised.
- The electron may spin clockwise or anti clockwise. Therefore, the spin quantum number takes two values +1/2 and –1/2. Clockwise spin or parallel spin is given +1/2 or ↑ and anti clockwise or anti parallel spin is given by –1/2 or ↓.

Wave nature of electron de-Broglie theory:

- de-Broglie proposed that the dual nature is associated with all the particles in motion and they are called matter waves.
- Electrons, protons, atoms and molecules which are treated as particles are associated with wave nature.
- Correlating Planck's equation E = hv and Einstein's equation $E = mc^2$, we can get wavelength of matter waves.

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

- de-Broglie applied this condition for the material particles in motion.
- The wavelength of a particle in motion is inversely proportional to its momentum.
- Smaller particles with very little mass have significant wavelength and bigger particles with large mass have negligible wavelengths.
- As electron has negligible mass, it has significant wavelength.
- The wave nature of electron was proved experimentally by Davisson and Germer in electron diffraction experiments.
- Hence electron exhibits both wave nature and particle nature.

Bohr's theory and de Broglie's concept:

- According to Bohr, electronic motion is permitted when the angular momentum is an integral multiple of $h/2\pi$.

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

- According to de Broglie, an electron behaves as a standing or stationary wave, which extends round the nucleus in a circular orbit.
- If the two ends of the electron wave meet, the electron wave is said to be in phase.
- In other words there is constructive interference of electron waves and the electron motion has a character of standing wave or non-energy radiating motion.
- For the electron wave in phase, the circumference of the Bohr's orbit should be an integral multiple of the wavelength of the electron wave.
- According to Bohr's quantum condition, $mvr = \frac{nh}{2\pi}$; $2\pi r = \frac{nh}{mv}$; $2\pi r = n\lambda$ $\left(\because \lambda = \frac{h}{mv}\right)$
- Thus, de-Broglie's theory and Bohr's theory are in agreement with each other.
- In case the circumference of the Bohr's orbit ($2\pi r$) is bigger or smaller than $n\lambda$, the electron wave is said to be out of phase.
- Then destructive interference of waves occurs causing radiation of energy.

- Such an orbit cannot exist.

Heisenberg's uncertainity principle:

- It is impossible to determine the exact position and velocity of the electron accurately and simultaneously.
- If the position is certain then the accurate determination of velocity is uncertain and vice-versa which is called Heisenberg's uncertainity principle.
- $\Delta x.\Delta p \geq \frac{h}{4\pi}$ or $\Delta x.m\Delta V \geq \frac{h}{4\pi}$ or $\Delta x.\Delta V \geq \frac{h}{4\pi m}$ If $\Delta x = 0$, Δv = infinity
- If $\Delta v = 0$, Δx = infinity
- Where Δx is uncertainity in position and Δp is the uncertainity in momentum.
- The radius of an atom is of the order of 10^{-10} m.
- Hence the uncertainity in the position of electron cannot be more than 10^{-10} m.
  When $\Delta x = 10^{-10}$ m.

  The uncertainity in velocity $\Delta v = \frac{h}{4\pi m\Delta x} = \frac{6.6x10^{-34}}{4x3.14x9.1x10^{-31}x10^{-10}} = 5.8x10^{5} ms^{-1}$
- Thus the minimum uncertainity in it's velocity can not be less than 5.8×10^5 m\sec
- The uncertainity is not of technical in nature but it lies in the nature of particle itself.

Schrodinger's wave equation:

- Schrodinger's wave theory is the basis for the modern quantum mechanical model of the atom.
- When the exact position of the electron cannot be determined we can predict the probability of finding the electron around the nucleus.
- This theory takes two facts into account.
  1) Wave nature of the electron
  2) The knowledge about the position of an electron is based on its probability.
- It describes electron as a three dimensional wave in the electric filed of positively charged nucleus.
- Schrodinger's wave equation describes the wave motion of electron along X, Y and Z axes.

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

- In the above equation 'm' is the mass of electron, E is its energy, U is its potential energy, ψ is called wave function or amplitude of the electronic wave.
- The above equation indicates the variation of the value of ψ along x, y and z axes.
- Since, the probability of finding electron can not be negative, ψ is replaced by ψ^2.
- ψ^2 is the probability function of the electron and it denotes the electron cloud density around the nucleus.
- The region or space around the nucleus where the probability of finding the electron is maximum (About 95%) is called an atomic orbital.
- The probability of finding the electron in the nucleus is zero.
- The probability of finding the electron in the radial space around the nucleus is called radial probability.
- The probability function of electron is called D function.
- Thus radial probability or electron probability function, $D = 4\pi r^2 dr.\psi^2$
- In hydrogen atom the probability of finding the electron is maximum at a distance 0.53 Å from the nucleus. The probability of electron at a distance of 1.3 Å is zero in H-atom.

- The plane in which the probability of finding the electron is zero is called node or nodal plane or nodal surface.

Shapes of orbitals:

- The shape of s-orbital is spherical and spherically symmetrical. It has no nodal planes.
- The number of radial nodes for s-orbital = (n – 1)
- p-orbital has dumb-bell shape. It has one nodal plane.
- The three p-orbitals are mutually perpendicular to one another.
- Each p-orbital has one nodal plane.
- The lobes are oriented along the respective axes.
- p_x orbital is along the x-axis and its nodal plane is along yz plane.
- p_y orbital is along the y-axis and its nodal plane is along xz plane.
- p_z orbital is along the z-axis and its nodal plane is along xy plane.
- For p-orbital l = 1 m = –1, 0, +1
- For p_x orbital; m = +1
- For p_y orbital; m = –1,
- For p_z orbital; m = 0;
- d orbital has 4 lobes and double dumb-bell shape.
- Each d-orbital has 2 nodal planes.
- d_{xy} orbital is in the xy plane between x and y axes.
- d_{yz} orbital is in the yz plane between y and z axes.
- d_{xz} orbital is in the xz plane between x and z axes.
- $d_{x^2-y^2}$ orbital is also in the xy plane but the lobes are oriented along x and y axes.
- d_z^2 orbital is along the z-axis.
- In d_{xy}, d_{yz}, d_{zx} orbitals, the lobes are in between the respective axes.
- In $d_{x^2-y^2}$, d_z^2 orbitals, the lobes are along the axes.
- d_z^2 contains a ring called torus or collar or tyre of negative charge surrounding the nucleus in the xy plane.
  It has only 2 big lobes oriented along z-axis.
- For d-orbital, I = 2, m = –2, –1, 0, +1, +2
- For d_{z^2} orbital, m = 0, for d_{xz} orbital, m = +1
- For d_{xy} orbital, m = –2 for d_{yz} orbital, m = –1
- For $d_{x^2-y^2}$ orbital, m = +2
- The energy of electron in hydrogen atom is determined only by the principal quantum number n.
- In multi electron atoms, the energy of electron depends on both principal quantum number and azimuthal quantum number.
- The magnetic quantum number ‘m’ indicates the number of degenerate levels or orbitals of equal energy.
- An orbital having a certain value for ‘m’ cannot accommodate more than 2 electrons.
- The maximum number of electrons in s, p, d and f sub energy levels is 2, 6, 10 and 14 respectively.
- The maximum number of electrons in a given principal quantum level 'n' is $2n^2$.
- The maximum number of sub orbitals in a main orbit = n.

- The maximum number of orbitals in a main orbit = n^2.
- The maximum number of orbitals in a sub orbit = (2l +1).
- The maximum number of e^-'s in a sub orbit = 4l + 2

Pauli's exclusion principle:

- No two electrons in the same atom can have the same set of values for all the four quantum numbers.
- Two electrons in a given orbital have the same values of *n, I* and *m* but differ in spin quantum numbers.

Aufbau principle:

- The orbitals are successively filled in the order of their increasing energy.
- Among the available orbitals, the orbitals of lowest energy are filled first.
- The relative energy of orbital can be known by (n+ℓ) formula.
- If two orbitals have the same value of (n + ℓ), the orbital having lower n value is first filled.
- As atomic number increases, (n + ℓ) formula is not useful to predict the relative energies of orbitals
  a) for example, up to z = 20, 3d > 4s
     Beyond z = 20, energy difference narrows up.
     Beyond z = 57, 3d < 4s.
  b) upto to z = 57,4f > 5p
     beyond z = 57, 4f > 5p ; At z = 90, 4f < 5s.
- The order of filling of orbitals can be known from Moellar's diagram.

Hund's rule of maximum multiplicity:

- Orbitals having the same values for n and ℓ are called degenerate orbitals.
- Pairing of orbitals will begin after the available degenerate orbitals are half filled.
- Orbitals with highest resultant spin value are more stable.
- The degenerate orbtials are filled to have like spins as far as possible.
- As per Hund's rule, the number of unpaired electrons in the ground state of C, N, O are 2, 3, 2 respectively.
- In the absence of Hund's rule, the number of unpaired electrons in C, N, O are 0, 1, 0 respectively.
- The filling of orbital is governed by Pauli's principle.
- The filling of sub-orbit is governed by Hund's rule.
- The filling of orbitals of various suborbits is governed by Aufbau principle.
- The maximum number of electrons that are present in the outer most shell of any atom = 8
- The maximum number of electrons that are present in the (n–1) most shell of any atom = 18
- The maximum number of electrons that are present in the (n–2) most shell of any atom = 32

Anomolous electronic configurations:

1. Half filled and completely filled degenerate orbitals give greater stability to atoms.
2. Chromium (Z = 24) and copper (Z = 29) have anamalous electronic configuration due to this reason.
3. Electronic configuration of chromium atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ or [Ar] $3d^5 4s^1$ but not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$.
4. Electronic configuration of copper atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ or [Ar] $4s^1 3d^{10}$ but not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$.

Magnetic properties:

- Atoms molecules, ions or any species having unpaired electrons exhibit para-magnetism.
- These are attracted into the magnetic field when they are placed in an external magnetic field.
- Atoms having the completely paired electrons are repelled by the external magnetic field and are called diamagnetic.
- The unpaired electrons produce magnetic field in atoms due to their resultant spin.
- The magnetic moment of atoms containing unpaired electrons is given by the formula $\mu = \sqrt{n(n+2)}$ B.M> Where 'n' is the number of unpaired electrons. Unit of magnetic moment is Bohr magneton (B.M.)

  If n = 1, μ = 1……B.M, If n = 2, μ = 2……B.M,

  If n = 3, μ = 3……B.M and so on.

Stability of atoms:

- Theory of exchange forces will explain why Cr has (Ar) $3d^5\ 4s^1$ but not (Ar) $3d^4 4s^2$.
- According to this theory, greater the number of unpaired electrons, greater is the number of possible exchange pairs of electrons and more is the exchange energy released and the atom is more stable.
- For $C_r \rightarrow$ (Ar) $3d^5\ 4s^1$, the possible number of exchange pairs = 15.
- If energy released for each exchange pair is k, the total exchange energy is 15 k.
- For Cr $\rightarrow$ (Ar) $3d^4\ 4s^2$, the possible number of exchange pairs = 10 and total exchange energy is only 10k.

Therefore Cr $\rightarrow$ (Ar) $3d^5\ 4s^1$ is more stable than Cr(Ar) $3d^4\ 4s^2$