ATOMIC STRUCTURE

1. Dalton's Atomic Theory:

John Dalton, in 1803, put forward his atomic theory. The following are the important points of the theory:

(i) Matter is composed of particles called atoms.

(ii) All the atoms of an element are similar in mass and properties.

(iii) Atom is indivisible.

(iv) Atoms of different elements combine in a simple ratio to give "compound atom".

- The discovery of phenomena of Radioactivity by Prof. Henri Becquerel showed that atom is divisible.
- The discovery of isotopes of an element by Soddy proved that the atoms of an element are different in mass and properties.
- The modern researches, such as discharge tube experiments have conclusively proved that atom is no longer an indivisible particle. It has definitely a complicated structure. Recent researches have shown that atom is composed of three, elementary, fundamental or sub-atomic particles, namely electron, proton and neutron.
- Electron ($_{-1}e^0$): It is (discovered by J.J. Thomson), negatively charged particle. It is the component particle of cathode rays.

MORE ABOUT ELECTRON

- Cathode rays were discovered by William Crooke's.
- Cathode rays originate from cathode in the discharge tube.
- Cathode rays are composed of stream of negatively charged particles.
- The magnitude of negative charge on electron was first determined by Millikan (oil drop experiment).
- The specific charge (e/m) on electron was first of all determined by J.J. Thomson using mass spectrometer.
- The value of $\frac{e}{m}$ of cathode ray particle does not depend upon the material of the cathode or the nature of the gas taken in the discharge tube.
- The name electron was suggested by J.S. Stoney.
- Magnitude of charge on electron = 1.6×10^{-19} coulomb = 4.8×10^{-10} e.s.u.
- Amount of charge on one mole of electrons is one Faraday.
- Rest mass of electron = 9.1×10^{-28} gram
  = 9.1×10^{-31} kg
  = 9.1×10^{-33} Quintal.
- Mass of electron on atomic scale = 0.000549 a.m.u = $\frac{1}{1837}$ of the mass of hydrogen atom.
- The mass of electron moving with a velocity 'v' is given as: $m_{(\text{in motion})} = \frac{m_{rest}}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$.
- Mass of a substance in motion increases with increase in velocity.
- Mass of electron moving with a velocity of light will become infinite.

- Mass of one mole of electrons is 0.55 mg.
- Electron is universal component of matter.
- Electron is the fundamental particle which takes part in chemical combination.
- The physical and chemical properties of an element depend upon the distribution of electrons in outer shells.
- Flow of electrons in a conductor means flow of electricity which can be detected by means of a Galvanometer.

2. Proton:

Proton ($_1H^1$, H^+, P): It was discovered by Rutherford. It is a positively charged particle. The magnitude of charge on proton is the same as that on an electron. Proton, like electron, is a fundamental particle and is universal component of matter.

MORE ABOUT PROTON

- Charge on proton $= 1.6 \times 10^{-19}$ coulomb
  $= 4.8 \times 10^{-10}$ e.s.u.
- Mass of proton = mass of hydrogen atom
  = 1837 times the mass of electron
  = 1.00747 a.m.u.
  $= 1.6726 \times 10^{-24}$ gram
  $= 1.6726 \times 10^{-27}$ kg.
- Volume of a proton $\left(\frac{4}{3}\pi r^3\right)$ is roughly close to 1.5×10^{-38} cm^3.
- Mass of one mole of protons is about 1.007 gm.
- Proton is protium nucleus.
- Proton is ionized hydrogen atom (H^+).
- Removal of solitary electron from hydrogen atom gives proton.
- Hydrogen atom minus electron is proton.

3. Neutron:

Neutron ($_0n^1$, N): It is a chargeless particle i.e., it is neutral. It was discovered by James Chadwick. The reason of its late discovery is its charge less ness.

When beryllium or boron is bombarded with α-particles, highly penetrating radiations are obtained. These radiations are not deflected from their path by strong magnetic or electric field. These radiations are composed of chargeless particles, known as neutrons.

$$_2He^4 + {}_4Be^9 \rightarrow {}_6C^{12} + {}_0n^1$$

MORE ABOUT NEUTRON

- Mass of neutron = 1.00899 a.m.u.
  $= 1.6749 \times 10^{-27}$ kg
- Actual mass of neutron is slightly greater than that of proton.
- Density of neutron is of the order 10^{12} kg/cc.
- Out of the three types of fundamental particles, neutron is the most unstable. It decays as follows:

$$\underset{\text{Neutron}}{{}_0n^1} \rightarrow \underset{\text{Proton}}{{}_1H^1} + \underset{\text{Electron}}{{}_{-1}e^0} + \underset{\text{Antineutrino}}{{}_0\nu^0}$$

4. Mass Number (A) and Atomic Number (Z):

The sum of protons and neutrons present in the nucleus is called mass number. It is always a whole number. The mass number is denoted by the symbol ‘A’. Since, electrons have negligible mass, therefore, the entire mass of atom is due to nucleons (neutrons and protons).

Mass number (A) = Number of protons + Number of neutrons

The concept of atomic number was given by Moseley. He observed that when a beam of highspeed electrons is bombarded on a metal, X-rays are emitted. The emitted X-rays have wavelength related to the number of protons present in the nucleus of metal atom. This number of protons present in the nucleus of the atom is called atomic number denoted by “Z”. The square root of the frequency of emitted X-rays is proportional to the atomic number of metals which is bombarded with the stream of electrons.

- Moseley’s relation is $\sqrt{v} = a(Z - b),$ where v = frequency of emitted X-rays, Z = atomic number of the metal, ‘a’ and ‘b’ are constants.
- Atomic number of an element is also equal to the number of electrons present in the outer shells around the nucleus since atom as a whole is electrically neutral.

  Atomic number = Number of protons in the Nucleus

  = Number of electrons in neutral atom
- Atomic number is fundamental property of an element.
- Two different elements can never have identical atomic numbers.
- The atom of an element ‘X’ having Mass number ‘A’ and atomic number ‘Z’ is represented by symbol, $_{Z}X^{A}$.
- Number of neutrons = A – Z.

5. Isotopes:

They were discovered by F. Soddy. They are atoms of a given element which have the same atomic number but differ in their mass numbers. Thus isotopes have the same nuclear charge but differ in the number of neutrons in the nucleus. Isotopes have identical chemical properties but differ in physical properties. They possess different charge: mass ratio, i.e., e/m of isotopes are different and they can be separated on this basis. The instrument which separates the particles according to their charge: mass ratio is called Mass spectrometer.

Examples:

(i) $_{1}H^{1}$ Hydrogen (Protium) (p =1, e = 1, n = 0); $_{1}H^{2}$ Heavy hydrogen (Deuterium) (p =1, e = 1, n = 1); $_{1}H^{3}$ Tritium (p =1, e = 1, n = 2)

(ii) $_{8}O^{16}$, $_{8}O^{17}$, $_{8}O^{18}$,

(iii) $_{17}Cl^{35}$, $_{17}Cl^{37}$,

(iv) $_{6}C^{12}$, $_{6}C^{13}$, $_{6}C^{14}$

Elements have non-integral atomic masses due to the existence of isotopes. The atomic weight of an element is the average of weights of all the isotopes of that element.

For example, the fractional atomic weight of chlorine (35.5) is due to the existence of isotopes $_{17}Cl^{35}$ and $_{17}Cl^{37}$ in the ratio of 3: 1. Their average atomic weight is the atomic weight of chlorine.

$$\text{Average weight} = \frac{\text{Weight of 3 atoms of } _{17}\text{Cl}^{35} + \text{Weight of one atom of } _{17}\text{Cl}^{37}}{\text{Total four atoms}}$$

$$= \frac{3\times35+1\times37}{4} = \frac{105+37}{4} = \frac{142}{4}$$

= 35.5 a.m.u.

6. Isobars:

They are atoms with the same MASS NUMBER but different ATOMIC NUMBERS. Thus isobars have different number of electrons, protons and neutrons but the sum of neutrons and protons in their nucleus is the same.

Examples: $_1H^3$ and $_2He^3$, $_{18}Ar^{40}$, $_{19}K^{40}$ and $_{20}Ca^{40}$; $_{52}Te^{130}$, $_{56}Ba^{130}$ and $_{54}Xe^{130}$.

As isobars are the atoms of different elements they possess different physical and chemical properties. In the periodic table, isobars are placed in separate groups.

Isotones (Isoneutronic species): They are the atoms possessing the same number of neutrons but different mass numbers.

Examples:

$_1H^3$ and $_2He^4$; $_{15}P^{31}$ and $_{16}S^{32}$; $_{19}K^{39}$ and $_{20}Ca^{40}$.

Since isotones differ in the number of protons (atomic number) in their nuclei, so their physical and chemical properties are different.

Isosters: These are the species with same number of atoms with equal number of electrons and similar bonding. e.g.,

$$O=C=O \text{ and } \overset{-}{N}=\overset{+}{N}=O \; or \; \overset{+}{O}\equiv C-\overset{-}{O} \; and \; N\equiv\overset{+}{N}—\overset{-}{O}$$

7. Rutherford's Atomic Model:

This model of an atom consists of two parts:

(i) Nucleus: It is very small (10^{-15} meter diameter), heavy, rigid, +vely charged part of the atom in which neutrons and protons are present. Thus, the whole mass of the atom is concentrated in the nucleus.

(ii) Extra Nuclear Part: It is the empty part of the atom. In this portion, the electrons (equal in number to the protons in the nucleus), the negatively charged particles, revolve at very high speed in fixed paths known as orbits or shells. The force of attraction between the positively charged nucleus and electrons balances the centrifugal force acting on the revolving electrons.

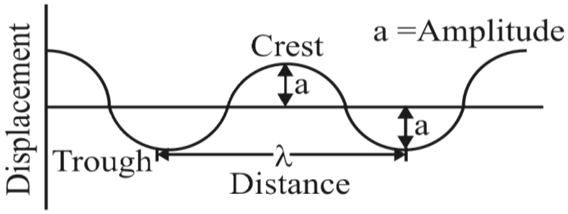
The Rutherford's atomic model is comparable to the solar system. The nucleus represents the sun, the electrons represent the planets. This atomic model was given the name planetary model of atom and the electrons were called planetary electrons.

Defects of the Rutherford's Atomic Model: Neils Bohr pointed out that Rutherford's model of atom is defective. He pointed out that according to classical electrodynamics; the electrons revolving around the nucleus are accelerated charged particles. Therefore, they should continuously emit radiation, lose energy, follow a spiral path and finally fall into the nucleus. Thus, Rutherford's atomic model represents an unstable atom. But an atom is found to be stable. In order to explain the stability of atom, Neil's Bohr postulated a theory which is based upon Planck's Quantum Theory.

Electromagnetic Radiations: Ordinary light, γ-rays, X-rays etc. are referred to as electromagnetic radiations because similar radiations can be produced by moving a charged body in a magnetic field or a magnet in an electric field. These radiations possess wave characteristics and are not in need of any medium for their propagation.

Wave characteristics: A wave is a type of disturbance whose origin is some vibrating source. The wave travels outwards as a continuous sequence of alternating crests and troughs. The following are the wave-characteristics:

1. Wave length (λ): It is the distance between two neighboring trough or crests.



It is expressed in cm, nanometers or angstrom (Å) units.

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

- The colour of a beam of visible light is determined by its wave length.

2. Frequency (v): The number of times, a wave passes through a given point in one second is known as the frequency of the wave. It is denoted by v (nu). It is expressed in cycles per second or Hertz (Hz) units.

1Hz = 1 cycle per second (cps)

3. Velocity (c): The distance travelled by the wave in one second is known as velocity of the wave. It is expressed in cm or meter per second. 'c' is related to v (nu) and λ (wave length) as follows:

$$c = \lambda v$$

or $$v(\text{nu}) = \frac{c}{\lambda}$$

All the electromagnetic radiations travel with the same velocity i.e. with the velocity of light i.e., 3×10^{10} cm sec^{-1}, 3×10^{8} m sec^{-1}, or 186000 miles sec^{-1}.

4. Wave number $\bar{v}$, (nu bar): The number of wave lengths per cm. is called wave number. It is reciprocal of wave length (λ). It is expressed in cm^{-1}

$$\bar{v} = \frac{1}{\lambda}$$

or $$\bar{v} = \frac{v}{c}$$

5. Amplitude (a): The height of the crest or depth of the trough of a wave is called its amplitude. It determines the intensity of brightness of the beam of light. The intensity of radiation is proportional to the square of amplitude (a^2).

7. Electromagnetic Spectrum:

When the different types of electromagnetic radiations are arranged in the increasing or decreasing order of their wave lengths or frequencies, we get a pattern, known as electromagnetic spectrum.

The following is the increasing order of wave length or decreasing order of energy of electromagnetic radiations:

Cosmic rays,
γ-rays,
X-rays
UV radiations
Violet.......Red
(visible spectrum)
Infra red
Microwaves
Radiowaves

λ increases ↓ | v Decreases ↓ | Energy decreases ↓

Black Body Radiations:

When solids are heated, they emit radiations over a wide range of wavelengths. For example, when an iron rod is heated in a furnance, it first turns a dull red and then progressively becomes more and more red as the temperature increases. On heating further it emits white radiations which turns blue at very high temperature. It is thus evident that radiations emitted goes from a lower frequency (low energy) to higher frequency (high energy) as the temperature increases. The ideal body which emits and absorbs all frequencies is called a black body and the radiations emitted by this body are called black body radiations.

8. Quantum Theory of Radiation:

This theory was proposed by German physicist, Max Planck in 1900, to explain the phenomena of black body radiations. According to this theory—

"Energy is emitted or absorbed by a body not continuously but discontinuously in the form of small packets or bundles of energy known as Quanta. The energy of a body can increase or decrease by 1,2,3,4,5,…..n quanta but not by fractions of a quanta.

- Quantum of light is called photon.
- The energy of a photon is given by the expression:

$E = h\nu$ …(i)

Where h = Planck's constant,

ν = frequency of radiation

Since $\nu = \frac{c}{\lambda}$

$\therefore \quad E = h\frac{c}{\lambda}$ …(ii)

Thus, the energy of radiation is proportional to its frequency and inversely proportional to wave length.

Example: The quantum theory assumes that energy changes are not continuous. Why do not we notice this effect in our every day activities?

Solution: In everyday activities, we deal with macroscopic particles such as our bodies, or cars which gains and loss total amount of energy much larger than a quantum. The gain and loss of the relatively miniscule quantum of energy is unnoticed.

Example: Calculate the energy per mole of photon of electromagnetic radiations of wavelength 4000Å.

Solution: E / Photon = hc/λ.

$$\therefore \; E/N_{Photon} = Nhc/\lambda$$

$$= \frac{6.023\times10^{23}\times6.626\times10^{27}\times3.0\times10^{10}}{4000\times10^{-8}}$$

= 2.99×10^{12} erg

9. Bohr's Model of Atom:

This atomic model is based on Planck's quantum theory. The following are the important points of the Bohr theory:

(i) The electrons revolve round the dense nucleus in circular orbits. So long as the electron remains in the same orbit, it neither absorbs nor emits energy i.e., the energy associated with the electron remains constant in an orbit.

- Such a state of electron in which its energy remains constant is called stationary state.
- Each orbit is called energy level or energy shell.
- Energy of an electron in nth orbit of hydrogen like ions is given by

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

(ii) Energy of electron in outer stationary state is greater than inner stationary state. Thus, the energy of electron increases with increasing distance from the nucleus.

(iii) Energy is emitted or absorbed by an electron when it jumps from one stationary state to another. This jumping of electron from one orbit to another is called electronic transition.

- When an electron jumps from outer (n_2) to inner (n_1) stationary state, the difference of energy is emitted in the form of radiation. The line of corresponding wave length or frequency is obtained in the Emission spectrum. Suppose the electronic transition takes place from n = 2 (Energy E_2) to n = 1 (energy E_1), then the difference of Energy, $E_2 - E_1$, is given out as radiation:

$E_2 - E_1 = h\nu$

Where v = frequency of emitted radiation.

- Energy is absorbed by an electron when it jumps from inner to outer stationary state. The energy absorbed is equal to the difference of the energy of orbits involved in electronic transition. The line of corresponding frequency is found absorbed in the absorption spectrum.

(iv) An electron can movearound the nucleus in that circular orbit for which its angular momentum (mvr) is equal to an integral multiple of h / 2π. Thus, the motion of an electron in a circular orbit is restricted i.e not all the orbits are permitted for revolution of an electron.

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

Where m = mass of electron,

v = velocity of the electron,

n = number of the orbit in which the electron is revolving

r = radius of the orbit.

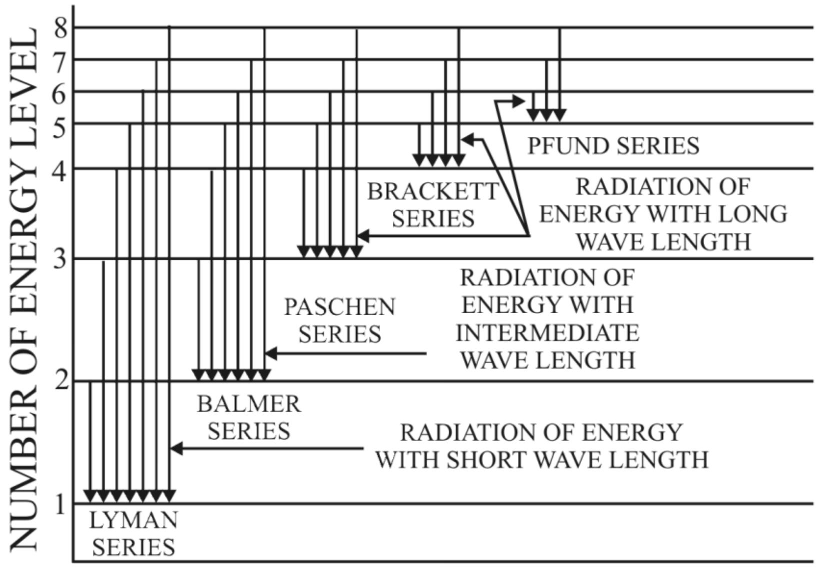
Advantage of Bohr Theory: Bohr's Theory satisfactorily explains the spectra of one electron systems such as hydrogen atom, singly ionized helium atom (He^+), doubly ionized lithium atom (Li^{++}) etc. The Bohr postulates can also be used for calculating the radii of various orbits in hydrogen atom or hydrogen like ions.

10. The Hydrogen Spectrum:

When energy is supplied to a sample of hydrogen gas, the atoms present in the sample, absorb energy and are excited from the ground state to different higher energy states, depending upon the amount of energy absorbed. When these excited electrons return to the normal state, energy is emitted in the form of radiations of different wave lengths which appear in the form of different lines in the emission spectrum. The wave length (or frequency) of the lines depends upon the amount of energy emitted. Greater the amount of energy liberated, shorter will be the wave length of radiation emitted.

The hydrogen spectrum contains a large number of closely spaced lines, hence, it is a line spectrum. Although, hydrogen atom contains only one electron in its atom, yet it gives a large number of lines in its spectrum. Its explanation is that a sample of hydrogen gas contains a very large number of atoms.

The electrons in these atoms are excited to different energy states on absorption of energy, which give very large number of lines in the spectrum on de-excitation. Its lines in the spectrum are grouped into five series each of which is named after the name of its discoverer. The various series of lines of the hydrogen spectrum are shown in the following figure.



Series of Lines of Hydrogen Spectrum:

(a) Lyman Series: Lines of this series are obtained when electrons fall from 2, 3, 4 …. etc. orbit to first orbit (ground state)

For Lyman series,

$n_1 = 1$, $n_2 = 2, 3, 4, 5, 6, 7, \ldots\ldots.$

The wave length of the lines in Lyman series can be calculated by using equation (13).

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

For the first line of Lyman series,

$n_2 = 2$, $n_1 = 1$

$$\frac{1}{\lambda} = 109678\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$$= 109678 \times \frac{3}{4} cm^{-1}$$

$$\lambda = 1215.7 \mathring{A}$$

For second line of Lyman series:

$n_2 = 3$, $n_1 = 1$

$$\frac{1}{\lambda} = 109678\left[1 - \frac{1}{9}\right] cm$$

$$\lambda = 1025.7 \mathring{A}$$

The wave length of the second line of Lyman series is less than that of the first line. Thus, the wave length of the other lines decreases continuously. The wave length of the last (limiting) line of the Lyman series is obtained when $n_2 = \infty$.

$$\frac{1}{\lambda} = 109678\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] cm^{-1}$$

$$\lambda = \frac{1}{109678} cm = 911.7\ \mathring{A}$$

- The lines of the Lyman series appear in the ultraviolet region of the spectrum.
- The intensities of spectral lines decreases with increase in the value of n. e.g., the intensity of first Lyman line ($2 \to 1$) is greater than second line $(3 \to 1)$.

(b) Balmer Series: Lines of this series are obtained when electrons fall from outer orbits to second orbit. Thus, for the various lines of this series, $n_1 = 2$, $n_2 = 3, 4, 5, 6, 7, 8\ldots\ldots$

The wave length of the first line in the Balmer series can be calculated by putting

$n_1 = 2$ and $n_2 = 3$

$$\frac{1}{\lambda} = 109678\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = 109678\left[\frac{1}{2^2} - \frac{1}{3^3}\right] \text{cm}^{-1}$$

$$= 109678\left[\frac{1}{4} - \frac{1}{9}\right] \text{cm}^{-1}$$

$$= 109678 \times \frac{5}{36} cm^{-1}$$

$$\lambda = \frac{36}{109678 \times 5} = \frac{36}{548390}$$

= 6.5646 × 10^{-5} cm,

or $\lambda = 6564.6 \mathring{A}$

The wave length of the last (limiting) line of Balmer series is:

$$\frac{1}{\lambda} = 109678\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] cm^{-1}$$

$$= \frac{109678}{4} cm^{-1}$$

$$\lambda = \frac{4}{109678} = 3.647 \times 10^{-5} cm$$

$$\lambda = 3647 \mathring{A}$$

- The lines of Balmer series fall in the visible region of the spectrum.
- In the Balmer series of hydrogen spectrum, the first line ($n_2 = 3 \rightarrow n_1 = 2$) is L_β line. The line from $n_2 = \infty$ to $n_1 = 2$ is called limiting line.

(c) Paschen Series: This series is produced when the electrons fall from outer orbits to third orbit i.e. for the lines of this series, $n_1 = 3$, $n_2 = 4, 5, 6, 7$……

For the first line of this series,

$n_1 = 3$, and $n_2 = 4$

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

$$\frac{1}{\lambda} = 109678\left[\frac{1}{3^2} - \frac{1}{4^4}\right] cm^{-1}$$

$$\frac{1}{\lambda} = 109678 \times \left[\frac{1}{9} - \frac{1}{16}\right] cm^{-1}$$

$$\frac{1}{\lambda} = 109678 \times \frac{7}{144} cm^{-1}$$

or $\lambda = \frac{144}{7 \times 109678} = \frac{144}{767746} cm$

= 1.87562 × 10^{-4} cm

or $\lambda = 18756.2 \mathring{A}$

- Lines of this series lie in the infra-red region of the spectrum.

(d) Brackett series: When the electronic transition takes place from outer orbits to the fourth orbit, lines of this series are obtained, i.e., for this series, $n_1 = 4$, $n_2 = 5, 6, 7, 8, 9$………

The wave length of the first line of the series can be calculated by putting $n_1 = 4$ and $n_2 = 5$ in the equation

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

$$\frac{1}{\lambda} = 109678\left[\frac{1}{4^2} - \frac{1}{5^2}\right] cm^{-1}$$

$$\frac{1}{\lambda}=109678\left[\frac{1}{16}-\frac{1}{25}\right]cm^{-1};\lambda=40523\,\mathring{A}$$

- This series also falls in the infra-red region of the spectrum.

(e) Pfund Series: The lines in this series of hydrogen spectrum are obtained when electrons are de-excited from higher orbits to fifth orbit, i.e., for this series, $n_1 = 5$, $n_2 = 6, 7, 8, 9, 10$……….

The wave length of the first line of the series can be calculated by putting, $n_1 = 5$ and $n_2 = 6$.

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

$$\frac{1}{\lambda}=109678\left[\frac{1}{25}-\frac{1}{36}\right]cm^{-1},\lambda=74600\,\mathring{A}$$

- This series also falls in the infra-red region of the spectrum.
- In the Rydberg formula when $n_2=\infty$, the line produced is called the limiting line of that series.
- The number of spectral lines produced when an electron jumps from nth level to ground level

$$\sum(n-1)=\frac{n(n-1)}{2}.$$

In the line spectrum of H–like systems, certain frequencies are common. These frequencies correspond to a transition between two energy levels which are divisible by their respective atomic numbers, e.g., $2\rightarrow1$ jump of e^- in hydrogen correspond to $4\rightarrow2$ jump, of e^- in He^+.

Advantages of Bohr's Theory:

(i) It satisfactorily explains the spectra of hydrogen atom and like ions such as He^+, Li^{++}, Be^{+++} etc, which have only one electron.

(ii) The experimental value of Rydberg constant, R for hydrogen agreed well with that calculated from Bohr theory.

(iii) The radii and energy of the orbits in hydrogen atom as calculated according to Bohr theory, agree well with the experimental values.

(iv) Bohr theory successfully explains why an electron does not fall into the nucleus. The lowest orbit for an electron in the Bohr's atomic model is first orbit for which n = 1. The electron has a fixed value of energy in this orbit (–13.6 eV/atom) and therefore it cannot fall into the nucleus.

(v) The concept of stationary states of electrons given by Bohr, explains the emission and absorption spectra of hydrogen atom and the like ions.

Limitations of Bohr's Theory:

(i) This theory satisfactorily explains the spectra of species containing one electron only such as hydrogen atom and ions iso-electronic with hydrogen (He^+, Li^{++}, Be^{+++}, etc). It does not explain the spectra of multi-electron atoms.

(ii) It does not explain the brightness of spectral lines.

(iii) Bohr theory does not offer any explanation for the fine structure of spectral lines in the hydrogen spectrum. Fine structure is obtained when the hydrogen spectrum is viewed through spectrometer of higher resolution power.

(iv) This theory contradicts (does not agree with) Heisenberg Uncertainty principle.

(v) No explanation is given for the quantization of angular momentum of an electron, i.e., why the angular momentum of the revolving electron is equal to $(nh/2\pi)$, has not bee explained by Bohr.

(iv) It fails to explain the splitting of spectral lines in the presence of magnetic field (Zeeman's effect) or electric field (Stark effect).

11. Wave-Particle Duality, Dual Nature of Electron:

It was suggested by Loius de Broglie in 1924 that a particle in motion also behaves like a wave. The wave length associated with the moving particle is given by the following equation,

$$\lambda = \frac{h}{mv} \qquad \ldots(i)$$

where, h = Planck's constant, m = mass of the moving particle, v = velocity of the particle.

This above equation (i) is known as de Broglie equation. De Broglie equation was derived on the basis of Einstein's equation, $E = mc^2$ and Planck's equation E = hv. From both of these relation,

$E = hv = mc^2$

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

or $\quad \lambda = \frac{h}{mv}, \qquad$ or $\quad \lambda = \frac{h}{p},$

where p is the momentum of the moving particle.

- The wave length associated with a particle in motion is inversely proportional to its momentum.
- As the mass of the moving particle increases, the momentum also increases; the wave length of the matter wave (associated with the matter in motion) decreases.
- For the particles of finite size, i.e., having appreciable mass, the momentum is very high, λ is very small and it can be said that macroscopic bodies in motion do not possess matter waves.
- When different particles move with the same velocity, the wave length of the matter wave is inversely proportional to the mass of the particle.

12. Heisenberg's Uncertainty Principle:

This principle was proposed by Werner Heisenberg in 1927. According to it, "It is impossible to determine simultaneously the exact position and momentum of a moving particle like electron, proton, neutron, etc."

If there is certainty of position of the particle, the momentum becomes uncertain and vice versa. Mathematically, the uncertainty principle is represented as:

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \qquad \ldots(ii)$$

where Δx = uncertainty in position of the particle, Δp = uncertainty in the momentum of the particle

Now $\Delta p = m\Delta v$, so equation (ii) takes the form

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

or $$\Delta x \times \Delta v \geq \frac{h}{4\pi m} \qquad \ldots(iii)$$

Equation (iii) can be used to calculate the uncertainty in the position or velocity of the particle.

The uncertainty principle is not in agreement with the Bohr theory as the latter gives a proper position to the electron with respect to the nucleus while according to the former, the position of electron is not certain. Hence, the idea of definite orbits for an electron is meaningless as suggested by Bohr. The wave-particle dual nature of electron and the uncertainty principle gave rise to a new concept called as "probability concept" for an electron.

Thus, we can predict the probability of locating an electron of particular energy in a given region of space around the nucleus at a given time. It gives rise to the concept of atomic orbital.

Example: The λ of H_a line of Balmer series is 6500Å. What is the λ of H_β line of Balmer series?

Solution: For H_a line of Balmer series $n_1 = 2$, $n_2=3$

For H_β line of Balmer series $n_1 = 2$, $n_2 = 4$

$$\therefore \qquad \frac{1}{\lambda_\alpha} = R_H\left[\frac{1}{2^2}-\frac{1}{3^2}\right] \qquad \ldots(i)$$

and

$$\frac{1}{\lambda_\beta} = R_H\left[\frac{1}{2^2}-\frac{1}{4^2}\right] \qquad \ldots(ii)$$

By Eqs. (i) and (ii)

$$\lambda_\beta = \lambda_\alpha \times (80/108) = 6500 \times (80/108)$$

$$= 4814.8 \text{ Å}$$

Example: Show that circumference of the Bohr orbit for hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving about that orbit.

Solutions: According to be Broglie:

$$\lambda = \frac{h}{mu} \qquad \ldots(i)$$

Also,

$$mur = \frac{nh}{2\pi} \qquad \ldots(ii)$$

By Eqs. (i) and (ii) $\lambda = \dfrac{h.2\pi r}{n.h}$

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

13. Quantum Mechanical Model of Atom:

In 1920, a new model of atom was developed by Ervin Schrodinger. In the atomic model proposed by Schrodinger, idea of quantization and conclusions of de Broglie principle and Heisenberg uncertainty principle were incorporated. In this model the behaviour of the electron in an atom is described by the mathematical equation known as Schrodinger Wave Equation, given below:

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

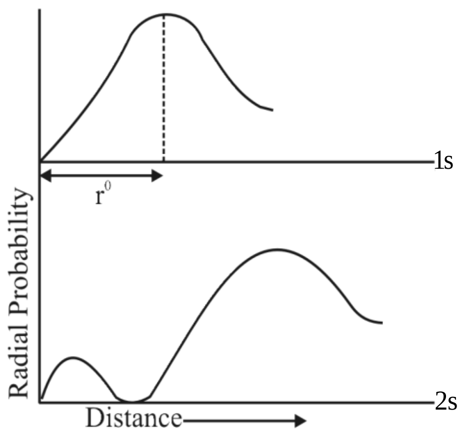
Here, in this equation, x,y and z are the three space co-ordinates, m = mass of electron, h = Planck's constant, E = total energy, U = Potential energy, ψ = wave function of electron wave. The permitted solutions of Schrodinger wave equation are known as wave functions which correspond to a definite energy state of an electron known as orbital. Thus, the discrete Bohr orbits are replaced by orbitals, i.e., "three-dimensional region of definite shape about the nucleus where the electron density is maximum or where the probability of finding an electron is maximum or where the electron passes its maximum time."

The Schrodinger wave equation may simply be interpreted by stating that a particle or body of mass m, energy E and velocity v possesses wave like properties associated with it, with amplitude given by the wave function ψ (Psi).

- ψ (Psi) gives the three-dimensional amplitude of electron wave.
- ψ^2 dV is the probability of finding an electron in a volume dV about the nucleus of an atom.
- The particular wave of ψ is called eigen function and the value of energy corresponding to this is called eigen value.
- The eigen function of an electron is called atomic orbital.

- The wave equation is applicable to atoms as well as molecules.

The solution of wave equation gives regions in space where ψ is +ve as well as —ve . But ψ^2 (probability of finding an electron) is always positive.



Probability Distribution: In wave mechanics, an electron in motion is described by a wave function, ψ . ψ has no physical significance and refers to the amplitude of the electron wave. However, ψ^2 is a significant term and give the probability of finding an electron or intensity of electron. An atomic orbital is a three dimensional region of definite shape about the nucleus where there is more intensity of electrons. An atomic orbital is considered as a diffused electron cloud having more electron density close to the nucleus. The probability of finding an electron in a given volume about the nucleus is understood best in the form of radial probability distribution curves. The probability distribution curves for some orbitals are given below. The distance of maximum radial probability is the radius of an atom. The point at which radial probability becomes zero is known as Nodal point. In general there are (n –1) nodal points for s-orbitals; (n –2) for p-orbitals; (n –3) for d-orbitals and (n –4) for f-orbitals (n = principal quantum number).

- The radius of maximum probability of 1s electron is 0.53 Å (Bohr radius).
- The number of regions of maximum probability for 1s, 2p, 3d, and 4f orbitals are one each.
- For 2s, 3p, 4d and 5f –atomic orbitals there are two regions of maximum probability.
- The small humps in the distribution curves show that the electron has a tendency to penetrate closer to the nucleus.
- In between the regions of maximum electron density, there is a region of zero electron density known as nodal point. Greater the number of nodal points, higher is the energy of an orbital.

Quantum Numbers: In order to define the 'state' of an electron in an atom, a set of four numbers is required known as Quantum numbers. The term 'state' includes, the energy, position with respect to the nucleus, orientation in space and the interaction of the electron with other electrons.

(i) Principal Quantum Number (n): This quantum number was introduced by Bohr. It gives the average distance of the electron from the nucleus. It also indicates the average volume of the electron cloud. It determines the main energy shell in which the electron is revolving round the nucleus. 'n' will have positive integral values only $n \neq 0$.

The main energy level (shell) corresponding to different values of n are:

Principal Quantum Number (n)	Main Energy Level
n =1	K- shell
n =2	L- shell
n =3	M- shell
n =4	N- shell

- Energy of electron in 'n'th shell of hydrogen atom and like ions is $E_n = -\frac{13.6Z^2}{n^2}$ eV/ atom where 'Z' is the atomic number.

- As the distance of the electron from the nucleus increases, energy of electron also increases.
- Energy of electron increases with increasing values of "n".
- Energy of electron at infinite distance from the nucleus is zero.
- Total number of electrons in nth shell is $2n^2$.
- The angular momentum of an electron in an orbit depends upon its principal quantum number and is given by $mvr = \frac{nh}{2\pi}$ where 'n' is principal quantum number.

(ii) Azimuthal, Angular, Secondary, Subsidiary or Serial Quantum Number (l): It was given by Sommerfeld. It explains the fine spectrum of hydrogen atom. It gives the angular momentum of electron in elliptical orbit while in motion round the nucleus. It also gives the shape of the sub-shell in which the electron is located. It (l) may have any +ve integral value ranging from 0 to (n –1).

- The total values of l are equal to the Principle quantum number of 'n'.
- Principal Quantum number (n) and azimuthal Quantum number (l) can never have identical numerical values.
- The orbital angular momentum of an electron depends upon the azimuthal quantum number (l) and is given by:
- Orbital angular momentum = $\sqrt{l(l+1)}.\frac{h}{2\pi}$ = $\sqrt{l(l+1)}.h \left(where\ h\ cross + h = \frac{h}{2\pi} \right)$.
- The total number of subshells (l) in a shell (n) is equal to shell number.
- The various sub shells corresponding to different values of 'l' are as follows:

Azimuthal Q. Number (l)	Sub-shell	Shape	Max. number of electrons
l = 2	s–	Symmetrically spherical shape	2
l = 1	p–	Dumb-bell	6
l = 2	d–	Double dumb-bell	10
l = 3	f–	Complicated shape	14
l = 4	g–	Highly complicated shape	18

The various shells are comprised of the following sub-shells:

(a)	n =1	K –shell	Designation
	l = 0	s-sub-shell	1s
(b)	n = 2,	L- shell	
	l = 0	s-sub-shell	$2s -$
	l = 1	p-sub-shell	$2p -$
			$not\ 2d$
(c)	n = 3	M-shell	$3s -$
	l = 0	s-sub-shell	$3p -$
	= 1	p-sub-shell	$3d -$
	=2	d-sub-shell	$not\ 3f$

(d)	n= 4,	N-shell	$4s-$
	l = 0	s-sub-shell	$4p-$
	=1	p-sub-shell	$4d-$
	=2	d-sub-shell	$4f-$
	=3	f-sub-shell	

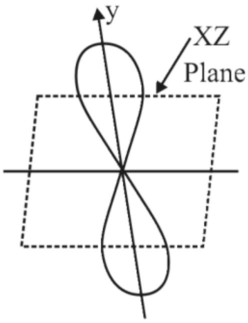
- Increasing order of energy of subshells is: s < p < d < f.
- Decreasing order of screening effect: s > p > d > f

(iii) Magnetic or Orientation Quantum Number (m): It explains Zeeman effect. It gives the atomic orbital in which the electron is present. It specifies the orientations of atomic orbitals in a magnetic field. The values of 'm' vary from – l, through 0 to +l. Thus, the total values of m are (2l + 1).

A subshell is made up of atomic orbitals which are described as follows:

Sub-shell (l)	Values of m (magnetic quantum number)	Atomic orbitals	Designations
l = 0	m = 0	1	s
l = 1	m =–1,0, + 1	3	p_x, p_z, p_y
l = 2	m = – 2, –1, 0, +1, +2	5	d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}
l = 3	m =0, ±1, ±2, ±3	7	Complicated

- The atomic orbitals p_x, p_y and p_z are dumb-bell shaped and posses equal energies but differ in their orientations in space. They are called degenerate orbitals.
- The plane where the electron density is almost zero is called nodal plane.
- Number of nodal plane for np orbital = 1.
- Pictorial representation of nodal plane:
- For p_y atomic orbital xz plane is the nodal plane:



Orbital	Designation of nodal plane
$2p_x$ or $3p_x$ etc.	yz
$2p_y$ or $3p_y$ etc.	xz
$2p_z$ or $3p_z$ etc.	xy

- The atomic orbitals dxy, dxz, dyz, $d_{x^2-y^2}$ and dz^2 are also degenerate (possess equal energies).
- The probability of finding the electron in the xy plane in the atomic orbital, $d_{x^2-y^2}$ is not zero.

- The atomic orbital having dough nut or a belly band or baby soother like shape is dz^2. It is dumb-bell shaped with a collar of high electron density in the xy plane.
- Nodal planes for d_{xy} d_{yz} and d_{xz} orbitals are 2 each.

Orbital	Nodal plane
d_{xy}	xz and yz planes
d_{xz}	xy and yz planes
d_{yz}	xy and xz planes

- f-orbitals are seven in number designated as,

$$f_{x^3}, f_{y^3}, f_{z^3}, f_{x^2-y^2}, f_{x^2-z^2}, f_{z^2-x^2}, f_{xyz}$$

(iv) Spin quantum Number (s): While in motion around the nucleus, the electron spins about its own axis. The spin may be clockwise or anticlockwise. The spinning electron would add to the angular momentum of the electron and therefore changes the energy associated with the electron. Assuming the spin to be quantized, there are two possible values of s, i.e. s $=+\frac{1}{2}$ and $-\frac{1}{2}$ depending upon whether the electron spins clockwise or anticlockwise. As a convention, the clockwise and anticlockwise spins are represented by an arrow $(\uparrow)$ and $(\downarrow)$ respectively. Two electrons having the same direction of spin are said to have parallel spins while the two having different direction of spins are said to have anti-parallel spins.

For each value of 'm' there are two values of spin quantum number, $s=+\frac{1}{2}$ and $-\frac{1}{2}$ i.e in any atomic orbital only two electrons can be accommodated having anti-parallel $(\uparrow\downarrow)$ spin.

- The solution of Schrodinger wave equation gives the principal (n), azimuthal (l) and magnetic quantum numbers (m) but not the spin quantum number (s). It was introduced on account of the spin of revolving electron.

  Significance of Quantum Numbers. The four quantum numbers are of physical significance. They give the address of an electron i.e they are capable of indicating the probable position (shell, sub-shell, atomic orbital) and energy of an electron in the atom. For example, if for an electron.

  n = 3, l = 1, m = –1, and $s=+\frac{1}{2}$, then it indicates that the electron is:

  — present in the third shell (M-shell)

  — present in the 3p sub-shell (since for p, l = 1)

  — present in the $3p_x$ or $3p_y$ atomic orbital

  — spinning in clockwise direction.

14. Pauli's Exclusion Principle:

This principle states, "No two electrons in an atom can have an identical set of all the four quantum numbers". If three quantum numbers are the same, the fourth will definitely be different. This principle shows that an atomic orbital cannot have more than two electrons and if there are two electrons in any atomic orbital, they will have anti parallel spins. This principle is very helpful in determining the maximum number of electrons in a shell or a sub-shell. For example:

For First Energy Level (K-Shell):

n = 1, l = 0, (1 s-sub-shell), m = 0 (1 s –atomic orbital) $s=\pm\frac{1}{2}$ (Two electrons having opposite spins)

These electrons are designated as $1s^2$

For Second Energy Level (L-Shell):

Principal Q. number(n)	Azimuthal Q. number (I)	Magnetic Q. number (m)	spin Q. number(s)	Designation

n = 2	l = 0 (2s)	m = 0 (2s)	$\pm\frac{1}{2}$	$2s^2$
	1 (2p)	m =–1($2p_x$)	$\pm\frac{1}{2}$	
		m = 0 ($2p_z$)	$\pm\frac{1}{2}$	$2p^6$
		m = 1 ($2p_y$	$\pm\frac{1}{2}$	

- Total electrons in second shell are eight.
- Similarly, it can be shown that d-sub-shell (l = 2) can accommodate 10 and f-subshell can have a maximum of fourteen (14) electrons.

  Shielding or Screening Effect: According to the screening rule, "the electrons in the completely filled inner shells screen the outer electrons against the attraction by the nucleus", i.e. the outer electrons are not attracted by the nucleus so effectively as they would have been attracted had the inner shell electrons not been present. This is known as Shielding or Screening Effect. Due to this effect, the ns orbitals are filled with electrons earlier than the (n – 1) d-orbitals. In a similar way the 5s, 5p and 6s-orbitals are occupied by electrons before the 4f-orbitals.
- In a given shell, the decreasing order of screening effect is: s > p > d > f.

15. Electronic Configuration of Elements:

The distribution of electrons in various shells and sub-shells is called electronic configuration of elements. This arrangement of electrons in the atom decides the properties of an element. The following rules are used for writing the electronic configuration:

1. Aufbau's Principle: Aufbau is not the name of any Scientist. It is a German word which means 'building up' or 'construction'. According to this principle, "sub-shells are filled with electrons in the increasing order of their energies", i.e. Sub-shell of lower energy will be filled first with electrons.

- Sub-shell having lower value of (n + l) will be of lower energy, where n is the principal and l, the azimuthal quantum number for the sub-shell.
- When the values of (n + l) for two or more sub-shells available for electrons, are the same, then that having lower value of 'n' will be of lower energy and hence will be occupied by the electrons first.

2.Hund's Rule of Maximum Multiplicity: According to this rule, "pairing of electrons in a sub-shell starts after all the available atomic orbitals of that sub-shell are singly filled (half-filled) with electrons having parallel spins" or pairing of electrons in a sub-shell is impossible in the presence of vacant atomic orbitals in that sub-shell".

- In p-sub shell, the fourth electron starts pairing, and the sixth electron starts pairing in d-sub-shell.
- In f-sub-shell, pairing starts with eight electron.
- This rule gives the number of unpaired electrons in an atom, ion or molecule.

3. Exactly half-filled sub-shells have lesser energy and thus assume more stability than any other arrangement. Thus, p^3 is more stable arrangement than p^2, p^4 or p^5.

4. When the electronic configuration ns^2np^6 is attained in the outermost shell of an atom, the next incoming electron enters the (n + 1) s-sub-shell. The nd and nf –sub- shells will be vacant.

Electronic configuration of the Elements

Element	Symbol	At. No.	Electronic Configuration
Hydrogen	H	1	$1s^2$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2$, $2s^1$
Beryllium	Be	4	$1s^2$, $2s^2$
Boron	B	5	$1s^2$, $2s^2\ 2p^1$
Carbon	C	6	$1s^2$, $2s^2\ 2p^2$
Nitrogen	N	7	$1s^2$, $2s^2\ 2p^3$
Oxygen	O	8	$1s^2$, $2s^2\ 2p^4$
Fluorine	F	9	$1s^2$, $2s^2\ 2p^5$
Neon	Ne	10	$1s^2$, $2s^2\ 2p^6$

Sodium	Na	11	$1s^2, 2s^2 p^6, 3s^1$
Magnesium	Mg	12	$1s^2, 2s^2 p^6, 3s^2$
Aluminium	Al	13	$1s^2, 2s^2 p^6, 3s^2 3p^1$
Silicon	Si	14	$1s^2, 2s^2 p^6, 3s^2 3p^2$
Phosphorus	P	15	$1s^2, 2s^2 p^6, 3s^2 3p^3$
Sulphur	S	16	$1s^2, 2s^2 p^6, 3s^2 3p^4$
Chlorine	Cl	17	$1s^2, 2s^2 p^6, 3s^2 3p^5$
Argon	Ar	18	$1s^2, 2s^2 p^6, 3s^2 3p^6$
Potassium	K	19	$1s^2, 2s^2 p^6, 3s^2 p^6, 4s^1$
Calcium	Ca	20	$1s^2, 2s^2 p^6, 3s^2 p^6, 4s^2$
Scandium	Sc	21	$1s^2, 2s^2 p^6, 3s^2 p^6 d^1, 4s^2$
Titanium	Ti	22	$1s^2, 2s^2 p^6, 3s^2 p^6 d^2, 4s^2$
Vanadium	V	23	$1s^2, 2s^2 p^6, 3s^2 p^6 d^3, 4s^2$
Chromium	Cr	24	$1s^2, 2s^2 p^6, 3s^2 p^6 d^5, 4s^1$
Manganese	Mn	25	$1s^2, 2s^2 p^6, 3s^2 p^6 d^5, 4s^2$
Iron	Fe	26	$1s^2, 2s^2 p^6, 3s^2 p^6 d^6, 4s^2$
Cobalt	Co	27	$1s^2, 2s^2 p^6, 3s^2 p^6 d^7, 4s^2$
Nickel	Ni	28	$1s^2, 2s^2 p^6, 3s^2 p^6 d^8, 4s^2$
Copper	Cu	29	$1s^2, 2s^2 p^6, 3s^2 p^6 d^{10}, 4s^1$
Zinc	Zn	30	$1s^2, 2s^2 p^6, 3s^2 p^6 d^{10}, 4s^2$
Gallium	Ga	31	$1s^2, 2s^2 p^6, 3s^2 p^6 d^{10}, 4s^2 p^1$
Germanium	Ge	32	$1s^2, 2s^2 p^6, 3s^2 p^6 d^{10}, 4s^2 p^2$
Arsenic	As	33	$1s^2, 2s^2 p^6, 3s^2 p^6 d^{10}, 4s^2 p^3$
Selenium	Se	34	$1s^2, 2s^2 p^6, 3s^2 p^6 d^{10}, 4s^2 p^4$

Example: (a) A compound of vanadium has a magnetic moment of 1.73 BM. Find the electronic configuration of vanadium ion in the compound

(b) Name the orbitals corresponding to given set of quantum numbers

(a) $n=3,\ l=2, m=\pm 2$ (b) $n=4,\ l=0, m=0$

(c) $n=2,\ l=1, m\pm 1$ (d) $n=2,\ l=1, m=2$

Solution: (a) Magnetic moment = $\sqrt{n(n+2)}$ where n = number of unpaired electrons

$\therefore\ \sqrt{n\,(n+2)} = 1.73 \Rightarrow n^2 + 2n = (1.73)^2\ \therefore\ n = 1$

Therefore vanadium atom must have one unpaired electron and thus its electronic configuration $_{23}V^{4+} : 1s^2 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$

(b) (a) $3dx^2 - y^2$ or 3dxy (b) 4s (c) 2px or 2py (d) no such orbital

Example: (a) Find the orbital angular momentum of an electron in the following orbital

(i) 3p (ii) 3d (iii) 3s

(b) Arrange the electrons represented by the following sets of quantum number in decreasing order of energy

(i) $n=4,\ l=0, m=0,\ ms=\pm 1/2$ (ii) $n=3,\ l=2, m=0,\ ms=\pm 1/2$

(iii) $n=3,\ l=0, m=0,\ ms=-1/2$ (vi) $n=3,\ l=0, m=0,\ ms=-1/2$

Solution: (a) $u=\sqrt{l(l+1)}\,\frac{h}{2\pi}=\sqrt{l(l+1)}\ h$ (i) $For\ 3p, l=1\ \mu_l=\sqrt{1(1+1)}=\sqrt{2}\ h$

(ii) $For\ 3d, l=2\ \mu_l=\sqrt{2(2+1)}=\sqrt{6}\ h$ (iii) $For\ 3s, l=0, \mu_1=0$

(b) Higher is the value of $(n+l)$ higher is the energy; if $(n+l)$ are same, higher the n values, higher the energy

For (i) $(n+l)=4\ 4s\ orbital$ For (ii) $(n+l)=5\ \ 3d\ orbital$

For (iii) $(n+l)=4\ \ 3p\ orbital$ For (iv), $(n+l)=3\ \ 3s\ orbital$

Decreasing order of energy = (i) > (i) > (iii) > (iv)

SOLVED EXAMPLES

Ex. 1 (i) What is the energy and wavelength o photons of frequency 3.4 MHz?
Also calculate the energy per mole o photons of the same wavelength

Sol. $v = 3.4\ MHz = 3.4\times10^{6}\ Hz = 3.4\times10^{6}\ s^{-1}$ $\quad \lambda = \frac{c}{v} = \frac{3\times10^{8}\,ms^{-1}}{3.4\times10^{-6}\ s^{-1}} = 88.2m$

Energy, $E = hv = 6.626\times10^{-34}\times3.4\times10^{6}\,J \quad = 1.356\times10^{-27}\ J$

Energy per mole of photon = $6.02\times10^{23}\times2.253\times10^{-27}\ J\ mol^{-1} = 1.356\times10^{-3}\ J\ mol^{-1}$

Ex. 2 What is the wavelength of he first line in Paschen series of the hydrogen spectrum?

Sol. $\bar{v} = RZ^{2}\left[\frac{1}{3^{2}} - \frac{1}{4^{2}}\right] = 15200cm^{-1}$ Paschen series. Z = 1

$= 109737\times0.0486 = 5334\ cm^{-1}$ $\quad \therefore\ \lambda = \frac{1}{v}1.875\times10^{-4}cm$

Ex. 3 The wave number of the first Balmer line in the hydrogen spectrum is 15200 cm^{-1}, Calculate the wavelength of the first Lyman line in the spectrum of He^{+}, Li^{2+}.

Sol. $\bar{v} = RZ^{2}\left[\frac{1}{2^{2}} - \frac{1}{3^{2}}\right] = 15200\,cm^{-1}$

$R = 15200\times\frac{36}{5}cm^{-1}\ (Z = 1\ for\ hydrogen)$

$For\ He^{+},\ \bar{v}4\times15200\times\frac{36}{5}\left(\frac{1}{1^{2}}\frac{1}{2^{2}}\right)cm^{-1}\ (Lyman\ Series) = 328320\ cm^{-1}$

$\therefore Wavelength\ of\ the\ first\ Lyman\ line = \frac{1}{328320}cm \quad = 3.046\times10^{-6}cm \quad = 304.6\ \mathring{A}$

Similarly for Li^{2+}., $\bar{v} = 9\times15200\times\frac{36}{5}\times\frac{3}{4}cm^{-1} = 738720cm^{-1}$

and $\quad \lambda = 1.354\times10^{-6}\ cm = 135.4\ \mathring{A}$

Ex. 4 What is de Broglie wavelength for a hydrogen atom moving with a velocity of 2000 ms^{-1} ? (Atomic mass of Hydrogen = 1.00797 a.m.u.)

Sol. Mass of a hydrogen atom =

$= \frac{1.0097}{6.023\times10^{-23}}9 = 1.673\times10^{-24} = 1.673\times10^{-27}\ kg \quad \lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}}{1.673\times10^{-27}\times2000}m$

$= 1.98\times10^{-10}\ m = 19.8\,nm$

Ex. 5 (a) The uncertainties in the position an velocity of a particle are 10^{-10} m and $5.27\times10^{-24}\ m/\sec$. respectively. Calculate the mass of the particle. Revolution in the 3rd Bohr orbit

Sol. (a) $As\ \Delta x.\Delta P=\frac{h}{4\pi}\Rightarrow\Delta x\times m\Delta V=\frac{h}{4\pi}\ \therefore\ m=\frac{h}{4\pi x\Delta x\times\Delta V}=\frac{6.625\times10^{-34}}{4\times3.14\times10^{-10}\cap5.27\times10^{-24}}$

$=0.10Kg$

(b) Circumference of 3rd orbit = 2 $2\pi r_3$ … (i)

Also $3\frac{h}{2\pi}=\frac{3h}{2\pi}$ … (ii)

From de Broglie equation $\lambda=\frac{h}{mv}$ … (iii)

$\lambda=\frac{h}{3h/2\pi r,}\Rightarrow3\lambda=2\pi r_3\ \Rightarrow3x=2\pi r_3,$ or $2\pi r_3=3\lambda$

Thus the circumference of the 3rd orbit is equal to three times the de-Brolie wavelength associated the electron

Ex. 6 A gas of identical H- like atom has some atoms in the lowest (ground energy level A(and some atoms in a particular upper excited energy level (B) and there are no atoms in any other energy level. The atoms of the gas make transition to a higher energy level by absorbing monochromatic light of photon energy 2.7 eV. Subsequently, the atoms emit radiation of only six different photons energies some of he emitted photons have energy 2.7 eV some have more and some have less than 2.78 eV.

(i) eV some have more and some have less than 2.78 eV.

(ii) Find the ionization energy of the gas atoms

(iii) Find the maximum and the minimum energies o the emitted photons

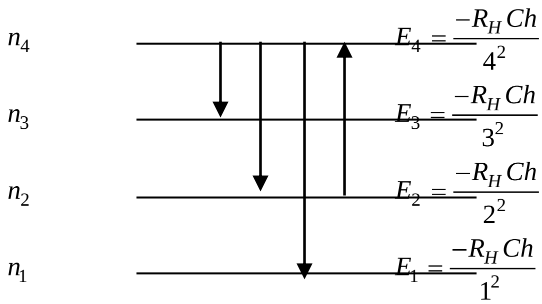
Sol. (i) A electrons are present in ground state and some excited state (say, n_1) and after absorbing 2.7 eV, electrons are excited to another excited state say n_2.

(ii) After dexcitation from n_2 level radiation of only six photon energies are emitted

$As\sum(n_2-1)=6,\ when\ n_2=4$

(iii) Absorption of 2.7 eV energy causing excitation to 4th shell and then re-emitting photons of energy equal to, more than, or less than 2.7 eV, is possible only when n_1= 2

$E_n=-\frac{R_H Ch}{n^2}\ (for\ H-like\ atom)$



$E_4 — E_2 = 2.7\ eV \quad E_4 — E_1 < 2.7\ eV \quad E_4 — E_3 < 2.7\ eV$

$$\frac{-R_h Ch}{4^2} - \left(\frac{-R_h Ch}{2^2}\right) = 2.7 \qquad \frac{-RHC}{4}(1/4-1) = 2.7$$

$$\Rightarrow \frac{E_1}{4}\left[\frac{-3}{4}\right] = 2.7 \quad \Rightarrow E_1 = -\frac{2.7\times 16}{3} = -14.4eV \quad \therefore \text{ Ionisation energy} = 14.4eV$$

$$E_{max} = E_4 - E_1 = \frac{-E_1}{4^2} + \frac{E_1}{1^2} \qquad = \frac{-14.4}{6} + 14.4 = 13.5\ eV \qquad E_{min} = E_4 - E_1 = \frac{-E_1}{4^2} + \frac{E_1}{1^2}$$

$$= \frac{-14.4}{6} + 14.4 = 13.5\ eV \qquad E_{min} = E_4 - E_3 = \frac{-E_1}{4^2} + \frac{E_1}{4^2} + \frac{E_1}{3^2} = 0.7\ eV$$

Ex. 7 Iodine molecule dissociates into atoms after absorbing light of $4500\,\overset{\circ}{A}$. If one quantum of radiation is absorbed by each molecule, Calculate the Kinetic energy of iodine atoms (B.E. of $I_2 = 240\ kJ / molecule$)

Sol. Energy given to I_2 molecules $= \frac{hc}{\lambda}$

$\frac{6.625\times 10^{-34}\times 3\times 10^{8}}{4500\times 10^{-10}} = 4.417\times 10^{-19}\ Joule$ Energy used for breaking up of I_2 molecule

$= \frac{240\times 10^{3}}{6.023\times 10^{3}} = 3.984\times 10^{-19}\ J$ $\therefore$ Energy used in imparting kinetic energy to two 1 atoms

$$= 4.417\ \times 10^{-19} - 3.984\times 10^{-19} = (4.417-3.984)\times 10^{-9}\ J \quad = 0.431\times 10^{-19}\ Joule$$

$$\therefore\ KE/1\,atom = \frac{0.431}{2}\times 10^{-19} = 0.216\times 10^{-19}\ J$$

Ex. 8 Photo –electrons are liberated by ultraviolet light of wavelength $9000\,\overset{\circ}{A}$ from a metallic surface for which the photoelectric threshold is $4000\,\overset{\circ}{A}$. Calculate de-Broglie wavelength of electrons emitted with maximum kinetic energy

Sol. $As,\ hv = hv^o + KE \Rightarrow \frac{hc}{\lambda} = \frac{hc}{\lambda^2} + KE \qquad \therefore\ K.E. = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda^o}\right) = \frac{hc\left(\lambda^o - \lambda\right)}{\lambda\times\lambda} =$

$$= \frac{6.625\times 10^{-34}\times 3\times 10^{8}\left(4000\times 10^{-10} - 3000\times 10^{-10}\right)}{3000\times 10^{-10}\times 4000\times 10^{-10}} = 1.6565\times 10^{-19}\ Joule$$

Also $\frac{1}{2}mv^2 = 1.6565\times 10^{-19} \Rightarrow m^2v^2 = 2\times 1.65665\times 10^{-19}\times m$

$$\Rightarrow m^2v^2 = 2\times 1.6565\times 10^{-19}\times 9.109\times 10^{-31} \Rightarrow mv = 5.49\times 10^{-25} \quad \lambda = \frac{h}{mv} = \frac{6.625\times 10^{-34}}{5.49\times 10^{-25}} = 1.2\times 10^{-9}\ m$$

Ex. 9 A mixture contains atoms of fluorine and chlorine. The removal of an electron from each atom of sample absorbs 284 kJ while the addition of an electron to each atoms of mixture releases 68.89 kJ. Determine the percentage composition of the mixture given that the ionization energies of F and $27..91\times 10^{-22}$ *and* $20.77\times 10^{-22}\ kJ$, respectively, and electron affinities are

Sol. Let atoms of chlorine and fluorine in the mixture be x and y respectively

$\therefore$ Energy absorbed $284\ kJ = (x)\times 20.77\times 10^{-22} + Y\times 27.91\times 10^{-22} --- (i)$

Energy released $= 68.8\ kJ = (x)\times 5.78\times 10^{-22} + Y\times 5.53\times 10^{-22} -- (ii)$

From solving equation (i) and (ii) e can get the vales of x and y respectively. % of Cl = 62.19% of F = 37.81

Ex. 10 Two hydrogen atoms collide head on and end up with zero kinetic energy. Each the emits a photon of wave length 121. 6 nm which transition leads to this wavelength? How fast were the hydrogen atoms traveling before collision?

$R_H = 1.09678\times 10^7\ m^{-1} \qquad M_H = 1.672\times 10^{-27}\ Kg$

Sol. As wavelength of emitted radiation is 121.6 nm, which falls in UV region of spectrum

Therefore, $n_1 = 1$

For hydrogen atom $\frac{1}{\lambda} = R_n\left[\frac{1}{1^2} - \frac{1}{n^2}\right] \qquad \therefore \frac{1}{121.6\times 10^{-9}} = 1.09678\times 10^7\left[\frac{1}{1} - \frac{1}{n^2}\right] \qquad n = 2$

Energy released is due to collision and all the kinetic energy released in form of radiant energy

$$\Rightarrow \frac{1}{2}1.67\times 10^{-27}\times V^2 = \frac{6.625\times 10^{-34}\times 3\times 10^8}{121.6\times 10^{-9}} \qquad \therefore V = 4.42\times 10^4\ m/\text{sec}$$

Ex. 11 The number of electrons in sulphur atom having $n + l = 3$?

(a) 2 (b) 4 (c) 6 (d) 8

Sol. The electronic configuration of sulphur atoms $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$, the orbitals with $(n+l) = 3$ *are* $2p$ *and* $6s$, therefore 8 electrons in sulphur atom have $(n+l) = 3$. $\therefore$ **(d)**

Ex. 12 Which atom contains an electron with quantum number $n = 3, l = 2, m = -1, s = -1/2$

(a) Ne (b) Co (c) Cl (d) K

Sol. Quantum numbers $n = 3, l = 2, m = -1\ S = -1/2$ represents 3d electron which is present in Co. $\therefore$ **(b)**

Ex. 13 The wavelength of a spectral line for an electronic transition is inversely related to :

(a) number of electrons undergoing transition

(b) the nuclear charge of the atom

(c) velocity an electron undergoing transition

(d) the difference in the energy levels involved in the transition.

Sol. $\Delta = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E}$ $\therefore$ **(d)**

Ex. 14 If E_1, E_2 *and* E_3 represent respectively the kinetic energies of an electron, α particle and a proton, each having same de Broglie's wave length then

(a) $E_1 > E_3 > E_2$ (b) $E_2 > E_3 > E_1$ (c) $E_1 > E_2 > E_3$ (d) $E_1 = E_2 = E_3$

Sol. $K.E. = 1/2\, mv^2, \lambda = \frac{h}{mv}$ $\therefore K.E. = 1/2\, m \frac{h^2}{(m\lambda)^2} = \frac{h^2}{2m\lambda^2}$ $\therefore$ **(a)**

Ex. 15 When the frequency of light incident on a metallic plate is doubled, the K.E. of the emitted photoelectrons will be

(a) doubled

(b) halved

(c) Increase but more than double of the previous K.E.

(d) unchanged

Sol. Upon doubling the frequency, energy of photon will be doubled with work function of metal will remain constant, So K.E. of photon electron will be more than the double of what it possessed previously.

$\therefore$ **(a)**

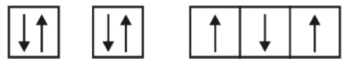
EXERCISE

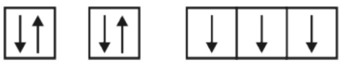
Q.1 A ball of mass 200 g moving with a velocity of 10 m sec^{-1}. If the error in measurement of velocity is 0.1%, the uncertainty in its position is:

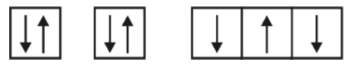
(A) 3.3×10^{-31} m (B) 3.3×10^{-27} m (C) 5.3×10^{-25} m (D) 2.6×10^{-32} m

Q.2 Ground state electronic configuration of nitrogen atom can be represented as:

(A) 

(B) 

(C) 

(D) 

Q.3 Which of the following set of quantum numbers belong to highest energy?

(A) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

(B) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$

(C) $n = 3, l = 1, m = 1, s = +\frac{1}{2}$

(D) $n = 3, l = 2, m = 1, s = +\frac{1}{2}$

Q.4 With increasing quantum number, the energy difference between adjacent orbits of hydrogen atom

(A) increase

(B) decrease

(C) remains constant

(D) first increases followed by a decrease.

Q.5 The number of orbitals in a subshell is equal to:

(A) n^2 (B) 2l (C) 2l + 1 (D) m

Q.6 Which of the following set of quantum numbers represents an impossible arrangement?

	n	l	m	s
(A)	3	2	–2	–1/2
(B)	4	0	0	–1/2
(C)	3	2	–3	–1/2
(D)	5	3	0	–1/2

Q.7 If the series limit of wavelength of the Lyman series for the hydrogen atoms is 912 Å, then the series limit of wavelength for the Balmer series of the hydrogen atom is:

(A) 912 Å (B) 912 × 2 Å (C) 912 × 4 Å (D) 912 / 2 Å.

Q.8 The shortest λ for the Lyman series of hydrogen atom is …. (Given R_H = 109678 cm^{-1})

(A) 912Å (B) 700 Å (C) 600 Å (D) 811 Å.

Q.9 If the radius of first Bohr orbit is x, then de Broglie wavelength of electron in 3rd orbit is nearly

(A) $2\pi x$ (B) $6\pi x$ (C) 9x (D) x/3.

Q.10 In Bohr's hydrogen atom, the electronic transition emitting light of longest wavelength is:

(A) n = 4 to n = 5

(B) n = 4 to n = 3

(C) n = 3 to n = 2

(D) n = 2 n = 4

Q.11 The frequency of first line of Balmer series in hydrogen atom is v_0. The frequency of corresponding line emitted by singly ionized helium atom is:

(A) $2v_0$ (B) $4v_0$ (C) $v_0/2$ (D) $v_0/4$.

Q.12 The magnetic quantum number for valence electron of sodium is:

(A) 3 (B) 2 (C) 1 (D) zero.

Q.13 The potential energy of the electron in an orbit of hydrogen atom would be:

(A) $-mv^2$ (B) $-e^2/r^2$ (C) $-1/2\ mv^2$ (D) $-e^2/2r$.

Q.14 Which of the following radiations has the highest wave number?

(A) X-rays (B) Microwaves (C) I.R. rays (D) Radio waves

Q.15 Which of the following particles moving with same velocity would be associated with smallest de–Broglie wavelength?

(A) Hydrogen molecule (B) Oxygen molecule (C) Helium molecule (D) Nitrogen molecule

Q.16 If the velocity of an electron in the first Bohr orbit of a hydrogen atom is V, then its velocity in the third Bohr orbit will be:

(A) V/9 (B) V/3 (C) 9 V (D) 3 V.

Q.17 What is the wavelength associated with an electron moving with a velocity of 10^6 m/s?

(Given $h = 6.63 \times 10^{-34}$ Js and $m = 9.11 \times 10^{-31}$ kg)

(A) 72.7 nm (B) 0.727 nm (C) 7.27 nm (D) none of these.

Q.18 If the ionization potential for hydrogen atom is 13.6 eV then the second ionization potential for helium atom should be:

(A) 13.6 eV (B) 27.2 eV (C) 54.4 eV (D) none of these.

Q.19 The ratio of the radius of Bohr first orbit for the electron orbiting the hydrogen nucleus to that of the electron orbiting the deuterium nucleus (mass nearly twice that of H nucleus) is approximately:

(A) 1 : 1 (B) 1 : 2 (C) 2 : 1 (D) 1 : 4

Q.20 Velocity of electron in the first orbit of H–atom as compared to that of velocity of light is nearly:

(A) $\frac{1}{10}th$ (B) $\frac{1}{100}th$ (C) $\frac{1}{1000}th$ (D) same

Q.21 Assuming the velocity to be same, which sub-atomic particle possesses smallest de Broglie wavelength:

(A) An electron (B) A proton

(C) An α-particle (D) All have same wavelength.

Q.22 An electron in H-atom in its ground state absorbs 1.50 times as much as energy as the minimum required for its escape (13.6 eV) from the atom. Thus KE given to emitted electron is:

(A) 13.6 eV (B) 20.4 eV (C) 34.0 eV (D) 6.8 eV.

Q.23 The velocity of an electron in a Bohr's orbit is:

(A) $\propto \frac{1}{n}$ (B) $\propto n$ (C) $\propto n^2$ (D) $\propto \frac{1}{n^2}$

Q.24 Bohr's theory is not valid for the species:

(A) H atoms (B) He^+ ion (C) Li^+ ion (D) Li^{2+} ion.

Q.25 Wavelength of an electron is equal to distance traveled by it in one second, then correct relation is:

(A) $\lambda = \frac{h}{p}$ (B) $\lambda = \sqrt{\frac{h}{p}}$ (C) $\lambda = \frac{h}{m}$ (D) $\lambda = \sqrt{\frac{h}{m}}$

Q.26. If kinetic energy of a proton is increased nine times the wavelength of the de–Broglie wave associated with it would become:

(A) 3 times (B) 9 times (C) $\frac{1}{3}$ *times* (D) $\frac{1}{9}$ *times*.

Q.27 If r_1 is the radius of the first orbit of hydrogen atom, then the radii of second, third and fourth orbitals in terms of r_1 are:

(A) r_1^2, r_1^3, r_1^4 (B) $8r_1, 27r_1, 64r_1$ (C) $4r_1, 9r_1, 16r_1$ (D) $2r_1, 6r_1, 8r_1$.

Q.28 The difference in angular momentum associated with the electron in two successive orbits of hydrogen atom is:

(A) h/π (B) $h/2\pi$ (C) h /2 (D) $(h-1)h/2\pi$.

Q.29 Difference between nth and (n + 1)th Bohr's radius of 'H' atom is equal to it's (n –1)th Bohr's radius. The value of n is:

(A) 1 (B) 2 (C) 3 (D) 4.

Q.30 Total number of transitions of an electron from nth shell to 2nd shell will be:

(A) $\frac{(n-1)(n-2)}{2}$ (B) $\frac{n(n-1)}{2}$ (C) $\frac{n(n+1)}{2}$ (D) $\frac{n}{2}$.

ANSWER KEY

EXERCISE

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	D	A	D	B	C	C	C	A	B	A	B	D	A	A	B	B	B	C	A	B

Q.No.	21	22	23	24	25	26	27	28	29	30
Ans.	C	D	A	C	D	C	C	B	D	A