1. IIT–JEE Syllabus

Atomic structure; Rutherford Model; Spectrum of hydrogen atom; Bohr model; de Broglie relations, Uncertainty principle, Quantum model; Electronic configuration of elements (upto to atomic number 36); Aufbau principle, Pauli's exclusion principle and Hund's rule, shapes of s,p, and d orbitals.

2. Dalton's Atomic Theory

All the objects around you, this book, your pen or pencil and things of nature such as rocks, water and plant constitute the matter of the universe. Matter is any substance which occupies space and has mass.

Dalton, in 1808, proposed that matter was made up of extremely small, indivisible particles called atoms. (In Greek atom means which cannot be cut). This concept was accepted for number of years.

The main postulates of Dalton's atomic theory are

- Matter is made up of small indivisible particles, called atoms.
- Atoms can neither be created nor destroyed. This means that a chemical reaction is just a simple rearrangement of atoms and the same number of atoms must be present before and after the reaction.
- Atom is the smallest particle of an element which takes part in a chemical reaction.
- Atoms of the same element are identical in all respects especially, size, shape and mass.
- Atoms of different elements have different mass, shape and size.
- Atoms of different elements combine in a fixed ratio of small whole numbers to form compound atoms, called molecules.

However, the researches done by various eminent scientists and the discovery of radioactivity have established beyond doubt, that atom is not the smallest indivisible particle but had a complex structure of its own and was made up of still smaller particles like electrons, protons, neutrons etc. At present about 35 different subatomic particles are known but the three particles namely electron, proton and neutron are regarded as the fundamental particles.

We shall now take up the brief study of these fundamental particles. The existence of electrons in atoms was first suggested, by J.J. Thomson, as a result of experimental work on the conduction of electricity through gases at low pressures and high voltage, which produces cathode rays consisting of negatively charged particles, named as electrons. The e/m ratio for cathode rays is fixed whose values is 1.76×10^8 C/g

We know that an atom is electrically neutral, if it contains negatively charged electrons it must also contain some positively charged particles. This was confirmed by Goldstein in his discharge tube experiment with perforated cathode. On passing high voltage between the electrodes of a discharge tube it was found that some rays were coming from the side of the anode which passed through the holes in the cathode. These anode rays (canal rays) consisted of positively charged particles formed by ionization of gas molecules by the cathode rays. The charge to mass ratio (e/m value) of positively charge particles was found to be maximum when the discharge tube was filled with hydrogen gas as hydrogen is the lightest element. These positively charged particles are called protons.

e/m varies with the nature of gas taken in the discharge tube. The positive particles are positive residues of the gas left when the gas is ionized.

The neutral charge particle, neutron was discovered by James Chadwick by bombarding boron or beryllium with α–particles.

Characteristics of the three fundamental particles are:

	Electron	**Proton**	**Neutron**
Symbol	e or e^-	p	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	–1	+1	No charge
Mass in kg	9.109×10^{-31}	1.673×10^{-27}	1.675×10^{-27}
Mass in amu	5.485×10^{-4}	1.007	1.008
Actual charge (coulomb)	1.602×10^{-19}	1.602×10^{-19}	0
Actual charge (e.s.u.)	4.8×10^{-10}	4.8×10^{-10}	0

The atomic mass unit (amu) is 1/12 of the mass of an individual atom of ${}_6C^{12}$, i.e., 1.660×10^{-27} kg.

The neutron and proton have approximately equal masses of 1 amu and the electron is about 1836 times lighter, its mass can sometimes be neglected as an approximation.

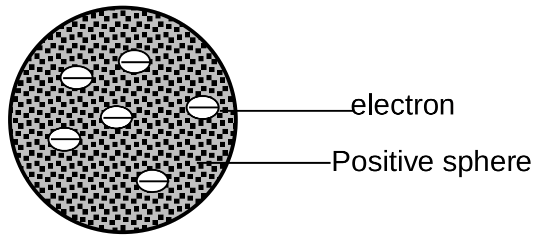
The electron and proton have equal, but opposite, electric charges while the neutron is not charged.

3. Atomic Models

We know the fundamental particles of the atom. Now let us see, how these particles are arranged in an atom to suggest a model of the atom.

3.1 Thomson's Model

J.J. Thomson, in 1904, proposed that there was an equal and opposite positive charge enveloping the electrons in a matrix. This model is called the plum – pudding model after a type of Victorian dissert in which bits of plums were surrounded by matrix of pudding.

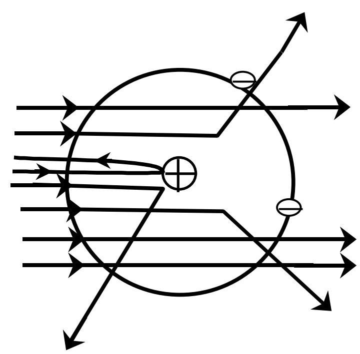


This model could not satisfactorily explain the results of scattering experiment carried out by Rutherford who worked with Thomson.

3.2 Rutherford's Model

α– particles emitted by radioactive substance were shown to be dipositive Helium ions (He^{++}) having a mass of 4 units and 2 units of positive charge.

Rutherford allowed a narrow beam of α–particles to fall on a very thin gold foil of thickness of the order of 0.0004 cm and determined the subsequent path of these particles with the help of a zinc sulphide fluorescent screen. The zinc sulphide screen gives off a visible flash of light when struck by an α particle, as ZnS has the remarkable property of converting kinetic energy of α particle into visible light. [For this experiment, Rutherford specifically used α particles because they are relatively heavy resulting in high momentum].



Observation

i) Majority of the α–particles pass straight through the gold strip with little or no deflection.

ii) Some α–particles are deflected from their path and diverge.

iii) Very few α–particles are deflected backwards through angles greater than 90°.

iv) Some were even scattered in the opposite direction at an angle of 180° [Rutherford was very much surprised by it and remarked that "It was as incredible as if you fired a 15–inch shell at a piece of tissue paper and it came back and hit you"]. There is far less difference between air and bullet than there is between gold atoms and α-particles assuming of course that density of a gold atom is evenly distributed.

Conclusions

1. The fact that most of the α - particles passed straight through the metal foil indicates the most part of the atom is empty.

2. The fact that few α - particles are deflected at large angles indicates the presence of a heavy positively charge body i.e., for such large deflections to occur α - particles must have come closer to or collided with a massive positively charged body.

3. The fact that one in 20,000 have deflected at 180° backwards indicates that volume occupied by this heavy positively charged body is very small in comparison to total volume of the atom.

Atomic model

On the basis of the above observation, and having realized that the rebounding α-particles had met something even more massive than themselves inside the gold atom, Rutherford proposed an atomic model as follows.

i) All the protons (+ve charge) and the neutrons (neutral charge) i.e nearly the total mass of an atom is present in a very small region at the centre of the atom. The atom's central core is called nucleus.

ii) The size of the nucleus is very small in comparison to the size of the atom. Diameter of the nucleus is about 10^{-13}cm while the atom has a diameter of the order of 10^{-8} cm. So, the size of atom is 10^{5} times more than that of nucleus.

ii) Most of the space outside the nucleus is empty.

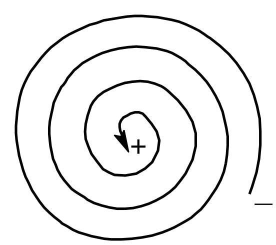
iv) The electrons, equal in number to the net nuclear positive charge, revolve around the nucleus with fast speed in various circular orbits.

v) The centrifugal force arising due to the fast speed of an electron balances the coulombic force of attraction of the nucleus and the electron remains stable in its path. Thus according to him atom consists of two parts (a) nucleus and (b) extra nuclear part.

Defects of Rutherford's atomic model

1. Position of electrons: The exact positions of the electrons from the nucleus are not mentioned

2. Stability of the atom: Neils Bohr pointed out that Rutherford's atom should be highly unstable. According to the law of electro–dynamics, the electron should therefore, continuously emit radiation and lose energy. As a result of this a moving electron will come closer and closer to the nucleus and after passing through a spiral path, it should ultimately fall into the nucleus.



It was calculated that the electron should fall into the nucleus in less than 10^{-8} sec. But it is known that electrons keep moving outside the nucleus.

To solve this problem Neils Bohr proposed an improved form of Rutherford's atomic model.

Before going into the details of Neils Bohr model we would like to introduce you some important atomic terms.

Atomic terms

a) ***Atomic Number (Z):*** The atomic number of an element is the number of protons contained in the nucleus of the atom of that element.

b) ***Nucleons:*** Protons and neutrons are present in a nucleus. So, these fundamental particles are collectively known as nucleons.

c) ***Mass Number (A):*** The total number of protons and neutrons i.e, the number of nucleons present in the nucleus is called the mass number of the element.

d) **Nuclide:** Various species of atoms in general. A nuclide has specific value of atomic number and mass number.

IUPAC notation of an atom (nuclide)

Let X be the symbol of the element. Its atomic number be Z and mass number be A. Then the element can be represented as $_{Z}X^{A}$

e) ***Isotopes:*** Atoms of the element with same atomic number but different mass number e.g. $_1H^1$, $_1H^2$, $_1H^3$. There are three isotopes of hydrogen.

f) ***Isobars:*** Atoms having the same mass number but different atomic numbers, e.g. $_{15}P^{32}$ and $_{16}S^{32}$ are called isobars.

g) ***Isotones:*** Atoms having the same number of neutrons but different number of protons or mass number, e.g. $_6C^{14}$, $_8O^{16}$, $_7N^{15}$ are called isotones.

h) ***Isoelectronic:*** Atoms, molecules or ions having same number of electrons are isoelectronic e.g. N_2,CO, CN^-.

i) ***Nuclear isomer:*** Nuclear isomers (isomeric nuclei) are the atoms with the same atomic number and same mass number but with different radioactive properties.

Example of nuclear isomers is
Uranium –X (half life 1.4 min) and
Uranium –Z (half life 6.7 hours)
The reason for nuclear isomerism is the different energy states of the two isomeric nuclei.
Other examples are

$_{30}Zn^{69}$	$_{30}Zn^{69}$
($T_{1/2}$ = 13.8 hr)	($T_{1/2}$ = 57 min)
$_{35}Br^{80}$	$_{35}Br^{80}$
($T_{1/2}$ = 4.4 hour)	($T_{1/2}$ = 18 min)

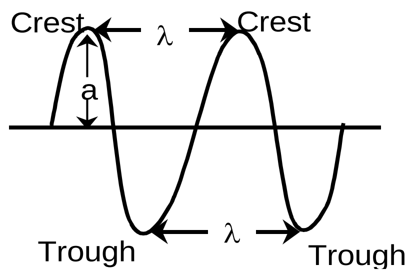
j) ***Isosters:*** Molecules having same number of atoms and also same number of electrons are called isosters.
E.g., (i) N_2 and CO
ii) CO_2 and N_2O
iii) HCl and F_2

k) ***Atomic mass unit:*** Exactly equal to 1/12 of the mass of $_6C^{12}$ atom

1 amu = 1.66×10^{-27} kg = 931.5 MeV

4. Some Important Characteristics of a Wave

A wave is a sort of disturbance which originates from some vibrating source and travels outward as a continuous sequence of alternating crests and troughs. Every wave has five important characteristics, namely, wavelength (λ), frequency (ν), velocity (c), wave number $(\bar{\nu})$ and amplitude (a).



Ordinary light rays, X–rays, γ–rays, etc. are called electromagnetic radiations because similar waves can be produced by moving a charged body in a magnetic field or a magnet in an electric field. These radiations have wave characteristics and do not require any medium for their propagation.

i) **Wave length (λ):** The distance between two neighbouring troughs or crests is known as wavelength. It is denoted by λ and is expressed in cm, m, nanometers ($1nm=10^{-9}m$) or Angstrom ($1Å=10^{-10}m$).

ii) **Frequency (ν):** The frequency of a wave is the number of times a wave passes through a given point in a medium in one second. It is denoted by ν(nu) and is expressed in cycles per second (cps) or hertz (Hz) 1Hz = 1cps.

The frequency of a wave is inversely proportional to its wave length (λ)

$$\nu \propto \frac{1}{\lambda} \text{ or } \nu = \frac{c}{\lambda}$$

iii) **Velocity:** The distance travelled by the wave in one second is called its velocity. It is denoted by c and is expressed in cm sec^{-1}.

$$c = \nu\lambda \text{ or } \lambda = \frac{c}{\nu}$$

iv) **Wave number $(\bar{\nu})$:** It is defined as number of wavelengths per cm. It is denoted by $\bar{\nu}$ and is expressed in cm^{-1}.

$$\bar{\nu} = \frac{1}{\lambda} \text{ (or) } \bar{\nu} = \frac{\nu}{c}$$

v) **Amplitude:** It is the height of the crest or depth of the trough of a wave and is denoted by a. It determines the intensity or brightness of the beam of light.

Wavelengths of electromagnetic radiations

Electromagnetic radiations	Wave length (Å)
Radio waves	3×10^{14} to 3×10^{7}
Micro waves	3×10^{9} to 3×10^{6}
Infrared (IR)	6×10^{6} to 7600
Visible	**7600 to 3800**
Ultra violet (UV)	3800 to 150
X–rays	150 to 0.1
Gamma rays	0.1 to 0.01
Cosmic rays	0.01 to zero

5. Atomic Spectrum

If the atom gains energy the electron passes from a lower energy level to a higher energy level, energy is absorbed that means a specific wave length is absorbed. Consequently, a dark line will appear in the spectrum. This dark line constitutes the ***absorption spectrum.***

If the atom loses energy, the electron passes from higher to a lower energy level, energy is released and a spectral line of specific wavelength is emitted. This line constitutes the ***emission spectrum.***

Hydrogen Atom

If an electric discharge is passed through hydrogen gas taken in a discharge tube under low pressure, and the emitted radiation is analysed with the help of spectrograph, it is found to consist of a series of sharp lines in the UV, visible and IR regions. This series of lines is known as line or atomic spectrum of hydrogen. The lines in the visible region can be directly seen on the photographic film.

Each line of the spectrum corresponds to a light of definite wavelength. The entire spectrum consists of six series of lines each series, known after their discoverer as the Balmer, Paschen, Lyman, Brackett, Pfund and Humphrey series. The wavelength of all these series can be expressed by a single formula.

$$\frac{1}{\lambda} = \bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where,

$\bar{\nu}$ = wave number

λ = wave length

R = Rydberg constant ($109678\ cm^{-1}$)

n_1 and n_2 have integral values as follows

Series	n_1	n_2	Main spectral lines
Lyman	1	2,3,4, etc	Ultra – violet
Balmer	2	3,4,5 etc	Visible
Paschen	3	4,5,6 etc	Infra – red
Brackett	4	5,6,7 etc	Infra – red
Pfund	5	6,7,8, etc	Infra – red

[Note: All lines in the visible region are of Balmer series but reverse is not true. i.e., all Balmer lines will not fall in visible region]

The pattern of lines in atomic spectrum is characteristic of hydrogen.

Types of Emission spectra

i) ***Continuous spectra:*** When white light from any source such as sun or bulb is analysed by passing through a prism, it splits up into seven different wide bands of colour from violet to red (like rainbow). These colour are so continuous that each of them merges into the next. Hence the spectrum is called as continuous spectrum.

ii) ***Line spectra:*** When an electric discharge is passed through a gas at low pressure light is emitted. If this light is resolved by a spectroscope, It is found that some isolated coloured lines are obtained on a photographic plate separated from each other by dark spaces. This spectrum is called line spectrum. Each line in the spectrum corresponds to a particular wavelength. Each element gives its own characteristic spectrum.

6. Planck's quantum theory

When a black body is heated, it emits thermal radiations of different wavelengths or frequency. To explain these radiations, Max Planck put forward a theory known as Planck's quantum theory. The main points of quantum theory are

i) Substances radiate or absorb energy discontinuously in the form of small packets or bundles of energy.

ii) The smallest packet of energy is called ***quantum***. In case of light the quantum is known as ***photon.***

iii) The energy of a quantum is directly proportional to the frequency of the radiation . $E \propto \nu$ (or) $E = h\nu$ were ν is the frequency of radiation and h is Planck's constant having the value 6.626×10^{-27} erg – sec or 6.626×10^{-34} J–sec.

iv) A body can radiate or absorb energy in whole number multiples of a quantum $h\nu$, $2h\nu$, $3h\nu$………..$nh\nu$. where n is the positive integer.

Neils Bohr used this theory to explain the structure of atom.

7. Bohr's Atomic Model

Bohr developed a model for hydrogen atom and hydrogen like one–electron species (hydrogenic species). He applied quantum theory in considering the energy of an electron bound to the nucleus.

Important postulates

- An atom consists of a dense nucleus situated at the centre with the electron revolving around it in circular orbits without emitting any energy. The force of attraction between the nucleus and an electron is equal to the centrifugal force of the moving electron.
- Of the finite number of circular orbits around the nucleus, an electron can revolve only in those orbits whose angular momentum (mvr) is an integral multiple of factor $h/2\pi$

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

  where, m = mass of the electron

  v = velocity of the electron

  n = orbit number in which electron is present

  r = radius of the orbit
- As long as an electron is revolving in an orbit it neither loses nor gains energy. Hence these orbits are called ***stationary states***. Each stationary state is associated with a definite amount of energy and it is also known as ***energy levels***. The greater the distance of the energy level from the nucleus, the more is the energy associated with it. The different energy levels are numbered as 1,2,3,4, (from nucleus onwards) or K,L,M,N etc.
- Ordinarily an electron continues to move in a particular stationary state without losing energy. Such a stable state of the atom is called as ***ground state*** or ***normal state***.
- If energy is supplied to an electron, it may jump (excite) instantaneously from lower energy (say 1) to higher energy level (say 2,3,4, etc.) by absorbing one or more quanta of energy. This new state of electron is called as ***excited state***. The quantum of energy absorbed is equal to the difference in energies of the two concerned levels.

  Since the excited state is less stable, atom will lose it's energy and come back to the ground state.

  Energy absorbed or released in an electron jump, (ΔE) is given by

  $\Delta E = E_2 - E_1 = h\nu$

  where E_2 and E_1 are the energies of the electron in the first and second energy levels, and ν is the frequency of radiation absorbed or emitted.

*[**Note:** If the energy supplied to hydrogen atom is less than 13.6 eV, it will accept or absorb only those quanta which can take it to a certain higher energy level i.e.,*

all those photons having energy less than or more than a particular energy level will not be absorbed by hydrogen atom. But if energy supplied to hydrogen atom is more than 13.6 eV then all photons are absorbed and excess energy appear as kinetic energy of emitted photo electron].

Radius and Energy levels of hydrogen atom

Consider an electron of mass 'm' and charge 'e' revolving around a nucleus of charge Ze (where, Z = atomic number and e is the charge of the proton) with a tangential velocity v. r is the radius of the orbit in which electron is revolving.

By Coulomb's Law, the electrostatic force of attraction between the moving electron and nucleus is

Coulombic force = $\frac{KZe^2}{r^2}$

K = $\frac{1}{4\pi \in_o}$ (where $\in_o$ is permittivity of free space)

K = 9×10^9 Nm^2 C^{-2}

In C.G.S. units, value of K = 1 dyne cm^2 (esu)$^{-2}$

The centrifugal force acting on the electron is $\frac{mv^2}{r}$

Since the electrostatic force balance the centrifugal force, for the stable electron orbit.

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \qquad \ldots (1)$$

$$\text{(or) } v^2 = \frac{KZe^2}{mr} \qquad \ldots (2)$$

According to Bohr's postulate of angular momentum quantization, we have

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

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

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \ldots (3)$$

Equating (2) and (3)

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

solving for r we get $r = \frac{n^2h^2}{4\pi^2mKZe^2}$

where n = 1,2,3 - - - - - ∞

Hence only certain orbits whose radii are given by the above equation are available for the electron. The greater the value of n, i.e., farther the energy level from the nucleus the greater is the radius.

The radius of the smallest orbit (n=1) for hydrogen atom (Z=1) is r_o.

$$r_o = \frac{n^2h^2}{4\pi^2me^2K} = \frac{1^2 \times \left(6.626 \times 10^{-34}\right)^2}{4 \times (3.14)^2 \times 9 \times 10^{-31} \times \left(1.6 \times 10^{-19}\right)^2 \times 9 \times 10^9} = 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ Å}$$

Radius of n^{th} orbit for an atom with atomic number Z is simply written as

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

Calculation of energy of an electron

The total energy, E of the electron is the sum of kinetic energy and potential energy.

Kinetic energy of the electron = $\frac{1}{2} mv^2$

Potential energy $= \frac{-KZe^2}{r}$

Total energy = $1/2\ mv^2 - \frac{KZe^2}{r}$ … (4)

From equation (1) we know that

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

$$\therefore \tfrac{1}{2} mv^2 = \frac{KZe^2}{2r}$$

Substituting this in equation (4)

Total energy (E) = $\frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$

Substituting for r, gives us

$$E = \frac{2\pi^2 mZ^2e^4K^2}{n^2h^2} \quad \text{where n = 1,2,3……….}$$

This expression shows that only certain energies are allowed to the electron. Since this energy expression consist of so many fundamental constant, we are giving you the following simplified expressions.

$$E = -21.8 \times 10^{-12} \times \frac{Z^2}{n^2} \text{ erg per atom}$$

$$= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J per atom} = -13.6 \times \frac{Z^2}{n^2} \text{ eV per atom}$$

(1eV = 3.83×10^{-23} kcal

1eV = 1.602×10^{-12} erg

1eV = 1.602×10^{-19}J)

$$E = -313.6 \times \frac{Z^2}{n^2} \text{ kcal / mole} \quad (1 \text{ cal} = 4.18 \text{ J})$$

The energies are negative since the energy of the electron in the atom is less than the energy of a free electron (i.e., the electron is at infinite distance from the nucleus) which is taken as zero. The lowest energy level of the atom corresponds to n=1, and as the quantum number increases, E becomes less negative.

When n = ∞, E = 0, which corresponds to an ionized atom i.e., the electron and nucleus are infinitely separated.

$H \longrightarrow H^+ + e^-$ (ionisation).

Exercise 1: ***Find out the value of electrostatic potential energy of two electrons separated by 3.0Å in vacuum./ Express your answer in joules and electron volt.***

Explanation for hydrogen spectrum by Bohr's theory

According to the Bohr's theory electron neither emits nor absorbs energy as long as it stays in a particular orbit. However, when an atom is subjected to electric discharge or high temperature, and electron in the atom may jump from the normal energy level, i.e., ground state to some higher energy level i.e, exited state. Since the life time of the electron in excited state is short, it returns to the ground state in one or more jumps.

During each jump, energy is emitted in the form of a photon of light of definite wavelength or frequency. The frequency of the photon of light thus emitted depends upon the energy difference of the two energy levels concerned (n_1, n_2) and is given by

$$h\nu = E_2 - E_1 = \frac{-2\pi^2 mZ^2 e^4 K^2}{h^2}\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$

$$\nu = \frac{2\pi^2 mZ^2 e^4 K^2}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

The frequencies of the spectral lines calculated with the help of above equation are found to be in good agreement with the experimental values. Thus, Bohr's theory elegantly explains the line spectrum of hydrogen and hydrogenic species.

Bohr had calculated Rydberg constant from the above equation.

$$\nu = \frac{c}{\lambda} = \frac{2\pi^2 mZ^2 e^4 K^2}{h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = \bar{\nu} = \frac{2\pi^2 mZ^2 e^4 K^2}{h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where $\dfrac{2\pi^2 me^4K^2}{h^3c}$ = $1.097 \times 10^{-7}m^{-1}$ or 109678 cm^{-1}

i.e., Rydberg constant (R)

$\therefore\ \bar{v} = \dfrac{1}{\lambda} = RZ^2\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

According to quantum mechanics the Rydberg constant is given by R = $\dfrac{e^4\mu}{8\pi\varepsilon_0^2h^3C}$

Were μ is reduced mass for the atom ε_0 is the permitivity of a vacuum. The reduced mass of an atom with one electron is given by

$\mu = \dfrac{m_{nuc}\cdot m_e}{m_{nuc} + m_e}$

where m_{nuc} = mass of nucleus

and m_e = mass of electron. For a nucleus with mass $m_{nuc} \longrightarrow \alpha$

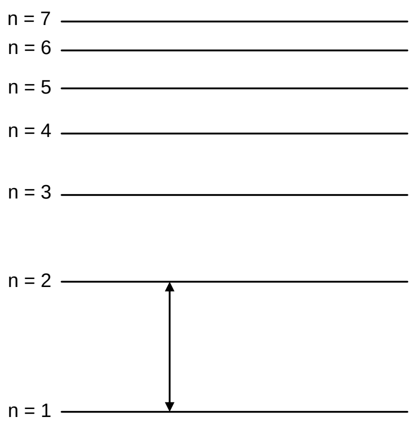
$\mu = m_e$

and $R_\alpha = 109673\ cm^{-1}$

Illustration 1: ***Find out the longest wavelength of absorption line for hydrogen gas containing atoms in ground state.***

Solution: $\dfrac{1}{\lambda} = RZ^2\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

for longest wavelength ΔE should be smallest i.e. transition occurs from n = 1 to n = 2



i.e. $\dfrac{1}{\lambda} = 109673\ cm^{-1} \times 1^2\left[\dfrac{1}{1} - \dfrac{1}{2^2}\right]$

$\therefore\ \dfrac{1}{\lambda} = 109673 \times \dfrac{3}{4}\ cm^{-1}$

$\therefore\ \lambda = \dfrac{4}{3 \times 109673\,cm^{-1}} = 1.2157 \times 10^{-5}$ cm = 121.6 nm

Exercise 2:

i) ***The series limit for the Paschen series of hydrogen spectrum occurs at 8205.8Å. Calculate.***

a) ***Ionization energy of hydrogen atom***

b) ***Wave length of the photon that would remove the electron in the ground state of the hydrogen atom.***

ii) ***Calculate frequency of the spectral line when an electron from 5th Bohr orbit jumps to the second Bohr orbit in a hydrogen atom.***

iii) ***Calculate the energy of an electron in 3rd Bohr orbit.***

Illustration 2 ***Calculate the energy in kJ per mole of electronic charge accelerated by a potential of 1 volt.***

Solution: Energy in joules = charge in coulombs $\times$ potential difference in volt

$= 1.6 \times 10^{-19} \times 6.02 \times 10^{23} \times 1$

$= 9.632 \times 10^{4}$ J or 96.32 kJ

Exercise 5:

i) ***What is highest frequency photon that can be emitted from hydrogen atom? What is wavelength of this photon?***

ii) ***Calculate the longest wavelength transition in the Paschenseries of He^+ .***

iii) ***Calculate the ratio of the wavelength of first and the ultimate line of Balmer series of Li^{2+}?***

Calculation of velocity

We know that

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

By substituting for r we are getting

$$v = \frac{2\pi KZe^2}{nh}$$

Where excepting n and z all are constants

$$v = 2.18 \times 10^8 \frac{Z}{n} \text{ cm/sec.}$$

Further application of Bohr’s work was made, to other one electron species (Hydrogenic ion) such as He^+ and Li^{2+}. In each case of this kind, Bohr’s prediction of the spectrum was correct.

Merits of Bohr’s theory

i) The experimental value of radii and energies in hydrogen atom are in good agreement with that calculated on the basis of Bohr’s theory.

ii) Bohr’s concept of stationary state of electron explains the emission and absorption spectra of hydrogen like atoms.

iii) The experimental values of the spectral lines of the hydrogen spectrum are in close agreement with that calculated by Bohr's theory.

Limitations of Bohr's theory

i) It does not explain the spectra of atoms having more than one electron.

ii) Bohr's atomic model failed to account for the effect of magnetic field (Zeeman effect) or electric field (Stark effect) on the spectra of atoms or ions. It was observed that when the source of a spectrum is placed in a strong magnetic or electric field, each spectral line further splits into a number of lines. This observation could not be explained on the basis of Bohr's model.

iii) De Broglie suggested that electrons like light have dual character. It has particle and wave character. Bohr treated the electron only as particle.

iv) Another objection to Bohr's theory came from ***Heisenberg's Uncertainty Principle***. According to this principle ***"It is impossible to determine simultaneously the exact position and momentum of a small moving particle like an electron"***. The postulate of Bohr, that electrons revolve in well defined orbits around the nucleus with well defined velocities is thus not tenable.

Exercise 4: ***Calculate the de Broglie wavelength of an electron that has been accelerated from rest through a potential difference of 1 KV.***

Illustration 3: ***A series of lines in the spectrum of atomic hydrogen lies at wavelengths 656.46, 482.7, 434.17, 410. 29 nm. What is the wave length of next line in this series.***

Solution: The given series of lines are in the visible region and thus appears to be Balmer series

Therefore $n_1 = 2$ and $n_2 = ?$ for next line

If $\lambda = 410.29 \times 10^{-7}$ cm and $n_1 = 2$

n_2 may be calculated for the last line

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

$$\frac{1}{410.29 \times 10^{-7}} = 109673\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

$n_2 = 6$

thus next line will be obtained during the jump of electron from 7th to 2nd shell i.e,

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{7^2}\right] = 109673\left[\frac{1}{4} - \frac{1}{49}\right]$$

$\lambda = 397.2 \times 10^{-7}$ cm **= 397.2 nm**

Exercise 5: ***Calculate wavelength of photon emitted when an electron goes from n = 3 to n = 2 level of hydrogen atom.***

Quantum Numbers

An atom contains large number of shells and subshells. These are distinguished from one another on the basis of their size, shape and orientation (direction) in space. The parameters are expressed in terms of different numbers called ***quantum numbers***.

Quantum numbers may be defined as a set of four numbers with the help of which we can get complete information about all the electrons in an atom. It tells us the address of the electron i.e., location, energy, the type of orbital occupied and orientation of that orbital.

i) ***Principal quantum number (n):*** It tells the main shell in which the electron resides and the approximate distance of the electron from the nucleus. It also tells the maximum number of electrons a shell can accommodate is $2n^2$, where n is the principal quantum number.

Shell	**K**	**L**	**M**	**N**
Principal quantum number (n)	1	2	3	4
Maximum number of electrons	2	8	18	32

ii) ***Azimuthal or angular momentum quantum number (l):*** This represents the number of subshells present in the main shell. These subsidiary orbits within a shell will be denoted as 1,2,3,4,… or s,p,d,f… This tells the shape of the subshells. The orbital angular momentum of the electron is given as $\sqrt{l(l+1)}\, h/2\pi$ (or) $\sqrt{l(l+1)}\,\hbar$ for a particular value of 'n' $\left(\text{where } \hbar = \frac{h}{2\pi}\right)$. For a given value of n values of possible l vary from 0 to n – 1.

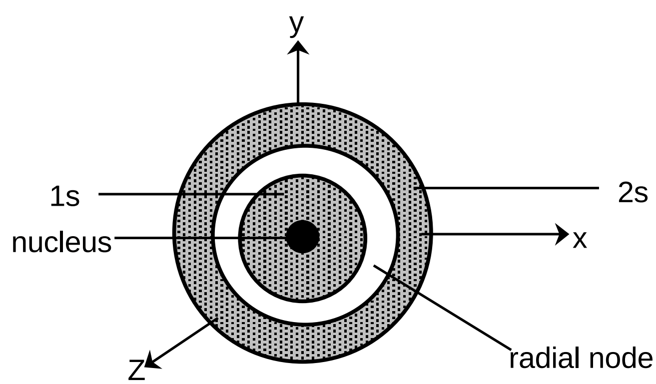
iii) ***The magnetic quantum number (m):*** An electron due to its angular motion around the nucleus generates an electric field. This electric field is expected to produce a magnetic field. Under the influence of external magnetic field, the electrons of a subshell can orient themselves in certain preferred regions of space around the nucleus called orbitals. The magnetic quantum number determines the number of preferred orientations of the electron present in a subshell. The values allowed depends on the value of *l*, the angular momentum quantum number, m can assume all integral values between –*l* to +*l* including zero. Thus m can be –1, 0, +1 for *l* = 1. Total values of m associated with a particular value of l is given by 2l + 1.

iv) ***The spin quantum number (s):*** Just like earth not only revolves around the sun but also spins about its own axis, an electron in an atom not only revolves around the nucleus but also spins about its own axis. Since an electron can spin either in clockwise direction or in anticlockwise direction, therefore, for any particular value of magnetic quantum number, spin quantum number can have two values, i.e., +1/2 and –1/2 or these are represented by two arrows pointing in the opposite directions, i.e., ↑ and ↓. When an electron goes to a vacant orbital, it can have a clockwise or anti clockwise spin i.e., +1/2 or –1/2. This quantum number helps to explain the magnetic properties of the substances.

Shapes and size of orbitals

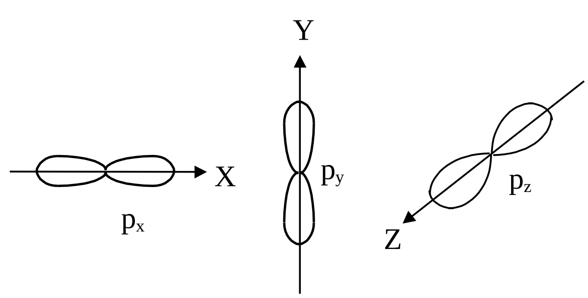
An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (90–95%). The shape of this region (electron cloud) gives the shape of the orbital. It is basically determined by the azimuthal quantum number *l*, while the orientation of orbital depends on the magnetic quantum number (m). Let us now see the shapes of orbitals in the various subshells.

s–orbitals: These orbitals are spherical and symmetrical about the nucleus. The probability of finding the electron is maximum near the nucleus and keep on decreasing as the distance from the nucleus increases. There is vacant space between two successive s–orbitals known as radial node. But there is no radial node for 1s orbital since it is starting from the nucleus.



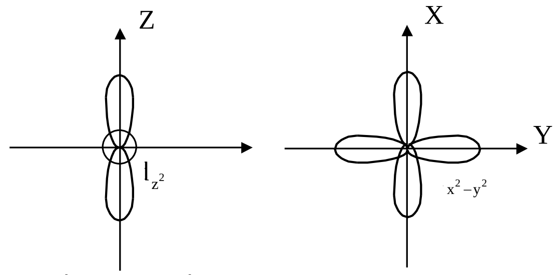
The size of the orbital depends upon the value of principal quantum number(n). Greater the value of n, larger is the size of the orbital. Therefore, 2s–orbital is larger than 1s orbital but both of them are non-directional and spherically symmetrical in shape.

p–orbitals (l =1): The probability of finding the p–electron is maximum in two lobes on the opposite sides of the nucleus. This gives rise to a dumb–bell shape for the p–orbital. For p–orbital l = 1. Hence, m = –1, 0, +1. Thus, p–orbital have three different orientations. These are designated as p_x,p_y & p_z depending upon whether the density of electron is maximum along the x y and z axis respectively. As they are not spherically symmetrical, they have directional character. The two lobes of p–orbitals are separated by a nodal plane, where the probability of finding electron is zero.



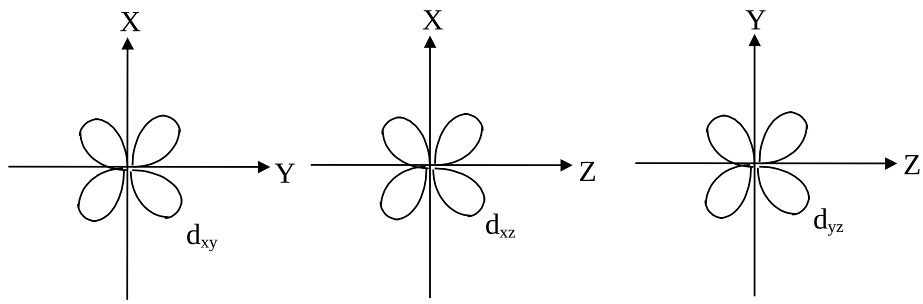
The three p-orbitals belonging to a particular energy shell have equal energies and are called ***degenerate orbitals***.

d–orbitals (l =2): For d–orbitals, l =2. Hence m=–2,–1,0,+1,+2. Thus there are 5 d orbitals. They have relatively complex geometry. Out of the five orbitals, the three (d_{xy}, d_{yz},d_{zx}) project in between the axis and the other two d_{z^2} and $d_{x^2-y^2}$ lie along the axis.



Dough–nut shape or Baby soother shape

Clover leaf shape



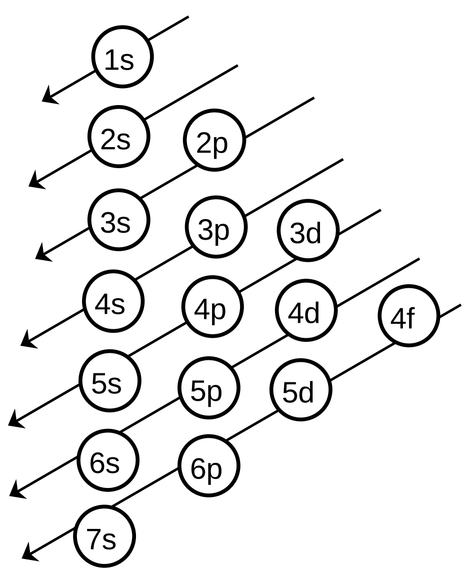
Rules for filling of electrons in various orbitals

The atom is built up by filling electrons in various orbitals according to the following rules.

Aufbau Principle: This principle states that the electrons are added one by one to the various orbitals in order of their increasing energy starting with the orbital of lowest energy. The increasing order of energy of various orbital is

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

How to remember such a big sequence? To make it simple we are giving you the method to write the increasing order of the orbitals. Starting from the top, the direction of the arrows gives the order of filling of orbitals.



Alternatively, the order of increasing energies of the various orbitals can be calculated on the basis of (n+*l*) rule.

The energy of an orbital depends upon the sum of values of the principal quantum number (n) and the azimuthal quantum number (*l*). This is called (n+ *l*) rule. According to this rule,

"In neutral isolated atom, the lower the value of (n+ l) for an orbital, lower is its energy. However, if the two different types of orbitals have the same value of (n+ l), the orbitals with lower value of n has lower energy".

Illustration of (n + *l*) rule

Type of orbitals	Value of n	Values of *l*	Values of (n+ *l*)	Relative energy
1s	1	0	1+0=1	Lowest energy
2s	2	0	2+0=2	Higher energy than 1s orbital
2p	2	1	2+1=3	2p orbital (n=2) have lower energy than 3s orbital (n=3)
3s	3	0	3+1=3	

Pauli's Exclusion principle

According to this principle, an orbital can contain a maximum number of two electrons and these two electrons must be of opposite spin.

Two electrons in an orbital can be represented by

$$\boxed{\uparrow\downarrow} \text{ or } \boxed{\downarrow\uparrow}$$

Hund's rule of maximum multiplicity

This rule deals with the filling of electrons in the equal energy (degenerate) orbitals of the same sub shell (p,d and f). According to this rule,

"Electron pairing in p,d and f orbitals cannot occur untill each orbital of a given subshell contains one electron each or is singly occupied".

This is due to the fact that electrons being identical in charge, repel each other when present in the same orbital. This repulsion can, however, be minimised if two electrons move as far apart as possible by occupying different degenerate orbitals. All the electrons in a degenerate set of orbitals will have same spin.

Illustration 4: ***Which hydrogen like ionic species has wavelength difference between the first line of Balmer and first line of Lyman series equal to 59.3 $\times$ 10^{-9} m? Neglect the reduced mass effect.***

Solution: Wave number of first Balmer line of an species with atomic number Z is given by

$$\bar{v}' = RZ^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

$\bar{v}' = \frac{5RZ^2}{36}$; Similarly wave number of $\bar{v}$ of first Lyman line is given by

$$v = RZ^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3}{4}RZ^2;\ \bar{v} = \frac{1}{\lambda} \text{ and } \bar{v}' = \frac{1}{\lambda'}$$

$$\therefore\ \lambda' - \lambda = \frac{36}{5RZ^2} - \frac{4}{3RZ^2} = \frac{1}{RZ^2}\left[\frac{36}{5} - \frac{4}{3}\right] = \frac{88}{15RZ^2}$$

$$\therefore Z^2 = \frac{88}{59.3\times10^{-9}\times15\times1.097\times10^{7}} = 9 \text{ or } Z = 3\ \therefore \text{ ionic species is } Li^{2+}$$

Electronic configuration of elements

Electronic configuration is the distribution of electrons into different shells, subshells and orbitals of an atom .

Keeping in view the above mentioned rules, electronic configuration of any orbital can be simply represented by the notation.]

Number of electrons in the subshell

$n\,l^{x}$

Principal quantum number

Symbol of subshell or orbitals (s,p,d,f)

Alternatively

Orbital can be represented by a box and an electron with its direction of spin by arrow. To write the electronic configuration, just we need to know (i) the atomic number (ii) the order in which orbitals are to be filled (iii) maximum number of electrons in a shell, sub–shell or orbital.

a) Each orbital can accommodate two electrons

b) The number of electrons to be accomodated in a subshell is 2 × number of degenerate orbitals.

Subshell	Maximum number of electrons
s	2
p	6
d	10
f	14

c) The maximum number of electron in each shell (K,L,M,N…) is given by $2n^2$. where n is the principal quantum number.

d) The maximum number of orbitals in a shell is given by n^2 where n is the principal quantum number.

e) The number of nodal planes associated with an orbital is given by l -1.

Importance of knowing the electronic configuration

The chemical properties of an element are dependent on the relative arrangement of its electrons.

Illustration 5: ***Write the electronic configuration of nitrogen (atomic number= 7)***

Solution:

$1s^2$	$2s^2$		$2p^3$	
↑↓	↑↓	↑	↑	↑

Exceptional Configurations

Stability of half filled and completely filled orbitals

Cu has 29 electrons. Its expected electronic configuration is

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

But a shift of one electron from lower energy 4s orbital to higher energy 3d orbital will make the distribution of electron symmetrical and hence will impart more stability.

Thus the electronic configuration of Cu is

$1s^2\ 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Fully filled and half filled orbitals are more stable.

Illustration 6: ***We know that fully filled and half filled orbitals are more stable. Can you write the electronic configuration of Cr(Z = 24)?.***

Solution: Cr (Z = 24)

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$.

Since half filled orbital is more stable one 4s electron is shifted to 3d orbital.

Exercise 6: ***1st I.P. of nitrogen is higher than oxygen. Explain.***

8. Dual Character
(Particle and Wave Character of Matter and Radiation)

In case of light some phenomenon like diffraction and interference can be explained on the basis of its wave character. However, the certain other phenomenon such as black body radiation and photoelectric effect can be explained only on the basis of its particle nature. Thus, light is said to have a dual character. Such studies on light were made by Einstein in 1905.

Louis de Broglie, in 1924 extended the idea of photons to material particles such as electron and he proposed that matter also has a dual character-as wave and as particle.

Derivation of de-Broglie equation

The wavelength of the wave associated with any material particle was calculated by analogy with photon.

In case of photon, if it is assumed to have wave character, its energy is given by

$E = h\nu$ ------------------ (i) (according to the Planck's quantum theory)

where ν is the frequency of the wave and 'h' is Planck's constant

If the photon is supposed to have particle character, its energy is given by

$E = mc^2$ ------------------ (ii) (according to Einstein's equation)

where 'm' is the mass of photon, 'c' is the velocity of light.

By equating (i) and (ii)

$h\nu = mc^2$

But $\nu = c/\lambda$

$h\dfrac{c}{\lambda} = mc^2$

(or) $\lambda = h/mc$

The above equation is applicable to material particle if the mass and velocity of photon is replaced by the mass and velocity of material particle. Thus for any material particle like electron.

$\lambda = h/mv$ (or) $\lambda = \dfrac{h}{p}$

where $mv = p$ is the momentum of the particle.

9. Derivation of Angular Momentum from de Broglie Equation

According to Bohr's model, the electron revolves around the nucleus in circular orbits. According to de Broglie concept, the electron is not only a particle but has a wave character also.

If the wave is completely in phase, the circumference of the orbit must be equal to an integral multiple of wave length (λ)

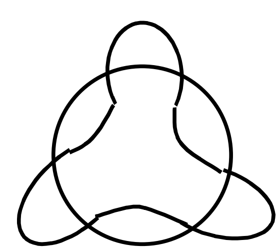
Therefore $2\pi r = n\lambda$

where 'n' is an integer and 'r' is the radius of the orbit

But $\lambda = h/mv$

$\therefore 2\pi r = nh/mv$

(or) $mvr = n\,h/2\pi$



which is Bohr's postulate of angular momentum, where 'n' is the principal quantum number.

"Thus, the number of waves an electron makes in a particular Bohr orbit in one complete revolution is equal to the principal quantum number of the orbit".

Alternatively

Number of waves 'n' $= \dfrac{2\pi r}{\lambda} = \dfrac{2\pi r}{h/mv} = \dfrac{2\pi mvr}{h}$

where v and r are the velocity of electron and radius of that particular Bohr orbit in which number of waves are to be calculated, respectively.

The electron is revolving around the nucleus in a circular orbit. How many revolutions it can make in one second

Let the velocity of electron be v m/sec. The distance it has to travel for one revolution $2\pi r$, (i.e., the circumference of the circle).

Thus, the number of revolutions per second is $= \dfrac{v}{2\pi r}$

Common unit of energy is electron volt which is amount of energy given when an electron is accelerated by a potential of exactly 1 volt. This energy equals the product of voltage and charge. Since in SI units coulombs × volts = Joules, 1 eV numerically equals the electronic charge except that joule replaces coulombs.

Illustration 7: ***Two particles A and B are in motion. If the wavelength associated with particle A is 5 ×10⁻⁸ m, calculate the wavelength associated with particle B if its momentum is half of A.***

Solution: According to de Broglie equation

$\lambda_A = \dfrac{h}{p_A}$ and $\lambda_B = \dfrac{h}{p_B}$

$\dfrac{\lambda_A}{\lambda_B} = \dfrac{p_B}{p_A}$

But $p_B = \frac{1}{2} p_A$ (given)

$\dfrac{\lambda_A}{\lambda_B} = \dfrac{1/2 p_A}{p_A} = \frac{1}{2}$

$\lambda_B = 2\lambda_A = 2 \times 5\times10^{-8}$ m $\mathbf{= 10^{-7}}$ **m**

Illustration 8: ***Calculate the de Broglie wavelength of a ball of mass 0.1kg moving with a speed of 60ms⁻¹.***

Solution: $\lambda = \dfrac{h}{mv} = \dfrac{6.6\times10^{-34}}{0.1\times 60}$

$\boldsymbol{\lambda = 1.1 \times 10^{-34}}$ **m.**

This is apparent that this wavelength is too small for ordinary observation.

Although the de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles.

Since, we come across macroscopic objects in our everyday life, de Broglie relationship has no significance in everyday life.

[Distinction between the wave- particle nature of a photon and the particle- wave nature of a sub atomic particle]

Photon	Sub Atomic Particle
1. Energy = $h\nu$	Energy = $\frac{1}{2}mv^2$
2. Wavelength = $\frac{c}{\nu}$	Wavelength = $\frac{h}{mv}$

[Note: We should never interchange any of the above]

10. Heisenberg's Uncertainty Principle

All moving objects that we see around us e.g., a car, a ball thrown in the air etc., move along definite paths. Hence their position and velocity can be measured accurately at any instant of time. Is it possible for subatomic particle also?

As a consequence of dual nature of matter, Heisenberg, in 1927 gave a principle about the uncertainties in simultaneous measurement of position and momentum (mass $\times$ velocity) of small particles.

This principle states

"It is impossible to measure simultaneously the position and momentum of a small microscopic moving particle with absolute accuracy or certainty" i.e., if an attempt is made to measure any one of these two quantities with higher accuracy, the other becomes less accurate.

The product of the uncertainty in position (Δx) and the uncertainty in the momentum ($\Delta p = m.\Delta v$ where m is the mass of the particle and Δv is the uncertainty in velocity) is equal to or greater than $h/4\pi$ where h is the Planck's constant.

Thus, the mathematical expression for the Heisenberg's uncertainty principle is simply written as

$$\Delta x \,.\, \Delta p \geq h/4\pi$$

Explanation of Heisenberg's uncertainty principle

Suppose we attempt to measure both the position and momentum of an electron, to pinpoint the position of the electron we have to use light so that the photon of light strikes the electron and the reflected photon is seen in the microscope. As a result of the hitting, the position as well as the velocity of the electron are disturbed. The accuracy with which the position of the particle can be measured depends upon the wavelength of the light used. The uncertainty in position is $\pm\lambda$. The shorter the wavelength, the greater is the accuracy. But shorter wavelength means higher frequency and hence higher energy. This high energy photon on striking the electron changes its speed as well as direction. But this is not true for macroscopic moving particle. Hence Heisenberg's uncertainty principle is not applicable to macroscopic particles.

Illustration 9: ***Why electron cannot exist inside the nucleus according to Heisenberg's uncertainty principle?***

Solution: Diameter of the atomic nucleus is of the order of 10^{-15}m

The maximum uncertainty in the position of electron is 10^{-15} m.

Mass of electron = 9.1×10^{-31} kg.

$$\Delta x.\ \Delta p = \frac{h}{4\pi}$$

$$\Delta x \times (m.\Delta v) = h/4\pi$$

$$\Delta v = \frac{h}{4\pi} \times \frac{1}{\Delta x.m} = \frac{6.63 \times 10^{-34}}{4 \times \frac{22}{7}} \times \frac{1}{10^{-15} \times 9.1 \times 10^{-31}}$$

$\mathbf{\Delta v = 5.80 \times 10^{10}\ ms^{-1}}$

This value is much higher than the velocity of light and hence not possible.

11. Quantum Mechanical Model of atom

The atomic model which is based on the particle and wave nature of the electron is known as wave or quantum mechanical model of the atom. This was developed by Ervin Schrodinger in 1926. This model describes the electron as a three dimensioinal wave in the electronic field of positively charged nucleus. Schrodinger derived an equation which describes wave motion of an electron. The differential equation is

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where x, y, z are certain coordinates of the electron, m = mass of the electron E = total energy of the electron. V = potential energy of the electron; h = planck's constant and zψ (psi) = wave function of the electron.

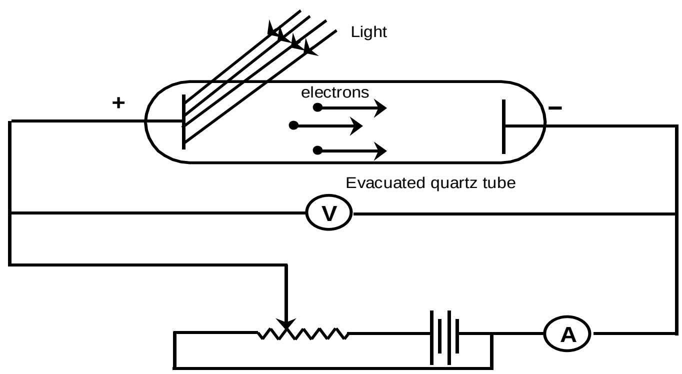
Significance of ψ The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y and z. The wave function may have positive or negative values depending upon the value of coordinates. The main aim of Schrodinger equation is to give solution for probability approach. When the equation is solved, it is observed that for some regions of space the value of ψ is negative. But the probability must be always positive and cannot be negative, it is thus, proper to use ψ^2 in favour of ψ.

Significance of ψ^2: ψ^2 is a probability factor. It describes the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is termed as orbital. The important point of the solution of the wave equation is that it provides a set of numbers called quantum numbers which describe energies of the electron in atoms, information about the shapes and orientations of the most probable distribution of electrons around nucleus.

12. Photo Electric Effect

Sir J.J. Thomson, observed that when a light of certain frequency strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is known as **photoelectric effect** and the ejected electrons are called photoelectrons.

A few metals, which are having low ionisation energy like Cesium, show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light.



An evacuated tube contains two electrodes connected to a source of variable voltage, with the metal plate whose surface is irradiated as the anode. Some of the photoelectrons that emerge from this surface have enough energy to reach the cathode despite its negative polarity, and they constitute the measured current. The slower photoelectrons are repelled before they get to the cathode. When the voltage is increased to a certain value V_o, of the order of several volts, no more photoelectrons arrive, as indicated by the current dropping to zero. This extinction voltage (or also referred as stopping potential) corresponds to the maximum photoelectron kinetic energy i.e., $eV_o = ½\, mv^2$

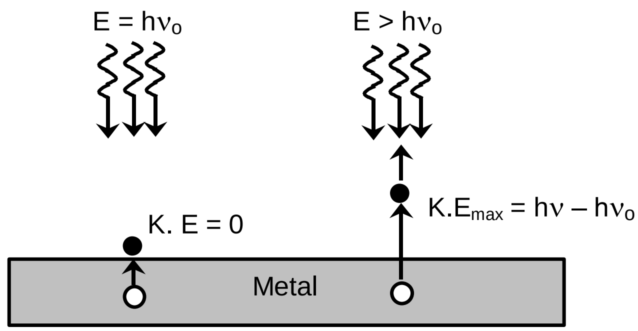
The experimental findings are summarised as below:

i) Electrons come out as soon as the light (of sufficient energy) strikes the metal surface .

ii) The light of any frequency will not be able to cause ejection of electrons from a metal surface. There is a minimum frequency, called the threshold (or critical) frequency, which can just cause the ejection. This frequency varies with the nature of the metal. The higher the frequency of the light, the more energy the photoelectrons have. Blue light results in faster electrons than red light.

iii) Photoelectric current is increased with increase in intensity of light of same frequency, if emission is permitted i.e., a bright light yields more photoelectrons than a dim one of the same frequency, but the electron energies remain the same.

Light must have stream of energy particles or quanta of energy (hν). Suppose, the threshold frequency of light required to eject electrons from a metal is ν_o, when a photon of light of this frequency strikes a metal it imparts its entire energy (hν_o) to the electron.



"This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus". Thus each photon can eject one electron. If the frequency of light is less than ν_o there is no ejection of electron. If the frequency of light is higher than ν_o (let it be ν), the photon of this light having higher energy (hν), will impart some energy to the electron that is needed to remove it away from the atom. The excess energy would give a certain velocity (i.e, kinetic energy) to the electron.

$h\nu = h\nu_o + K.E$

$h\nu = h\nu_o + ½\, mv^2$

$½\, mv^2 = h\nu – h\nu_o$

where, ν = frequency of the incident light

ν_o = threshold frequency

hν_o is the threshold energy (or) the work function denoted by $\phi = h\nu_o$ (minimum energy of the photon to liberate electron). It is constant for particular metal and is also equal to the ionization potential of gaseous atoms.

The kinetic energy of the photoelectrons increases linearly with the frequency of incident light. Thus, if the energy of the ejected electrons is plotted as a function of frequency, it result in a straight line whose slope is equal to Planck's constant 'h' and whose intercept is hν_o.

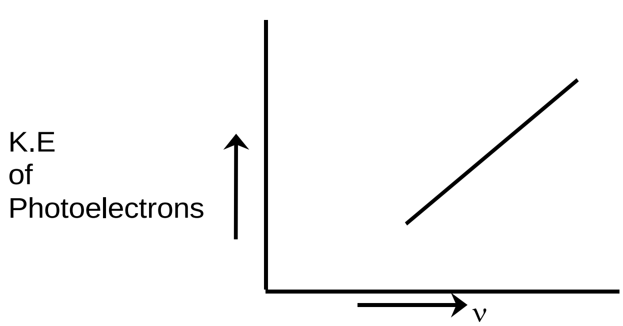


Illustration 10: ***A photon of wavelength 5000 A strikes a metal surface, the work function of the metal being 2.20 eV. Calculate (i) the energy of the photon in eV (ii) the kinetic energy of the emitted photo electron and (iii) the velocity of the photo electron.***

Solution:

i) Energy of the photon

$E = h\nu = \frac{hc}{\lambda} = \frac{(6.6\times10^{-34}\,Js)(3\times10^{8}\,ms^{-1})}{5\times10^{-7}\,m} = 3.96\times10^{-19}$ J

1 eV = 1.6×10^{-19} J

Therefore $E = \frac{3.96\times10^{-19}\,J}{1.6\times10^{-19}\,J/ev} = 2.475$ eV

ii) Kinetic energy of the emitted photo electron

Work function = 2.20 eV

Therefore, KE = 2.475 – 2.20 = 0.275 eV = 4.4×10^{-20} J

iii) Velocity of the photo electron

$KE = \frac{1}{2}mv^2 = 4.4\times10^{-20}$ J

Therefore, velocity (v) = $\sqrt{\frac{2\times4.4\times10^{-20}}{9.1\times10^{-31}}} = 3.11\times10^{5}\ ms^{-1}$

13. Solution to Exercises

Exercise 1:

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

$K = \frac{1}{4\pi\varepsilon_0} = 9 \times 10^9\ Nm^2\ C^{-2}$

$= \frac{9\times10^9 \times 1\times(1.6\times10^{-19})^2}{3\times10^{-10}} = 7.68 \times 10^{-19} J$

$\because$ 1 eV = 1.6×10^{-19}J

$\therefore E = \frac{7.68\times10^{-19}}{1.6\times10^{-19}} = 4.8$ eV

Exercise 2:

i) a) Energy corresponding to 8205.8 A° $= \frac{6.626\times10^{-34}\times3\times10^8}{8205.8\times10^{-10}}$

$= 2.422 \times 10^{-19}$ J = 1.572 eV

$\Delta E = E_{1H} \times Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

1.512 eV = $E_{1H} \times (1)^2 \times \left(\frac{1}{3^2} - \frac{1}{\infty^2}\right)$

1.512 eV = $\frac{E_{1H}}{9}$

$E_{1\,H}$ = 13.608 eV

$\therefore$ Ionisation energy of hydrogen atom = **13.6 eV**

b) $\lambda = \frac{hc}{E} = \frac{6.626\times10^{-34}\times3\times10^8}{13.6\times1.602\times10^{-19}}$

= 916 A°

ii) $\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 109673\left[\frac{1}{2^2} - \frac{1}{5^2}\right] = 2.304 \times 10^6\ m^{-1}$

$\therefore v = \frac{C}{\lambda} = 2.304 \times 10^6\ m^{-1} \times 2.998 \times 10^8$ m/s

$= 6.906 \times 10^{14}$ Hz

iii) $E_n = -\frac{13.6}{n^2}$ eV

$= -\frac{13.6}{3^2} = -1.51$ eV

$= -2.42 \times 10^{-19}$ J

Exercise 3:

i) Highest frequency photon is emitted when electron comes from infinity to 1st energy level.

$$E = -\frac{13.6Z^2}{1^2} = -13.6\text{eV}$$

or $13.6 \times 1.6 \times 10^{-19}$ Joule = 2.176×10^{-18} Joule

$E = h\nu$

$$\therefore v = \frac{E}{h} = \frac{2.176 \times 10^{-18}\,\text{J}}{6.626 \times 10^{-34}\,\text{JS}} = 0.328 \times 10^{16}\ \text{Hz}$$

$$v = \frac{C}{\lambda} \ \therefore \lambda = \frac{3 \times 10^8}{0.328 \times 10^{16}} = 9.146 \times 10^{-8}\ \text{m}$$

ii) $\bar{\upsilon} = R_H \times Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

For He; Z = 2; For Paschen series $n_1 = 3$

For longest wavelength $n_2 = 4$

$$\frac{1}{\lambda} = 109678 \times (2)^2 \times \left[\frac{1}{3^2} - \frac{1}{4^2}\right] = 109678 \times 4 \times \left[\frac{1}{9} - \frac{1}{16}\right] = 109678 \times 4 \times \frac{7}{144}$$

λ = 4689 A°

iii) Wave number of first line of Balmer,

$$\bar{\nu}_1 = RZ^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5 \times 9R}{36} = \frac{5R}{4}$$

$\therefore$wave length of first line of Balmer = $\frac{4}{5R}$

wave number of ultimate line of Balmer, $\bar{\nu}_2 = RZ^2\left[\frac{1}{2^2} - \frac{1}{\infty}\right] = \frac{9R}{4}$

$\therefore$wave length of ultimate line of Balmer = $\frac{4}{9R}$

$\therefore$**Ratio =** $\mathbf{\frac{9}{5}}$

Exercise 4: Energy in Joules = Charge on the electron in coloumb $\times$ pot. diff. in volts.

$= 1.609 \times 10^{-19} \times 1000 = 1.609 \times 10^{-16}$ J

Kinetic energy ($1/2\ mv^2$) = 1.609×10^{-16} J

$$\frac{1}{2} \times 9.1 \times 10^{-31}\ v^2 = 1.609 \times 10^{-16}$$

$v^2 = 3.536 \times 10^{14}$

$v = 1.88 \times 10^7\ \text{ms}^{-1}$

$h = 6.626 \times 10^{-34}$ J sec

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 1.88 \times 10^7} = \mathbf{3.87 \times 10^{-11}\ m.}$$

Exercise 5:

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

$$\therefore \frac{1}{\lambda} = 109673 \times 1^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

$$= 109673 \times \frac{5}{36}$$

$$\therefore \lambda = \frac{36}{109673 \times 5} = 6.56 \times 10^{-7} \text{ m or } 656 \text{ nm}$$

Exercise 6: Due to presence of half filled orbital in nitrogen which impart it extra stability.

14. Solved Problems

14.1 Subjective

Problem 1: ***Calculate the wavelength emitted during the transition of electron in between two levels of Li^{2+} ion whose sum is 4 and difference is 2.***

Solution: Let the transition occurs between the level n_1 and n_2 and $n_2 > n_1$

Given that $n_1 + n_2 = 4$

$n_2 - n_1 = 2$

$\therefore$ $n_1 = 1$ and $n_2 = 3$

Therefore, $\frac{1}{\lambda} = R_h \times Z^2\left[\frac{1}{(1)^2} - \frac{1}{(3)^2}\right] = 109678 \times (3)^2\left[\frac{8}{9}\right]$

$\therefore$ $\lambda = 1.14 \times 10^{-6}$ cm

Problem 2: ***Find the quantum number 'n' corresponding to the excited state of He^+ ion if on transition to the ground state that ion emits two photons in succession with wavelengths 108.5 and 30.4 nm.***

Solution: $\lambda_2 = 30.4 \times 10^{-7}$ cm

$\lambda_2 = 108.5 \times 10^{-7}$ cm

Let excited state of He^+ be n_2. It comes from n_2 to n_1 and then from n_1 to 1 to emit two successive photon.

$$\frac{1}{\lambda_2} = R_H Z^2\left[\frac{1}{(1)^2} - \frac{1}{n_1^2}\right]$$

$$\therefore \frac{1}{30.4 \times 10^{-7}} = 109678 \times (2)^2\left[\frac{1}{(1)^2} - \frac{1}{(n_1)^2}\right]$$

$\therefore n_1 = 2$

Now for λ, $n_1 = 2$, $n_2 = ?$

$$\frac{1}{108.5 \times 10^{-7}} = 10.9678 \times 4\left[\frac{1}{(2)^2} - \frac{1}{(n_2)^2}\right]$$

$\therefore$ $n_2 = 5$

Hence excited state for He is 5^{th} orbit.

Problem 3: ***The Lymann series of the hydrogen spectrum can be represented by the equation.***

$$\nu = 3.2881 \times 10^{15}\ s^{-1}\left[\frac{1}{(1)^2} - \frac{1}{(n)^2}\right]$$

(where n = 2, 3,…..)

Calculate the maximum and minimum wavelength of lines in this series.

Solution:

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{3.2881 \times 10^{15}}{3 \times 10^8} m^{-1}\left[\frac{1}{(1)^2} - \frac{1}{n^2}\right]$$

Wavelength is maximum ($\bar{\nu}_{min}$) when n is minimum so that $\frac{1}{n^2}$ is maximum

$$\therefore \ \bar{\nu}_{min} = \frac{1}{\lambda_{max}} = \frac{3.2881\times10^{15}}{3\times10^{8}}\left[\frac{1}{(1)^2}-\frac{1}{(2)^2}\right]$$

$$\therefore \lambda_{max} = \frac{3\times10^{8}}{3.2881\times10^{15}}\times\frac{4}{3}$$

$= 1.2165 \times 10^{-7}$ m = 121.67 nm

Wavelength is minimum $(\bar{\nu}_{max})$ when n is $\propto$

i.e. series converge

$$\therefore \ \nu_{max} = \frac{1}{\lambda_{min}} = \frac{3.2881\times10^{15}}{3\times10^{8}}$$

$\therefore \lambda_{min} = 0.9124\times 10^{-7}$ m 91.24 nm

Problem 4: ***When certain metal was irradiated with light frequency 1.6 $\times 10^{16}$ Hz the photo electrons emitted had twice the kinetic energy as did photo electrons emitted when the same metal was irradiated with light frequency 1.0 $\times$ 10^{16} Hz. Calculate threshold frequency (v^0) for the metal.***

Solution: $hv = hv^0 + KE$

$KE_1 = h(v_1 - v^0)$

$KE_2 = h(v_2 - v^0) = \frac{KE_1}{2}$

$$\therefore \ \frac{v_2 - v_0}{v_1 - v^0} = \frac{1}{2} \Rightarrow \frac{1.0\times10^{16} - v^0}{1.6\times10^{16} - v^0} = \frac{1}{2} \Rightarrow v^0 = 4 \times 10^{15}\text{Hz}$$

Problem 5: ***Iodine molecule dissociates into atoms after absorbing light of 4500Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (Bond energy of I_2 = 240 kJ (mol).***

Solution: Energy given to iodine molecule

$$\frac{hc}{\lambda} = \frac{6.625\times10^{-34}\times3\times10^{8}}{4500\times10^{-10}} = 4.417 \times 10^{-19}\text{J}$$

Also energy used for breaking up

$$I_2 \text{ molecule} = \frac{240\times10^{5}}{6.023\times10^{23}} = 3.984 \times 10^{-19}\text{J}$$

$\therefore$ Energy used in imparting kinetic to two atoms

$= (4.417 - 3.984) \times 10^{-19}$J

$$\therefore \text{ KE of iodine atom} = \frac{(4.417 - 3.984)}{2}\times10^{-19} = 0.216\times 10^{-19}\text{J}$$

Problem 6: ***Two hydrogen atoms collide head on and end up with zero kinetic energy. Each atom then emits a photon of wavelength 121.6 nm. Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before collision?***

Solution: Wavelength is emitted in UV region and thus $n_1 = 1$

For H atom = $\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$

$\therefore \frac{1}{121.6\times10^{-9}} = 1.097\times10^7\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$

$\therefore$ n = 2

Also the energy released is due to collision and all the kinetic energy is released in form of photon.

$\therefore \frac{1}{2}mv^2 = \frac{hc}{\lambda}$

$\therefore \frac{1}{2}\times1.67\times10^{-27}\times v^2 = \frac{6.625\times10^{-34}\times\times10^3}{121.6\times10^{-9}}$

$\therefore$ v = 4.43 × 10^4 m/sec

Problem 7: ***Find out the angular momentum of an electron in***

a) 4s orbital

b) 3p orbital

c) 4th orbital

Solution: Angular momentum in an orbital = $\frac{h}{2\pi}\sqrt{\ell(\ell+1)\ell}$

i) ℓ = 0 for 4s orbital, hence orbital angular momentum = 0

ii) ℓ = 2 for 3p orbital

$\therefore$ angular momentum = $\frac{h}{2\pi}\sqrt{(1+1)\times1}$ = $\frac{h}{\sqrt{2}\pi}$

iii) Angular momentum in an orbit

= $\frac{nh}{2\pi} = \frac{4h}{2\pi} = \frac{2h}{\pi}$

Problem 8: ***Given below are the sets of quantum numbers for given orbitals. Name these orbitals.***

i) n = 2, ℓ = 1, m = –1

ii) n = 4, ℓ = 2, m = 0

iii) n = 3, ℓ = 1, m = ± 1

iv) n = 4, ℓ = 0, m = 0

v) n = 3, ℓ = 2, m = ± 2

Solution: i) $2p_x$ or $2p_y$

ii) $4dz^2$

iii) $3p_x$ or $3p_y$

iv) 4s

v) $3d_{x^2-y^2}$ or $3d_{xy}$

Problem 9: ***A compound of vanadium has a magnetic moment of 1.73 BM work out the electronic configuration of the vanadium in the compound.***

Solution: Magnetic moment = $\sqrt{n(n+2)}$

Where n is number of unpaired electrons

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

Vanadium atom must have the unpaired electron and thus its configuration is:
$_{23}V^{4+}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$

Problem 10: ***An electron beam can undergo defraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54Å.***

Solution: For an electron

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

(Where V is accelerating potential)

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

$$\therefore\ \frac{1}{2}m\left(\frac{h}{m\lambda}\right)^2 = eV$$

$$\therefore\ V = \frac{1}{2}\times\frac{h^2}{m\lambda^2 e} = \frac{1\times(6.625\times10^{-34})^2}{2\times9.108\times10^{-31}\times(1.54\times10^{-10})^2\times1.602\times10^{-19}} = 63.3 \text{ volt}$$

14.2 Objective

Problem 1: ***For a d–electron, the orbital angular momentum is:***

(A) $\sqrt{6}\hbar$ ***(B)*** $\sqrt{2}\hbar$
(C) $\hbar$ ***(D)*** $2\hbar$

Solution: For d–electron, ℓ =2, orbital angular momentum
= $\sqrt{\ell(\ell+1)}\hbar = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$
$\therefore$ **(A)**

Problem 2: ***If the nitrogen atoms had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2\ 2s^2\ 2p^3$ because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates***

(A) Heisenberg's uncertainity principle
(B) Hund's rule
(C) Pauli exclusion principle
(D) Bohr's postulate of stationary orbits

Solution: According to Pauli's exclusion principle, an orbital cannot have more than two electrons and these two with opposite spin.
$\therefore$ **(C)**

Problem 3: ***The energy of an electron in the first Bohr orbit of H atom is – 13.6 eV. The possible energy value(s) of excited state(s) for electron in Bohr orbitls of hydrogen is are***

(A) – 3.4 eV ***(B) – 4.2 eV***
(C) 6.8 eV ***(D) +6.8 eV***

Solution: $E_n = \frac{-13.6}{n^2}\text{eV}$

When n = 2, $E_2 = \frac{-13.6}{4} = -3.4\text{eV}$

Problem 4: ***The electronic configuration of an element is $1s^2\ 2s^2\ 2p^6,\ 3s^2,\ 3p^6,\ 3d^5,\ 4s^1$. This represents its***

(A) Excited state ***(B) Ground state***
(C) Cationic form ***(D) Anionic from***

Solution: The given electronic configuration is ground state for chromium.
$\therefore$ **(B)**

Problem 5: ***Which of the following sets of quantum number is./are not permitted?***

(A) $n = 3, \ell = 3, m = 0, s = \frac{3}{2}$ ***(B)*** $n = 3, \ell = 2, m = 2, s = -\frac{1}{2}$

(C) $n = 3, \ell = 1, m = 2, s = -\frac{1}{2}$ ***(D)*** $n = 3, \ell = 0, m = 0, s = +\frac{1}{2}$

Solution: When n = 3, ℓ cannot be 3. so (A) is not permitted when ℓ = 1, m cannot be = –2.

So (C) is not permitted
$\therefore$ **(A) and (C)**

Problem 6: ***Which of the following pairs of ions have the same electronic configuration?***
(A) ***Cr^{3+}, Fe^{3+}*** ***(B)*** ***Fe^{3+}, Mn^{2+}***
(C) ***Fe^{3+}, Co^{3+}*** ***(D)*** ***Se^{3+}, Cr^{3+}***

Solution: Fe^{3+} and Mn^{2+} have same electronic configuration
$\therefore$ **(B)**

Problem 7: ***If an electron in H–atom has an energy of – 78.4 kcal/mol. The orbit in which the electron is present is:***
(A) ***1^{st}*** ***(B)*** ***2^{nd}***
(C) ***3^{rd}*** ***(D)*** ***4^{th}***

Solution: $E^{n} = \frac{-313.6}{n^2}$ kcal/mol $\Rightarrow -78.4 = \frac{-313.6}{n^2}$ $\therefore$ n = 2

Problem 8: ***What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n = 4 to n = 2 in the He^+ spectrum.***
(A) ***n = 4 to n = 2*** ***(B)*** ***n = 3 to n = 2***
(C) ***n = 3 to n = 1*** ***(D)*** ***n = 2 to n = 1***

Solution: $\bar{\nu} = \frac{1}{\lambda} = \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \frac{3}{4}R$

In H–spectrum for the same $\bar{\nu}$ or λ as Z = 1, n = 1, n_2 = 2
$\therefore$ **(D)**

Problem 9: ***Principal. Azimuthal and magnetic quantum numbers are respectively related to***
(A) ***Size, orientation and shape*** ***(B)*** ***Size shape and orientation***
(C) ***Shape, size and orientation*** ***(D)*** ***None of these***

Solution: Principal gives ie, azimuthal gives shape and magnetic quantum number gives the orientation
$\therefore$ **(B)**

Problem 10: ***If the radius of 2^{nd} Bohr orbit of hydrogen atom is r_2. The radius of third Bohr orbit will be***
(A) $\frac{4}{9}r_2$ ***(B)*** ***$4r_2$***
(C) $\frac{9}{4}r_2$ ***(D)*** ***$9r_2$***

Solution: $r = \frac{n^2h^2}{4\pi^2 mZe^2}$ $\therefore$ $\frac{r_2}{r_3} = \frac{2^2}{3^2}$ $\therefore$ $r_3 = \frac{9}{4}r_2$
$\therefore$ **(C)**

15. Assignments

15.1 Subjective problems

LEVEL – I

1. Calculate the longest wavelength in the Paschen series of He^{+}ion.

2. Calculate the ratio of the wavelength of first and the ultimate line of Balmer series of Li^{2+}.

3 Calculate the number of photons emitted in 10 hours by a 60 W sodium lamp (λ = 5893Å).

4. An electron collides with a hydrogen atom in its ground state and excited it to a state of n=3. How much energy was given to the hydrogen atom in this inelastic collision?

5. Hydrogen atom in states of high quantum number have been created in the laboratory and observed in space.
   a) find the quantum number of the Bohr orbit in a H–atom whose radius is 0.0100 mm ?
   b) what is the energy of H–atom in this state?

6. With what velocity should an α–particle travel towards the nucleus of a copper atom so as to arrive at a distance 10^{-13} metre from the nucleus of the copper atom.

7. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated. So that its wave length becomes equal to 1.54 Å.

8. If the uncertainty in position and momentum are equal. Calculate the uncertainty in velocity for an electron.

9. Calculate the kinetic energy of an electron emitted from the surface of a metal by light of wavelength 5.5×10^{-8} cm. Threshold energy for the metal is 2.62×10^{-9} ergs.

10. Suppose 10^{-17}J of energy is needed by the interior of human eye to see an object. How many photons of green light (λ=550 nm) are needed to generate this minimum amount of energy?

LEVEL – II

1. The power output for a certain laser transition was found to be 2.79 watt per square meter. Given λ = 520 nm, calculate the number of quanta emitted per square meter per second.

2. An electron in a hydrogen like atom is in an excited state. It has a total energy of –3.4 eV. Calculate (i) kinetic energy and (ii) de-Broglie wavelength of the electron.

3. Light from a discharge tube containing hydrogen atoms falls on the surface of a piece of sodium. The kinetic energy of the fastest photo electrons emitted from sodium is 0.73 eV. The work function for sodium is 1.82 eV. Find
   a) The energy of the photons causing the photo electric emission?
   b) The quantum numbers of the two levels involved in the emission of these photons?

4. Find the threshold wavelengths for photoelectric effect from a copper surface, a sodium surface and a caesium surface? The work function of these metals are 4.5 eV, 2.3 eV and 1.9 eV respectively.

5. Calculate
   a) The de-Broglie wavelength of an electron moving with a velocity of 5.0×10^5 ms^{-1} and
   b) Relative de-Broglie wavelength of an atom of Helium and an atom of oxygen moving with same velocity (h = 6.63×10^{-34} kg m^2 sec^{-1}).

6. The series limit for the Paschen series of hydrogen spectrum occurs at 8205.8Å. Calculate.
   a) Ionization energy of hydrogen atom
   b) Wave length of the photon that would remove the electron in the ground state of the hydrogen atom.

7. The angular momentum of an electron in a particular orbit of Li^{2+}ion is 5.2728×10^{-34} kg m^2/sec. Calculate the frequency of the spectral line when electron falls from this level to the level where angular momentum of electron will be 3.1636×10^{-34} kg – m^2/sec.

8. The electron energy in hydrogen atom is given by E = $21.7 \times 10^{-12}/ n^2$ ergs. Calculate the energy required to remove an electron completely from n = 2 orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition?

9. The wavelength corresponding to a transition when electron falls from a certain quantum level to the ground state of an He^+ ion is 24.31 nm. Find the ratio of velocity of the electron in the next quantum level to that of velocity of light?

10. Calculate the energy emitted when electron of 1.0 g atom of hydrogen undergo transition giving the spectral lines of lowest energy in u.v. region of its atomic spectrum.
    ($R_H = 1.1 \times 10^7$ m^{-1}, c = 3×10^8 ms^{-1}, h = 6.62×10^{-34} J–sec)

15.2 Objective

LEVEL – I

1. If the electronic structure of oxygen atom is written as $1s^2\ 2s^2\ 2p^4$ it would violate
(A) Hund's rule (B) Paulis exclusion principle
(C) Both Hunds' and Paulis' principles (D) None of these

2. Number of nodal planes for f-orbital are
(A) 3 (B) 2
(C) 1 (D) 0

3. One Bohr magneton equals
(A) $\frac{ehc}{4\pi n}$ (B) $\frac{ec}{4h\pi m}$
(C) $\frac{hc}{me^4\pi}$ (D) $\frac{eh}{4\pi mc}$

4. Three isotopes of an element have mass numbers M, (M + 1) and (M + 2). If the mean mass number is (M + 0.5) than which of the following ratio may be accepted for M, (M + 1), (M + 2) in that order.
(A) 1 : 1 : 1 (B) 4 : 1 : 1
(C) 3 : 2 : 1 (D) 2 : 1 : 1

5. A possible set of quantum numbers for the last electron added to a gallium atom (Z = 31) in its ground state is

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

6. The angle made by angular momentum vector of an electron with z axis is given by
(A) $\cos\theta = l/m$ (B) $\cos = \sqrt{l}/m$
(C) $\cos\theta = \sqrt{\frac{(l+1)}{m}}$ (D) $\cos\theta = \frac{m}{\sqrt{l(l+1)}}$

7. The distance between 3rd and 2nd orbit of hydrogen atom is
(A) 2.646×10^{-8} cm (B) 2.116×10^{-8} cm
(C) 1.058×10^{-8} cm (D) 0.529×10^{-8} cm

8. An atom has four unpaired electrons. The total spin of this atom will be
(A) 1 (B) 1.5
(C) 2 (D) 4

9. For a 'd' electron, the orbital angular momentum is
(A) $\sqrt{6}\hbar$ (B) $\sqrt{2}\hbar$
(C) $\hbar$ (D) $2\hbar$

10. Which of the following pairs can form correct set of isosters ?
(A) MgS, CaF_2 (B) C_6H_6, $B_3N_3H_6$
(C) CO, N_2O (D) All the above

11. Electromagnetic radiation (Photon) with least wavelength result when an electron in the hydrogen atom falls from n = 5 to
(A) n = 1 (B) n = 2
(C) n = 3 (D) n = 4

12. The first five ionization energies of an element are 801, 2428, 3660, 25030, 32835 in kJ/mol. Then the element could be
(A) a halogen (B) a noble gas
(C) a third group element (D) a second group element

13. The energy required to melt 1g ice is 33J. The number of quanta of radiation of frequency 4.67×10^{13} sec^{-1}, that must be absorbed to melt 10 g ice is
(A) 1.065×10^{22} (B) 3.205×10^{23}
(C) 9.076×10^{20} (D) none of these

14. If the wave length of first line of the Balmer series of hydrogen atom is 656.1 nm, the wave length of second line of this series would be
(A) 218.7 nm (B) 328.0 nm
(C) 486.0 nm (D) 640.0 nm

15. The energy of an electron in the first Bohr orbit for He^+ ion is –54.4 eV. Which one of the following is a possible excited state for electron in Bohr orbit of He^+ ion?
(A) –6.04 eV (B) – 6.8eV
(C) – 1.7 eV (D) +1.36 eV

16. The outermost electronic configuration of the most electronegative element is
(A) ns^2,np^3 (B) ns^2,np^4
(C) ns^2,np^5 (D) ns^2,np^6

17. The first four ionization energies of an element are 191, 578,872 and 5962 kcal. The number of valence electrons in the element is
(A) 1 (B) 2
(C) 3 (D) 4

18. The quantum numbers of +1/2 and –1/2 for the electron spin represent
(A) Rotation of the electron in clockwise and anticlockwise direction respectively
(B) Rotation of the electron in anticlockwise and clockwise direction respectively
(C) Magnetic moment of the electron pointing up and down respectively
(D) Two quantum mechanical spin states which have no classical analogue.

19. A atom forms an ion by the loss of three electrons. The ion has an electronic configuration $[Ar]3d^6$. The symbol of the ion is
(A) Fe^{3+} (B) Ni^{3+}
(C) Co^{3+} (D) Mn^{+3}

20. Given that in H–atom, the transition energy for n=1 to n=2 is 10.2 eV, the energy for the same transition in Be^{3+} is
(A) 20.4 eV (B) 30.6 eV
(C) 40.8 eV (D) None of these

LEVEL – II

1. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because:
(A) alpha particles are much heavier than electrons
(B) alpha particles are positively charged
(C) most part of the atom is empty space
(D) alpha particle move with high velocity

2. Which represent a possible 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	½

3. Which set of quantum number is consistent with theory
(A) $n = 2, \ell = 1, m = 0, s = –1/2$ (B) $n = 4, \ell = 3, m = 2, S = –1/2$
(C) $n = 3, \ell = 2, m = 3, S = +1/2$ (D) $n = 4, \ell = 3, m = 3, S = +1/2$

4. Which of the following statements are false:
(A) The uncertainty in position and momentum in Heisenberg's principle due to electron wave.
(B) The energy level order 4s < 3d < 4p < 5s may not hold good for all elements
(C) The quantum nature of light radiation is manifested in photoemission of electrons
(D) According to Bohr's theory the energy decreases as n increases.

5. Five valence electrons of $_{15}P$ are labeled as

Pq		x	y	z
3s			3P	

If the spin quantum number of q and z is + 1/2
The group of electrons with three of the quantum number same are :
(A) Pq (B) (xyz), (pq)
(C) (pq), (xyz), (pz) (D) (pq), (xyz), (qy)

6. Which of the following is/are correct?
(A) the energy of an electron depends only on the principal quantum numbers not on the other quantum numbers

(B) the energy of an electron depends only on the principal quantum number in case of hydrogen and hydrogen like atoms.
(C) The difference in potential energies of any two energy level is always more than the difference in kinetic energies of these two levels.
(D) An electron in an excited state can always emit a photon or two but can not absorb a photon

7. The ratio of the e/m values of a proton and a α-particle is
(A) 2 : 1
(B) 1 : 1
(C) 1 : 2
(D) 1 : 4

8. Let A_n be the area enclosed by the nth orbit in a hydrogen atom. The graph of $\ln(A_n/A_1)$ against $\ln(n)$:
(A) will pass through origin
(B) will be straight line with slope = 4
(C) will be a monotonically increasing non-linear curve
(D) will be a circle

9. Which of the following is the nodal plane of d_{xy} orbital ?
(A) XY
(B) YZ
(C) ZX
(D) all

10. Ground state electronic configuration of nitrogen atom can be represented by
(A) [↑↓] [↑↓] [↑][↑][↑]
(B) [↑↓] [↑↓] [↑][↓][↑]
(C) [↑↓] [↑↓] [↑][↓][↓]
(D) [↑↓] [↑↓] [↓][↓][↓]

COMPREHENSION

WRITE-UP I

For hydrogen atom or 1-electron ions, the wave functions of 1s and 2s atomic orbitals are given as under:

$$\psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}} \cdot e^{-\frac{Zr}{a_0}}$$

$$\psi_{2s} = \left(\frac{Z}{2a_0}\right)^{1/2}\left(2 - \frac{Zr}{a_0}\right)e^{-\frac{Zr}{a_0}}$$

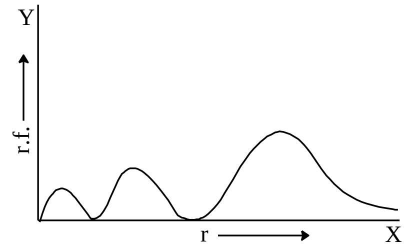
The wave functions for any 1-electron system is given by

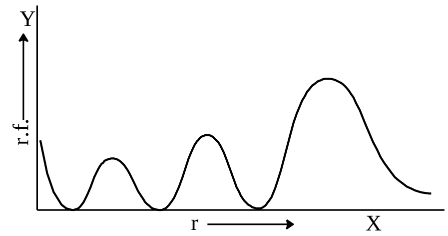
$\psi = k' e^{-kr}$ where k and k′ are constants.

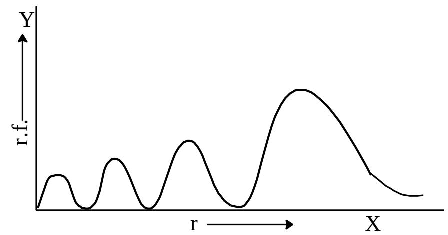
The number of angular nodes are given by the value of angular quantum number and angular node is directional in nature. Total number of nodes is nothing but it is the sum of radial nodes ($n - \ell - 1$) and angular nodes (ℓ).

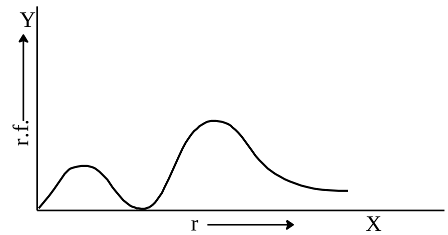
On the basis of the above write up, answer the following questions.

1. Which of the following is the correct representation of plot radial function (r.f.) in Y-axis vs distance from the nucleus in X-axis for 1-elelectron of 3p-atomic orbital?

(A) 

(B) 

(C) 

(D) 

2. If the nodes at infinity is not neglected, then what is the total number of radial and angular nodes of $3p_x$-orbitals?

(A) 4 (B) 3
(C) 5 (D) infinity

3. The distance from the nucleus of the radial nod of 2s-electron of Li^{2+} ion (a_0 = Bohr's radius is equal to

(A) $0.67a_0$ (B) $2a_0$
(C) a_0 (D) $0.5a_0$

WRITE-UP II

According to Bohr's theory, when electron jumps from higher orbit of lower orbit, then it radiates energy in the form of electromagnetic radiations and provides emission spectrum. If

$\Rightarrow \Delta E = E_{n_2} - E_{n_1}$

$$\Delta E = 13.6 \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{eV/atom}$$

$$\Rightarrow \frac{1}{\lambda} = \bar{\nu} = R_H \times Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{eV/atom} \quad \ldots(i)$$

where R_H is Rydberg's constant and $R_H = 10^7\ m^{-1}$

So far in Bohr's theory, we have assumed that nucleus is at rest and the electron is revolving around it. The assumption of nucleus to be at rest is entirely valid if an only if the mass of nucleus is infinite.

So far, for the finite mass of the nucleus, both the nucleus and the electron will revolve around the common centre of mass which lies on the line connecting the two particles.

Thereby Bohr's theory (i.e. expression for energy, Rydberg's constant, etc.) needs to be modified. So Rydberg's constant of Ritz equation (i) needs to be modified. Simply the mass of electron i.e., m_e has to be replaced by reduced mass (μ) which is related as:

$$= \frac{1}{\mu} = \frac{1}{m_N} + \frac{1}{m_e}$$

where m_N = mass of nucleus
m_e = mass of electron

Keep in mind that the minimum amount of energy needed to remove electron or carry out electron from ground state to infinite from gaseous and isolated atom, is known as ionization energy.

4. What will be the value of modified Rydberg's constant, if the ratio of mass of nucleus to the mass of electron is 3:2

(A) $\frac{3}{5} \times 10^7 m^{-1}$ (B) $\frac{5}{3} \times 10^7 m^{-1}$
(C) $\frac{2}{5} \times 10^7 m^{-1}$ (D) $\frac{8}{5} \times 10^7 m^{-1}$

5. If the mass of the nucleus be 5 times than that of the mass of electron and both the nucleus and the electron revolves around the common centre of mass which lies on the same line connecting the two spheres; then what will be the wave length of the transition of 1st line of Balmer series for He^+ ion ?

(A) 8.64×10^{-7}m (B) 1.1×10^{-7}m
(C) 2.16×10^{-7}m (D) $3.5 \times 10^{-7}m^{-1}$

6. If the ratio of mass of electron to mass of nucleus be 1:1 and both the nucleus and the electron revolve around the common centre of mass which lies on the same line connecting the two; then what will be the value of ionization energy for Li^{2+} ions? Given that I.P. of H-atom is 13.6eV/atom.

(A) 61.2 eV (B) 13.6 eV
(C) 54.4 eV (D) 6.8 eV

MATCH THE COLUMN

1. Match the following

	LIST – I		LIST – II
(A)	Orbital angular momentum = $\sqrt{2}\frac{h}{2\pi}$	(p)	d–orbital.
(B)	$mvr = \frac{nh}{2\pi}, n = 1,2,3....$	(q)	Classical analogue of angular momentum.
(C)	Orbital with five fold degeneracy but four lobes	(r)	p–orbital
(D)	N–shell	(s)	No. of waves made by electron is 4.

2. Match the List – I and List – II.

List – I	List - II

(A) Radius of nth orbit	(p) inversely proportional to n^2
(B) Energy of nth Shell	(q) Integral Multiple of $h/2\pi$
(C) Angular momentum of electron	(r) Proportional of n^2
(D) Velocity of electron in nth orbit	(s) Inversely proportional to 'n'

16. Hints to Subjective Assignments

LEVEL – I

1. Longest wavelength is associated with least energy.
3. Total energy emitted = number of photons emitted × energy of 1 photon
6. At the closest distance of approach, the alpha particle will have the same kinetic and potential energies

LEVEL – I

2. a) KE for a H – like atom is same as the magnitude of total energy
5. b) $\lambda \propto 1/m$ if the velocity is same.
7. Use quantization condition for a Bohr orbit in order to evaluate the n values.

17. Answers

17.1 Subjective

LEVEL – I

1. 4689Å
2. 9/5
3. 6.4×10^{24}
4. 12.08 eV
5. a) 435; b) -7.18×10^{-5} ev
6. 6.3×10^{6}m/sec
7. 63.40
8. 7.98×10^{12} m/sec
9. 9.93×10^{-10} ergs
10. 28

LEVEL – II

1. 7.30×10^{18}
2. i) 3.4 eV; ii) 6.654Å
3. a) 2.55 eV b) $2 \leftarrow 4$
4. For Cu = 276 nm; For Mg = 540 nm; For Cs = 654 nm
5. a) 1.46×10^{-9} m; b) λ for He is 4 times greater than the λ of oxygen atom
6. a). I.P. = 13.6 eV; b) λ = 916Å
7. 2.1058×10^{15}
8. 5.42×10^{-12} ergs, 3.67×10^{-5} cm
9. 1:344
10. 978.75 kJ mole^{-1}

17.1 Objective

LEVEL – I

1.	(D)	2.	(A)
3.	(D)	4.	(B)
5.	(A)	6.	(D)
7.	(A)	8.	(C)
9.	(A)	10.	(B)
1.	(A)	2.	(C)
3.	(A)	4.	(C)
5.	(A)	6.	(C)
7.	(C)	8.	(D)
9.	(C)	10.	(D)

LEVEL – II

1.	(A), (C)	2.	(A), (B), (D)
3.	(A), (B), (D)	4.	(B), (D)
5.	(A), (B)	6.	(B), (D)
7.	(A), (B)	8.	(A),(B),(C)
9.	(B), (C)	10.	(A), (D)

COMPREHENSION

1.	(D)	2.	(B)
3.	(A)	4.	(A)
5.	(C)	6.	(A)

MATCH THE COLUMN

1. (A - R), (B - Q), (C – P), (D - S)
2. (A – R), (B – P), (C - Q), (D - S)