ATOMIC STRUCTURE

1. INTRODUCTION

John Dalton 1808, believed that matter is made up of extremely minute indivisible particles, called **atom** which takes part in chemical reactions. These particle can neither be created nor be destroyed. However, modern researches have conclusively proved that atom is no longer an indivisible particle. Modern structure of atom is based on Rutherford's scattering experiment, quantization of energy and wave mechanical model.

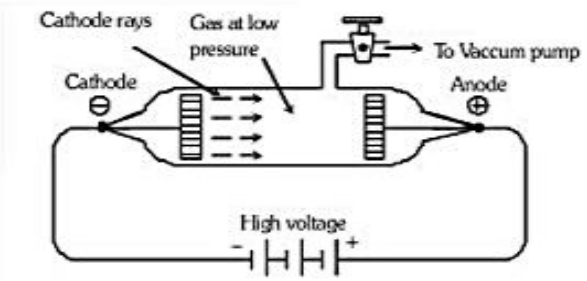
2. COMPOSITION OF ATOM

The works of J.J. Thomson and Ernst Rutherford actually laid the foundation of the modern picture of the atom. It is now verified that the atom consists of several sub-atomic particles like electron, proton, neutron, positron, neutrino, meson etc. Out of these particles, the electron, proton and the neutron are called fundamental subatomic particles.

3. ELECTRON ($_{-1}e^0$, e)

3.1 Electron was discovered by **J.J. Thomson (1897)** and it is a negatively charged particle.

3.2 Cathode rays were discovered by **William Crooke** & **J.J. Thomson** using a cylindrical hard glass tube fitted with two metallic electrodes. This tube was known as discharge tube. They passed electricity (10,000V) through a discharge tube at very low pressure. Blue rays emerged from the cathode. These rays were termed as Cathode rays.



Discharge tube experiment for production of cathode rays

3.3 Properties of Cathode rays

(i) Cathode rays travel in straight line.
(ii) Cathode rays produce mechanical effect, as they can rotate the wheel placed in their path.
(iii) Cathode rays consist of negatively charged particles known as electron.
(iv) Cathode rays travel with high speed.
(v) Cathode rays can cause fluorescence.
(vi) Cathode rays heat the object on which they fall due to transfer of kinetic energy to the object.
(vii) When cathode rays fall on heavy metals, X-rays are produced.
(viii) Cathode rays possess ionizing power i.e., they ionize the gas through which they pass.
(ix) The cathode rays produce scintillation on the photographic plates.
(x) They can penetrate through thin metallic sheets.
(xi) The nature of these rays does not depend upon the nature of gas or the cathode material used in discharge tube.

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Note : The television picture tube is a cathode ray tube in which a picture is produced due to fluorescence on the television screen coated with suitable material. Similarly, fluorescent light tubes are also cathode rays tubes coated inside with suitable materials which produce visible light on being hit with cathode rays.

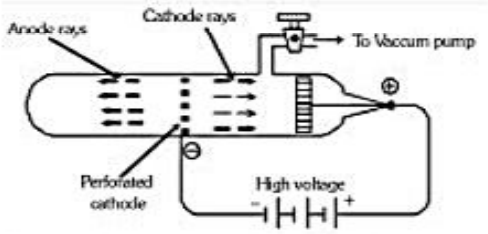
3.4 R.S. Mullikan measured the charge on an electron by oil drop experiment. The charge on each electron is -1.602×10^{-19} C.

3.5 The specific charge (e/m) on electron was first determined by J.J. Thomson.
$e/m = 1.758 \times 10^{-11}$ C/kg

3.6 Rest mass of electron is 9.109×10^{31} kg or, 0.00054 amu

4. PROTON ($_1H^1$, H^+, P)

4.1 Proton was discovered by **Goldstein** and it is positively charged particle. It is a component particle of anode rays. **Goldstein** (1886) used perforated cathode in the discharge tube and repeated cathode rays experiment and observed the formation of anode rays. These rays were also termed as **positive or canal rays**.



Perforated tube experiment for production of anode rays

4.2 Properties of anode rays
(i) Anode rays travel in straight line.
(ii) Anode rays are material particles.
(iii) Anode rays are positively charged.
(iv) Anode rays may get deflected by external magnetic field.
(v) Anode rays also affect the photographic plate.
(vi) The e/m ratio of these rays is smaller than that of electrons.
(vii) Unlike cathode rays, their e/m value is dependent upon the nature of the gas taken in the tube. It is maximum when gas present in the tube is hydrogen.
(viii) These rays produce flashes of light on ZnS screen.

4.3 Charge on proton = 1.602×10^{-19} coulombs

4.4 Mass of proton = 1.673×10^{-27} kg = 1.00728 amu

4.5 Proton is ionized hydrogen atom H^+

4.6 Specific charge of a proton is 9.58×10^7 Coulomb/kg

5. NEUTRON ($_0n^1$, n)

5.1 Neutron was discovered by James Chadwick (1932) according to the following nuclear reaction,

$$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1 \text{ or } {}_5B^{11} + {}_2He^4 \rightarrow {}_7N^{14} + {}_0n^1$$

5.2 The reason for the late discovery of neutron was its neutral nature.

5.3 Mass of neutron = 1.675×10^{-27} kg = 1.00866 amu

5.4 Specific charge of a neutron is zero.

5.5 Neutron is fundamental particle of all the atomic nucleus, except hydrogen or protium.

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Illustration

The mass to charge ratio for A^+ ion is 1.97×10^{-7} kg C^{-1}. Calculate the mass of A atom.

Sol. Given $\frac{m}{e} = 1.97 \times 10^{-7}$

(since $e = 1.602 \times 10^{-19}$ C) $\therefore m = 1.97 \times 10^{-7} \times 1.602 \times 10^{-19}$ kg

Exercise

Arrange the following particles in increasing order of values of e/m ratio : Electron (e), proton (p), neutron (n) and α-particle (α) -

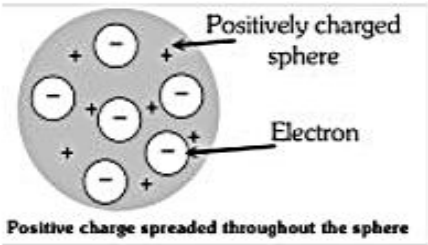
(A) n, p, e, α (B) n, α, p, e (C) n, p, α, e (D) e, p, n, α

Ans. **(B)**

6. THOMSON'S MODEL

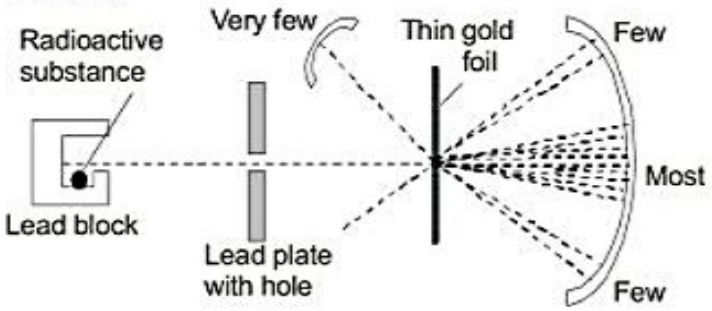
After discovery of electron and proton attempts were made to find out their arrangement in an atom. The first simple model was proposed by J.J. Thomson known as Thomson's atomic model.
He proposed that the positive charge is spread over a sphere of the size of the atom (i.e. 10^{-8} cm radius) in which electrons are embedded to make the atom as whole neutral.

This model could not explain the experimental results of Rutherfords α-particle scattering, therefore it was rejected.



7. RUTHERFORD'S MODEL

Rutherford carried out α-particles scattering experiment by the bombardment of high speed α-particle on thin foil of gold, emitted from radium and gave the following observations, which was based on his experiment.



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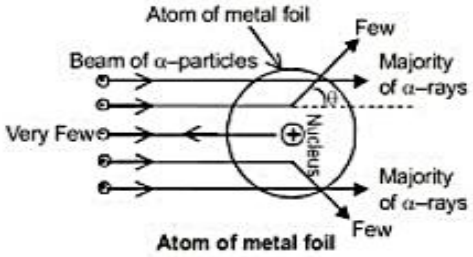
7.1 Observations :

(a) Most of the α - particles (nearly 99%) continued with their straight path.

(b) Some of the α - particles passed very close to the centre of the atom and deflected by small angles.

(c) Very few particles thrown back (180°).



7.2 Main features :

(a) Most of the α - particles were continued their straight path that means most of the space inside the atom is empty.

(b) The centre of an atom has a positively charged body called **nucleus** which repel positively charged α - particles and thus explained the scattering phenomenon.

(c) Almost all mass of an atom is concentrated in its nucleus.

(d) The size and volume of the nucleus is very small as compared to the total size and volume of atom.

7.3 Properties of the Nucleus

(i) Nucleus is a small, heavy, positively charged part of the atom and is located at the centre of the atom.

(ii) All the positive charge of atom (i.e. protons) are present in nucleus.

(iii) Nucleus contains neutrons and protons, and hence these particles collectively are also referred to as nucleons.

(iv) The size of nucleus is measured in Fermi (1 Fermi = 10^{-13} cm = 10^{-15} m). Generally, the radius of the nucleus (r_n) is given by the following relation :

$$r_n = r_o \times A^{1/3}$$

where r_0 is a constant and A is the mass number.

(v) The Volume of the nucleus is about 10^{-45} m^3 and that of atom is 10^{-27} m^3 , i.e., volume of the nucleus is 10^{-15} times that of an atom.

7.4 Distance of closest approach : When the α-particle approaches the nucleus to made a head-on collision with a the nucleus, the α-particle approaches the nucleus until coulombic potential energy of repulsion , $k\frac{Z_1Z_2e^2}{r}$, becomes equal to its initial K.E., $\frac{1}{2}$ $m.v^2$.

Thus $\frac{1}{2}mv^2 = k\frac{Z_1Z_2e^2}{r}$

Hence, the distance of closest approach, $r = \frac{k\ z_1z_2e^2}{\left(\frac{1}{2}mv^2\right)}$

The nucleus must be further smaller than the distance of closest approach.

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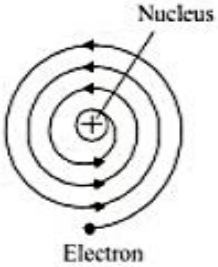
7.5 Drawbacks of Rutherford's model

(i) It does not obey the Maxwell theory of electrodynamics. According to this theory a small charged particle moving around an oppositely charged centre continuously loses its energy. If an electron does so, it should also continuously lose its energy and should set up spiral motion ultimately falling into the nucleus.



(ii) It could not explain the line spectra of atom.

Illustration

1. Atomic radius is of the order of 10^{-8} cm and nuclear radius is of the order of 10^{-13} cm. Calculate what fraction of atom is occupied by nucleus ?

Sol. Volume of nucleus $= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (10^{-13})^3 \text{ cm}^3$

Volume of atom $= \frac{4}{3}\pi (10^{-8})^3 \text{ cm}^3$, $\frac{V_N}{V_{Atom}} = \frac{10^{-39}}{10^{-24}} = 10^{-15}$

$V_{Nucleus} = \mathbf{10^{-15} \times V_{Atom}}$

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

Sol. $\frac{1}{2} m_\alpha v_\alpha^2 = \frac{kz_1z_2}{r_{min}^2} = \frac{k(2e)(63e)}{r_{min}^2}$

$v_\alpha = \frac{k(2e)(63e)}{m_\alpha . r_{min}^2}$

$v\alpha = \sqrt{\frac{2k.2e.63e}{m_\alpha . r_{min}^2}} = \mathbf{6.3 \times 10^6 \text{ m/s}}$

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Exercise

Assuming a spherical shape for fluorine nucleus, calculate the radius and the nuclear density of fluorine nucleus of mass number 19.

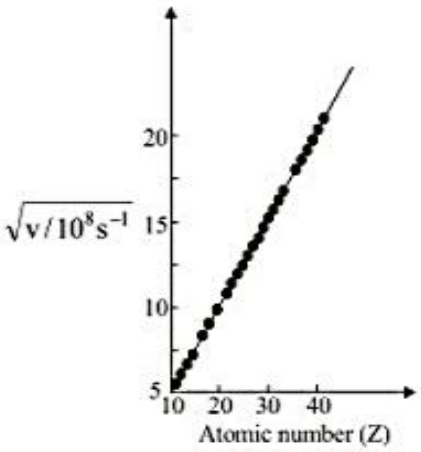
Ans. 3.73×10^{-13} cm, $7.616 = 10^{13}$ g cm^{-3}

8. MOSELEY EXPERIMENT (DISCOVERY OF ATOMIC NUMBER)

Moseley (1912–1913), investigated the X–rays spectra of 38 different elements, starting from aluminium and ending in gold. He measured the frequency of principal lines of a particular series (the α-lines in the K series) of the spectra. It was observed that the frequency of a particular spectral line gradually increased with the increase of atomic mass of the element. But, it was soon realised that the frequency of the particular spectral line was more precisely related with the serial number of the element in the periodic table which he termed as atomic number (Z). He presented the following relationship :

$$\sqrt{v} = a(Z - b)$$

where, v = frequency of X-rays, Z=atomic number, 'a' and 'b' are constants. When the values of square root of the frequency were plotted against atomic number of the elements producing X–rays, a straight line was obtained.



Illustration

If the straight line is at an angle 45° with b= 1 calculate frequency when atomic number Z is 50.

(A) 2000 (B) 2010 (C) 2401 (D) None

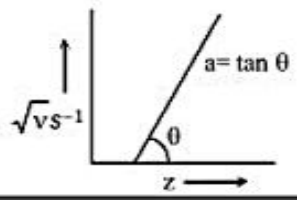
Ans. (C)

Sol. $\sqrt{v} = \tan 45° = 1 = a$

$b = 1$

$\therefore \sqrt{v} = 50 - 1 = 49$

$v = 2401 s^{-1}$.



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Exercise

What is atomic number Z when $v = 2500\ s^{-1}$ and value of a = 1 and b = 1

(A) 50 (B) 40 (C) 51 (D) 53

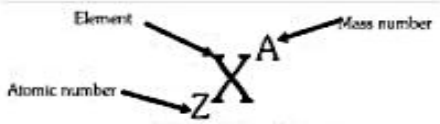
Ans. (C)

9. SOME ATOMIC TERMS

9.1 **Atomic number** = Number of unit positive charge on nucleus = Number of protons in nucleus = Number of electrons in neutral atom.
Two different elements can never have identical atomic number.

9.2 **Mass number (A)** = Number of protons + Number of neutrons or Atomic number (Z)
Hence Number of neutrons = A - Z .

The atom of an element X having mass number (A) and atomic number (Z) may be represented by a symbol,



e.g. ${}_9F^{19}$, ${}_8O^{16}$, ${}_7N^{14}$ etc.

9.3 A part of an atom up to penultimate shell is a **kernel** or atomic core.

9.4 Negative ion (anion) is formed by gaining electrons and positive ion (cation) by the loss of electrons.

9.5 **Isotopes :** Atoms of an element with the same atomic number but different mass number.

eg.	${}_1H^1$	${}_1H^2$	${}_1H^3$
	Protonium	deuterium	Tritium

9.6 **Isodiapheres :** The elements which have same value of (n – p) is called Isodiapheres.

eg.	${}_7N^{14}$	${}_8O^{16}$
Values of (n – p)	0	0

9.7 **Isotone :** Elements which contain same no. of neutron is called **Isotone**.

eg.	${}_{14}Si^{30}$	${}_{15}P^{31}$	${}_{16}S^{32}$
number of neutrons	16	16	16

9.8 **Isobar :** The two different atoms which have same mass number but different atomic number is called Isobar.

eg. ${}_{18}Ar^{40}$ ${}_{19}K^{40}$ ${}_{20}Ca^{40}$

9.9 **Isoelectronic :** Ion or atom or molecule which have the same number of electron is called Isoelectronic species.

eg.	${}_{17}Cl^-$	${}_{18}Ar$	${}_{19}K^+$	${}_{20}Ca^{+2}$
No. of electrons	18	18	18	18

9.10 **Isosters :** Substance which have same number of electrons and the same number of total atoms are called Isosters.

eg.	CO_2	N_2O
No. of electrons	22	22
No. of atoms	3	3

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Illustration

1. From the following list of atoms, choose the isotopes, isobars and isotones -

$^{16}_{8}O$, $^{39}_{19}K$, $^{235}_{92}U$, $^{40}_{19}K$, $^{14}_{7}N$, $^{18}_{8}O$, $^{14}_{6}C$, $^{40}_{20}Ca$, $^{238}_{92}U$

Sol. Isotopes : ($^{16}_{8}O$, $^{18}_{8}O$), ($^{39}_{19}K$, $^{40}_{19}K$), ($^{235}_{92}U$, $^{238}_{92}U$)

Isobars : ($^{40}_{19}K$, $^{40}_{20}Ca$), ($^{14}_{7}N$, $^{14}_{6}C$)

Isotones : ($^{39}_{19}K$, $^{40}_{20}Ca$), ($^{14}_{6}C$, $^{16}_{8}O$)

2. Total number of electrons, protons and neutrons present in the nucleus of $_{92}U^{238}$ is

(A) e = 92, p = 92, n= 146 (B) e = 92, p = 92, n= 148

(C) e = 0, p = 92, n= 146 (D) None of these

Ans. (C)

Sol. There is no electron in the nucleus.

$n_e = 0$, $n_p = 92$, $n_n = 238–92 = 146$

Exercise

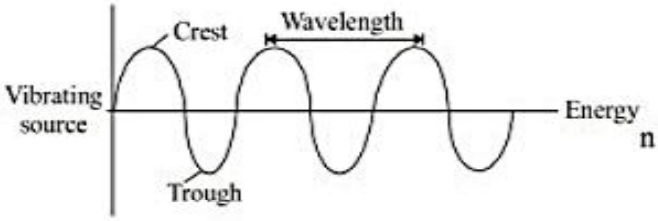
Nitrogen atom has Atomic number 7 & oxygen has Atomic number 8. Calculate the total number of electrons in nitrate ion -

Ans. 32

10. WAVE

A wave motion is a means of transferring energy from one point to another point without any actual transportation of matter between these points. When we throw a piece of stone on the surface of water in a pond, we observe circles of ever increasing radius, till they strike the wall of the pond. When we put a piece of cork on the surface of this water, we observe that the cork moves up and down as the wave passes, but the piece does not travel along with the waves. The water waves carries the energy but there is no transfer of matter. Thus in a wave motion, disturbance travels through the medium, but the medium does not travel along with the disturbance.

Some important terms related with wave motion.



(i) Wave length (λ) : The distance between two adjacent crest or trough of the wave (or the distance between two similar neighbouring points)

OR

(ii) Time period (T) : Time for one complete oscillation of wave is called the period (T).

Time taken by the wave to travel a distance equal to one wavelength. If C is the speed of wave, then $C = \frac{\lambda}{T}$

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(iii) Frequency (v) : Number of oscillations per unit time is called frequency.

$$\nu = \frac{C}{\lambda}$$

(iv) Wave number ($\bar{\nu}$) : Number of wavelength per unit length.

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

(v) Amplitude (A) : It is the height of crest or depth of a trough of a wave.

10.1 Electromagnetic Wave :

Light is also a type of wave which is known as electromagnetic wave i.e. wave consisting of oscillating electric and magnetic field.

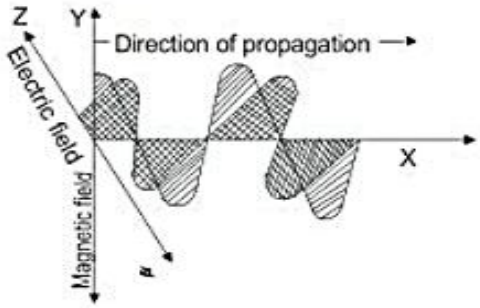
There are various types of electromagnetic waves (radiation) which differs from one another in wavelengths e.g. Visible light, ultraviolet rays, X-rays, infra-red rays, radio waves etc.

Characteristics of electromagnetic radiations:

(a) All electromagnetic waves move or travel with the same speed equal to that of light.

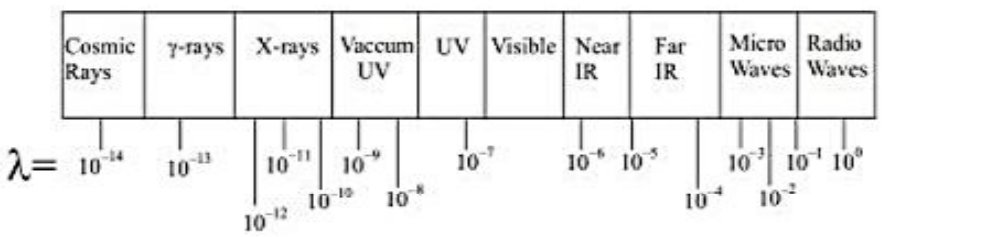
(b) They do not require any medium to propagate.

(c) These consist of electric and magnetic field that oscillate in the direction perpendicular to each other and to the direction in which the wave propagates (as shown in above diagram)



10.2 Electromagnetic Spectrum

Arrangement of various types of electromagnetic radiations in order of their increasing (or decreasing) wavelengths or frequencies is known as electromagnetic spectrum.



11. SPECTRUM

When light coming from a source is dispersed by a prism, light of different wavelength are deviated through different angles and get separated. This phenomenon is called dispersion and such a dispersed light may be received on a photographic plate or it may be viewed directly by eye. A collection of dispersed light giving its wavelength composition is called a spectrum.

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11.1 Types of spectrum

1. Emission spectrum : A substance gets excited on heating at a very high temperature or by giving energy and subsequently radiations are emitted. These radiations when analysed with the help of spectroscope, spectral lines are obtained. A substance may be excited-

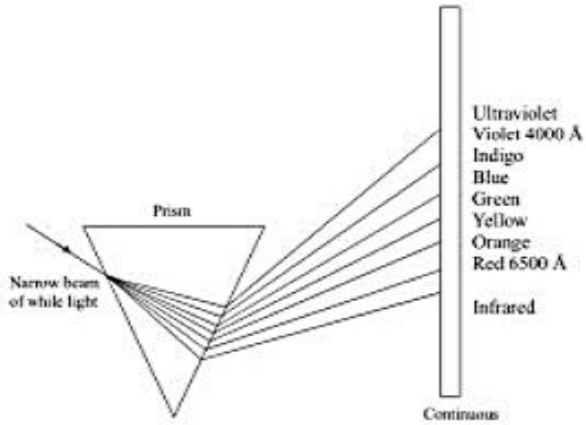
(a) By heating at a higher temperature.

(b) By passing electric current at a very low pressure in a discharge tube filled with a gas.

(c) By passing electric current into metallic filament.

Emission spectra may be classified as :

(i) **Continuous spectrum :** When sunlight is passed through a prism, it gets dispersed into continuous bands of different colours. If the light of an incandescent object is resolved through prism or spectroscope, it also gives continuous spectrum of colours.



Continuous spectrum of white light

(ii) **Line spectrum :** If the radiations obtained by the excitation of a substance are analysed with the help of a spectroscope, a series of thin bright lines of specific colours are obtained. There is dark space in between two consecutive lines. This type of spectrum is called line spectrum or atomic spectrum. For example on heating sodium chloride or any other salt of sodium in Bunsen flame bright yellow light is emitted. The emitted light when viewed through a spectroscope two isolated yellow lines separated by dark space are obtained. The wave lengths of these lines are 5890Å and 5896Å.

2. **Absorption spectrum**

When the white light of an incandescent substance is passed through any other substance, this substance absorbs the radiations of certain wavelength from the white light. On analysing the transmitted light we obtain a spectrum in which dark lines of specific wave lengths are observed. These lines constitute the absorption spectrum. The wave length of the dark lines correspond to the wavelength of light absorbed.

12. MAXWELL THEORY OF ELECTROMAGNETIC WAVE

(i) All the radiations have wave nature which explains interference (linear superposition) and diffraction.

(ii) They consist of oscillating electric and magnetic field perpendicular to each other and to the direction of propagation.

(iii) All the radiations (radio waves, micro waves, infra red waves, visible, UV, X-rays, γ-rays) travel at the speed of light in vaccum.

(iv) Energy of electromagnetic wave is proportional to amplitude and not linked with frequency of waves.

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Draw backs : This theory could not explain the following
(a) Phenomenon of black body radiations (b) Photoelectric effect (c) Line spectra of atoms

13. PLANCK'S QUANTUM THEORY

According to this theory atoms or molecules could emit or absorb energy only in discrete quantities (small packets) and not in any arbitrary amount. Planck gave the name quantum to the smallest quantity of energy that can be emitted in the form of E.M. radiation.
The energy of a photon is proportional to its frequency and is given by

$E = h\upsilon$ where $h = 6.626 \times 10^{-34}$ Jsec.

A body can emit or absorb energy only in terms of the integral multiples of quantum, i.e.

$E = n \,.\, h\upsilon$, where $n = 1, 2, 3, ...$

i.e. a body can emit or absorb energy as $h\upsilon$, $2h\upsilon$ ..... but it can not emit or absorb energy in fractional values of $h\upsilon$ such as $1.5\, h\upsilon$, $2.5\, h\upsilon$.

Einstein supported the planck's theory and explained the photoelectric effect considering that electromagnetic radiations also propagate in the form of photon. Energy of each photon depends on frequency of light $\left(E = h\upsilon = \frac{hc}{\lambda}\right)$.

Since wave character of light explains the interference and diffraction phenomenon while the particle character explains, black body radiations and photoelectric effect, the light was considered to have wave as well as particle character [Dual character of light.]

1. Wave nature : diffraction, interference, polarisation.
2. Particle nature : photoelectric effect.

Illustration

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

Sol. $\nu = 3.4\text{MHz} = 3.4\times10^{6}\text{HZ} = 3.4\times10^{6}\,s^{-1}$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{8} ms^{-1}}{3.4 \times 10^{6} s^{-1}} = 88.2m$$

Energy, $E = h\nu = 6.626 \times 10^{-34} \times 3.4 \times 10^{6}$ J
$= 2.253 \times 10^{-27}$J
Energy per mole of photon $= 6.02 \times 10^{23} \times 2.53 \times 10^{-27}$ J mol^{-1}
$= 1.356 \times 10^{-3}$ J mol^{-1}

2. The vapours of Hg absorb some electrons accelerated by a potential diff. of 4.5 volt as a result of which light is emitted. If the full energy of single incident e^- is supposed to be converted into light emitted by single Hg atom, find the wave no. of the light.

Sol. $E = e.V = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{e.V}$ **$= 3.63 \times 10^{6}$ m^{-1}**

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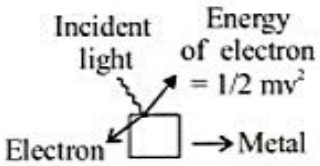
Exercise

Calculate the number of photons emitted in 10 hours by a 60 W(J/s^{-1}) sodium lamp (λ of photon = 5893 Å)

Ans. 6.43×10^{24}

14. PHOTOELECTRIC EFFECT

Emission of electrons from a metal surface when exposed to light radiations of appropriate wavelength is called photoelectric effect. The emitted electrons are called **photoelectrons**.



Work function or threshold energy may be defined as the minimum amount of energy required to eject electrons from a metal surface.
According to Einstein,
Maximum kinetic energy of the ejected electron = absorbed energy - work function

$$\frac{1}{2}\, mv^2_{max} = h\nu - h\nu_0 = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$$

where, ν_0 and λ_0 are threshold frequency and threshold wavelength respectively.

Stopping potential : The minimum potential at which the photoelectric current becomes zero is called stopping potential.
If V_0 is the stopping potential , then

$$eV_0 = h\,(\nu - \nu_0) \text{ or } V_0 = \frac{h(\nu - \nu_0)}{e} = \frac{K.E._{max.}}{e}$$

Some facts of Photoelectric Effect

(i) There is no time lag between incidence of light and emission of photoelectrons.

(ii) For emission of photoelectrons, the frequency of incident light must be equal to or greater than the threshold frequency.

(iii) Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.

(iv) The maximum kinetic energy of photoelectrons depends on the frequency of incident radiation; but, it is independent of the intensity of light used.

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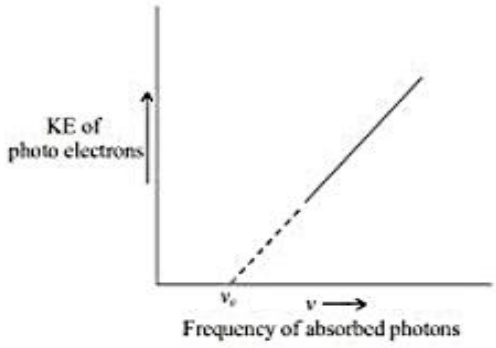

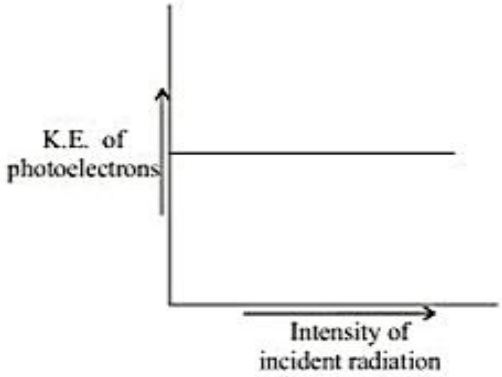

Illustration

1. The minimum energy required to overcome the attractive forces electron and surface of Ag metal is 7.52 $\times 10^{-19}$ J. Calculate the maximum K.E. of electron ejected out from Ag which is being exposed to U.V. light of $\lambda = 360$ Å

Sol.

$$\text{Energy absorbed} = \frac{hc}{\lambda}$$

$$= \frac{6.62 \times 10^{-27} \times 3.0 \times 10^{10}}{360 \times 10^{-8}}$$

$$= 5.52 \times 10^{-11} \text{ erg}$$

$$= 5.52 \times 10^{-18} \text{ Joule}$$

$$\text{Maximum kinetic energy of electron} = (7.52 \times 10^{-19}) - (0.552 \times 10^{-19})$$

$$= 6.968 \times 10^{-19} \text{ Joule}$$

2. A metal was irriadated by light of frequency $3.2 \times 10^{15}\ S^{-1}$. The photoelectron produced had its KE, 2 times the KE of the photoelectron which was produced when the same metal was irriadated with a light of frequency $2.0 \times 10^{15}\ S^{-1}$. What is work function.

Sol. $E_1 = h\nu_1 - \phi_0$, $E_2 = h\nu_2 - \phi_0$

$$\frac{E_1}{E_2} = \frac{h\nu_1 - \phi_0}{h\nu_2 - \phi_0}, 2 = \frac{h \times 3.2 \times 10^{15} - \phi_0}{h \times 2 \times 10^{15} - \phi_0}$$

$$\boldsymbol{\phi_0 = 319.2 \text{ KJ/Mol}}$$

Exercise

Light of wavelength 4000 Å falls on the surface of cesium. Calculate the maximum kinetic energy of the photoelectron emitted. The critical wavelength for photoelectric effect in cesium is 6600 Å

Ans. 1.95×10^{-19} Joule

15. BOHR'S ATOMIC MODEL

This model was based on the quantum theory of radiation and the classical law of physics. It gave new idea of atomic structure in order to explain the stability of the atom and emission of sharp spectral lines.

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15.1 Postulates

(i) The atom has a central massive core nucleus where all the protons and neutrons are present. The size of the nucleus is very small.

(ii) The electron in an atom revolve around the nucleus in certain discrete orbits. Such orbits are known as stable orbits or non - radiating or stationary orbits.

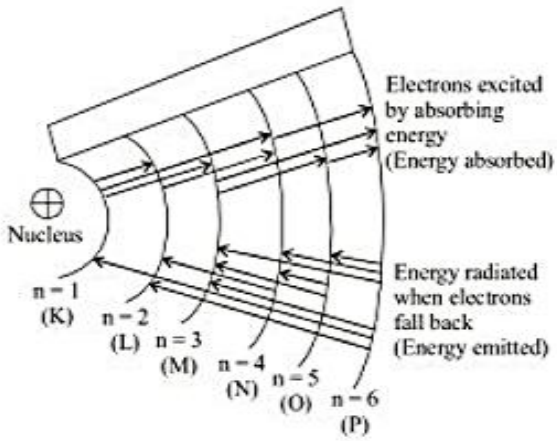
(iii) An electron can move only in those permissive orbits in which the angular momentum (mvr) of the electron is an integral multiple of $h/2\pi$ Thus,

$$mvr = n\frac{h}{2\pi}$$

where, m = mass of the electron, r = radius of the electronic orbit, v = velocity of the electron in its orbit.

(iv) The angular momentum can be $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}, \ldots\ldots \frac{nh}{2\pi}$. This principal is known as quantization of angular momentum. In the above equation 'n' is positive integer which has been called as principal quantum number. It can have the values n=1,2,3, ------- (from the nucleus). Various energy levels are designed as K(n=1), L(n=2), M(n=3) ------- etc. Since the electron present in these orbits is associated with some energy, these orbits are called energy levels.

(v) The emission or absorption of radiation by the atom takes place when an electron jumps from one stationary orbit to another.



(vi) The radiation is emitted or absorbed as a single quantum (photon) whose energy is equal to the difference in energy of the electron in the two orbits involved. Thus, $\Delta E = h\nu$, where h = Planck's constant and ν, frequency of the radiant energy. Hence the spectrum of the atom will have certain fixed frequency.

(vii) The lowest energy state (n=1) is called the ground state. When an electron absorbs energy, it gets excited and jumps to an outer orbit. It has to fall back to a lower orbit with the release of energy.

15.2 Advantage of Bohr's theory

(i) Bohr's theory satisfactorily explains the spectra of species having one electron, viz. hydrogen atom, He^+, Li^{2+} etc.

(ii) Calculation of the radius of the Bohr's orbit:

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

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

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

Where : K = constant = $\frac{1}{4\pi\varepsilon_0} = 9 \times 10^9\ Nm^2/C^2$

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

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

or, $v^2 = \frac{KZe^2}{mr}$ ...(1)

From the postulate of Bohr,

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

or, $v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$ ...(2)

From equation (1) and (2) :

$\therefore \quad r = \frac{n^2h^2}{4\pi^2mKZe^2}$

On putting the value or e, h, m,

$$\boxed{r = 0.529 \times \frac{n^2}{Z} \text{Å}}$$

(iii) Calculation of velocity of an electron in Bohr's orbit :

Velocity of the revolving electron in n^{th} orbit is given by –

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

Putting the value of r in above equation

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

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

on putting the values of e and h,

$$v = 2.188 \times 10^6 \times \frac{Z}{n} m/sec$$

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(iv) Calculation of energy of an electron :

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

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

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

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

Hence, $T.E. = \frac{1}{2}mv^2 - \frac{KZe^2}{r}$ .....(3)

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

Substituting the value of mv^2 in the equation (3)

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

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

Substituting the value of 'r' in the equation of T.E. .

$$E = -\frac{kZe^2}{2} \times \frac{4\pi^2 Ze^2 mk}{n^2h^2} = -\frac{2\pi^2 Z^2 e^4 mk^2}{n^2h^2}$$

Thus, the total energy of an electron in n^{th} orbit is given by

$$E_n = \frac{2\pi^2 Z^2 e^4 mk^2}{n^2h^2}$$

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

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

$$= -313.6 \times \frac{Z^2}{n^2} \text{ Kcal / mole}$$

(v) Relation between P. E., K. E. & T. E. :

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

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

(vi) Calculation of the number of revolutions of the electron in an orbit per second

$$\text{Number of revolutions per sec.} = \frac{\text{velocity of the electron}}{\text{Circumference of the orbit}}$$

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$$= \frac{v}{2\pi r} = \frac{nh}{2\pi mr} \times \frac{1}{2\pi r}$$ [On substituting the value of v from $mvr = \frac{nh}{2\pi}$]

$$= \frac{nh}{4\pi^2 mr^2}$$

No. of revolutions per second $= \frac{nh}{4\pi^2 mr^2} = \frac{nh}{4\pi^2 m} \times \left(\frac{4\pi^2 mze^2k}{n^2h^2}\right)^2$

$$= \frac{4\pi^2 mz^2e^4k^2}{n^3h^3}$$

Time taken for one revolution (Time period) $= \frac{4\pi^2 mr^2}{nh} = \frac{n^3h^3}{4\pi^2 mz^2e^4k^2}$

Illustration

1. The radius of the an orbit of hydrogen atom is 0.85 nm. Calculate the velocity of electron in this orbit.

Sol. $r = r_0 n^2$ $\quad n^2 = 16,$
$n = 4$

$V = V_0 \cdot \frac{Z}{n} = 2.186 \times 10^6 \times \frac{1}{4}$ **$= 5.44 \times 10^5$ m/s**

2. The energy of an excited H-atom is –3.4 eV. Calculate angular momentum of e^- in the given orbit.

Sol. $E = -13.6 \frac{Z^2}{n^2} \Rightarrow n^2 = \frac{13.6}{3.4} = 4$

$n = 2$

Angular momentum $= mvr = \frac{nh}{\pi} = \frac{h}{\pi}$

3. Ionisation energy of hydrogen atom is 13.6 eV. Calculate the ionisation energy for Be^{3+} in the first excited state.

Sol. Ionization energy of hydrogen = $-E_1$ (Energy of first Bohr orbit)

$$I.E. = -E_1 = -\left(-13.6\frac{Z^2}{n^2}\right) = +13.6 \times \frac{1^2}{1^2} = 13.6\,eV$$

Ionization energy of Be^{3+}
$Z = 4$
$n = 2$ (for 1st excited state)

$$I.E. = \left(13.6\frac{4^2}{2^2}\right) = 54.4\ eV$$

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Exercise

The ionization energy of H-atom is 13.6 eV. Calculate the ionization energy of Li^{+2} ion -

Ans. **122.4 eV**

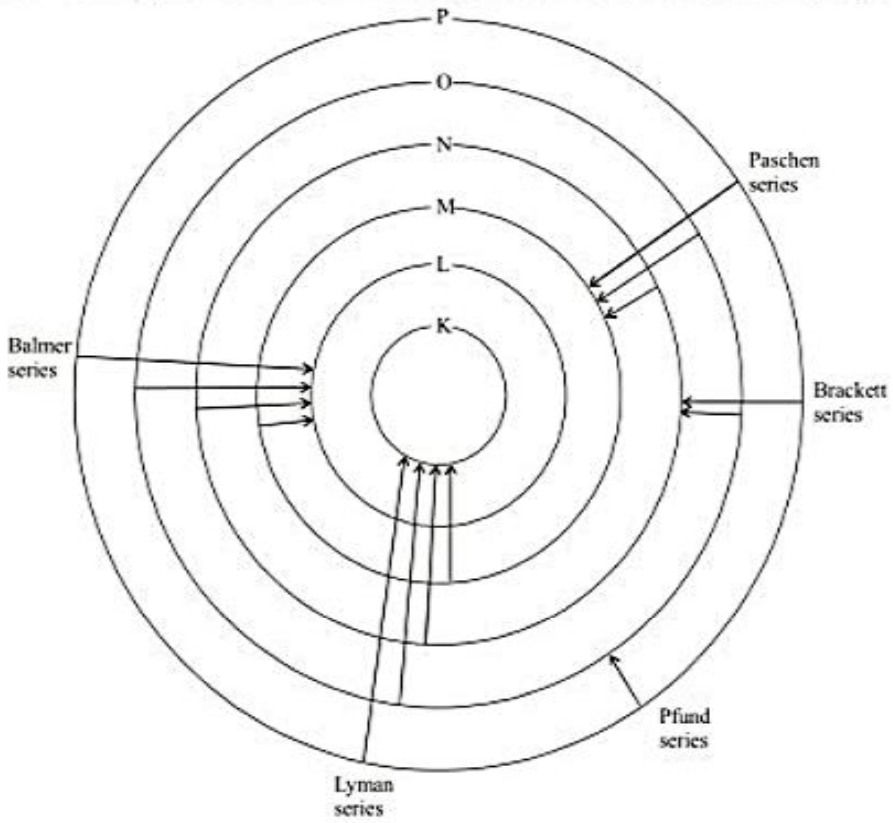
15.3 Hydrogen Spectrum

Hydrogen spectrum is an example of line or atomic emission spectrum. When an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted. This light shows discontinuous line spectrum of several isolated sharp lines through prism. All these lines of H-spectrum have Lyman, Balmer, Paschen, Barckett, Pfund and Humphrey series. These spectral series were named by the name of scientist discovered them. To evaluate wavelength of various H-lines Rydberg introduced the following expression,

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

Where R is a constant known as Rydberg's constant its value is 109, 67800 m^{-1} .

Although H- atom consists only one electron yet it's spectra consist of many spectral lines because electrons in different hydrogen atoms absorb different amount of energies and are excited to different energy levels. Since life time of electrons in these excited states is very small, they return to some lower energy level or even to the ground state in one or more jumps



Maximum number of lines produced when an electron jumps from nth level to ground level $= \frac{n(n-1)}{2}$.

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(A) Lyman Series

(a) It is a first series of spectral series of H.

(b) It was found out in ultraviolet region in 1898 by ***Lyman***.

(c) It's value of $n_1 = 1$ and $n_2 = 2, 3, 4$ where 'n_1' is ground state and 'n_2' is called excited state of electron present in a H - atom.

(d) If the electron goes to $n_1 = 1$ from $n_2 = 2$ — first Lyman series
If the electron goes to $n_1 = 1$ from $n_2 = 3$ — Second Lyman series
If the electron goes to $n_1 = 1$ from $n_2 = 4$ — third Lyman series ----- so on.

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

(f) For marginal line or limiting line $n_2 = \infty$. Hence the wavelength of marginal line $= \frac{n_1^2}{R_H}$ for all series.

So, for lyman series it is $\frac{1}{R_H}$

(B) Balmer series :

(a) It is the second series of H-spectral series.

(b) It was found out in 1892 in visible region by **Balmer**.

(c) Balmer series was found out before all series because it was found in visible region.

(d) It's value of $n_1 = 2$ and $n_2 = 3, 4, 5$ .....

(e) If the electron goes to $n_1 = 2$ from $n_2 = 3$ — First Balmer series
If the electron goes to $n_1 = 2$ from $n_2 = 4$ — Second Balmer series
If the electron goes to $n_1 = 2$ from $n_2 = 5$ — third Balmer series .... so on

(f) The wavelength of marginal line of Balmer series $= \frac{n_1^2}{R_H} = \frac{2^2}{R_H} = \frac{4}{R_H}$

(g) $\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$ where $n_2 > 2$ always

(C) Paschen series :

(a) It is the third series of H - spectrum.

(b) It was found out in infra red region by ***Paschen***.

(c) It's value of $n_1 = 3$ and $n_2 = 4, 5, 6$ .....

(d) If the electron goes to $n_1 = 3$ from $n_2 = 4$ — First paschen series
If the electron goes to $n_1 = 3$ from $n_2 = 5$ — second paschen series
If the electron goes to $n_1 = 3$ from $n_2 = 6$ — third paschen series ------ so on.

(e) The wavelength of marginal line of paschen series $= \frac{n_1^2}{R_H} = \frac{3^2}{R_H} = \frac{9}{R_H}$.

(f) $\frac{1}{\lambda} = R_H\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right]$ where $n_2 > 3$ always.

(D) Brackett series :

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

(b) It was found out in infra red region by **Brackett**.

(c) It's value of $n_1 = 4$ and $n_2 = 5, 6, 7$ .....

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(d) If the electron goes to $n_1 = 4$ from $n_2 = 5$ — first brackett series
If the electron goes to $n_1 = 4$ from $n_2 = 6$ — second brackett series
If the electron goes to $n_1 = 4$ from $n_2 = 7$ — third brackett series ------ so on.

(e) The wavelength of marginal line of brackett series = $\frac{n_1^2}{R_H} = \frac{4^2}{R_H} = \frac{16}{R_H}$

(f) $\frac{1}{\lambda} = R_H\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right]$ Where $n_2 > 4$ always.

(E) Pfund series :

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

(b) It was found out in infra red region by Pfund.

(c) It's value of $n_1 = 5$ and $n_2 = 6, 7, 8$ .....

(d) If the electron goes to $n_1 = 5$ from $n_2 = 6$ — first Pfund series
If the electron goes to $n_1 = 5$ from $n_2 = 7$ — second Pfund series
If the electron goes to $n_1 = 5$ from $n_2 = 8$ — third Pfund series -----so on.

(e) The wavelength of marginal line of Pfund series = $\frac{n_1^2}{R_H} = \frac{5^2}{R_H} = \frac{25}{R_H}$

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

(F) Humfrey series :

(a) It is the sixth series of H - spectrum.

(b) It was found out in infra-red region by ***Humfrey***.

(c) It's value of $n_1 = 6$ and $n_2 = 7, 8, 9$ ---------

(d) If the electron goes to $n_1 = 6$ from $n_2 = 7$ — first Humfrey series
If the electron goes to $n_1 = 6$ from $n_2 = 8$ — second Humfrey series
If the electron goes to $n_1 = 6$ from $n_2 = 9$ — third Humfrey series ... so on.

(e) The wavelength of marginal line of Humfrey series = $\frac{n_1^2}{R_H} = \frac{6^2}{R_H} = \frac{36}{R_H}$

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

Note : α - line = first line of series.

Similarly β-line = second line of series

For example : First line (α-line) of Paschen series will be from $n_2 = 4$ to $n_1 = 3$

15.4 Calculation of Rydberg Constant from bohr's atomic model

Suppose that an electron transist from first energy level to second energy level. Then, the change of energy is given by

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

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$$\text{or, } = \left[\frac{-2\pi^2 mZ^2e^4k^2}{n_2^2h^2}\right] - \left[\frac{-2\pi^2 mZ^2e^4k^2}{n_1^2h^2}\right] \qquad \text{or, } \frac{hc}{\lambda} = \frac{-2\pi^2 mZ^2e^4k^2}{h^2} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\text{or, } \frac{1}{\lambda} = \frac{2\pi^2 mz^2e^4k^2}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = R_H.Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{or, } R_H = \frac{2\pi^2 me^4k^2}{ch^3} = \text{Rydberg constant}$$

Illustration

1. Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.

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

$$\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{4^2}\right]$$ (For H-atom, Z = 1, Lyman series; $n_1 = 1$)

$\boldsymbol{\lambda = 9.7 \times 10^{-8}}$ **m**

2. Calculate the wave no. for the shortest wavelength transition in the Balmer series of atomic hydrogen.

Sol. For shortest wavelength $n_2 \to \infty$

$$\overline{V} = R\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] = \frac{R}{4} = \mathbf{27419.25\ cm^{-1}}$$

3. Calculate the energy emitted when electrons of 1.0 gm atom of Hydrogen undergo transition giving the spectral lines of lowest energy in visible region of its atomic spectra. Given that, $R_H = 1.1 \times 10^7\ m^{-1}$, $c = 3 \times 10^8$ m / sec, $h = 6.625 \times 10^{-34}$ J sec.

Sol. Visible region of H- spectrum correspond to Balmer series $n_1 = 2$, $n_2 = 3$ (for minimum energy transition)

$$1/\lambda = R_H = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \Rightarrow \frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{3^2}\right] \Rightarrow \frac{1}{\lambda} = 1.1 \times 10^7\left[\frac{1}{4} - \frac{1}{9}\right]$$

[RH = 109677 cm^{-1} = 109677 × 100 $m^{-1} \approx 1.1\ 10^7\ m^{-1}$]

$$\lambda = 6.55 \times 10^{-7}\ m$$

$$E = \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{6.55 \times 10^{-7}} = \mathbf{3.03 \times 10^{-19}\ Joule}$$

∴ Energy released by 1 gm atom of H (1 mol)

$= 3.03 \times 10^{-19} \times 6.023 \times 10^{23} = 18.25 \times 10^4$ J $= 182.5$ k J

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Exercise

Calculate ratio of wavelength of limiting line of Balmer and Paschen series for an atom .

Ans. 4/9

15.5 Failure of Bohr Model

(i) Bohr theory was very successful in predicting and accounting the energies of line spectra of hydrogen i.e. one electron system. It could not explain the line spectra of atoms containing more than one electron.

(ii) This theory could not explain the presence of multiple spectral lines.

(iii) This theory could not explain the splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect). The intensity of these spectral lines was also not explained by the Bohr atomic model.

(iv) This theory could not explain uncertainty principle.

16. PARTICLE AND WAVE NATURE OF ELECTRON

In 1924, de Broglie proposed that an electron, like light, behaves both as material particle and as a wave. This proposal gave a new theory, known as wave mechanical theory of matter. According to this theory, the electrons, protons and even atoms, when in motion, posses wave properties.

de Broglie derived an expression for calculating the wavelength of the wave associated with the electron. According to Planck's equation

$$E = h\nu = h.\frac{c}{\lambda} \qquad .....(1)$$

The energy of a photon on the basis of Einstein's mass-energy relationship is

$$E = mc^2 \qquad .....(2)$$

where, c is the velocity of the electron.

From (1) and (2) equation

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

$$\lambda = \frac{h}{mc} = \frac{h}{p} \qquad .....(3)$$

Momentum of the moving electron is inversely proportional to its wavelength.

Let kinetic energy of the particle of mass 'm' is E.

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

$$2Em = m^2v^2$$

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

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}} \qquad .....(4)$$

Let a charged particle, with charge q be accelerated with a potential of V; then the kinetic energy may be given as : $E = qV$

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

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$$m^2v^2 = 2qVm$$

$$mv = \sqrt{2qVm}$$

and, $$\lambda = \frac{h}{\sqrt{2qVm}} \quad \text{.....(5)}$$

(A) de Broglie wavelength associated with charged particles

For electron : $\lambda = \frac{12.27}{\sqrt{V}}$ Å

For proton : $\lambda = \frac{0.286}{\sqrt{V}}$ Å

For α - particles : $\lambda = \frac{0.101}{\sqrt{V}}$ Å

where, V = accelerating potential of these particles

(B) de Broglie wavelength associated with neutron

For neutron : $\lambda = \frac{h}{\sqrt{2Em}} = \frac{6.62\times10^{-34}}{\sqrt{2\times1.67\times10^{-27}\times E}} = \frac{0.286}{\sqrt{E(eV)}}$ Å

The wavelength decreases if the value of mass (m) increases i.e. de Broglie equation is applicable in the case of smaller particles like electron and has no significance for larger particles.

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

$$2\pi r = n\lambda$$

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

But $\lambda = h/mv$

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

or $mvr = nh/2\pi$

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".

Illustration

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 = $\frac{1.0097}{6.02\times10^{23}}$ g = 1.68×10^{-24} g = 1.68×10^{-27} kg

$$\lambda = \frac{h}{mv} = \frac{6.62\times10^{-34}}{1.68\times10^{-27}\times2000} = 1.97 \times 10^{-10}\ m$$

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Exercise

Determine the de Broglie's wavelength of electron emitted by a metal whose threshold frequency is 2.25×10^{14} Hz when exposed to visible radiation of wavelength 500 nm.

Ans. **9.84 A**

17. HEISENBERG'S UNCERTAINTY PRINCIPLE

(a) While treating e^- as a wave it is not possible to ascertain simultaneously the exact position and velocity of the e^- more precisely at a given instant since the wave is extending throughout a region of space

(b) As the photons of longer wavelengths are less energetic, hence they have less momentum and cannot be located exactly

(c) In 1927, Warmer Heisenberg presented a principle known as Heisenberg's uncertainty principle

(d) According to this principle it is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron.

(e) If uncertainty of measurement of position is Δx and uncertainty of measurement of momentum is Δp or $m\Delta v$, then according to Heisenberg

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

where h is planck's constant

(f) For other conjugates of motion the equation for Heisenberg's uncertainty principle may be given as

$$\Delta E.\ \Delta t \geq \frac{h}{4\pi} \text{ (for energy and time)}$$

(g) Like de Broglie equation, this principle has significance only for microscopic particles.

Illustration

An electron having velocity 2×10^6 m/s has uncertainty in kinetic energy is $\frac{6.62}{\pi} \times 10^{-21}$ J, then calculate the uncertainty in position (in Angstrom, Å) of the electron. [Given : $h = 6.62 \times 10^{-34}$ J-sec]

Sol. $KE = \frac{1}{2} mv^2 \quad v = 2 \times 10^6$ m/s

$d(KE) = mvdv$

$$dv = \frac{d(KE)}{mv} \quad ....(1) \qquad \text{But} \quad \Delta x = \frac{h}{4\pi m \Delta v} \quad ....(2)$$

$$\Delta x = \frac{h}{4\pi m \frac{d(KE)}{mv}} \quad ; \quad \Delta x = \frac{6.62 \times 10^{-34} \times 2 \times 10^6}{4\pi \times \frac{6.62}{\pi} \times 10^{-21}} = 500 \text{ Å}$$

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Exercise

1. A measurement establishes position of a proton with an accuracy of $\pm 10^{-10}$ m. Find the minimum uncertainty in proton's position 1 second later.

Sol. $\Delta x = \pm 10^{-10}$ m

$\therefore$ According to Heisenberg's Uncertainty Principle

$$\Delta v = \frac{h}{4\pi m(\Delta x)} = \frac{6.62\times10^{-34}}{4\times3.14\times1.67\times10^{-27}\times10^{-10}} = 0.3156 \times 10^3$$

$\Delta v = \Delta x / \Delta t$

hence Δx (minimum uncertainty in position after one sec.) $= \Delta v \times \Delta t$

$= 0.3156 \times 10^3 \times 1 \quad = 3.15 \times 10^2$ m **Ans.**

WAVE MECHANICAL MODEL OF ATOM

The atomic model which is based on the particle and wave nature of the electron is known as wave mechanical model of the atom. This was developed by Erwin Schrodinger in 1926. This model describes the electron as a three-dimensional wave in the electronic field of positively charged nucleus. Schrodinger derived an equation which described 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 and z are cartesian 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 ψ(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 values of coordinates.

The main aim of Schrodinger equation is to give a solution for the probability approach. When the equation is solved, it is observed that for some regions of space, the value of ψ is positive and for other regions 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 this equation is that it provides a set of number, called quantum numbers, which describe energies of the electrons in atoms, information about the shapes and orientations of the most probable distribution of electron around the nucleus .

Wave function ψ can be plotted against distance 'r' from nucleus as,

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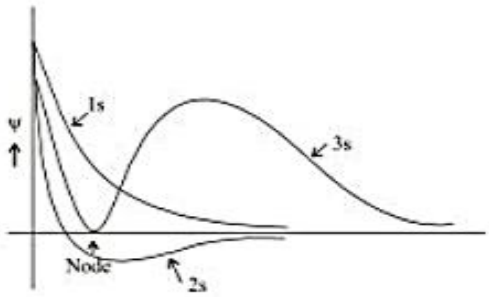

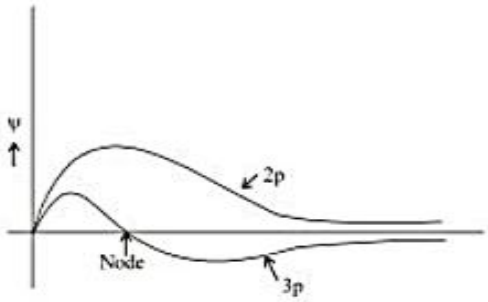

For hydrogen wave function, number of nodes can be calculated as,
(i) Number of radial nodes = $(n - l - 1)$
(ii) Number of angular nodes = l
(iii) Total number of nodes = $(n - 1)$

Examples : (i) For 1s – orbital n = 1, l = 0, it will have no radial or angular node
(ii) For 2s–orbital, n = 2, l = 0, it will have only one radial node
(iii) For 3s-orbital, n = 3, l = 0, it will have two radial nodes
(iv) For 2p-orbital, n = 2, l = 1, it will have no radial node but it has only one angular node
(v) For 3p-orbital, n = 3, l = 1, it will have one radial and one angular node

Solution of Schrodinger wave equation :

In spherical co-ordinates $\psi(x, y, z)$ is represented by $\psi(r, \theta, \phi)$ such that complete wave function can be given as

$$\psi(r, \theta, \phi) = \underbrace{R(r)}_{\text{Radial part}} \underbrace{\Theta(\theta)\Phi(\phi)}_{\text{Angular part}}$$

Dependance of the wave function on quantum number can be given as,

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\ \Theta_{lm}(\phi)\ \Phi_m(\phi)$$

The function R depend only on r, therefore they describe the distribution of the electron as a function of r from the nucleus. These functions depend upon two quantum numbers, n and l. The two functions Θ and Φ taken together give the angular distribution of the electron.
The radial part the wave function for some orbitals may be given as,

	n	l	R_{nl}
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-zr/a_0}$
2s	2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-zr/2a_0}$
2p	2	1	$\frac{1}{\sqrt{3}}\left(\frac{Zr}{2a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$

where, Z = atomic number, a_0 = radius of first Bohr orbit of hydrogen.

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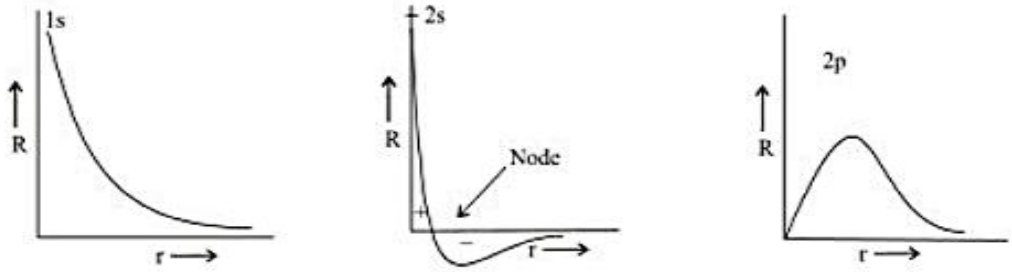
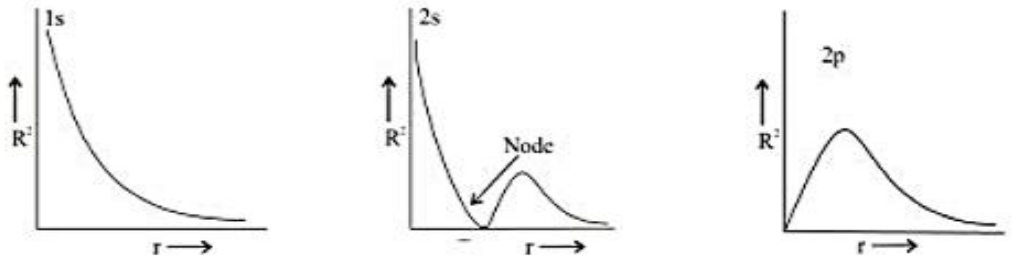
Plot of Radial Wave Function 'R' :



At node, the value of 'R' changes from positive to negative.

Plot of Radial Probability Density 'R^2' :

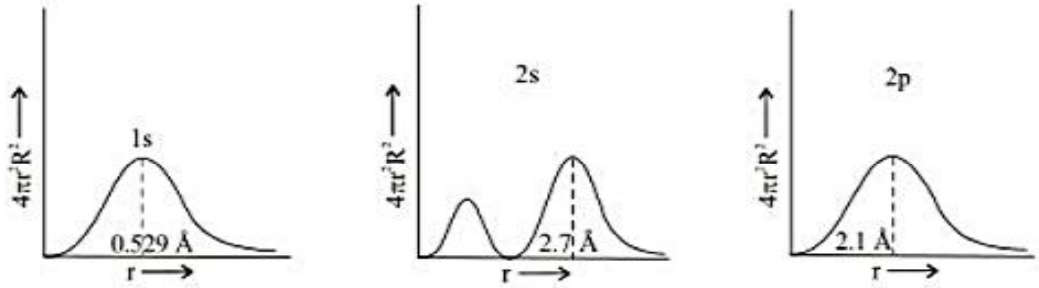


The plot of probability i.e. R^2 or Ψ^2 are more meaningful than the plots of function themselves. It can be seen that for both 1s and 2s orbitals, the probability has a maximum value at r = 0, i.e. in the nucleus. In case of 2s orbital, one more maximum in the probability plot is observed.

Plot of Radial probability Function ($4\pi r^2R^2$) :

In order to visualize the electron cloud within a spherical shell is placed at radii 'r' and 'r + dr' from the nucleus. Thus radial probability function describes the total probability of finding the electron in a spherical shell of thickness 'dr' located at the distance r from the nucleus.

R.P.E. = (Volume of spherical shell) × Probability density = $(4\pi r^2\, dr) \times R^2$



In the plot of radial probability against 'r', number peaks, i.e. region of maximum probability = n – 1.

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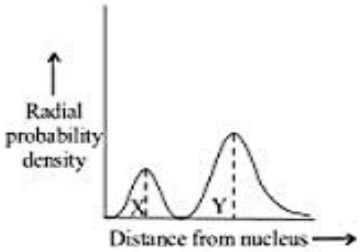
Illustration



If the above radial probability curve indicates '2s' orbital, the distance between the peak points X & Y is-

(A) 2.07 Å (B) 1.59 Å (C) 0.53 Å (D) 2.12 Å

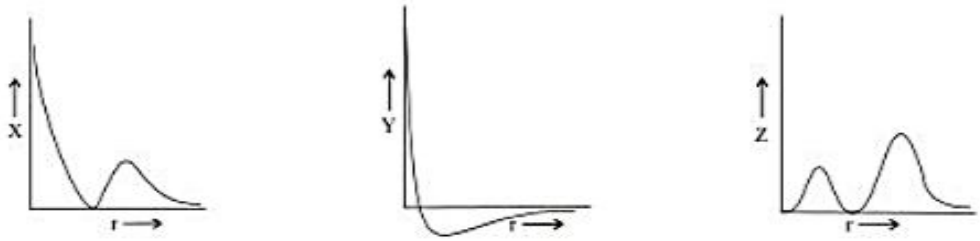
Ans. (A)

Sol. X = 0.53 Å, Y = 2.6 Å

Y – X = 2.6 – 0.53 = 2.07 Å

Exercise

Plots for 2s orbital are :



X, Y and Z are respectively

(A) R, R^2 and $4\pi r^2R^2$ (B) R^2, R and $4\pi r^2R^2$ (C) $4\pi^2R^2$, R^2 and R (D) R^2, $4\pi r^2R^2$ and R

Ans. **(B)**

19. QUANTUM NUMBERS

(a) The measurement scale by which the orbitals are distinguished, can be represented by sets of numbers called as quantum number.

(b) Quantum numbers are to specify and display to complete information about size, shape and orientation of the orbital. These are principle, azimuthal and magnetic quantum number, which follows directly from solution of schrodinger wave equation.

(c) Except to these quantum numbers, one additional quantum number designated as spin quantum number, which specify the spin of electron in an orbital.

(d) Each orbital in an atom is specified by a set of three quantum numbers and each electron is designated by a set of four quantum numbers.

19.1 Principal quantum number (n) :

(a) It was proposed by Bohr and denoted by 'n'.

(b) It determines the average distance between electron and nucleus, means it is denoted the size of atom.

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(c) It determine the energy of the electron in an orbit where electron is present.

(d) The maximum number of an electron in an orbit represented by this quantum number as $2n^2$.

(e) It gives the information of orbit K, L, M, N, ...

(f) The value of energy increases with the increasing value of n.

(g) It represents the major energy shell from which the electron belongs.

19.2 Azimuthal quantum number or angular quantum number (ℓ) -

(a) It was proposed by Sommerfield and denoted by 'ℓ'.

(b) It determines the number of subshells or sublevels to which the electron belongs.

(c) It tells about the shape of subshells.

(d) It also expresses the energies of subshells s < p < d < f (Increasing energy).

(e) The value of ℓ is integral values upto (n – 1), starting from zero where 'n' is the number of principle shell.

(f)

Value of ℓ	0	1	2	3
Name of subshell	s	p	d	f
Shape of orbital	spherical	Dumbbell	Clover leaf (Except d_{z^2} doughtnut)	Complex

(g) It represent the orbital angular momentum, which is equal to $\frac{h}{2\pi}\sqrt{\ell(\ell+1)}$.

(h) The number of electrons in subshell = $2(2\ell + 1)$.

(i) For a given value of 'n' the total value of 'ℓ' is always equal to the value of 'n'.

19.3 Magnetic quantum number (m) :

(a) It was proposed by Linde and denoted by 'm'.

(b) It gives the number of permitted orientation of subshells.

(c) The value of m varies from $-\ell$ to $+\ell$ through zero.

(d) It tells about the splitting of spectral lines in the magnetic field i.e. this quantum number proved the Zeeman effect.

(e) For a given value of 'n' the total value of 'm' is equal to n^2.

(f) For a given value of 'ℓ' the total value of 'm' is equal to $(2\ell + 1)$.

(g) *Degenerate orbitals* - Orbitals having the same energy are known as degenerate orbitals. e.g. for p subshell P_x, P_y and P_z are degenerate orbital

(h) The number of degenerate orbitals of s subshell = 0.

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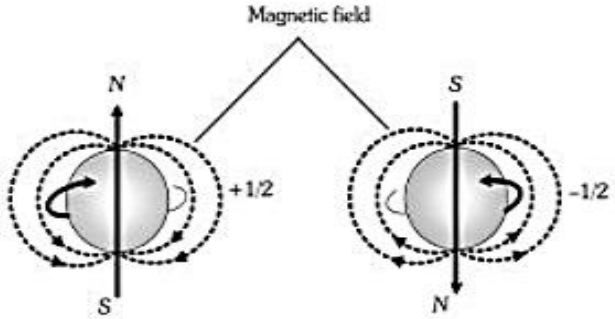
19.4 Spin quantum number (s) :

(a) It was proposed by ***Goldshmidt*** & ***Uhlenbeck*** and denoted by the symbol of 's'.



(b) The value of 's' is + ½ or – ½, which is signified as the spin or rotation or direction of electron on it's axis during the movement.

(c) The spin may be clockwise or anticlockwise.

(d) It represents the value of spin angular momentum is equal to $\frac{h}{2\pi}\sqrt{s(s+1)}$.

(e) Maximum spin of an atom = ½ × number of unpaired electron.

Illustration

1. The correct order of atomic orbitals in terms of energy between 8s and 8p orbital are

(A) 7d, 6f (B*) 5g, 6f, 7d (C) 6d, 7f (D) 4h, 5g, 6f, 7d

Sol. (n+l): 8s ⟶ 8 + 0 = 8
8p ⟶ 8 + 1 = 9
5g ⟶ 5 + 4 = 9
6f ⟶ 6 + 3 = 9
7d ⟶ 7 + 2 = 9
correct order ⟶ 8s 5g 6f 7d 8p

2. Which of the following set of quantum number is valid/invalid. In case of valid set write the symbol of the orbital it represents [may have more than one answers] & in case it is invalid mention the reason.

	n	l	m
(i)	3	not known (but less than 3)	0
(ii)	–2	–1	+1
(iii)	4	2	–1

Sol. (i) Valid, $3s/3p_x/3p_y/3p_z/3d_{x^2-y^2}/3d_{z^2}/3d_{xy}/3d_{xz}/3d_{yz}$
(ii) Invalid 'n' cannot be negative
(iii) Valid $4d_{x^2-y^2}/4d_{z^2}/4d_{xy}/4d_{xz}/4d_{yz}$

Exercise

How many electrons in a given atom can have the following quantum numbers –

(a) n = 4, ℓ = 1 (b) n = 2, ℓ = 1, m = – 1, s = + ½
(c) n = 3 (d) n = 4, ℓ = 2, m = 0

Ans. (a) 6 (b) 1 (c) 18 (d) 2

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20. SHAPE 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).

20.1 s-orbital ($l = 0$) : These orbitals are spherical and symmetrical about the nucleus. The probability of finding the electron is maximum near the nucleus and keeps 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.

20.2 p-orbital ($l = 1$): 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.

20.3 d-orbital ($l = 2$):

For d-orbitals, l = 2. Hence m = -2,-1, 0, +1, +2. Thus there are 5d 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.

20.4 Spherical nodes : The spherical surface where probability of finding the electron is zero, is called spherical nodes.

No. of spherical nodes in any orbital = $n - l - 1$

20.5 Nodal Plane : This is a plane passing through the nucleus where the probability of finding the electron is zero.

Number of nodal plane in a orbital = l

Orbital	Nodal plane
p_x	yz
p_y	xz
p_z	xy
d_{xy}	yz, zx
d_{yz}	xy, xz
d_{zx}	xy, yz

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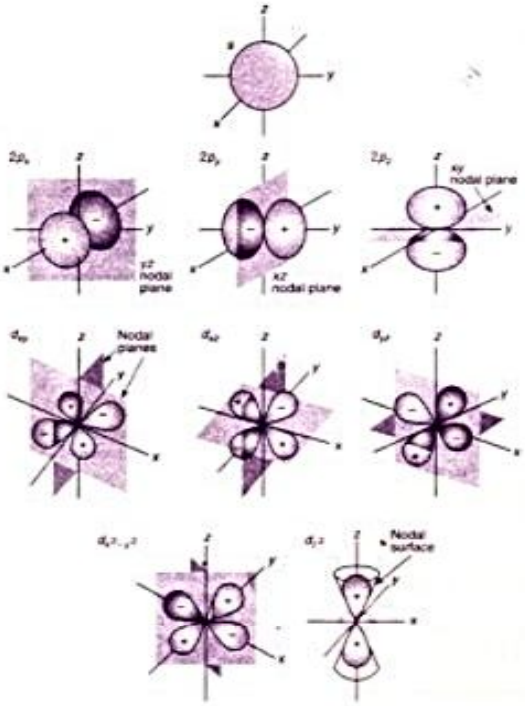

21. ELECTRONIC CONFIGURATION

The distribution of electrons in different orbitals of atom is known as electronic configuration of the atoms.

Filling up of orbitals in the ground state of atom is governed by the following rules:

21.1 Aufbau principle

(i) Auf bau is a German word, meaning 'building up'.

(ii) According to this principle, "In the ground state, the atomic orbitals are filled in order of increasing energies i.e. in the ground state the electrons first occupy the lowest energy orbitals available".

(iii) In fact the energy of an orbital is determined by the quantum number n and *l* with the help of (n+*l*) rule or Bohr Bury rule. According to this rule

(a) Lower the value of n + *l*, lower is the energy of the orbital and such an orbital will be filled up first.

(b) When two orbitals have same value of (n + *l*) the orbital having lower value of "n" has lower energy and such an orbital will be filled up first .

Thus, order of filling up of orbitals is as follows:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d

However, in one electron system, orbital of same principal quantum number have same energy, which is independent of (*l*). In this system *l* only determines the shape of the orbital. Energy of orbitals are

1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f

21.2 Pauli's exclusion principle

(i) According to this principle, "No two electrons in an atom can have same set of all the four quantum numbers n, *l*, m and s .

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(ii) In an atom any two electrons may have three quantum numbers identical but fourth quantum number must be different.

(iii) Since this principle excludes certain possible combinations of quantum numbers for any two electrons in an atom, it was given the name exclusion principle. Its results are as follows :

(a) One orbital cannot have more than two electrons.

(b) The maximum capacity of a main energy shell is equal to $2n^2$ electrons.

(c) The maximum capacity of a subshell is equal to $2(2l + 1)$ electrons.

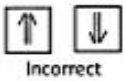
(d) Number of sub-shells in a main energy shell is equal to the value of n.

(e) Number of orbitals in a main energy shell is equal to n^2

(iv) According to this principle an orbital can accommodate at the most two electrons with spins opposite to each other. It means that an orbital can have 0, 1, or 2 electron.

(v) If an orbital has two electrons they must be of opposite spin.

Correct


Incorrect

21.3 Hund's Rule of maximum multiplicity

(i) This rule provides the basis for filling up of degenerate orbitals of the same sub-shell.

(ii) According to this rule "Electron filling will not take place in orbitals of same energy until all the available orbitals of a given subshell contain one electron each with parallel spin".

(iii) This implies that electron pairing begins with fourth, sixth and eighth electron in p, d and f orbitals of the same subshell respectively.

(iv) The reason behind this rule is related to repulsion between identical charged electron present in the same orbital.

(v) They can minimise the repulsive force between themselves by occupying different orbitals.

(vi) Moreover, according to this principle, the electron entering the different orbitals of subshell have parallel spins. This keep them farther apart and lowers the energy through electron exchange.

(vii) The term maximum multiplicity means that the total spin of unpaired is maximum in case of correct filling of orbitals as per this rule.

Spin multiplicity = (no. of unpaired electron + 1)

Electronic configuration of some elements

S.No.	Elements	Symbol	Atomic No.	Electronic configuration
(1)	Hydrogen	H	1	$1s^1$
(2)	Nitrogen	N	7	$1s^2\ 2s^2\ 2p^3$ or [He] $2s^2\ 2p^3$
(3)	Sulphur	S	16	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ or [Ne] $3s^2\ 3p^4$
(4)	Manganse	Mn	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$ or [Ar] $3d^5\ 4s^2$

Exceptional electronic configuration

S.No.	Elements	Symbol	Atomic No.	Electronic configuration
(1)	Chromium	Cr	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ or [Ar] $3d^5\ 4s^1$
(2)	Copper	Cu	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ or [Ar] $3d^{10}\ 4s^1$

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Element	At.No.	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	6d	5f
H	1	1													
He	2	2													
Li	3	2	1												
Be	4	2	2												
B	5	2	2	1											
C	6	2	2	2											
N	7	2	2	3											
O	8	2	2	4											
F	9	2	2	5											
Ne	10	2	2	6											
Na	11	2	2	6	1										
Mg	12	2	2	6	2										
Al	13	2	2	6	2	1									
Si	14	2	2	6	2	2									
P	15	2	2	6	2	3									
S	16	2	2	6	2	4									
Cl	17	2	2	6	2	5									
Ar	18	2	2	6	2	6									
K	19	2	2	6	2	6		1							
Ca	20	2	2	6	2	6		2							
Sc	21	2	2	6	2	6	1	2							
Ti	22	2	2	6	2	6	2	2							
V	23	2	2	6	2	6	3	2							
*Cr	24	2	2	6	2	6	5	1							
Mn	25	2	2	6	2	6	5	2							
Fe	26	2	2	6	2	6	6	2							
Co	27	2	2	6	2	6	7	2							
Ni	28	2	2	6	2	6	8	2							
*Cu	29	2	2	6	2	6	10	1							
Zn	30	2	2	6	2	6	10	2							
Ga	31	2	2	6	2	6	10	2	1						
Ge	32	2	2	6	2	6	10	2	2						
As	33	2	2	6	2	6	10	2	3						
Se	34	2	2	6	2	6	10	2	4						
Br	35	2	2	6	2	6	10	2	5						
Kr	36	2	2	6	2	6	10	2	6						
Rb	37	2	2	6	2	6	10	2	6			1			
Sr	38	2	2	6	2	6	10	2	6			2			
Y	39	2	2	6	2	6	10	2	6	1		2			
Zr	40	2	2	6	2	6	10	2	6	2		2			
*Nb	41	2	2	6	2	6	10	2	6	4		1			
*Mo	42	2	2	6	2	6	10	2	6	5		1			
Tc	43	2	2	6	2	6	10	2	6	5		2			
*Ru	44	2	2	6	2	6	10	2	6	7		1			
*Rh	45	2	2	6	2	6	10	2	6	8		1			
*Pd	46	2	2	6	2	6	10	2	6	10					
*Ag	47	2	2	6	2	6	10	2	6	10		1			
Cd	48	2	2	6	2	6	10	2	6	10		2			
In	49	2	2	6	2	6	10	2	6	10		2	1		
Sn	50	2	2	6	2	6	10	2	6	10		2	2		

*** Exceptional electronic configuration**

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21.4 Extra stability of half filled and completely filled orbitals

Half-filled and completely filled sub-shell have extra stability due to the following reasons :

(i) Symmetry of orbitals

(a) It is a well known fact that symmetry leads to stability.

(b) Thus, if the shift of an electron from one orbital to another orbital differing slightly in energy results in the symmetrical electronic configuration. It becomes more stable.

(c) For example p^3, d^5, f^7 configurations are more stable than their near ones.

(ii) Exchange energy

(a) The electron in various subshells can exchange their positions, since electron in the same subshell have equal energies.

(b) The energy is released during the exchange process with in the same subshell.

(c) In case of half filled and completely filled orbitals, the exchange energy is maximum and is greater than the loss of energy due to the transfer of electron from a higher to a lower sublevel e.g. from 4s to 3d orbitals in case of Cu and Cr .

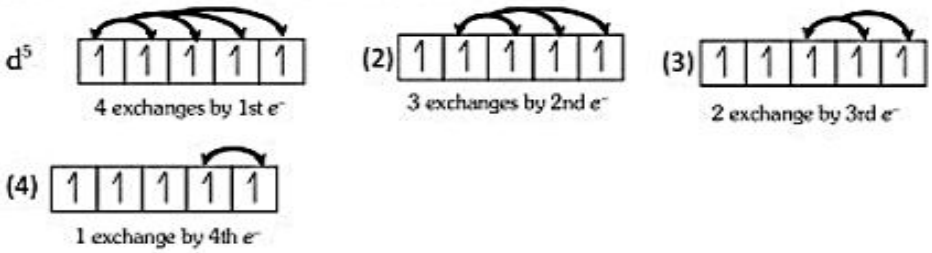
(d) The greater the number of possible exchanges between the electrons of parallel spins present in the degenerate orbitals, the higher would be the amount of energy released and more will be the stability.

(e) Let us count the number of exchange that are possible in and configuration among electrons with parallel spins.

d^4 (1)

To number of possible exchanges = 3 + 2 + 1 =6

d^5 (1)



To number of possible exchanges = 4 + 3 + 2 +1 = 10

21.5 Writing electronic configuration of ions

In ionizaiton electron(s) are removed from outer-shell first (i.e. 4s) while, electrons are filled according to energy level.

For example : -

(i) Fe : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

(ii) Fe^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

(iii) Fe^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

(iv) Cr : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

(v) Cr^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

(vi) Cl^- : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

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SOLVED EXAMPLES

Q.1 Electromagnetic radiations of wavelength 242 nm is just sufficient to ionise sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

Sol. Energy associated with a photon of 242 nm $= \dfrac{6.62\times10^{-34}\times3.0\times10^{8}}{242\times10^{-9}} = 8.21 \times 10^{-19}$ joule

$\because$ 1 atom of Na for ionisation requires $= 8.21 \times 10^{-19}$ J

$\therefore$ 6.023×10^{23} atoms of Na for ionisation requires $= 8.21 \times 10^{-19} \times 6.023 \times 10^{23}$

$= 49.45 \times 10^{4}$ J = **494.5 kJ mol^{-1}**

Q.2 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He^{+} spectrum ?

Sol. For He^{+}, Z = 2 $\quad \dfrac{1}{\lambda} = R_H Z^2 \left[\dfrac{1}{2^2} - \dfrac{1}{4^2}\right]$

For H, Z = 1 $\quad \dfrac{1}{\lambda} = R_H \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

Since λ is same

$\therefore \quad 4\left[\dfrac{1}{2^2} - \dfrac{1}{4^2}\right] = \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

$\therefore \quad \left[\dfrac{1}{1^2} - \dfrac{1}{2^2}\right] = \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] \qquad \therefore \quad n_1 = \mathbf{1}$ and $n_2 = \mathbf{2}$

Q.3 Calculate the longest wavelength which can remove the electron from I^{st} Bohr's orbit. Given $E_1 = 13.6$ eV.

Sol. The photon capable of removing electron from I Bohr's orbit must possess energy

$= 13.6$ eV

$= 13.6 \times 1.602 \times 10^{-19}$ J $\quad = 21.787 \times 10^{-19}$ J

$\because \quad E = \dfrac{hc}{\lambda}$;

$21.787 \times 10^{-19} = \dfrac{6.62\times10^{-34}\times3.0\times10^{8}}{\lambda}$

$\therefore \quad \lambda = 912.24 \times 10^{-10}$ m = **912.24 Å**

Q.4 Show that the wavelength of a 150 g rubber ball moving with a velocity 50 m sec^{-1} is short enough to be observed -

Sol. $\because \lambda = \dfrac{h}{mv}$

Given v = 50 m sec^{-1}

$= 50 \times 10^{2}$ cm sec^{-} ; m = 150 g

$\therefore \lambda = \dfrac{6.62\times10^{-27}}{150\times50\times10^{2}} = \mathbf{8.83 \times 10^{-33}}$ **cm**

The wavelength is much lesser than that of visible region and thus it will not be visible.

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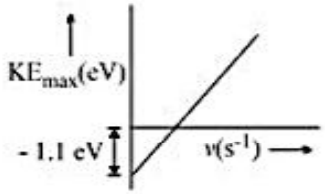
Q.5 An element undergoes a reaction as shown –
$X + 2e^- \longrightarrow X^{2-}$, energy released = 30.87 eV/atom. If the energy released, is used to dissociate 8 gms of H_2 molecules, equally into H^+ and H^*, where H^* is an excited state of H atoms where the electron travels in orbit whose circumference equal to four times its de Broglie's wavelength.
(a) Calculate the excited state of H
(b) Determine the least amount of X that would be required.
Given : IE of H = 13.6 eV/atom, Bond energy of H_2 = 4.526 eV/molecule.

Sol. (a) $2\pi r = 4\lambda$
$\therefore$ $n = 4$
(b) $\therefore$ Total energy required
$= 4 \times 4.526\text{eV} \times 6.023 \times 10^{23} + 4 \times 13.6 \times 6.023 \times 10^{23} + 4 \times 12.75 \text{ eV} \times 6.023 \times 10^{23}$
$= 4 \times 6.023 \times 10^{23}$ [30.876]
$\therefore$ moles of X required = 4 moles

Q.6 Light of frequency 7.5×10^{14} Hz is incident on a metal surface. A curve between KE_{max} v/s incident frequency is plotted as shown. Find
(a) The stopping potential
(b) Magnitude of the slope of curve given.
(c) Intercept on x-axis



Sol. $KE_{max} = h\nu - h\nu_0$ ....(1)
$h\nu_0 = 1.1$ eV (from the given curve)
Incident energy = $h\nu$

$$= 6.62 \times 10^{-34} \times 7.5 \times 10^{-14} \text{ J} \Rightarrow \frac{6.62 \times 10^{-20} \times 7.5}{1.6 \times 10^{-19}} \text{eV} \Rightarrow 3.1 \text{ eV}$$

$KE_{max} = 3.1 - 1.1 = 2$ eV
We know that
(a) Stopping potential $= KE_{max} / e$
$= 2V$
(b) Magnitude of slope of curve $= h$

$$= \frac{6.62 \times 10^{-34} \text{Js}}{1.6 \times 10^{-19}} \Rightarrow 4.14 \times 10^{-15}$$

(c) Intercept on x-axis = Threshold frequency

$$= \nu_0 = \frac{1.1 \text{eV}}{h \text{eV} - s} = \frac{1.1}{4.14 \times 10^{-15}} = 2.66 \times 10^{14} \text{ Hz}$$ **Ans.**

Q.7 How many electrons in a given atom can have the following quantum numbers –
(a) $n = 4, l = 1$
(b) $n = 2, l = 1, m = -1, s = +\frac{1}{2}$
(c) $n = 3$
(d) $n = 4, l = 2, m = 0$

Sol. (a) $l = 1$ refers to p - subshell which has three orbitals (p_x, p_y and p_z) each having two electrons. Therefore, total number of electrons are **6**.
(b) $l = 1$ refers to p - subshell, $m = -1$ refers to p_x or p_y orbital whereas, $s = +\frac{1}{2}$ indicate for only 1 electron.
(c) Number of electrons for any energy level is given by
$2n^2$ i.e. $2 \times 3^2 = 18$ electrons
(d) $l = 2$ means d-subshell and $m = 0$ refer to dz^2 orbital
$\therefore$ Number of electrons are **2.**

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Q.8 What designation will you assign to an orbital having following quantum number –
(a) $n = 3$, $l = 1$, $m = -1$
(b) $n = 5$, $\ell = 0$, $m = 0$
(c) $n = 2$, $\ell = 1$, $m = 0$

Sol. (a) Since $\ell = 1$ corresponds to p-orbital and $m = -1$ shows orientation either in x or y axis, thus this orbital refers to $3p_x$ or $3p_y$ or $3p_z$
(b) 5s
(c) $2p_z$ or $2p_x$ or $2p_y$

Q.9 Which of the following set of quantum numbers are not permitted
(a) $n = 3, \ell = 2, m = -2, s = +1/2$
(b) $n = 3, \ell = 2, m = -1, s = 0$
(c) $n = 2, \ell = 2, m = +1, s = -1/2$

Sol. (a) This set of quantum number is permitted.
(b) This set of quantum number is not permitted as value of 's' cannot be zero.
(c) This set of quantum number is not permitted as the value of 'l' cannot be equal to 'n'.

Q.10 (a) For any multielectron specie, compare the energies of following orbitals. **Justify** [External magnetic & electric fields are absent]
Orbitals to be compared $3d_{xy}$, 2s, $4p_x$, $4p_y$
(b) Compare the "average distance" of the following orbitals from the nucleus. Also comment on their 'Chances of closeness to the nucleus" if they have same average distance"
Orbitals to be compared 1s, 2s, 3s, $3p_x$, $3d_{xy}$

Sol. (a) $2s < 3d_{xy} < 4p_x = 4p_y$
Justification compare $(n + l)$ & if $(n + l)$ same then 'n'
(b) Average distance (on the basis of n)
$1s < 2s < 3s = 3p_x = 3d_{xy}$
Closeness comparison
3s will be more close as compared to $3p_x$ as compared to $3d_{xy}$

Q.11 Calculate energy of electron which is moving in the orbit that has its radius, sixteen times the radius of first Bohr orbit for H–atom.

Sol. $r = r_0 n^2$ $\Rightarrow n^2 = 16$ $\Rightarrow n = 4$

$$E = \frac{-2.18\times10^{-18}}{n^2} = \mathbf{-1.36 \times 10^{-19}\ J/atom}$$

Q.12 Wavelength of the Balmer H_α line is 6565 Å. Calculate the wavelength of H_β, line of same hydrogen like atom.

Sol. For α-line of Balmer Series

$$\frac{1}{\lambda_\alpha} = RZ^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

For β-line of Balmer series

$$\frac{1}{\lambda_\beta} = RZ^2\left[\frac{1}{2^2} - \frac{1}{4^2}\right]$$

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$$\frac{\lambda_\beta}{\lambda_\alpha} = \frac{\left[\frac{1}{2^2} - \frac{1}{4^2}\right]}{\left[\frac{1}{2^2} - \frac{1}{3^2}\right]}$$

λ_β **= 4.863 × 10^{-7} m**

Q.13 The electron energy in hydrogen atom is given by $E_n = \frac{-21.7 \times 10^{-12}}{n^2}$ ergs. Calculate the energy required to remove an e^- completely from n = 2 orbit . What is the largest wavelength in cm of light that can be used to cause this transition.

Sol. For complete removal from n = 2

$$\Delta E_n = +2.1 \times 10^{-12}\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right]$$

= 5.4 25 × 10^{-12} erg

$$\frac{hc}{\lambda} = \Delta E_n \quad \Rightarrow \quad \lambda = \frac{hc}{\Delta E_n} = \mathbf{3.7 \times 10^{-5}\ cm}$$

Q.14 Calculate the threshold frequency of metal if the binding energy is 180.69 KJ mol^{-1} of electron.

Sol. $$\Delta E\left(\text{in}\ \frac{eV}{atom}\right) = \frac{1.80.69 \times 10^3}{6.02 \times 10^{23} \times 1.6 \times 10^{-19}} = h\nu$$

ν **= 4.5 × 10^{14} S^{-1}**

Q.15 U.V. light of wavelength 800 Å & 700 Å falls on hydrogen atoms in their ground state & liberates electrons with kinetic energy 1.8 eV and 4 eV respectively. Calculate planck's constant.

Sol. $E_1 = \frac{hc}{\lambda_1} - \phi_0 \qquad E_2 = \frac{hc}{\lambda_2} - \phi_0$

$$E_1 - \frac{hc}{\lambda_1} = E_2 - \frac{hc}{\lambda_2} = \phi_0$$

$$hc\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) = E_1 - E_2$$

$$h = \frac{(E_2 - E_1)\lambda_1\lambda_2}{(\lambda_1 - \lambda_2)c} = \mathbf{6.57 \times 10^{-34}\ Js}$$

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Q.16 Through what potential difference must an electron pass to have a wavelength of 500 Å.

Sol. $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2m.e.V}}$

$$V = \left(\frac{h}{\lambda}\right)^2 \frac{1}{2me} = \frac{(6.63\times10^{-34})^2}{(5\times10^{-18})^2\times2\times9.01\times10^{-31}\times1.6\times10^{-19}}$$

$$= \mathbf{6.03 \times 10^{-4}\ V}$$

Q.17 Calculate magnitude of orbital angular momentum of an e^- that occupies 1s, 2s, 2p, 3d, 3p.

[Ans. 0 ; 0 ; $\sqrt{2}\frac{h}{2\pi}$; $\sqrt{6}\frac{h}{2\pi}$; $\sqrt{2}\frac{h}{2\pi}$]

Sol. Orbital angular momentum

$$= \frac{h}{2\pi}\sqrt{\ell(\ell+1)}$$

for 1s, 2s, $l = 0$ O.A. M. = 0

for 2p, $l = 1$ O.A.M. = $\frac{h}{2\pi}\sqrt{2}$

for 3d, $l = 2$ O.A.M. = $\frac{h}{2\pi}\sqrt{6}$

for 3p, $l = 1$, O.A.M. = $\frac{h}{2\pi}\sqrt{2}$

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