ATOMIC STRUCTURE

1. Dalton's Theory of Atom

ATOMS AS IT IS ?

Basically atom was an idea derived from the element. Although its presence was proved by various means but people did not think that they could see them directly, but now science has made it possible to see them directly by using powerful microscope like electron microscope, through scanning tunneling microscopy. (STM)



(STM Image of Silicon atom)

The journey of atoms starts from John Dalton's (1803) atomic theory to J. J. Thoson (1904) who proved divisibility of atom by inventing electron and further advanced by Lord Rutherford (1911) both worked at Cambridge University (U. K.) and

DALTON'S THEORY OF MATTER

On the basis of large number of experiments performed, John Dalton proposed that matter was made up of extremely small particles called atoms. The main postulates of Dalton's atomic theory are:

- * Matter is made up of small indivisible particle atom.
- * 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 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.
- * 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 has a complex structure of its own and is 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.

Drawbacks: It fails to explain why atoms of different kinds should differ in mass and valency etc.

The discovery of isotopes and isobars showed that atoms of same elements may have different atomic masses (isotopes) and atoms of different kinds may have same atomic masses (isobars).

Sub-Atomic Particles: The discovery of various sub-atomic particles like electrons, protons etc. during late 19th century led to the ideal that the atom was no longer an indivisible and the smallest particle of the matter.

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 at high voltage, which produces cathode rays consisting of negatively charged particles, named as electrons. The e/m ratio for cathode rays is

fixed whose value 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 charged 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 electrically neutral charge particle, neutron was discovered by James Chadwick by bombarding boron or beryllium with α -particles.

$${}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

Discharge Tube Experiment

DISCHARGE TUBE EXPERIMENT

At atmospheric pressure air is non conductor.

Upto 10 torr pressure no-change in the tube.

At 10 torr discharge initiate with cracking sound and a stream of glow appears from anode to cathode. At 5 torr the glow becomes steady and extends from anode to cathode called positive column and its colour is related from the nature of gas in the tube. Example ; Neon-red ; Hydrogen-blue ; Nitrogenred ; Air-purple red : Carbondioxide-bluish white.

At one torr glow splits into two parts surrounding cathode and anode and in between them black space is created called Faraday's dark space.

At 0.5 torr glows are detached and narrow dark space is created round cathode and anode called Crookes dark space and thereafter pinky disk of light is formed called **Striations**.

At 0.01 torr cathode rays are produced and this pressure is called Mother pressure of electron.

At 0.0001 torr again no discharge passes through the tube and gas becomes non-conductor.

	Electron	Proton	Neutron
Symbol	e or e ⁻¹	Р	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

Characteristics of the three fundamental particles are:

The atomic mass unit (amu) is 1/12 of the mass of an individual atom of ${}_{6}C^{12}$, 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 charge while the neutron is not charged. *MOSLEY'S LAW*:

According to Mosley, the atomic number of elements is directly proportional to the square root of the frequency of the X-ray.

i.e.,
$$z \propto \sqrt{v}$$
 or, $\sqrt{v} = a(z-b)$
 $\therefore \qquad z = \frac{1}{a}\sqrt{v} + b$ (i) $[y = mx + c]$

2. Models of Atom



Thomson's Model: Putting together all the factsknown at that time, Thomson assumed that an atom is a sphere of positive charges uniformly distributed, with the electrons scattered as points throughout the sphere.

This was known as plum-pudding model at that time. However this idea was dropped due to the success of α -particle scattering experiments studied by Rutherford and Mardson.



RUTHERFORD A-SCATTERING EXPERIMENT & ATOMIC MODEL :

Lord Rutherford in 1911 studies the scattering of alpha (α) He⁴(II) by very thin sheet of gold foil using radium gun as source of alpha particles and observed following facts about internal structure of atom.



Most of the α -particles passes the gold foil without any deviation from the original straight line path and their percentage was 99.9%.

Some of the particles deviates through small angle and their ratio was 1:10⁴.

* Few of the alpha particles scattered or deflected through large angle and their ratio was $1:2 \times 10^3$.



Alpha particles move toward nucleus at the cost of their kinetic energy and it has to face potential energy of repulsion from protons present in the atom at the centre. and at the point where potential energy of repulsion becomes equal to kinetic energy of the alpha particle is called dead point and their distance from nucleus is called distance of closest approach d.c.a.

At the dead point KE = PE of repulsion

$$\frac{1}{2} \text{ mv}^2 = \frac{2e \times Ze}{4\pi\epsilon_0 r} \text{ in SI unit} \qquad \text{and in c. g. s. unit}$$
$$\frac{1}{2} \text{ mv}^2 = \frac{2e \times Ze}{r} \text{ as } 4\pi\epsilon_0 = 1 \qquad r = \frac{4Ze^2}{mv^2} = \frac{4Ze^2}{4\pi\epsilon_0 mv^2}$$
$$r = \frac{4Ze^2}{mv^2}$$

TIPS :

*

 $r\,{\propto}\,Z$ when m and V are constant

$$r \propto \frac{1}{v^2}$$
 When Z and m are constant.
 $r \propto \frac{1}{m}$ When Z and V constant
 $r \propto \frac{Z}{v^2}$ When only m is constant.

Here m is the mass of particles used having velocity (v) and z is the atomic number of the foil. According the Rutherford average scattering was poor and the number of scattered particles with angle θ may be obtained by Rutherford scattering formula given as

$$N = \frac{Q.n.t.Z^2 e^4}{m^2 v^4 r^2 \sin^4 \theta / 2}$$

Where N = number of scattered α -particles, q = total number of α particles, v = velocity of alpha particle, z = atom number of foil, r = distance between source of alpha particles and foil, n = number of atoms per unit volume of the foil, t = thickness of the foil, e = change of proton, θ = scattering angle, m = mass of alpha particles.

TIPS :

For objective questions

$$N \propto t = K_{1}t \qquad N \propto (PE)^{2} = K_{2}PE^{2} \qquad N \propto \frac{1}{(KE)^{2}} = \frac{K_{3}}{KE^{2}}$$
$$N \propto \frac{1}{\sin^{4}\theta/2} = \frac{K_{3}}{\sin^{4}\theta/2} = ka \operatorname{cosec}^{4}\theta/2 \qquad N \propto \frac{1}{V_{4}} = \frac{K}{V_{4}}$$

Where corresponding K is constant according to the constant parameters. Tips for numerical problem

$$N_{A} = K.t_{A}$$
 $N_{B} = K.t_{B}$

 $\frac{N_A}{N_B} = \frac{t_A}{t_B}$ rest parameters are constant, the value of N-may be in terms of rate of particles per unit time and similar tips may be applied for other parameters also Graphical study :



Conclusions

On the basis of above facts he proposed the following 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 charged body i.e., for such large deflections to occur α -particles must have come closer to or collided with a massive positively charged body, and he named it nucleus.
- 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} while the atom has a diameter of the order 10^{-8} of cm. So, the size of atom is

 10^5 times more than that of nucleus.

- (iii) 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 high speed in various circular orbits.
- (v) The centrifugal force arising due to the high speed of an electron balances the columbic 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 outsided 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.

Complete the follo	Wing table:	ractice	e Problem	5 - 01	
Particle	Atomic No.	Mass No.	No. of Elecrrons	No. of Protons	No. of neutrons
Sodium atom	11	_	—	_	12
Aluminium ion	_	27	10	_	_
Chloride ion	_	_	18	_	18
Phosphorus atom	_	31	—	15	_
Cuprous ion	_		28	_	35

1.

- If radius of the nucleus is 3.5×10^{-15} m then find the space occupied by the nucleus. 2.
- The approximate radius of a H-atom is 0.05 nm, and that of proton is 1.5×10^{-14} m. Assuming 3. both the hydrogen atom and the proton to be spherical, calculate fraction of the space in an atom of hydrogen that is occupied by the nucleus.
- The mass-charge ratio for A⁺ ions is 1.97×10^{-7} kg C⁻¹. Calculate the mass of A atom. 4.
- Calculate the force of attraction between an electron and a body having two proton charge when 5. they are 0.529×10^{-8} cm apart. Charge on one electron and one proton is -1.6×10^{-19} C and $+ 1.6 \times 10^{-19}$ C.
- Two carbon discs of 1.0 g each are 1.0 cm apart have equal and opposite charges. If forces of 6. attractions between them is 1.00×10^{-5} N, Calculate the ratio of excess electrons to total atoms on the negatively charged disc. (permittivity constant is 9.0×10^9 N m²C⁻²)
- 7. Write down the numerical value of h and its unit.
- Calculate the charge in coulomb on Fe³⁺ ion. 8.
- An oil drop has 6.39×10^{-19} coulomb charge. How many electrons does this oil drop has? 9.
- 10. (A) Find the radius of nucleus of an atom having atomic mass number equal to 125.
 - Find the distance of closest approach when an a particle is projected towards the nucleus **(B)** of silver atom having speed V. (mass of α particle m)
- 11. α -particles of 6 MeV energy is scattered back from a silver foil. Calculate the maximum volume in which the entire positive charge of the atom is supposed to be concentrated. (Z for silver = 47) $K = 9.0 \times 10^{-9} \text{ Nm}^2 \text{C}^{-2}.$

- 12. 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?
- 13. An alpha particle after passing through a potential difference of 2×10^6 volt falls on a silver foil. The atomic number of silver is 47. Calculate (i) the K.E. of the alpha-particles at the time of falling on the foil. (ii) K.El. of α -particle at a distance of 5×10^{-14} m from the nucleus, (iii) the shortest distance from the nucleus of silver to which the α -particle reaches.
- 14. In Rutherford experiment the number of alpha particles scattered through and angle of 90° in 28 per minute. Then find the number particles scattered through an angle of 60° per minute.
- 15. X-rays emitted from a copper target and a molybdenum target are found to contain a line of wavelength 22.85 nm attributed to the Ka line of an impurity element. The Ka lines of copper (Z = 29) and molybdenum (Z = 42) have wavelength 15.42 nm and 15.42 nm and 7.12 nm respectively. Using Moseley's law $\gamma^{1/2} = a(Z-b)$ calculate the atomic number of the impurity element.
- 16. With what velocity should an α -particle travel towards the nucleus of a copper atom so as to arrive at a distance 10⁻¹³ meter from the nucleus of the copper atom.
- 17. A beam of α -particle of velocity 2.1 × 10⁷ m/s is scattered by the gold (z = 79) foil. Find out the distance of closest approach of the α -particle to the gold nucleus. The value of the charge/mass for α -particle is 4.9 × 10⁷ coulomb/Kg.

3. Electromagnetic Energy

Newton was first person to comment on the nature of light in terms of Corpuscular. Theory of Light. According to this theory light is a stream of particles commonly known as corpuscles of

light. He was able to explain reflection and refraction, the most common phenomenon of light. But the other phenomenon like diffraction and interference could not be explained on the basis of this theory.

Maxwell, in 1956 proposed that radiant energy (light) has wave characteristics. Light according to him is Electromagnetic Wave arising due to the disturbance created by electric and



magnetic fields oscillating perpendicular to each other in space. Like all other mechanical waves, it is characterised by velocity c, frequency ν , wavelength λ which are related as :

 $c = v\lambda$. The value of c is constant and equal to $3 \times 10^8 \text{ m/s}$.

Wavelength (λ) :

The shortest separation between two consecutive crests and troughs.



Frequency (v): It is the number of waves or cycles passing through a particular point per unit time.



v = 2 Two waves are passing through "P" per unit time.

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

Wave number (\overline{v}) : It is the reciprocal of the wavelength i.e., number of wavelengths per centimeter. **Amplitude :** It is the height of depth of either a crest or a trough.



a = amplitude Z

4. Electromagnetic Spectrum

Electromagnetic wave or radiation is not a single wavelength radiation, but a mixture of various wavelength or frequencies. All the frequencies have same speed.

If all the components of Electromagnetic Radiation (EMR) are arranged in order of decreasing or increasing wavelengths or frequencies, the pattern obtained is known as Electromagnetic Spectrum. The following table shows all the components of light.

	Name	Wavelength	Frequency(Hz)	Source
S.No.				
1.	Radio wave	$3 \times 10^{14} - 3 \times 10^{7}$	$1 \times 10^{5} - 1 \times 10^{9}$	Alternating current of high frequency
2.	Microwave	$3 \times 10^{7} - 6 \times 10^{6}$	$1 \times 10^9 - 5 \times 10^{11}$	Klystron tube
3.	Infrared (IR)	$6 \times 10^{6} - 7600$	$5 \times 10^{11} - 3.95 \times 10^{16}$	Incandescent objects
4.	Visible	7600–3800	$3.95 \times 10^{16} - 7.9 \times 10^{14}$	Electric bulbs, sun rays
5.	Ultraviolet(UV)	3800-150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, arc lamps with mercury vapours
6.	X-Rays	150-0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate
7.	γ-Rays	0.1–0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Secondary effect of radioactive decay
8.	Cosmic Rays	0.01-zero	3×10 ²⁰ –Infinity	Outer space

Continuous Spectrum: When sunlight (white light) is passed through a prism, it is dispersed or resolved into a continuous spectra of colours. It extends from RED (7600 Å) at one end to the VIOLET (3800Å) at other end. In this region, all the intermediate frequencies between red and violet are present. The type of spectrum is known as Continuous Spectrum., Hence continuous spectra is one which contains radiation of all the frequencies.

Discontinuous Spectrum: Light emitted from atoms heated in a flame or excited electrically in gas discharge tube, does not contain a continuous spread of wavelengths (or frequencies). It contains only certain well-defined wavelength (or frequencies). The spectrum pattern appears as a series of bright lines (separated by gaps of darkness) and hence called as Line-Spectrum.

One notable feature observed is, that each element emits a characteristic spectrum, suggesting that there is discrete relation between the spectrum characteristics and the internal atomic structure of an atom.

5. 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. $E \propto v$ (or E = hv were v 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 hv, 2hv, 3hv nhv where n is the positive integer.

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

6. Photoelectric Effect

Hertz (1887) discovered that a metallic surface in vacuum can emit electricity when light of very short wavelength falls on it and in 1898 Thomson showed that the e/m value of emitted particles was the same as that for cathode rays. It is now known of course that particle are dielectron. The important facts of photoelectric effects are

- If light of a given frequency can liberate electrons from a surface, the electron current is proportional to the intensity of the light.
- For a given metallic surface there is a smallest value of the frequency for which the incident light can liberate electrons; light of smaller frequency than this can not eject electrons no matter how long it falls on the surface or how greater is its intensity.
- Light of frequency greater than this critical value causes immediate emission of electron, the time interval between the incidence of it light on the metallic surface and appearance of electrons is not more than 3×10^{-9} sec.
- The maximum kinetic energy of the emitted electrons is a linear function of the frequency of the light which causes the emission and is independent of the intensity of the incident light.



While explaining the action of photo electric effect EINSTIENE suggested that photon's energy is used in two ways.

• A part of the total energy of photon's is used to overcome the attractive forces between the electrons and the metal.

• Rest part of the energy is used to move the electrons by adding them kinetic energy. On the basis of conservation of energy principle we have

Energy of photon = energy to release electrons + K. E. of electrons.

E = W + KE where W is termed as photo electric work function

$$E = W + \frac{1}{2} mv^2$$
(i)

When the photon's energy is only sufficient to overcome the attractive forces of electrons to nucleus of the atom their K. E = 0 hence from equation (i) \uparrow

$$E = h_{1} hv = hv_{0} hv = hv_{0} + \frac{1}{2} mv^{2} KE$$

$$\frac{1}{2} mv^{2} = hv - hv_{0} = h(v - v_{0}) (y) = mx - c$$
For a given metal w = hv_{0} is constant and
$$KE = \frac{1}{2} mv^{2} \propto hv$$

$$v^{2} \propto v$$

Thus increase of frequency of the incident radiation causes an increase in the velocity of electron provided intensity of incident light is constant.

Note: The electromagnetic Radiation (or wave) now emerges as an entity which shows dual nature i.e., sometimes as Wave and sometimes as Particle (quantum aspect).

Illustration 4:

In a photoelectric experiment, the collector plate is at 2.0 V with respect to emitter plate made of copper (work function 4.5 eV). The emitter is illuminated by a source of monochromatic light of wavelength 200 nm. Find the minimum and maximum kinetic energy of photoelectrons reaching the collector.

Solution:

Since plate potentials 2 V, minimum K.E. will be 2 eV. For max. K.E. use the following relation: Absorbed energy = Threshold energy + K.E.

$$h\frac{c}{\lambda} = 4.5 \times 1.6 \times 10^{-19} + K.E. \qquad \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{200 \times 10^{-9}} = 4.5 \times 1.6 \times 10^{-19} + K.E$$

K.E. =
$$2.739 \times 10^{-19} \text{ J} = 1.7 \text{ eV}$$
 Max

Max K.E. = 2eV + 1.7 eV = 3.7 eV.

Daily Practice Problems - 02

- 1. Let a light of wavelength λ and intensity 'I' strikes a metal surface to emit x electrons per second. Average energy of each electron is 'y' unit. What will be happen to 'x' and 'y' when (a) l is halved (b) intensity I is doubled?
- 2. Work function of sodium is 2.5 eV. Predict whether the wavelength 65000Å is suitable for a photoelectron or not?

- 3. The threshold frequency for a certain metal is 3.3×10^{14} cycle/sec. If incident light on the metal has a cut-off frequency 8.2×10^{14} cycle/sec, calculate the cut-off potential for the photoelectron.
- 4. The photoelectric cut-off voltage in a certain experiment is 1.5 volt. What is the maximum kinetic energy of the photoelectrons emitted?
- 5. In a photoelectric effect experiment, irradiation of a metal with light of frequency $5.2 \times 10^{14} \text{ sec}^{-1}$ yields electrons with maximum kinetic energy 1.3×10^{-19} J. Calculate the v_0 of the metal.
- 6. The stopping potential for the photoelectric emitted from a metal surface of work function 1.7 eV is 10.4V. Find the wavelength of the radiation used. Also identity the energy levels in hydrogen atom, which will emit this wavelength.
- 7. What will be the maximum kinetic energy of the photoelectrons ejected from magnesium (for which the work function W = 3.7 eV) when irradiated by ultraviolet light of frequency $1.5 \times 10^{15} \text{ sec}^{-1}$.
- 8. A metallic surface is irradiated with monochromatic light of variable wavelength. Above a wavelength of 5000 Å, no photoelectrons are emitted from the surface. With an unknow wavelength, stopping potential of 3 V is necessary to eliminate the photocurrent. Find the unknown wavelength.
- 9. A graph regarding photoelectric effect is shown between the maximum kinetic energy of electrons and athe frequency of the incident light. On the basis of data as shown in the graph, calculate:



- (a) Threshold frequency, (b) Work function, (c) Planck's constant **10.** A metallic surface is illuminated alternatively with light wavelengths 3000 $\stackrel{0}{A}$ and 6000 $\stackrel{0}{A}$. It is observed that the maximum speeds of the photoelectrons under these illuminations are in the ratio 3:1. Calculate the work function of the metal and the maximum speed of the photoelectrons in two cases.
- 11. When a beam of 106 eV photons of intensity 2.0 Wm⁻² falls on a platinum surface of area 1.0×10^{-4} m² and work function 5.6 eV, 0.53% of the incident photons eject photoelectrons. Find the number of photoelectrons emitted per second and their minimum and maximum energies (in eV).
- 12. Light described at a place by the equation $E = (100 \text{ V/m}) [\sin(5 \times 10^{15} \text{ s}^{-1})t + \sin(8 \times 10^{15} \text{ s}^{-1})t]$ falls on a metal surface having work function 2.0 eV. Calculate the maximum kinetic energy of the photoelectrons.
- 13. Light described at a place by the equation $E = E_0 \sin[(1.57 \times 10^7 \text{ m}^{-1}) (x \text{ct})]$. Find the stopping potential when this light is used in an experiment on photoelectric effect with the similar having work function 1.9 eV.
- 14. In a photo–emissive cell, with exciting wavelength λ , the maximum kinetc energy of electron is K. If the exciting wavelength is changed to $\frac{31}{4}$, kinetic energy of the fastest emitted electron will be (A) 3K/4 (B) 4K/3 (C) less than 4K/3 (D) greater than 4K/3

15.	The threshold wavelength for photoelectric emission from a material is 5200Å. Photoelectrons will be		
	emitte	ed when this material is illuminated with m	(D) 1 see the formed laws
	(A) 50	J watt infrared lamp	(B) I watt infrared lamp
	(C) 5() watt ultraviolet lamp	(D) I watt ultraviolet lamp
16.	Photo	electric effect supports quantum nature of	of light because
	(A)	there is a minimum frequency of light	below which no photoelectrons are emitted
	(B)	the maximum kinetic energy of photoe not on its intensity	electrons depends only on the frequency of light and
	(C)	even when the metal surface is faintly immediately	y illuminated, the photoelectrons leave the surface
	(D)	electric charge of the photoelectrons is	s quantized.
17.	When a monochromatic point source of light is at a distance of 0.2 m from a photoelectric cell, the cut-off voltage and the saturation current are respectively 0.6 volt and 18 mA. If the same source is placed 0.6 m away from the photoelectric cell, then		
	(A) th (C) th	e stopping potential will be 0.2 volt e saturation current will be 6 mA	(B) the stopping potential will be 0.6 volt(D) the saturation current will be 2 mA
18.	When maxim energy $T_B = ($ (A) th (C) T	in photons of energy 4.25 eV strike the sumum kinetic energy. T_A expressed in eV a by of photoelectrons liberated from an $T_A - 1.50$ eV). If the de-Broglie wavele work function of A is 2.25 eV = 2 eV	arface of a metal A, the ejected photoelectrons have nd de-Broglie wavelength λ_A . The maximum kinetic nother metal B by photons of energy 4.70 eV is ngth of these photoelectrons is $\lambda_B = 2\lambda_A$, then (B) the work function of B is 4.20 eV (D) T = 2.75 eV
19.	Theg	raph between the stopping potential (V_0) and wave number $(1/\lambda)$ is as shown in the figure. ϕ
	is the	work function, then	*
	(A) ∳ (B) ∳	$\phi_1: \phi_2: \phi_3 = 1:2:4$ $\phi_1: \phi_2: \phi_3 = 4:2:1$	Metal 1 Metal 2 Metal 3 ϕ_1 ϕ_2 ϕ_3

(C) $\tan\theta \propto \frac{hc}{e}$ where θ is the slope

<u>λθ</u><u>λ</u>θ<u>λ</u>θ 0.001 0.002 0.004 1/λ

(D) ultraviolet light can be used to light photoelectrons from metal 2 and metal 3 only

Daily Practice Problems - 03

- 1. AIR service on Vividh Bhrati is transmitted on 219 m band. What is its transmission frequency in Hertz?
- 2. Certain sun glasses having small crystals of AgCl incorporated in the lenses, on exposure to light of appropriate wavelength turns to gray colour to reduce the glare following the reaction:

AgCl
$$\xrightarrow{hv}$$
 Ag $+$ Cl (Gray)

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

- 3. If Einstein E is total energy absorbed by 1 mole of a substance and that each molecule absorbs one quantum of energy, then calculate the value of E in terms of λ in cm.
- 4. Calculate the energy involved when one mole of a substance absorbs red light of frequency 4×10^{14} sec⁻¹.

- 5. Calculate the energy involved when one mole of a substance absorbs red light of frequency 4×10^{14} sec⁻¹. Given that one molecule absorbs one quantum.
- 6. Calculate the no. of quanta of radiation of frequency $4.67 \times 10^{13} \text{ sec}^{-1}$, that must be absorbed to melt 10 g ice. The energy required to melt 1 g ice is 33 J.
- 7. Calculate the wavelength of photon associated with an energy of 1 electron volt.
- 8. If takes approximately, 1 eg of energy for a fly to lift off from a table top. How many flies could get air borne by Avogadro's number of photon of yellow sodium light of l = 5800Å
- **9.** A photon of light of wavelength 6000Å has energy E. Calculate the wavelength of photon of a light which has energy/photon 4E.
- 10. How many photons of frequency 2.45×10^9 s⁻¹ are required to raise the temperature of 225 g water from 24.5°C to 99.5°C? Specific heat of water is $4.18 \times Jg^{-1}K^{-1}$?
- 11. A beam of electron accelerated with 4.64 V is passed through a tube containing mercury vapours. As a result of absorption, electronic changes occurred with mercury atoms and light was emitted. If the full energy of single electron was converted into light, what was the wave number of emitted light?
- 12. 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.
- 13. The minimum energy required to overcome the attractive forces between and electron and the surface of Ag metal is 5.52×10^{-19} J. What will be the maximum kinetic energy of electrons ejected out from Ag which is being exposed to UV light of 1 = 360 Å?
- 14. Calculate the number of photons emitted in 10 hour by a 60 W sodium lamp. ($\lambda_{photon} = 5893$ Å)

Daily Practice Problems - 04

- 1. The dissociation energy of H_2 is 430.53 kJ mol⁻¹. If H_2 is exposed to radiation energy of wavelength 253.7 nm, what percentage of radiant energy will be converted into kinetic energy?
- 2. O_2 undergoes photochemical dissociation into one normal oxygen atom and one oxygen atom, 1.967 eV more energetic than normal. The dissociation of O_2 into two normal atoms of oxygen requires 498 kJ mol⁻¹. What is the maximum wavelength effective for photochemical dissociation of O_2 ?
- 3. A certain laser transition emits 6.37×10^{15} quanta per second per square metre. Calculate the power out put in joule per square metre per second. Given $\lambda = 632.8$ nm.
- 4. Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda = 550$ nm) are needed to generate this minimum amount of energy?
- 5. A certain dye absorbs light of $\lambda = 4530$ Å. Assuming that under given conditions 47% of the absorbed energy is re-emitted out as fluorscence, calculate the ratio of quanta emitted out to the no. of quanta absorbed.
- 6. A photon of 300 nm is absorbed by a gas and then re-emits two photons. One re-emitted photon has wavelength 496 nm. Calculate energy of other photon re-emitted out.
- 7. The dissociation $I_2 \xrightarrow{hv} 2I$ utilizes one photon per iodine molecule dissociated. The maximum l for this is 4995 Å. Calculate number of moles of I, dissociated per kJ of photon energy.

- 8. (a) An atom initially in an energy level with E = -6.52 eV absorbs a photon that has wavelength 860 nm. What is the internal energy of the atom after it absorbs the photon? (b) An atom initially in an energy level with E = -2.68 eV emits a photon that has wavelength 420 nm. What is the internal energy of the atom after it emits the photon?
- **9.** Ultraviolet light of wavelength 800 Å and 700Å when allowed to fall on hydrogen atoms in their ground state is found to liberate electrons with kinetic energy 1.8 eV and 4 eV respectively. Find the value of Planck's constant.

7. Bohr's Atomic Model

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

Important postulates of Bohr's Model

(1) Electrons revolve around the nucleus along certain circular paths known as "ORBIT" or "SHELLS"

K, L, M, are shells

 $K \rightarrow 1$ st orbit

 $L \rightarrow 2nd \text{ orbit}$

 $M \rightarrow 3rd \text{ orbit}$

- (2) Electron is associated with a fixed energy in a particular orbit. The change in electronic energy is possible only when; electron changes its orbit number.
 - (a) When an electron goes to higher orbit from lower orbit, then energy is absorbed.

$$\bigoplus_{\substack{n=1\\n=2}}^{E_1} E_2$$

$$E_1 - E_2 = \Delta E \text{ (Absorbed energy)}$$

(b) If an electron jumps to lower orbit from higher orbit, then energy is radiated.

$$\bigoplus_{\substack{n=1\\n=2}}^{E_1} E_2$$

$$E_2 - E_1 = \Delta E \text{ (Emission of energy)}$$

(3) The electrostatic force of attraction acting between the electron and the nucleus is counterbalance by the centrifugal force

$$\frac{mV^2}{r} = \frac{Ze^2}{r^2}$$

or
$$mv^2 = \frac{Ze^2}{r^2} \qquad (i)$$
$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{r} \qquad (ii)$$



 $[*\epsilon_{_0}\,8.8\times10^{_{-12}}\,C^2\,N^{_{-1}}\,m^{_{-2}}]$



(4) Electrons can revolve only in those orbits in which angular momentum is integral multiple of $\frac{h}{2\pi}$



where, h = Planck's constant = 6.62×10^{-34} J s⁻¹ = 6.62×10^{-27} erg. sec⁻¹ m = mass of electron

v = Electronic velocity

- n=orbit number
- **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.

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 the calculated by Bohr's theory.

Limitations of Bohr's Theory

- (i) It does not explain the spectra of atoms or ions 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 attainable.

By Bohr's theory

(i) 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
$$=\frac{KZe^2}{r^2}$$

 $K = \frac{1}{4\pi\epsilon_0}$ (where ϵ_0 is permitivity of free space)
 $K = 9 \times 10^9 \text{ Nm}^2 \text{C}^{-2}$



In C.G.S. units, value of K = 1 dyne cm²(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.

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \qquad \dots (i)$$
(or) $v^2 = \frac{KZe^2}{mr} \qquad \dots (ii)$

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

$$mvr = \frac{nh}{2\pi} \qquad v = \frac{nh}{2\pi mr}$$
$$v^{2} = \frac{n^{2}h^{2}}{4\pi^{2}m^{2}r^{2}} \qquad \dots \text{ (iii)}$$
$$mr(2) \text{ and } (2) \qquad \frac{KZe^{2}}{2\pi} = \frac{n^{2}h^{2}}{2\pi}$$

Equating (2) and (3)
$$\frac{1}{mr} = \frac{1}{4\pi^2 m^2 r^2}$$

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

where $n = 1, 2, 3, ... \infty$

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 level from the nucleus the greater is the radius.

The radius of the smallest orbit (n = 1) for hydrogen atom (Z = 1) is r_0 .

$$r_{0} = \frac{n^{2}h^{2}}{4\pi^{2}me^{2}K} = \frac{1^{2} \times (6.626 \times 10^{-34})^{2}}{4 \times (3.14)^{2} \times 9 \times 10^{-31} \times (1.6 \times 10^{-19})^{2} \times 9 \times 10^{9}} = 5.29 \times 10^{-11} m$$

$$r_{0} = 0.529 \text{\AA}$$

Radius of nth orbit for an atom with atomic number Z is simply written as

$$r_n = r_0 \frac{n^2}{z} = 0.529 \times \frac{n^2}{z} \text{\AA}$$

Illustration :

Calculate the ratio of the radius of Li^{+2} ion in 3^{rd} energy level to that of He+ ion in 2^{nd} energy level.

Solution:

$$r \propto \frac{n^{2}}{z} \qquad \frac{r_{1}}{r_{2}} = \left(\frac{n_{1}}{n_{2}}\right)^{2} \left(\frac{z_{2}}{z_{1}}\right)$$

$$n_{1} = 3 \quad n_{2} = 2 \qquad z_{1} = 3 \text{ (for } Li^{2+}) \qquad z_{2} = 2 \text{ (for } He^{+})$$

$$\frac{r_{1}}{r_{2}} = \left(\frac{3}{2}\right)^{2} \times \left(\frac{2}{3}\right) = \frac{3}{2}$$

(ii) **Energy level of Hydrogen atom:** The total energy, E of the electron is the sum of kinetic energy and potential energy. Kinetic energy of the electron = $\frac{1}{2} \text{mv}^2$

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

Total energy $= \frac{1}{2}mv^2 - \frac{KZe^2}{r}$... (4)
From equation (1) we know that

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

Substituting this in equation (4)

Total energy (e)
$$= \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$
 $KE = -\frac{1}{2}PE, KE = -TE$
Substituting for r, gives us $E = \frac{2\pi^2 mZe^2 e^4 K^2}{n^2 h^2}$ where n = 1, 2, 3, ...

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

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

= $-21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J per atom}$
= $-13.6 \times \frac{Z^2}{n^2} \text{ eV per atom}$
 $E_n = -13.6 \frac{Z^2}{n^2} \text{ eV per atom}$
(1eV = $3.83 \times 10^{-23} \text{ Kcal}$) (1eV = $1.602 \times 10^{-12} \text{ erg}$) (1eV = $1.602 \times 10^{-19} \text{ J}$)
 $E = -313.6 \times \frac{Z^2}{n^2} \text{ kcal/mole}$ (1 cal = 4.18 J)
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$$E_n = -\frac{2\pi^2 mze^4}{n^2 h^2}$$

The negative sign before energy expression suggest that electron is not free, but it is bound to the nucleus. So, if we will try to remove the electron outside the atom, we have to do some work against the force of attraction acting between the electron and the nucleus.



 $E_{\infty} - E_1 = \Delta E = 0 - (-13.6) = +13.6 \text{ ev}$ *.*.

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

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

Illustration :

How far from the nucleus is the electron in a hydrogen atom if it has energy of _ 0.850 eV.

Solution:

$$E_{n} = -\frac{Z^{2}}{n^{2}} \times 21.69 \times 10^{-19} \qquad -\frac{Z^{2}}{n^{2}} \times 21.69 \times 10^{-19} = -0.85 \times 1.6 \times 10^{-19}$$

$$n = 4 \ (Z = 1) \qquad r = \frac{n^{2}}{Z} \times 0.529 = \frac{16}{1} \times 0.529 = 8.46 \text{\AA}$$

(iii) Velocity of electron

We know that, mvr $=\frac{nh}{2\pi}$; v $=\frac{nh}{2\pi mr}$

By substituting for r we are getting

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

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

Where excepting n and z all are constant, $v = 2.18 \times 10^8 \frac{2}{n}$ 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.

DATA FOR FIRST ORBIT OF HYDROGEN ATOM :

(i) Total energy = -13.6 eV(ii) Potential energy = -27.2 eV(iii) Kinetic energy = +13.6 eV(iv) Radius = 0.529 Å(v) Velocity = $2.188 \times 10^8 \text{ cm}\text{-sec}^{-1}$

Energy of K, L, M, N ∞ (hypothetical) orbit of H-atom :

Orbit	Energy		
	J/atom	eV/atom	K cal/mode
K (n =1)	$-21.8 imes 10^{-19}$	-13.6	-313.6
L (n=2)	-5.45×10^{-19}	-3.4	-78.4
M (n=3)	$-2.42 imes 10^{-19}$	-1.51	-34.84
N (n =4)	$-1.36 imes 10^{-19}$	-0.85	-19.6
8	0	0	0

Graphical representation of radius energy and velocity Radius



(a) Ground state (G. S.) :

The lowest energy state of an atom or ion or molecule

G.S. for H-atom	n = 1
He ⁺ - ion	n = 1
Ne - atom	n = 3

(b) Excited state (E. S.)

The energy states above the ground state are referred to as an excited

n = 2	1st E. S.
n = 3	2nd E. S.
n = 4	3rd E. S.
	Total E. S. = $(n - 1)$

(c) Excitation Potential (E. P.) :

The amount of energy needed to promote an electron from ground sat to 'n' level 1st I. P. = $E_2 - E_1 = -3.4 - (13.6) = 10.2 \text{ eV}$ 2nd E. P. $E_3 - E_1 = -1.51 - (-13.6) = 12.09$

(d) Ionization potential (I. P..)/Energy/Enthalpy

Corresponding energy required to remove the electron from G.S. to the infinite excited state. I. P. $= E_{\infty} - E_{1}$ = 0 - (-13.6) = 13.6 eV

(e) Separation Energy (S. E.)

The amount of energy needed to remove to infinity the electron from the excited state. e.g., S. E. = $E_{\infty} - E_2 = 0 - (-3.4) = 3.4 \text{ eV}$ also S. E. = $E_{\infty} - E_3 = 0 - (-1/51) = 1.51 \text{ eV}$

Daily Practice Problems - 05

1. Prove that $\sqrt{\left(\frac{Ze^2}{mr_n}\right)}$ where u is velocity of electron in a one electron atom of at. no. Z at a distance

 r_n from the nucleus, m and e are mass and charge of electron.

- 2. Calculate the velocity of an electron placed in III orbit of H atom. Also calculate the no. of revolution/sec round the nucleus.
- 3. Findout the energy of H atom in first excitation state. The value of permittivity factor $4\pi\epsilon_0 = 1.11264 \times 10^{-10} \text{ C}^2\text{N}^{-1} \text{ m}^{-2}.$
- 4. What is the principal quantum no. of H atom orbital if the electron energy is -3.4 eV? Also report the angular momentum of electron/
- 5. The ionisation energy of H atom is 13.6 eV. What will be ionisation energy of He⁺ and Li²⁺ ions?
- $\label{eq:constant} \textbf{6.} \qquad \text{The ionisation energy of } He^+ \text{ is } 19.6 \times 10^{-18} \text{ J atom}^{-1}. \ \text{Calculate the energy of first stationary state of } Li^{2+}.$
- 7. Energy required for excitation of electron in 1 mole H atom form ground state to 2nd excited state is 2.67 times lesser than dissociation energy per mole of $H_2(g)$. Calculate the amount of energy needed to excite each H atom of $H_2(g)$ confined in 1.0 litre at 27°C and 1 bar pressure. R = 0.083 bar litre K^{-1} mol⁻¹; $R_{\rm H} = 1.1 \times 10^7$ m⁻¹.

- 8. 1.8 g hydrogen atoms are excited to radiation. the study of spectra indicates that 27% of the atoms are in 3rd energy level and 15% of atoms in 2nd energy level and the rest in ground state. If I.P. of H is $21.7 \times 10-12$ erg. Calculate–
 - (i) No. of atoms present in III & II energy level.
 - (ii) Total energy evolved when all the atoms return to ground state.
- **9.** One mole He⁺ ions are excited. Spectral analysis showed existence of 50% ions in 3rd orbit, 25% in 2nd and rest in ground state. Calculate total energy evolved when all the ions return to the ground state.

Daily Practice Problems - 06

- 1. An electron, in a hydrogen atom, in tis ground state absorbs 1.5 times as much energy as the minimum required for its escape (i.e., 13.6 eV) from the atom. Calculate the value of λ for the emitted electron.
- 2. The radius of the fourth orbit of hydrogen in 0.85 nm. Calculate the velocity of an electron in this orbit $(m_e = 9.1 \times 10^{-31} \text{ kg}]$
- 3. The radius of the fourth orbit in H atom is 0.85 nm. Calculate the velocity of electron in this orbit.
- 4. The first ionisation energy of H is 21.79×10^{-19} J. Calculate the second ionisation energy of He atom.
- 5. The radius of I bohr's orbit of the H atom is 0.529 Å. Calculate the (a) radius of III orbit of He^+ (b) II orbit of Li^{+2} ion.
- 6. To which quantum level does the electron jump in H atom from the lowest level if it is given an energy corresponding to 99% of the ionisation potential?
- 7. The first ionisation energy of potassium is 100 kcal mol⁻¹. Calculate the lowest possible frequency of light that can ionise a potassium atom [Ans. 1.052×10^{15} Hz]
- 8. Calculate the shortest frequency, longest λ and the minimum photon energy which will remove the 2nd electron of He atom with a velocity of 10^5 metre sec⁻¹.
- 9. How many times does the electrons go round the first Bohr's orbit of hydrogen in one second?
- 10. The circumference of first Bohr's orbit is 3.32×10^{-10} m. If this circumference represents one wavelength, what is the velocity of electron in this orbit.

Daily Practice Problems - 07

- 1. Convert the value of Rydberg constant ($R_{\rm H} = 109678 \text{ cm}^{-1}$) into Rydberg an unit of energy (i.e. Rydberg (1 Rh) = $2.18 \times 10^{-18} \text{ J}$)
- 2. Wavelength of high energy transition of H atom is 91.2 nm. Calculate the corresponding wavelength of He⁺ ion.
- 3. Wavelength of the K_a characteristic X-ray of iron and potassium are 1.9321×10^{-8} and 3.737×10^{-8} cm respectively. What is the atomic number and name of the element for which characteristic K_a wavelength is 2289×10^{-8} cm?

- 4. The velocity of an electron in certain Bohr orbit of H-atom bears the ratio 1:275 to the velocity of light. (a) what is the quantum number 'n' of the orbit? (b) Calculate the wave number of the radiation when the electron jumps from (n + 1) state to ground state.
- 5. Calculate the ionisation energy of the hydrogen atom. How much energy will be required to ionise 1 mole of hydrogen atoms? Given, that the Rydberg constant is 1.974×10^7 m⁻¹.
- 6. Calculate the ionisation energy of (a) one Li^{2+} ion and (b) one mole of Li^{2+} ion. (Given $R = 1.0974 \times 10^{-7} m^{-1}$)
- 7. Calculate the speed of an electron in the ground state of hydrogen atom. What fraction of the speed of light is this value? How long does it take for the electron to complete on revolution around the nucleus? How many times does the electron travel around the nucleus in one second?
- 8. If the average life time of an excited state of H atom is of order 10^{-8} sec, estimate how many orbits an e⁻ makes when ti is in the state n = 2 and before it suffers a transition to n = 1 state.
- **9.** A single electron orbits around a stationary nucleus of charge + Ze where Z is a constant from the nucleus and e is the magnitude of the electric charge. The hydrogen like species required 47.2 eV to excite the electron from the second Bohr orbit to the third Bohr orbit. Find
 - (i) the value of Z and give the hydrogen like species formed.
 - (ii) the kinetic energy and potential energy of the electron in the first Bohr orbit.
- 10. A particle of charge equal to that of an electron and mass 208 times the mass of the electron moves in a circular orbit around a nucleus of charge +3e. Assuming that the Bohr model of the atom is applicable to this system, (a) derive an expression for the radius of the nth bohr orbit, (b) find the value of n form which the radius of the orbit is approximately the same as that of the first bohr orbit for the hydrogen atom, and (c) find the wavelength of the radiation emitted when the revolving particle jumps from the third orbit to the first.

8. Atomic Spectrum

ATOMIC SPECTRA :

Nature of radiant energy :

Einstein suggested that light is made of a stream of particles known as PHOTONS. But, according to maxwell light is an electromagnetic wave, arising due to the disturbance created by electric and magnetic fields oscillating perpendicular to each other in space. Like all the mechanical wave it is characterised by velocity c, wavelength λ and frequency v, which are related

$$r = \frac{c}{2}$$
(i)

For electromagnetic wave ; c is a constant and is equal to $3 \times 10^8 \text{ ms}^{-1}$.

Spectrum :

It is a photographic impression obtained on a photographic film when a ray of particular wavelength is analysed through a prism and then made to fall on the photographic film.

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.

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.



Line spectrum of hydrogen

It is evident that the energy gap between the two consecutive energy levels is going to decrease from lower energy level to higher energy levels. This energy gap suggests that energy levels are trying to converge into a single energy level. In fact the significance of quantisation is going to be lost particular in the higher energy levels of H-spectrum.

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.

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

$$\overline{v} = \text{wave number}$$

$$\lambda = \text{wave length}$$

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

 n_1 and n_2 have integral values as follows



A mechanical analogy for the emission processes. The ball can rest on any step but not between steps

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 also 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.



(iii) 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 jumps, 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

$$n_{2} - E_{n_{2}} = -\frac{2\pi^{2}mz^{2}e^{4}}{n_{2}^{2}h^{2}}$$

$$n_{1} - E_{n_{1}} = -\frac{2\pi^{2}mz^{2}e^{4}}{n_{1}^{2}h^{2}}$$

$$n_{2} > n_{1}$$

$$hv = E_2 - E_1 = \frac{-2\pi^2 m Z^2 e^4 K^2}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \qquad v = \frac{2\pi^2 m Z^2 e^4 K^2}{h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

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.

$$v = \frac{C}{\lambda} = \frac{2\pi^2 m Z^2 e^4 K^2}{h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \qquad \qquad \frac{1}{\lambda} = \overline{v} = \frac{2\pi^2 m Z^2 e^4 K^2}{h^3 c} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where $\frac{2\pi^2 m e^4 K^2}{h^3 c} = 1.097 \times 10^{-7} m^{-1}$ or 109678 cm⁻¹
i.e. Rydberg constant (R) $\therefore \qquad \overline{v} = \frac{1}{\lambda} = R Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$
 \overline{v} = wave number.

Series Limit :

If $n_2 = \infty$, then the corresponding wavelength of any series is called limit of Lyman, Balmer, Paschen,

Bracket, Pfund and humphery series respectively $\frac{1}{R}$, $\frac{4}{R}$, $\frac{9}{R}$, $\frac{16}{R}$, $\frac{25}{R}$, $\frac{36}{R}$

Illustration :

Find the wavelengths of the first line of He⁺ ion spectral series whose interval between

extreme lines is
$$\frac{1}{\lambda_1} - \frac{1}{\lambda_2} = 2.7451 \times 10^4 \text{ cm}^{-1}$$

Solution:

Extreme lines means first and last.

$$\frac{1}{\lambda} - \frac{1}{\lambda_2} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{\infty^2} \right] - RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2} \right] = \frac{RZ^2}{(n_1 + 1)^2}$$
$$2.7451 \times 10^4 = \frac{109677.76 \times 2^2}{(n_1 + 1)^2} \qquad (n_1 + 1) = 4 \qquad n_1 = 3$$

Wavelength of first line,

$$\frac{1}{\lambda} = 109677.76 \times 2^2 \times \left[\frac{1}{3^2} - \frac{1}{4^2}\right] \qquad \lambda = 4689 \times 10^{-8} \,\text{cm} = 4689 \,\text{\AA}$$

Daily Practice Problems - 08

- 1. How many spectral lines are emitted by atomic hydrogen excited to the nth energy level?
- 2. Calculate the Rydberg constant R if He⁺ ions are known to have the wavelength difference between the first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7 nm.
- 3. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He⁺ spectrum?
- 4. 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.

- 5. Consider the following two electronic transition possibilities in a hydrogen atom as pictured given:
 - (1) The electron drops from third Bohr's orbit to second Bohr's orbit followed with the next transition from second to first Bohr's orbit.



(2) The electron drops from third Bohr's orbit to first Bohr's orbit directly.

Show that:

- (a) The sum of the energies for the transition n = 3 to n = 2 and n = 2 to $n_1 = 1$ is equal to the energy of transition for n = 3 to n = 1.
- (b) Are wavelengths and frequencies of the emitted spectrum are also additive in the same way as their energies are?
- 6. A gas of identical H-like atom has some atoms in the lowest (ground) energy level A and some atoms in a particular upper (excited) energy level B and there are no atoms in any other energy level. The atoms of the gas make transition to a higher energy level by absorbing monochromatic light of photon energy 2.7 eV. Subsequently, the atoms emit radiation of only six different photons energies. Some of the emitted photons have energy 2.7 eV. Some have more ans some have less than 2.7 eV.
 - (i) Find the principal quantum number of initially excited level B.
 - (ii) Find the ionisation energy for the gas atoms.
 - (iii) Find the maximum and the minimum energies of the emitted photons.
- 7. The wavelength of the first member of the Balmer series of hydrogen is 6563×10^{-10} m. Calculate the wavelength of its second member.
- 8. According to Bohr theory, the electronic energy of hydrogen atom in the nth Bohr orbit is given by.

$$E_{n} = \frac{21.76 \times 10^{-19}}{n^{2}} J$$

Calculate the longest wavelength of light that will needed to remove an electron from the 2nd orbit of Li^{2+} ion.

- **9.** Calculate the frequency, energy and wavelength of the radiation corresponding to spectral line of lowest frequency in Lyman series in the spectra of hydrogen atom. Also calculate the energy of the corresponding line in the spectra of Li²⁺.
- 10. What hydrogen-like ion has the wavelength difference between the first lines of Balmer and Lyman series equal to 59.3 nm ($R_{\rm H} = 109678 \, {\rm cm}^{-1}$)?

Daily Practice Problems - 09

- 1. Find out the wavelength of the next line in the series having lines of spectrum of H-atom of wavelengths 6565Å, 4863Å, 4342 Å and 4103 Å.
- 2. Which jump is responsible for the wave number of emitted radiation equal to $9.7490 \times 10^6 \text{ m}^{-1}$ in Lyman series of hydrogen spectrum? [R = $1.0974 \times 10^7 \text{m}^{-1}$]
- **3.** A series of lines in the spectrum of atomic hydrogen lies at 656.46nm, 486.27 nm, 439.17 nm and 410.29 nm. What is the wavelength of the next line in this series? What is the ionisation energy of the atom when it is in the lower state of transition?
- 4. A certain line of the Lyman series of hydrogen and a certain line of the Balmer series of He⁺ ion have nearly the same wavelength. To what transition do they belong? Small differences between their Rydberg constant may be neglected.

- 5. What element has a hydrogen-like spectrum whose lines have wavelengths four times shorter than those of atomic hydrogen?
- 6. What lines of atomic hydrogen absorption spectrum fall within the wavelength range from 94.5 to 130 nm.
- 7. What is the ratio of the speeds of an electron in the first and second orbits of a hydrogen atom?
- 8. Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit.
- **9.** The wave number of first line in Balmer series of hydrogen i 15200 cm⁻¹. What is the wave number of first line in Balmer series of Be³⁺?
- **10.** By what factor does the velocity of an electron in H atom changes when it is excited from the first to the second orbit?
- 11. The wavelength of certain line in Balmer series is observed to be 4341Å. To what value of n_2 does this correspond, $R_{\rm H} = 109678 \text{ cm}^{-1}$?

Daily Practice Problems - 10

- 1. Find the ionization energy of a doubly ionized lithium atom.
- 2. The total energy of an electron in the first excited state of the hydrogen atom is about -3.4 eV.
 - (a) What is the kinetic energy of the electron in this state?
 - (b) What is the potential energy of the electron in this state?
 - (c) Which of the answers above would change if the choice of the zero of potential energy is changed?
- 3. Hydrogen atom in its ground state is excited by means of monochromatic radiation of wavelength 1023 $\stackrel{0}{A}$. How many different lines are possible in the resulting spectrum? Calculate the longest wavelength among them. You may assume the ionization energy of hydrogen atom as 13.6 eV.
- **4.** A doubly ionized lithium atom is hydrogen-like with atomic number 3. Find the wavelength of the radiation require to excite the electron in Li⁺⁺ from the first to third Bohr orbit (ionization energy of the hydrogen atom equals 13.6 eV).
- 5. Find the quantum number n corresponding to nth excited state of He^+ ion if on transition to the ground state the ion emits two photons in succession with wavelengths 108.5 nm and 30.4 nm. The ionization energy of the hydrogen atom is 13.6 eV.
- 6. A hydrogen like atom (described by the Bohr model) is observed to emit six wavelength, originating from all possible transitions between a group of levels. These levels have energies between -0.85 eV and -0.544 eV(including both these values).
 - (a) Find the atomic number of the atom.
 - (b) Calculate the smallest wavelength emitted in these transitions.
- 7. The energy levels of a hypothetical one electron atom are shown in the figure.

~	0 eV
n = 5	
n = 4	
n = 3	

- n = 2 ______ 5.30 eV
- n = 1 ______ 15.6 eV

(a) Find the ionization potential of this atom.

- (b) Find the short wavelength limit of the series terminating at n = 2.
- (c) Find the excitation potential for the state n = 3.
- (d) Find wave number of the photon emitted for the transition n = 3 to n = 1.

Q.8.to 11

A single electron orbits around a stationary nucleus of charge + Ze, where Z is a constant and e is the magnitude of the electronic charge. It requires 47.2 eV to excite the electron from second Bohr orbit to the third Bohr orbit. Find:

- 8. The value of Z,
- 9. The energy required to excite the electron from n = 3 to n = 4,
- 10. The wavelength of radiation required to remove electron from the first Bohr Orbit to infinity,
- 11. The kinetic energy, potential energy and angular momentum of the electron in the first Bohr orbit and the radius of first Bohr orbit.

9. Quantum Mechanical Model of Atom

Quantum mechanical treatment of hydrogen atoms & Schrodinger wave equation

Bohr considered the electron as particle and offered a satisfactory explanation of the hydrogen spectra but could not explain the spectra of multieletron atoms. If also failed to provide any answer for electronic configuration of atoms. This theory faced a greater challenge from the discoveries of de-Broglie equation and Heisenberg uncertainty principle which consider electron a negatively charged wave distributed round the positive nucleus. This new model of the structure of atom is known as its

Quantum Mechanical Model.

This model has gained wide acceptance as the results obtained are in excellent agreement with experimental findings.

On the basis of above concept Erwin schrodinger on Austrian physicst in 1926 developed a new branch of science called quantum mechanics or wave mechanics. He also proposed an equation for the electronic wave in atom like hydrogen. Since hydrogen is the simplest chemical system consisting of one proton and one electron and has no change of repulsive energy between negative electron as it has only one electron in their atom.

He considered nucleus as the commanding point of electronic wave called nodal point and schrodinger has taken it as the origin in the co-ordinate system. The main target of the schrodinger was to locate the exact position of electron which could not be done by Heisenberg so accurately, to solve the problem he applied Cartesian co-ordinate (x, y, z) as well as polar co-ordinate (δ , θ , ϕ) to locate the best position of electron with respect to nucleus. Based on the above two co-ordinate system he first derived his equation in Cartesian system and then by trigonometric transformation it could be converted into polar co-ordinate system.

SCHRODINGER EQUATION OF CARTESIAN SYSTEM/RADIAL EQUATION

Schrodinger considered negativity charged electronic wave as stationary wave around the positively charged nucleus. (nodal point) The stationary wave equation or Sine wave used by him was.

where A = amplitude of the wave

x = displacement of wave along x-axis

 $\lambda =$ wavelength of the wave

 $\psi(Psi)$ = wave function representation of wave on differentiating equation (i) with respect to x.

$$\frac{d\psi}{dx} = \left[A\cos\frac{2\pi x}{\lambda}\right] \frac{2\pi}{\lambda} = \frac{2\pi}{\lambda} A \frac{A\cos\frac{2\pi}{\lambda}}{\lambda}$$

Again differentiation with respect to x

$$\frac{\partial^2 \psi}{dx^2} = \frac{2\pi A}{\lambda} \left[-\sin \frac{2\pi x}{\lambda} \right] \frac{2\pi}{\lambda}$$

or $\frac{\partial^2 \psi}{dx^2} = -\frac{4\pi^2 A}{\lambda^2} \sin \frac{2\pi x}{\lambda}$
Using equation for ψ we have
 $\frac{\partial^2 \psi}{dx^2} = -\frac{4\pi^2 A}{\lambda^2} \psi$ (ii)
Now we have from de Broglie equation
 $\lambda = \frac{h}{p} = \frac{h}{mv}$
or $\lambda_2 = \frac{h^2}{m^2 v^2}$ (iii)
From equation (ii) and (iii) we have

 $\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2 A m^2 v^2}{\lambda^2}$ (iv) since the negative electron is in motion and placed around a positively charged nucleus i.e., nodal point hence it has kinetic as well as potential energy hence total energy E = KE + PE

$$E = \frac{1}{2} mv^{2} + E_{p}$$

$$mv^{2} = 2(E - E_{p})$$

$$m^{2}v^{2} = 2m (E - E_{p}) \dots \dots \dots \dots (v)$$
From equation (iv) on adjusting for (v)
$$\frac{\partial^{2}\psi}{\partial x^{2}} = \frac{8\pi^{2}A \times m(E - E_{p})\psi}{h^{2}}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{8\pi^2 m(E - E_P)\psi}{h^2}$$
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m(E - E_P)\psi}{h^2} = 0 \dots (vi)$$

or

This is the schrodinger wave equation only along x-axis but atom is spherical and electrons are bound to move in three dimensional space i.e. along x, y and z-axis but the energy parameters are constant for we specific situation hence we have for space model of electronic wave.

$$\frac{\partial^2 \psi}{dx^2} + \frac{\partial^2 y}{dy^2} + \frac{\partial^2 y}{dz^2} + \frac{8\pi^2 m(E - E_P)\psi}{h^2} = 0 \dots (vii)$$

This is the Cartesian form of schrodinger wave equation. The value of potential energy Ep for hydrogen atom is taken as

$$E_{\rm p} = -\frac{e^2}{4\pi \epsilon_0 r} \text{ hence we have}$$
$$\frac{\partial^2 \psi}{dx^2} + \frac{\partial^2 y}{dy^2} + \frac{\partial^2 y}{dz^2} + \frac{8\pi^2 m(E - E_{\rm P})\psi}{h^2} = 0$$

It is a second degree differential equation of electronic wave ψ , as $\frac{dx}{dt}$ represent velocity i.e., rate of

displacement and $\frac{\partial^2 x}{dx^2}$ the rate of change in velocity i.e., acceleration similarly $\frac{\partial^2 y}{dx^2}$ may be taken as for electronic wave ψ .

Schrodinger equation in Polar co-ordinate system -

since atom has spherical symmetry hence it is more convenient to express schrodinger equation in terms of polar co-ordinate (r, θ , ϕ)

The transfer of Cartesian Co-ordinate (x, y, z) into polar co-ordinate may successfully be carried out with the help of following axial model of the atom in which both co-ordinate systems are represented having θ = angle with z-axis called zenith angle

r = radial vector of angular distance (OP) of electron (p) from nucleus (origin)

 ϕ = angle with x-axis from the perpendicular PP' drawn in xy-plane called longitudinal or Azimuthal angle.



The radial vector (r) is related to x, y, z as $r^2 = x^2 + y^2 + z^2$

When the Cartesian Co-ordinate (x, y, z) are transferred into polar co-ordinate (r, θ , ϕ) from the relation (i), (iii), (iv) and (v) and datas are substituted in Cartesian Schrodinger equation whose computing process is very complicated mathematical operation. Which in beyond the scope of discussion at this level the polar equation of schrodinger may be written as.

..... (v)

$$\frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} + \frac{1}{r^2 d^2 \theta} \cdot \frac{r^2 \psi}{\partial \phi^2} + \frac{1}{r^2} \frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} \right) \right] \frac{8\pi^2 m}{h^2} (E - E_p) \psi = 0$$

Solution of Schrodinger Equation :

Schrodinger wave equation is represented in radial form for Cartesian co-ordinate (x,y,z) and angular form (polar co-ordinate (r, θ, ϕ) and can be solved by various advance level mathematical operations which is beyond the scope of our discussion at this stage but its solution have got strong meaningful interpretation in deciding the position of electron in terms of orbital and their shape.

It's solution falls into two group called angular and radial solution and the product of the corresponding two solution gives the normalized wave function which decides the shape of corresponding orbitals. Some important solution within scope of our discussion are listed below.

Angular solution : It is represented as ' $\theta \phi$ ' (theta, fi)

ns-orbital
$$-\frac{1}{2\sqrt{\pi}}$$

 $\psi p_x - \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cdot \cos\phi$
 $\psi p_y - \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cdot \sin\phi$
 $\psi p_z - \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \cdot$
 $3dz^2 \sqrt{\frac{15}{4\pi}} (3\cos^2\theta - 1)$

here θ is zenith angle (with z-axis) and θ is azimuthal angle (with x-axis)

Radial solution : R(r)

$$\psi_{1s} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$$\psi_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} \left[2 - \frac{2Zr}{2a_0}\right] e^{-\frac{Zr}{2a_0}}$$

$$\psi_{3s} = \frac{1}{a\sqrt{3}} \left(\frac{Z}{a_0}\right)^{3/2} \left[6 - \frac{4Zr}{a_0} + \frac{4}{9} \frac{Z^2 r^2}{a_0^2}\right] e^{-\frac{Zr}{3a_0}}$$

$$\psi_{3p} = \frac{1}{a\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \left[4 - \frac{2Zr}{3a_0}\right] \frac{2Zr}{3a_0} e^{-\frac{Zr}{3a_0}}$$
liced upon function: $P(r) \times (0.4)$

Normalized wave function: $R(r) \times (\theta \phi)$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{\frac{Zr}{a_0}}$$

$$\begin{split} \psi_{2s} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left[2 - \frac{Zr}{a_0}\right] e^{-\frac{Zr}{2a_0}} \\ \psi_{2p_z} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \cos\phi \\ \psi_{2p_x} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin\theta . \cos\phi \\ \psi_{2p_y} &= \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin\theta . \sin\phi \end{split}$$

Schrodinger equation and quantum number

The natural solution of the schrodinger wave equation provides the concept of three quantum number n, ℓ and m. It also explain all aspect of the hydrogen spectrum which Bohr's theory failed to explain. Schrodinger equation cannot be solved for a multielectron atom. However solution of reasonable accuracy can be obtained using approximate methods.

The total wave function for a multielectron atom can be constructed from atomic orbitals having different energies. From the concept of angular solution and radial solution energy level for different orbitals maybe assigned and these atomic orbitals form the basis of designing electronic structure of the atom having more than one electron, it has been done keeping in mind to repulsion energy among the electron also.

Concept of atomic orbitals from schrodinger wave equation

In the light of wave mechanics an atomic orbital is one electron wave function $\psi(r, \theta, \phi)$ that is obtained from the solution of schrodinger wave equation for the hydrogen like atom. The position of the electron in polar co-ordinate is (r, θ, ϕ) can be factorised into three separate parts each of which is a function of only one co-ordinate.

 $\psi(\mathbf{r}, \theta.\phi) = \mathbf{R}(\mathbf{r}) \,\theta[\theta] \,\phi[\phi]$

R(r) = radial wave function which denotes the dependence of wave function on distance (r) of the electron from their nucleus.

 $\theta[\theta]$ is angular function showing its relation with zenith angle (θ) $\phi(\theta)$ = is angular function showing its dependence over azimuthal angle ϕ from x-axis.

The radial function R(r) depends upon the quantum number n and ℓ where an angular part $\theta(\theta)$ and $\phi(\theta)$ depends upon quantum number (ℓ) and (m) and is independent of (n).

The total wave function may be expressed as

 $\psi(\mathbf{r}, \theta, \phi) = \mathbf{R}_{\mathbf{n},\ell}(\mathbf{r}) \,\theta_{\ell,m}[\theta] \,\phi_{m}[\psi]$

The orbital wave function ψ has no physical significance, but the absolute value $[\psi]$ has physical significance as the square of the amplitude of photo-radiation (light) gives the intensity of photon falling at the given point $[\psi^2]$ gives the electron probability density at a given point in an atom.

The variation of ψ and ψ^2 with three co-ordinate (r, θ , ϕ) for different orbitals, in space can be displayed only with the help of fourth co-ordinate, the fourth co-ordinate will represent ψ or ψ^2 and remaining three (r₁, θ , ϕ) axial participation showing fourth axis is a very-very difficult for plane paper diagram hence a difficult work.

To get rid of from the fourth axis we may draw separate graph for radial and angular function.

When ψ is plotted against (r) the nature of the curve is



High Light of the solutions and wave function

Angular part solution of ns orbital is free from Zenith and Azimuthal angle.

Normalized wave function of ns is free from Zenith and Azimuthal angle.

Normalized wave function of Pz is dependent on only cos value of zenith angle.

Px and Py are jointly regulated by Zenith and Azimuthal angle.

The distribution curve shows a maxima near the nucleus for ns showing that their probability is maximum round the nucleus.

P-orbital has maxima farther from nucleus hence it stands at large distance from the nucleus.

Percentage ionic character of the bond is given by $\frac{\lambda_2}{1+\lambda^2} \times 100$ where $\lambda =$ Fraction of the contribution of ionic structure in the total wave function.

Radial probability density [R²]

The square of the radial wave function $[R^2]$ for an orbital gives the radial density and radial density given the probability density of finding the electron at a point along a particular radius line. The nature of the graph is like below. Node = n - l - 1





In above graph gives information about probability density or relative electron density at point for different distance (r) values. It may be noted here that for ns-orbitals the maximum electron density is at the nucleus and remaining orbitals np, nd, have zero electron density at the nucleus.

Each curve becomes finally parallel to x-axis showing one imaginary node for every orbital at infinity.

- * Node is defined as a region where the probability of finding an electron is zero.
- * The planes passing through the angular nodal points are called nodal planes.
- * No. of radial or spherical nodes = n l 1
- * No. of angular nodes = l, Total no. of nodes = n-1

Radial probability functions $D = 4\pi r^2 R^2$

The radial density $(R)^2$ for an orbital gives the probability density of finding the electron at a point at a distance (r) from the nucleus but atom is spherical and a means to find the probability of finding electron at a distance (r) from the nucleus in any possible direction in space between rand. Hence this probability in independent of direction is called radial probability is equal to $4\pi r^2 dr R^2$.

The radial probability may be obtained by considering a spherical shell between the spheres of radius (r + dr) and (r). The volume of the shell is

$$\frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3 = 4\pi r^2 dr$$

on neglecting dr³ function & dr² which are too small.

The nodal probability distribution curves obtained by plotting $4\pi r^2 dr R^2$ against (r) from the nucleus are given below.



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

Comment on the Curve :

- For 1s the probability distribution curve shows a maximum at r = 0.529 Å which is the radius of the Bohr's first orbit.
- The probability at nucleus is zero.
- In case of 2s there are two peaks the smaller peak at $0.8r_1$ and higher at $5r_1$ this shows that electron spends small time near nucleus and maximum at $5r_1$ from the nucleus. This effect is called penetration effect.
- The point where amplitude is zero called real radial node it is equal to (n l 1) here the probability becomes zero/amplitude also becomes zero.
- There is probability of amplitude to be zero in each case at infinity also which is called imaginary node hence each orbital has one imaginary node.
- The number of angular node is also called nodal plane where probability is also zero it si equal to (1).
- Hence total number of real nodes = $n-1-1+\ell = (n-1)$ if imaginary is also include it is equal to (n).
- Since ψ^2 is always positive hence curve never goes below zero.
- It appears that probability in the nucleus is zero and becomes quite small at large distance but never becomes zero so there is no fixed boundary to the size of the atom and having highest principal quantum equal to infinity as proposed by Bohr's is supported here also.
- For the hydrogen atom in the ground state, the 90 percent contour is at 4 = 0.141 nm. This means that 90 percent of the time the electron will be located with in this distance fro the nucleus.
- The radial probability function $4\pi r^2 \psi^2 dr$ at r = 0 the volume element is zero and hence radial probability is zero but as r increases the volume element $(4\pi r^2)$ increase enough to overcome the decrease of ψ^2 .

Comparision of probability $[R]^2$ and radial probability density $4\pi r^2 dr R^2$

 $[R]^2$ is the probability of finding electron at particular point at some distance (r) from the nucleus but the radial probability density $4\pi r^2 dr R^2$ is the chance of finding electron at all the points which are at a distance between r and (r + dr) from the nucleus.

High light of radial distribution curve $4\pi r^2 dr R^2$ and (r).

Angular wave function $\phi_{lim}[\theta]$

The angular wave function part $[\theta]$ depends only on the quantum number (l) and (m) and has no relation with (n) for the given orbital. It means that all the s-orbitals i.e., ns will have the same function. The plots of wave function $\theta_{lm}[\theta]$ and angular probability density $|\phi\theta|^2$

For s and pz orbitals are like





Angular probability function of (p_{y})

For an s-orbital the angular wave function is free from θ and ϕ and is of constant value hence the graphic circular but becomes spherical in space function.

For the angular wave function plots the distance from the nucleus is proportional to the numerical

value of $\phi(\theta)$ in that direction and is not the distance from the centre of the nucleus. For p_z we get two tangential sphere and same for $p_x & p_y$ along x and y-axis .

Angular probability density $[\phi \theta]^2$

The angular probability plots can be obtained by squaring the angular wave function plots on doing so for S-orbital there is no change in shape since the function in constant but another sphere is obtained. But for p and d. The plots becomes more elongated as seen in above fig.

Plots of total probability density : Shapes of atomic orbitals.

Analysis of S-orbitals :

The normalized wave function of 1s orbital is

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

But squaring this function we obtain an expression which gives probability of finding electron in an unit volume as a function distance (r) from the nucleus.

$$\psi_{1s}^2 = \frac{1}{\pi} \left(\frac{Z}{a_0}\right)^3 e^{-\frac{2Zt}{a_0}}$$

From this expression we find that the probability of finding an electron in a 1s-orbital is independent of the angular co-ordinate θ and ϕ and also decreases monotonically as r-increases.



From the graph it is seen that there is finite probability of finding electrons at any value of (r) between zero and infinity. It also indicates that this probability is zero in nucleus but maximum just around the nucleus.

This contradicts the Bohr's theory which proposes that electron is fixed at one radius. For 2s-orbital the normalized wave function is

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left[2 - \frac{Zr}{a_0}\right] e^{-\frac{Zr}{2a_0}} \qquad \text{or} \qquad \psi_{2s} \propto \left[2 - \frac{Zr}{a_0}\right] e^{-\frac{Zr}{2a_0}}$$

The function $\frac{Zr}{2a_0}$ appears increases the 2s-function decreases in amplitude more slowly than does the 1s function. Which has $\frac{Zr}{a_0}$ in its exponential factor. This is one of the reason that 2s electrons tends to stay for the reason that $\frac{1}{a_0}$ is the stay for the reason the reason that $\frac{1}{a_0}$ is the stay for the reason that $\frac{1}{a_0}$ is the stay for the reason that $\frac{1}{a_0}$ is the reason the reason that $\frac{1}{a_0}$ is the reason the reason that $\frac{1}{a_0}$ is the reason the re

tends to stay farther from nucleus and has higher energy than 1s.

The factor $\left(2 - \frac{Zr}{a_0}\right)$ in the 2s-wave function controls the sign of the wave function for small value of (r) $\frac{Zr}{a_0}$ is smaller than two and wave function is positive but for larger value of (r), $\frac{Zr}{a_0}$ is greater than two and the function is negative at $r = \frac{2a_0}{2}$ to pre exponential factor $e^{-\frac{Zr}{2a_0}}$ is zero, since the radial function vanishes on the circle of the radius $r = \frac{2a_0}{2}$ this said to be the locus of a radial node. For 3s-orbital the normalized wave function is

$$\psi_{3s} = \frac{1}{a\sqrt{3}} \left(\frac{Z}{a_0}\right)^{1/2} \left[6 - 6K + K^2\right] e^{-\frac{K}{2}}$$
 where $K = \frac{2Zr}{a_0}$

A similar analysis os possible for 3s-wave function the exponential factor is now $e^{-\frac{Zr}{3a_0}}$ which decreases even more slowly with increasing (r) than the corresponding exponential part of (1s) and (2s). Therefore 3s-electron are farther from nucleus of the ψ_{3s} is prehaving on

$$\Psi_{2s} \propto \left[6 - 6K + K^2\right] e^{-\frac{K}{2}}$$

On squaring the probability density is

$$\psi_{3s}^2 \propto \left[6 - 6K + K^2\right]^2 e^{-k}$$

At nodes $\psi^2 = 0$ hence

$$6-6\mathbf{K}+\mathbf{K}^2 = 0 \qquad \text{or} \qquad 6-6\times\frac{2\mathbf{Zr}}{3\mathbf{a}_0} + \left(\frac{2\mathbf{Zr}}{3\mathbf{a}_0}\right)^2$$
$$\text{or} \qquad \frac{4}{9}\left(\frac{\mathbf{Zr}}{\mathbf{a}_0}\right)^2 + \left[-4\left(\frac{\mathbf{Zr}}{\mathbf{a}_0}\right)\right]^2 + 6 = 0$$

The above equation will locate the position of radial nodes, since it is a quadratic equation in r we expect two solution and thus two radial nodes. Hence in general for ns orbital there are (n-1) radial nodes hence the number of nodes increases with increasing energy level (n).

Analysis of p-orbitals

The axial location view of the electron n For px orbital the wave function is proportional to $\sin\theta.\cos\phi$, $\psi_{px} \propto \sin\theta.\cos\phi$ and nodal plane is yz-plane and $\theta = 0$ and $\phi = 90^{\circ}$ for every point in the yz-plane hence $\psi_{px} \propto \sin\theta.\cos90 = 0$ x0 = 0 hence yz plane has zero electronic wave and in nodal plane but along to positive



§ show variation in axis

side of x-axis $\theta = 90^{\circ}$ and $\phi = 0$ hence the wave function $\psi_{px} \propto \sin 90^{\circ} \cdot \cos 0^{\circ}$, $\psi_{px} \propto 1$. Hence maximum wave function are on positive x-axes so its name is px. For py-orbital the wave function is proportional as $\psi_{py} \propto \sin \theta \cdot \sin \phi$ and zx-plane if nodal plane for which $\theta = 0$ and $\phi = 0$ at every point on zx-plane hence $\psi_{py} \propto \sin 0 \sin \phi = 0$. Hence ψ_{py} electronic wave function is zero in zx plane and is called nodal plane, but along positive y-axis $\theta = 90^{\circ}$ and $\phi = 90^{\circ}$ hence the wave function. $\psi_{py} \propto \sin 90^{\circ} \sin 90^{\circ} = K$. Hence maximum wave function is along positive y-axis hence it was assigned as py. For pz orbital the wave function is proportional to $\cos \theta$, $\psi_{pz} \propto \cos \theta$. Every where is xy-plane $\theta = 90^{\circ}$ and hence $\psi_{pz} \propto \cos 90 = 0$. Hence no place for electron wave and an called nodal plane for pz. At positive side of z-axis $\theta = 0$ and the wave function becomes maximum along positive z-axis on $\psi_{pz} \propto \cos \theta = 1$. Hence the name pz it is θ becomes equal to 180° at negative z-axis hence wave function $\psi_{pz} \propto \cos 180^{\circ} = -1$.

Analysis of d-orbitals :

Out of five degenerate of d-orbitals the significant feature is that of two orbitals point along co-ordinate axes while other three are in co-ordinate plane pointing between caresian co-ordinate (x, y, z) the labelling of the d-orbitals in derived from the directions or planes in which the orbitals

The angular wave function are proportional as

Analysis of nodes :

We have seen that some of the orbital wave function depends only on radial distance (r) ex-ns orbital whereas for p and d-orbital their wave depends on both (r) and angle θ and ϕ . One way to understand the wave function in through nodes which in a place where either $\psi^2 = 0$ or value of radial wave function changes from positive to negative or the point when amplitude is zero.

For hydrogen atom wave function there is total (n-1) nodes which occurs at finite value of radial distance out of (n-1) nodes some one located radially out from nucleus at any fixed angle. These are called radial nodes others are located as we proceed around the atom at a fixed distance from the nucleus. These are called angular nodes.

The outcome of wave mechanics points out to be

Total radial real nodes = $n - \ell - 1$ Total angular nodes = ℓ

Number of imaginary node = 1 for all orbitals at infinity.

Total real nodes = n - 1

total real and imaginary nodes = n

Analysis of the orbital's shape :

S-orbitals spherical





 dz^2 may be viewed as hybrid or combination of two hypothetical d-orbitals namely dz^2-x^2 and dz^2-y^2 whose shape may be assigned as



When we view the combination $dz^2 - x^2 + z^2 - y^2 = d_{2z^2 - x^2 - y^2}$ it appears as dz^2 as shown above since we can't have more than five d-orbital so $d_{z^2 - x^2}$ and $d_{z^2 - y^2}$ are compounded to dz^2 . For the f-orbital their wave function is beyond the scope of our discussion at this stage however their

shapes are reported as



Nodes and Nodal plane for d-orbitals



Nodal planes for $d_X 2_{-y} 2$ at angle 45° to x and y axis



The three 2p orbitals and Nodal Planes

10. Quantum Numbers

To understand the concept of Quantum Numbers, we must known the meaning of some terms clearly so as to avoid any confusion.

Energy Level: The non-radiating energy paths around the nucleus are called as Energy Levels of Shells. These are specified by numbers having values 1, 2, 3, 4, ... or K, L, M, N, ... in order of increasing energies. The energy of a particular energy level is fixed.

Sub-Energy Level: The phenomenon of splitting of spectral lines in electric and magnetic fields reveals that there must be extra energy levels within a definite energy level. These were called as Sub-Energy Levels or Sub-Shells. There are four types of sub-shells namely; **s**, **p**, **d**, **f**. First energy level (K or) has one sub-shell designated as 1s, the second energy level (L or 2) has two sub-shell as 2s & 2p, the third energy level (M or 3) has three sub shell as 3s, 3p and 3d, and the fourth energy level (N or 4) has four sub-shells as 4s, 4p, 4d and 4f. The energy of sub-shell increases roughly in the order: s .

Orbital: Each sub-energy level (sub-shell) is composed of one or more orbitals. These orbitals belonging to a particular sub-shell have equal energies and are called as degenerate orbitals. **s**-sub-shell has one orbital, **p** has three orbitals, **d** have five orbitals and **f** has seven orbitals.

To describe or to characterize the electrons around the nucleus in an atom, a set of four numbers is used, called as Quantum Numbers. These are specified such that the states available to the electrons should follows the laws of quantum mechanics or wave mechanics.

Quantum number are those dimensionless parameter which can determine all the quantized properties of an electron in a particular energy level inside an atom, it is taken as addres of electron.

Energy and angular momentum of the electron are the quantized properties of the electron.

n = 1, E₁ =
$$-\frac{13.6}{12}$$
 eV = -13.6 eV
mv₁r₁ = 1× $\frac{h}{2\pi}$
n = 2, mv₂r₂ = 2, $\frac{h}{2\pi} = \frac{h}{\pi}$

$$E_2 = -3.4 \text{ eV}$$

n=3 n=2 n=1 E_1 E_2 E_3

There are four quantum numbers :

(a) Principal quantum number(c) Magnetic quantum number (m)

(b) Azimuthal quantum number (l)(d) Spin quantum number (s)

Principal Quantum Number: (n): This quantum number represents the main energy levels (principal energy levels) designated as n = 1, 2, 3, ... or the corresponding shells are named as K, L, M, N, ... respectively. It gives an idea of position and energy of an electron. The energy

level n = 1 corresponds to minimum energy and subsequently n = 2, 3, 4, ..., are arranged in order of increasing energy.

Higher is the value of n, greater is its distance from the nucleus, greater is its size and also greater is its energy.

It also gives the total electrons that may be accommodated in each shell, the capacity of each shell is given by the formula $2n^2$, where n : principal quantum number.

It gives ideal about the following :

(i) Orbit number in which electron revolves

(ii)Atomic size

(iii) Distance of the electron from the nucleus

(iv) Energy of the electron in an orbit

(v) Angular momentum of the electron in an orbit

 $(vi) n \neq 0$ or fraction

Azimuthal Quantum Number: (*l*): This number determines the energy associated with the angular momentum of the electron about the nucleus. It is also called as the angular momentum quantum number. It accounts for the appearance of groups of closely packed spectral lines in electric field. It can assume all integral values from 0 to n-1. The possible values of *l* are :

0, 1, 2, 3, ..., n-1.

Each value of l describes a particular sub-shell in the main energy level and determines the shape of the electron cloud.

When n = 1, l = 0, i.e., its energy level contains one sub-shell which is called as a s-sub-shell. So for l = 0, the corresponding sub-shell is a s-sub-shell. Similarly when l = 1, 2, 3, the sub-shells are called **p**, **d**, **f** sub-shells respectively.

As you known for n = 1, l = 0, there is only one sub-shell. It is represented by 1s. Now for n = 2, *l* can take two values (the total number of values taken by *l* is equal to the value of n in a particular energy level). The possible values of *l* are 0, 1. The two sub-shell representing the IInd energy level are 2s, 2p. In the same manner, for n = 3, three sub-shells are designated as 3s, 3p, 3d corresponding to l = 0, 1, 2, and for n = 4, four sub-shells are designated as 4s, 4p, 4d, 4f corresponding to l = 0, 1, 2, 3.

It gives idea about the shape of atomic orbitals. It depends upon n. The total number of values of l will be equal to n but maximum value of l will be (n-1)

If l = 0, s-orbital

- l = 1, p-orbital
- l = 2, d-orbital
- l = 3, f-orbital

* An orbital is the wave mechanical concept of electronic motion. While an orbit is the old classical concept of electronic motion.

* Maximum number of electron in an orbital = (4n-2) where n = 1, 2, 3, 4



Magnetic Quantum Number (m): An electron with angular momentum can be thought as an electric current circulating in a loop. A magnetic field due to this current is observed. This induced magnetism is determined by the magnetic quantum number. Under the influence of magnetic field,

the electrons in a given sub-energy level prefer to orient themselves in certain specific regions in space around the nucleus. The number of possible orientations for a sub-energy level is determined by possible values of m corresponds to the number of orbitals in a given sub-energy level).

m can have any integral values between -l to +l including 0, i.e., m = -l, 0 +, l, ..., 0, 1, 2, 3, 4, ..., l-1 + l. We can say that a total of (2l + 1) values of m are there for a given value of l-2, -1, 0, 1, 2, 3.

In s sub-shell there is only one orbital $[l = 0, \Rightarrow m = (2l+1) = 1]$.

In p sub-shell there are three orbitals corresponding to three values of m : -1, 0+1.

 $[l = 1 \implies m = (2l + 1) = 3]$. These three orbitals are represented as p_x, p_y, p_z along X, Y, Z

axes perpendicular to each other.

In d sub-shell, there are five orbitals corresponding to -2, -1, 0+1, +2,

 $[l=2 \implies m = (2 \times 2 + 1) = 5]$. These five orbitals are represented as $d_{xy}, d_{zx}, d_{y^2-y^2}, dz^2$.

In f sub-shell there are seven orbitals corresponding to -3, -2, -1, 0, +1, +2, +3

$$[l=3 \implies m = (2 \times 3 + 1) = 7]$$

It gives information about the orientation of atomic orbital in presence of external magnetic field. It depends upon *l*.

total no. of values of m = (2l+1)

Values of m will be in between + l to -l including O. If l = 0, if l = 1, $m = 2l + 1 = 2 \times 0 + 1 = 1$ $m = 2l + 1 = 2 \times 1 + 1 = 3$

$$m = +1, 0, -1$$

$$px \quad py \quad pz$$

$$1, -2$$

$$m = 2l + 1 = 2 \times 2 + 1$$

$$m = +2, +1, 0, -1, -2$$

$$+2 + 1 0 -1 -2$$

$$dxy dyz dzx dx^2 - y^2 dz^2$$

Spin quantum Number (s): When an electron rotates around a nucleus it also spins about its axis. If the spin is clockwise, its spin quantum number is +1/2 and is represented as \uparrow . If the spin is anti-clockwise, its value is -1/2 and is represented as \downarrow . If the value of s is +1/2, then by convention, we take that electron as the first electron in that orbital and if the value of s is -1/2, it is taken as second electron.

It arises due to the spinning nature of an electron about its own axis. An electron can rotate either in a clockwise or anticlockwise direction.



s = +1/2 s = +1/2 s = +1/2 s = -1/2Since, a spinning charge is associated with a magnetic field, an electron must have a magnetic moment associated with it.

Illustration :

l = 2,

Write down the values of quantum numbers of all the electrons present in the outermost orbit of argon (At. No. 18)

Solution:

 $1s^2, 2s^2 2p^6, 3s^2 3p_x^2 3p_y^2 3p_z^2$

The electronic configuration of argon is Values of quantum numbers are:

	n	1	m	S
$3s^2$	3	0	0	+1/2, -1/2
$3p_x^2$	3	1	± 1	+1/2, -1/2
$3p_y^2$	3	1	±1	+1/2, -1/2
$3p_z^2$	3	1	0	+1/2, -1/2

Illustration :

- (a) An electron is in 5f-orbital. What possible values of quantum numbers n, l, m and s can it have?
- (b) What designation is given to an orbital having (i) n = 2, l = 1, and (ii) n = 3, l = 0?

Solution:

(a) For an electron in 5f-orbital, quantum number are:

n = 5, 1 = 3; m = -3, -2, -1, 0, +1, +2, +3 and s = either +
$$\frac{1}{2}$$
 or $-\frac{1}{2}$ (b) (i) 2p, (ii)3s

11. Electronic Configuration of Elements

The arrangement of electrons in different orbitals outside the nucleus for multielectron atoms are done on the guide lines of the following principles

- * Aufbau principle
- * Pauli's exclusion Principle
- * Hunds rule of maximum multiplicity

However above mentional principle are only guide line but finally it is done to satisfy

- * Magnetic moment value
- * Over all stability of the system

(1) Aufbau Principle

Aufbau is a German word meaning 'building up'. This gives us a sequence in which various subshells are filled up depending on the relative order of the energy of the subs-hells. The sub-shell with minimum energy is filled up first and when this obtains maximum quota of electrons, then the next sub-shell of higher energy starts filling.



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

Sub-shell	n	1	(n+l)	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	Lowest value of n
3s	3	0	3	
3p	3	1	4	Lowest value of n
4s	4	0	4	
3d	3	2	5	Lowest value of n
4p	4	1	5	
5s	5	0	5	
4d	4	2	6	Lowest value of n
5p	5	1	6	
6s	6	0	6	
4f	4	3	7	Lowest value of n
5d	5	2	7	
6p	6	1	7	
7s	7	0	7	
5f	5	3	8	Lowest value of n
6d	6	2	8	
7p	7	1	8	

Exceptions to Aufbau Principle: In some cases it is seen that actual electronic arrangement is slightly different from arrangement given by Aufbau principle. A simple reason behind this is that half-filled and full-filled sub-shell have got extra stability.

$$Cr(24) \longrightarrow 1s^{2}, 2s^{2}2p^{6}, 3s^{2}3p^{6}3d^{4}, 4s^{2}$$
(wrong)
$$\longrightarrow 1s^{23}, 2s^{2}2p^{6}, 3s^{2}3p^{6}3d^{5}, 4s^{1}$$
(right)
$$Cu(29) \longrightarrow 1s^{2}, 2s^{2}2p^{6}, 3s^{2}3p^{6}3d^{9}, 4s^{2}$$
(wrong)
$$\longrightarrow 1s^{2}, 2s^{2}2p^{6}, 3s^{2}3p^{6}3d^{10}, 4s^{1}$$
(right)

Similarly the following elements have slightly different configurations than expected.

$Nb \longrightarrow [Kr] 4d^45s^1$	$Mo \longrightarrow [Kr] 4d^4 5s^1$
$\operatorname{Ru} \longrightarrow [\operatorname{Kr}] 4d^7 5s^1$	$Rh \longrightarrow [Kr] 4d^8 5s^1$
$Pd \longrightarrow [Kr] 4d^{10} 5s^{0}$	$Ag \longrightarrow [Kr] 4d^{10} 5s^1$
$Pt \longrightarrow [Xe] 4f^{14} 5d^9 6s^1$	Au \longrightarrow [Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹

Electronic Configuration of Elements: Quantum numbers can now characterize the electrons in an atom. To describe the arrangements and distribution of electrons for different elements, following rules an selective principles are used. The distributions of electrons in an atom is known as the electronic configuration of that element.

Aufbau Principle: An atom in its lowest state of energy is said to be in ground state. The ground state is the most stable in an atom. According to Aufbau principle.

"Electrons are added progressively to the various orbitals in their order of increasing energy starting with the orbital of lowest energy".

The order of increasing energy may be summed up as follows

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

As a working rule, a new electron enters an empty orbital for which the value of (n + l) is minimum. If the value (n + l) is same for two or more orbitals, the new electron enters an orbital having lower value of n.

Pauli's Exclusion Principle :

According to Pauli, "No two electrons in an atom can have the same sets of all the four quantum numbers.



But according to rule ; set –I is correct.

Hund's rule of maximum multiplicity :

The placing of electron in different degenerate orbitals are decided by Hund's rule keeping in mind the validity of Aufbau principle and Pauli's exclusion principle. The possible number of arrangement

for the given orbitals and given number of electrons are obtained from the formula $\frac{2m!}{2(2m-r)!}$ where m = number of available orbitals, r = number of electrons to be arrangement.

Illustrations :

For p² we have m = 3 and r = 2 the number of possible arrangements are $\frac{2 \times 3!}{2(2 \times 3)! - 2} = 15$

Out of these 15 arrangements the following four possible arrangements are A, B, C and D.

+1	0 -1	+1	0	-1	+1	0	1	+1	0	-1	+1	0	1_
$\uparrow\downarrow$			1			\uparrow	\uparrow	\uparrow		\uparrow	\rightarrow	\rightarrow	
$+\frac{1}{2}$ $-\frac{1}{2}$		$+\frac{1}{2}$	$+\frac{1}{2}$			$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$		$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	
((A)		(B)			(C)			(D))		(E)	

The correct one is decided from Hund's rule as discussed below :

First rule : That arrangement is correct which has highest value of spinmulplicities calculated from the formula

 $S = 2\sum s+1$ Where $\sum s = sum of the spin quantum number Applying this rule A, B, C and D.$

$$S_{A} = 2\left(+\frac{1}{2} - \frac{1}{2}\right) + 1 = 2 \times 0 + 1 = +1$$

$$S_{B} = 2\left(+\frac{1}{2} + \frac{1}{2}\right) + 1 = 2 \times 1 + 1 = +3$$

$$S_{C} = 2\left(+\frac{1}{2} + \frac{1}{2}\right) + 1 = 2 \times 1 + 1 = +3$$

$$S_{D} = 2\left(+\frac{1}{2} + \frac{1}{2}\right) + 1 = 2 \times 1 + 1 = +3$$

$$S_{E} = 2\left(-\frac{1}{2} - \frac{1}{2}\right) + 1 = 2 \times (-1) + 1 = -1$$

Arrangement (A) and (E) are rejected because they have lowest value of S but B, C and D having same value of S are equally correct but the best possible arrangement is obtained by applying second rule.

Second Rule : If for the same number of electrons in the given orbital the spinmultiplicity becomes equal then that arrangement will be correct for which net orbital angular momentum (L) is highest.

 $L = \sum$ magnetic quantum number

Applying for B, C and D, we have

For structure B the value of S and L both are highest hence it is the correct arrangement for p^2 system. **Conclusive Tips : Electrons in different orbitals are first added single and then pairing is done. Comments :** The concept of high spin multiplicity successfully explains the stability of fulfilled orbital (p^3 , d^5 , f^7) orbital as it has highest value of spin multiplicity but he extra stability of full filled orbital could not be explained from this concept because the value of spinmultiplicity becomes lowest for fulfill orbitals where as their stability is highest.

To account the extra stability to full filled orbital the concept of exchange energy and pair energy are utilized.

Since the electrons are in motion naturally there is regular change in their positions without charging the quantum positions and they undergo exchange and in the course of exchange work is done by the electron and energy of the system is decreased and it stabilises the system where paired electrons exerts repulsive forces as they are in the same orbital and the energy increases for such is called pairing energy and it is taken as positive and it tends to destabilise the system. Although magnitude of the both energy are almost same, hence the sum of exchange and pairing energy finally decide the overall stability of the system.

The number of possible exchange pair is calculated as

Number of exchange pair = $\frac{x!}{2(x-2)!} + \frac{y!}{2(y-2)!}$

Where x is the number electrons with (+1/2) spin and y is the number of (-1/2) spin. Pairing energy is equal to number of paired electrons present in the system.

Illustration of the rule :

We have two possible electronic configuration of Cr-atom (Z = 24) and the point of difference is with only valence electrons hence it may be either as (a) or (b).



The number of exchange pair and their corresponding exchange energy (E) for (a) is

 $E = \frac{5!}{2(5-2)!} + \frac{1!}{2(1-2)!} = \frac{5 \times 4 \times 3 \times 2 \times 1}{2 \times 3 \times 2 \times 1} + 0 = 10 + 0$

 $E_a = 10E = -10E$ (E = energy consumed in exchange process)

Pairing energy $E_p = 1P = P$

Total of $E_a = -10E + P$ where as in the arrangement (b) $E_b = -15E + 0 = -15E$

Since much energy is decreased in (b) as compared to (a) hence the most stable configuration of Cr is (b). It was also confirmed through the magnetic moment value which is $\sqrt{48}$ B.M. and supports the arrangement (b).

Electronic configuration of an element is represented by the notation nl^x .

x : number of electrons present in an orbital

l : denotes the sub-shell n : principal quantum number.

Daily Practice Problems - 11

1. Suggest the angular and spherical nodes in (a) 4p (b) 3p

(c) 3s

2. The wave function (ψ) of 2s-orbital is given by:

$$\psi_{2s} = \frac{1}{2\sqrt{2\pi}} \cdot \left[\frac{1}{a_0} \right]^{1/2} \left[2 - \frac{r}{a_0} \right] e^{-r/2a}$$

At $r = r_0$, radial node is formed. Calculate r_0 in terms of a_0 .

3.	Nitrogen atom has at. no. 7 and oxygen has at no. 8. Calcuate total no. of electrons in nitrate ion.								
4.	A neutral atom of an elment has 2K, 8L (a) atomic no. (c) Total no. of p electrons (e) Valency of elemnent			 and 2N electrons. Find out the following: (b) Total no. of s electson (d) total no. of d electrons (f) No. of unpiared electrons. 					
5.	Oxygen consists of ise How many types of Co	ptopes of O^{16} , O^{17} O_2 molecule can be	and C e form	¹⁸ and carbon e? Also report	consists their mo	of isotopes of C ¹² and C ¹³ . l wt.			
6.	The atomic mass of tw (A) No. of neutrons	vo isotopes of O an (b) No. of proton	re 15.9 ns	936 and 17.00 (c) No. of ele)36. Calc ctrons	ualte in each atom: (d) Mas no.			
7.	Write down electronic (a) Mn^{+4} (e) Cl^- (i) Mg	$\begin{array}{c} \text{configuration of th} \\ \text{(b) } Cr^{+2} \\ \text{(f) } Zn^{+2} \\ \text{(j) } Cr^{+3} \end{array}$	ne follo	owing and repo (c) Fe ⁺³ (g) Fe ⁺²	ort no. of (d) N (h) Na	unpaired elecctron in each. Ii ⁺²			
8.	Predict total spin for ea (a) $1s^2$ (d) $1s^2$, $2s^2 2p^3$	(b) 1s ² , 2s ² , 2p ⁶ (e) 1s ² , 2s ² , 2p ⁶	⁵ , 3s ² , 2	(c) 1s 3p ⁶ 3d ⁵ , 4s ²	$s^2, 2s^2, 2j$	D ⁵			
9.	A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the wanadium ion in the compound.								
10.	DescriptionPoint out the angular momentum of electron in (a) 4s orbital(b) 3p orbital(c) 4th orbital								
		nihy Draati		Droblem	1	2			

1.	The shape of an orbit: (A) Spin quantum nu: (C) Azimuthal quantur	al is governed by : mber m number	(B) Principal quantum number(D) Magnetic quantum number			
2.	The number of neutro (A) 30	ons present in ${}_{19}K^{39}$ is :	(C) 20	(D) none of these		
3.	(A) 59 For which species, B (A) H	(B) 19 Bohr's theory does not a (B) Be (C) H	apply . e^+	(D) Li^{2+}		
4.	Which represents the (A) $4, 3, 2, +1/2$	correct set of four quar (B) 4, 2, 1, 0	ntum number of (C) $4, 3, -2$,	$\begin{aligned} &fa 4 d - electron ? \\ &+ 1/2 (D) 4, 2, 1, + 1/2 \end{aligned}$		
5.	When the value of azir $(A) - 1$ only	nuthal quantum number (B) + 1 only	ris1, magnetic qu (C) +1, 0, -	tantum number can have values : -1 (D) $+1$ and -1		
6.	For a given value of at quantum number 'm' (A) $l + 1$	zimuthal quantum numl are given by : (B) $2l + 1$	ber l , the total nu (C) $2l - 1$	umber of values for the magnetic (D) $l+2$		
7.	Which of the subshell (A) s	has double dumb-bell (B) p	shape ? (C) d	(D) f		
8.	The order of filling of (A) 3 d, 4 s, 4 p, 4 (C) 5 s, 4 p, 3 d, 4	electrons in the orbital d, 5 s	l of an atom will be : (B) 4s, 3d, 4p, 5s, 4d (D) 3d, 4p, 4s, 4d, 5s			
9.	In ground state of chr more electrons is : (A) 15	romium atom (Z = 24) t (B) 16	the total number (C) 20	r of orbitals populated by one or (D) 14		

10.	An atom has 2 electrons in K-shell, 8 electrons in L-shell and 6 electrons in M-shell. The number of s-electrons present in the element is :							
	(A) 10	(B) 7	(C) 6	(D) 4				
11.	The number of vacant	t orbitals of element wit	th atomic number 14 is	:				
	(A) 2	(B) 4	(C) 8	(D) 6				
12.	Suppose a completely filled or half filled set of p or d-orbitals is spherically symmetrical. Point out the species which is spherical symmetrical.							
	(A) O	(B) C	(C) Cl ⁻	(D) Fe				
13.	Number of electrons	in the outermost orbit o	f the element of atomic	e number 15 is :				
	(A) 7	(B) 5	(C) 3	(D) 2				
14.	When 3d-orbital is c	omplete , the newly ent	ering electron goes inte	o:				
	(A) 4f	(B) 4s	(C) 4 p	(D) 4 d				
15.	Which neutral atom h	as 18 electrons in its ou	iter shell ?					
	(A) Cu^+	(B) Pd	(C) Mn^{4+}	(D) Zn				

			D	aily	Practice	Pro	blen	ns - 1	3	
1.	Whicl	h set of	quantu	m numb	ers is wrong?					
		n	l	m	s		n	l	m	S
	(A)	2	1	0	+1/2	(B)	2	2	0	+1/2
	(C)	3	2	0	+1/2	(D)	3	2	0	+1/2
2.	The la	st elec	tron pla	ced in t	he third $(n=3)$	quantun	n shell	for :		
	(A) k	Kr	-	(B)	Zn	(C) (Cu		(D)	Ca
3.	Anele	ectron	will hav	e the hi	ghest energy in	the set :				
	(A) 3	,2,1	, 1/2	(B)	4, 2, -1, 1/2	(C) 4	4,1,0	, -1/2	(D)	5,0,0,1/2
4.	The n	naximu	ım numl	ber of e	lectrons in a p-	orbital w	vith n=	= 6 and 1	n = 0 ca	an be :
	(A) 2	2		(B)	6	(C)	10		(D)	14
5.	Numb	ber of t	f-orbita	ls assoc	viated with $n = 3$	5 is :				
	(A) 7	,		(B)	5	(C) 9	9		(D)	10
6.	In wh	ich orb	ital elec	tron is 1	nost tightly bou	ind to the	e nucle	us.		
	(A) 5	s		(B)	4 p	(C) 4	4 d		(D)	5 d
7.	Aneu	tral atc	om of an	elemer	t has $2K, 8L$,	11 M and	d 2 N el	lectrons	. Total r	number of electrons
	with a	l = 2 w	ill be :							
	(A) z	ero		(B)	3	(C) (6		(D)	10
8.	A neu	tral at	om of ar	1 eleme	ent has 2 K , 8 L	, 11 M a	nd 2 N	electron	ns . The	total number of s-
	electr	ons in	the atom	n are :						
	(A) 2			(B)	8	(C)	10		(D)	6
9.	Whic	h set of	fquantu	m numł	per is not consis	tent with	n the th	eory?		
		n	l	m	S		n	l	m	S
	(A)	2	1	0	-1/2	(B)	4	3	2	-1/2
	(C)	3	2	3	+1/2	(D)	4	3	3	+1/2
10.	Electr	onic co	onfigurat	tion of 1	Ni is $[Ar] 3 d^8$, 4	s ² . The	electro	nic confi	guration	n of next element is:
	(A) [Ar] 3 c	$1^{10}, 4s^{1}$			(B) [[Ar] 3 ($d^9, 4 s^2$	-	
	(C) [Ar] 3 c	1^{8} , $4 s^{2}$,	$4 p^1$		(D) r	none of	these		

11.	Total number of unp	aired electrons , in an ı	inexcited atom of atom	nic number 29 is :				
	(A) 1	(B) 2	(C) 3	(D) 4				
12.	The number of unpaired electrons in fluorine atom is :							
	(A) 7	(B) 5	(C) 1	(D) 2				
13.	Wave mechanical model of the atom depends upon :(A) de Broglie concept of dual nature of electron(B) Heisenberg's uncertainty principle(C) Schrodinger wave equation(D) All of these							
14.	Which ion has the ma	aximum magnetic mom	nent?					
	(A) Mn^{3+}	(B) Cu^{2+}	(C) Fe^{3+}	(D) V^{3+}				
15.	The possibility of fin	ding an electron in an o	orbital was conceived	by:				
	(A) Rutherford	(B) Bohr	(C) Heisenberg	(D) Schrodinger				

Daily Practice Problems - 14

1.	Which set has the sar (A) N, P, V (C) Na ⁺ , Mg ²⁺ , Al	ne number of unpaired	 electrons in their ground state ? (B) Na, P, Cl (D) Cl⁻, Fe³⁺, Cr³⁺ 				
2.	The three quantum n (A) Bohr's atomic th (C) Heisenberg's und	umbers n, <i>l</i> , m are the leory certainty principle	e outcome of : (B) Solution of Schro (D) Aufbau principle	odinger equation			
3.	Which orbital has two (A) s	o angular nodal planes . (B) p	(C) d	(D) f			
4.	A node is a surface of (A) zero	n which the probability (B) > 1	of finding an electron i (C) > 10	s: (D) > 90			
5.	Which of the followin (A) Zn ⁺	ng has more number of (B) Fe ²⁺	unpaired 'd' electrons ' (C) Ni ³⁺	? (D) Cu ⁺			
6.	The statements which(A) Number of to(B) Number of ratio(C) Number of an anti-	h is/are correct . tal nodes in an orbital = dial nodes in an orbita ngular nodes in an orbita	= n - 1 l = n - l - 1 al = l	(D) All			
7.	A 3 p-orbital has : (A) two non-spheric (C) one spherical and	al nodes d one non-spherical noc	(B) two spherical n le (D) one spherical an	odes Id two non-spherical node			
8.	The number of nodal (A) 1 s	planes is greatest for th (B) 2 p	ne orbital : (C) 3 d	(D) 3 p			
9.	Number of unpaired (A) 2	electrons in the electron (B) 3	nic configuration $1s^2$, 2 (C) 4	$2s^2, 2p^4 \text{ are }:$ (D) 6			
10.	How many unpaired (A) zero	electrons are there in N (B) 2	$i^{2^+}?$ (C) 4	(D) 8			
11.	Which orbital is repr (A) 4 d	esented by the complete (B) 3 d	e wave function ψ_{420} ? (C) 4 p	(D) 4s			

12.	The number of unpair	red electrons in Mn ⁺ is	:					
	(A) 3	(B) 5	(C) 4	(D) 6				
13.	Which has highest number of unpaired electrons ?							
	(A) Mn	(B) Mn^{5+}	(C) Mn^{3+}	(D) Mn^{4+}				
14.	Which of the following	ng has the maximum nu	mber of unpaired electr	rons?				
	(A) Mg^{2+}	(B) Ti ³⁺	(C) V^{3+}	(D) Fe^{2+}				
15.	The zero probability of finding the electron in p_x orbital is :(A) Maximum on two opposite sides of the nucleus along x-axis(B)None(C) Same on all the sides around the nucleus(D)In the nucleus							
16.	The number of unpair	red electrons present in	Cr^{3+} is :					
	(A) 3	(B) 1	(C) 2	(D) 5				
17.	The number of orbita	ls that could be associa	ted with a principal qua	antum number are :				
	(A) n^2 (B) $2n^2$ (C) $n^2 + 2$ (D) $n^2 - 2$							
18.	Which metal cation h	as maximum number of	funpaired electrons?					
	(A) Mn^{2+}	(B) Ni ²⁺	(C) Co ²⁺	(D) Fe^{2+}				

12. Dual Character

De Broglie equation wave particle duality

Louis de Broglie in 1924 while opening the door of quantum mechanics through electromagnetic radiation as a wave phenomenon on and at the same Einstein had shown that waves have properties of particles or photons de-broglie thought about it's converse that can particles have wave character. Starting with the einstein relation between energy and frequency of photon de Broglie derives his own equation on

From the theory of relativity of Einstein

$$E = cp \qquad \qquad \frac{hc}{\lambda} = cp \qquad \qquad \lambda = \frac{hc}{cp} = \frac{h}{p} = \frac{h}{mv}$$
$$\lambda = \frac{h}{p} \qquad \qquad \lambda \propto \frac{1}{p} \text{ as h is constant}$$

The properties of light like reflection photoelectric effect etc. leads to the particle character of the light.

Where as properties like diffraction interference etc. can be explained only when it has wave character. de Broglie suggested that his equation could be used to calculate the wave length associated with any particle whose momentum is p = mv. He verified his equation for various particles and the results are tabulated on

Particle	Mass (gm)	Velocity cm/sec	Wave length λ		
			= h/mv [A]		
Electron	9.1×10^{-28}	1.2×10^{7}	61.00		
1-volt electron	9.1×10^{-28}	5.9×10^{7}	12.30		
100 volt electron	9.1×10^{-28}	5.9×10^{8}	01.20		
He atom at 300 K	2.6×10^{-24}	1.4×10^{5}	00.72		
Xe-atom at 300 K	2.2×10^{-22}	2.4×10^{4}	00.12		

Experimental out come of de Broglie equation

de-Broglie equation proved a land mark in the success of quantum mechanics and finally the conflict of wave particle duality in no longer a conflict. Therefore we just accept the fact that whatever electrons and photons are they have a dual nature.

de-Broglie extended his theory to co-relate Bohr's orbit and proposed that electron can revolve only in those orbits where the number of waves are complete and waves will be in phase and will show constructive interference and wave will be there and electron will show their presence. If the number of waves will be incomplete the wave will be out of phase and will show destructive interference and naturally orbit will automatically vanish.

Validity of de-Broglie equation

Let 'n' number of waves are created in one complete revolution of electron then we have

 $2\pi r = n\lambda \qquad(1)$ $2\pi r = n. \frac{h}{mv} \qquad \text{from de-Broglie equation}$ or mvr = n. $\frac{h}{2\pi}$ i.e., quantization of angular momentum. If mvr $\neq \frac{nh}{2\pi}$ orbit will vanish or Angular momentum = $n \times \frac{h}{2\pi}$ h

as proposed by Bohr himself in his theory hence $\lambda = \frac{h}{p}$ equation is acceptable factor.

de-Broglie equation may be used to calculate the wave length of electron when it is accelerated by some electric field i.e. if an electron is accelerated by potential V creating their velocity μ with λ as their wavelength, then $K_{\rm e} = \text{charge } \times \text{ potential}$

K. E. =
$$\frac{1}{2}$$
 mu² = e × V
m²u² = m × 2eV
 $\left(\frac{h}{\lambda}\right)^2 = 2meV$
 $\lambda = \frac{h}{\sqrt{2meV}}$
 $\lambda = \frac{h}{\sqrt{2m(KE)}} = \frac{h}{\sqrt{2meV}}$
he walks of m. Land h are computed the result comes as

when the value of m, l and h are computed the result comes as

$$\lambda = \sqrt{\frac{150}{V}} \text{ Å}$$

This relation may be used for finding λ under accelerated potential V. volt.

Illustration :

13.6 eV is needed for ionization of a hydrogen atom. An electron in a hydrogen atom in its ground state absorbs 1.50 times as much energy as the minimum required for it to escape from the atom. What is the wavelength of the emitted electron? ($m_e = 9.109 \times 10^{-31}$ kg, $e = 1.602 \times 10^{-19}$ coulomb, $h = 6.63 \times 10^{-34}$ J.s)

Solution:

1.5 times of 13.6 eV i.e., 20.4 eV is absorbed by the hydrogen atom out of which 6.8 eV (20.4 –13.6) is converted to kinetic energy. KE = 6.8 eV = 6.8 (1.602×10^{-19} coulomb) (1 volt) = 1.09×10^{-18} J.

Now,
$$KE = \frac{1}{2}mv^2$$
 or, $v = \sqrt{2\frac{KE}{m}} = \sqrt{\frac{2(1.09 \times 10^{-18} \text{ J})}{(9.109 \times 10^{-31} \text{ kg})}} = 1.55 \times 10^6 \text{ m/s}$
 $\therefore \quad \lambda = \frac{h}{mv} = \frac{(6.63 \times 10^{-34} \text{ J.s})}{(9.109 \times 10^{-31} \text{ kg})(1.55 \times 10^6 \text{ m/s})} = 4.70 \times 10^{-10} \text{ metres}$

Illustration :

Show that de-Broglie wavelength of electrons accelerated V volt is very nearly given by

$$\lambda$$
 (in $\mathbf{A} = \left(\frac{150}{V}\right)^{1/2}$.

Solution:

$$\begin{split} \lambda &= \sqrt{\frac{h}{2e \ Vm}} \\ \lambda &= \left[\frac{h^2}{2e \ Vm} \times 10^{20}\right]^{1/2} \text{ \AA} = \left[\frac{(6.626 \times 10^{-34})^2 \times 10^{20}}{2 \times 1.6 \times 10^{-19} \times V \times 9.1 \times 10^{-31}}\right]^{1/2} = \left[\frac{150}{V}\right]^{1/2} = \frac{12.25}{\sqrt{V}} \text{ \AA} . \end{split}$$

13. Heisenberg's Uncertainty Principle

Heisenberg uncertainty principle

Werner Heisenberg presented a principle known as Heinsenberg uncertainty principle to locate the position of electron and their momentum under certain limit. It may be stated as

"It is impossible to measure simultaneously the exact position and exact momentum of a body as small as electron."

Heinsenberg pointed out some practical limitation in course of locating the position of electron. We use light to locate the electron and the general principle of vision tell us that we can not locate the electron much more accurately than λ i.e., the wave length of light used. Naturally we would try to make λ as small as possible and so in principle to locate to electron to any required degree of

accuracy. The smaller value of λ will increase to energy of light photon $E = \frac{hc}{\lambda}$ and collision of photon with electron will occur and some unknown fraction of the momentum of photon will be transferred to the electron and locating momentum will be come difficulty with accuracy.

Thus the result of locating the electron to within a distance $\Delta x = \pm \lambda$ is to produce an uncertainty in As

momentum which is roughly $\Delta \approx \frac{h}{\lambda}$ The product of these to uncertainties is

$$\Delta P \times \Delta x \cong \frac{h}{\lambda} . \lambda \cong h$$

This is the crude derivation of this principle which states that there is a limit to the precision to which the position and momentum of a particle may be determined simultaneously.

Heinsenberg proposed a more accurate relation for the same job as.

$$\Delta x. \ \Delta p \ge \frac{h}{4\pi} \qquad \Delta x. \ \Delta v \ge \frac{h}{4\pi m}$$

The concept may be extended to the uncertainty of energy and some also as

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

The acceptability of this principle is limited to only smaller particles like electron. In the case of bigger particle having considerable mass the value of the $\Delta x.\Delta p$ is negligible.

It is the position is known quite accurately i.e., very small then 4v become large and vice-versa.

Proof of validity of this principle

let us suppose for a moment that electron is present in the nucleus of an atom then we have Range of uncertainty in position = diameter of nucleus.

$$\Delta x = 2r = 2 \times 10^{-15} \text{ m} \qquad Me = 9.1 \times 10 \times 10^{-31} \text{ kg}$$

$$\Delta x. \ \Delta p = \frac{h}{4\pi} \qquad 2 \times 10^{-15} \times Me \Delta V = \frac{h}{4\pi}$$

$$\Delta V = \frac{h}{4\pi \times m_e \times 2 \times 10^{-15}} \qquad \Delta V = \frac{6.63 \times 10^{-34}}{4 \times (22/7) \times 2 \times 10^{-15} \times 9.1 \times 10^{-31}}$$

$$\Delta V = 2.9 \times 10^{10} \text{ m sec}^{-1}$$

This value is much higher than the velocity of light 3×10^8 ms⁻¹ which is impossible hence the presumption of having electron in the nucleus is out rightly respected and validity of the uncertainty principle is accepted.

Illustration :

If a 1 g body is traveling along the x-axis with an uncertainty in velocity of 1 cm/s, what is theoretical uncertainty in its position? (b) If an electron is traveling with uncertainty in velocity of 1 m/s, what is the theoretical uncertainty in its position? Solution:

(a) According the uncertainty

$$\Delta x \times m\Delta v = \frac{h}{4\pi}, \ \Delta x = \frac{\lambda}{4\pi m\Delta v} = \frac{6.628 \times 10^{-27} \text{ ergs sec.}}{4 \times 3.14 \times 19 \times 1 \text{ cms}^{-1}} = 3 \times 10^{-28} \text{ cm} = 3 \times 10^{-30} \text{ m}$$

(b)
$$\Delta X = \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 9.1 \times 10^{031} \text{ kg} \times 1 \text{ ms}^{-1}} \qquad 3 \times 10^{-5} \text{ m} = 30 \text{ } \mu \text{ m}$$

Daily Practice Problems - 15

- 1. Calculate the wavelength of a photon in Angstroms having an energy of 1 electron volt.
- 2. A photon of light with wavelength 6000Å has an energy E. Calculate the wavelength of photon of a light which corresponds to an energy equal to 2E.
- 3. Calculate the energy in kilocalorie per mol of the photon of an electromagnetic radiation of wavelength 5700Å.
- 4. Light of what frequency and wavelength is needed to ionise sodium atom. The ionisation potential of sodium is 8.2×10^{-19} J.
- 5. Determine the energy of 1 mole photons of radiation whose frequency is $5 \times 10^{10} \text{s}^{-1}$.
- 6. Calculate momentum of radiations of wavelength 0.33 nm.
- 7. How much will the kinetic energy and total energy of an electron in H atoms change if the atom emits a photon of wavelength 4860 Å?
- 8. Calculate the wavelength of moving electron having 4.55×10^{-25} joule kinetic energy.
- 9. Calculate the momentum of electron moving with 1/3rd velocity of light.
- **10.** An electron has a total energy of 2 MeV. Calculate the effective mass of the electron in kg and its speed. Assume rest mass of electron 0.511 MeV.
- 11. (a) A photon is moving at a speed such less than the speed of light. It has kinetic energy K_1 and momentum p_1 . If the momentum of the proton is doubled, so $p_2 = 2p_1$, how is its new kinetic energy K_2 related to K_1 ?
 - (b) A photon with energy E_1 has momentum p_1 . If anoather photon has momentum p_2 that is twice p_1 , how is the energy E_2 of the second photon retated to E_1 ?

Atomic Structure

• No. of total exchange pair =
$$\frac{x!}{2(x-2)!} + \frac{y!}{2(y-2)!}$$

•
$$m_u = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}}$$
 Where $m_0 = \text{rest mass of electron}$

 $r_n = 1.4 \times 10^{-13} A^{1/3}$ where A = mass no. *

•
$$\lambda = h/p = h/mu = de Broglie equation$$

•
$$V_n = 2.182 \times 10^6/n$$

• No. of real radial nodes
$$(n - \ell - 1)$$

$$\qquad \qquad \frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - U) \psi = 0 \text{ is radial schrodinger equation}$$

• Specific charge of electron
$$(e/m_e) = 1.76 \times 10^8$$
 coulomb/gram

• Specific charge of proton
$$e/m_p = 9.58 \times 10^4$$
 coulomb/gram

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

Frequency v is the number of wave passing per second 2+5 unit is cycle per second (Cps) \Leftrightarrow or Hertz (Hz.) 1 Cps = 1 Hz; 1 KHz = 10^3 hz; 1 MHz = 10^6 Hz.

• Number of waves in one orbit =
$$2\pi r/\lambda$$
 = Number of orbit (n)

• Fitzerald factor =
$$\sqrt{1 - u^2 / c^2}$$

• One electron volt (eV) =
$$1.602 \times 10^{-19}$$
 (J) = 3.827×10^{-20} Cal.

• One e.s.u. =
$$3.3356 \times 10^{-10}$$
 coulomb

• One calory =
$$4.184 (J) = 2.163 \times 10^{19} (e.v.)$$

• d.c.a. =
$$4ze^2/mV^2$$
 in c. g. s. = $\frac{1}{4\pi\epsilon_0}\left(\frac{4Ze^2}{mv^2}\right)$ in S. I.

$$\bullet \qquad N = Q n t z^2 e^4 / r^2 m^2 v^4 \sin^4 \theta / 2$$

N = No. of a-particles striking unit area, Q = total no. of α -particles, n = no. of atoms per ÷ unit volume of the foils, t = thickness of the foil, θ = scattering angle.

Number of possible arrangement for (r) number of electron in (m) number of orbitals

 $=\frac{2m!}{2(2m-r)!}$

Number of wave length of Number of waves created in one circular orbit = n(No. of orbit)Number of spherical nodes = Azimuthal quantum number (ℓ) Total number of real nodes = n - 1

÷ Schrodinger wave equation in polar co-ordinates is

Here r = radial line, $\theta = zenith$ angle

 ϕ = Azimuthal angle.

- Atoms having more than eight electrons in the outermost orbit = Palladium (46) has 18 electrons in the outermost orbit.
- Selection rules : as a result of electronic transition. Atomic spectra is obtained which obeys following rule called selection rule.
 - (i) $\Delta n =$ any value i.e., n-may change by any integer
 - (ii) Change in azimuthal quantum number is only by ± 1 i.e., $\Delta \ell = \pm 1$.

(iii) Magnetic quantum number may change by ± 1 or remains unchanged hence $\Delta m = 0$ or ± 1

- Total energy of electron = $(n + \ell)$
- Degenerate orbitals : orbitals of same energy
- Orbital is defined by = ψ^2
- Normalized wave function = Radial solution × angular solution of corresponding orbital Polar wave functions

$$p_{x} = \sqrt{\left(\frac{3}{4\pi}\right)} \sin\theta \cos\phi \qquad p_{y} = \sqrt{\left(\frac{3}{4\pi}\right)} \sin\theta \sin\phi$$
$$p_{z} = \sqrt{\frac{3}{4\pi}} \cos\theta \qquad d_{z}^{2} = \sqrt{\frac{15}{4\pi}} [3\cos^{2}\theta - 1]$$

• Wave length of electron when accelerated through potential (V)volt = $\sqrt{\frac{150}{V}}$ Å

• Maximum kinetic energy of the ejected electron = hc
$$\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$$

h(V - V_0)

• Stopping potential
$$(V_0) = \frac{h(V - V_0)}{c}$$

$$\overline{e}^{-}$$
 Length of minor axis

• Radial momentum = $n\phi \frac{h}{2\pi}$ = Azimuthal momentum

• One B. M. =
$$9.27 \times 10^{-24}$$
 Ampere square meter.

Series limit

(i) Lyman series
$$n_1 = 1$$
 and $n_2 = \infty$
 $\lambda = 912 \text{\AA}$
(ii) Balmer series $n_1 = 2$, $n_2 = \infty$
 $\lambda = 6563 \text{\AA}$
(iii) Paschen series $n_1 = 3$, $n_2 = \infty$
 $\lambda = 8208 \text{\AA}$
(iv) Bracket series $n_1 = 4$, $n_2 = \infty$
 $\lambda = 14592 \text{\AA}$

 Lyman series are in ultraviolet region, Balmer are in visible region and rest are in infrared region.

ANSWER SHEET

Daily Practice Problems - 01

	Particle	Atomic No.	Mass No.	No. of Elecrrons	No. of Protons	No. of neutrons	
	Sodium atom	11	23	11	11	12	
	Aluminium ion	13	27	10	13	14	
	Chloride ion	17	35	18	17	18	
1.	Phosphorus atom	15	31	15	15	16	
	Cuprous ion	29	64	28	29	35	
2.	$1.80 \times 10^{-43} \text{ m}^3$	3.	2.7×10^{-1}	4	4. 3	$3.16 \times 10^{-26} \text{ kg}$	
<u>5.</u>		6.	4.17×10^{-1}	⁻¹⁴ electron/atom			
7.	6.625×10^{-34} joule	e sec 8.	4.80×10^{-10}	$^{-19}$ C	9. 4		
10.	(A) 6Å (B) $\frac{188 \text{Ke}}{\text{m}_{\alpha} \text{V}}$	$\frac{e^2}{2}$ 11.	12.40 × 1	0 ⁻⁷ m	12. 10	$V^{-15} imes V_{Atom}$	
13.	6.4 × 10 ⁻¹³ J, 2.1 >	× 10 ⁻³ J, 3.4	$\times 10^{-14} \mathrm{m}$		14 11	2	
15.	24	16.	6.32×10^{-10}	06	17. 2	2.471×10^{-14}	

Daily Practice Problems - 02

1.			2. 7	.3 × 1	10 ⁻¹¹ me	etre	3.	2 volt		
4.	2.4×10^{-19} jou	le	5. 3	.2 ×	10 ¹⁴ sec-	-1	6.	1022 Å	$^{\circ}_{\rm A}$, n = 3	to $n = 1$
7.	2.48 eV	8.	2260 Å	9.	(a) 10^{11}	⁵ Hz	(b) 4 eV	V	(c) 6.4	imes 10 ⁻³⁴ J -s
10.	1.81 eV, 9.0 ×	$10^{5} m/s$	$, 3.0 \times 10^{5}$	m/s		11.	$6.25 \times$	10^{11} s^{-1}	, zero, 5	.0 eV
12.	0.148 m	13.	1.2 V	14.	D	15.	C D		16.	ABCD
17.	ВD	18.	ABC	19.	AC					

Daily Practice Problems - 03

1.	$1.37 imes 10^6 \mathrm{Hz}$	2.	$4.83 \times 10^{-7} m$	3.	$\frac{1.198 \times 10^8}{\lambda} \text{ erg mol}^{-1}$
4.	$2 \times 10^{18} \text{ sec}^{-1}$	5.	$1.596 \times 10^{5} \text{ J}$	6.	1.065×10^{22}
7.	$12.41 \times 10^{-5} \text{ cm}$	8.	2.1×10^{12}	9.	1500Å
10.	4.345×10^{28}	11.	$3.75 \times 10^4 \mathrm{cm}^{-1}$	12.	$3.63 imes 10^6 m^{-1}$
13.	$47.68 \times 10^{-19} \text{J}$	14.	6.40×10^{24}		

Daily Practice	Problems - 04
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1.	8.68 %	2.	1740.2 Å	3.	2×1	$0^{-3} \text{ Jm}^{-2} \text{sec}^{-1}$	4.	28
5.	0.527	6.	2.625×10^{-1}	⁹ joule	7.	4.175×10^{-3}	mole o	fI,
8.	(a) - 5.08 eV	, (b) –	5.63 eV		9.	6.58×10^{-34}	Js	-

Daily Practice Problems - 05

1.	$\sqrt{\left(\frac{\mathrm{Ze}^2}{\mathrm{mr}_{\mathrm{n}}}\right)}$	2.	2.44×10^{14}	3.	5.443×10^{-19} joule
4.	$2.1 \times 10^{-34} \text{ J-sec}^{-1}$	5.	54.4 eV, 122.4 eV	6.	44.1 ×10 ⁻¹⁸ J atom ⁻¹
7.	$21.87 \times 10^4 \text{ J}$	8.	292.68×10^{21} atom,	, 162.60 >	< 10 ²¹ atom, 832.50 KJ
9.	$331.13 \times 10^4 \text{ J}$				

Daily Practice Problems - 06

1. 4.69 Å2. $5.44 \times 10^5 \text{ m sec}^{-1}$ 3. $5.44 \times 10^5 \text{ m sec}^{-1}$ 4. $87.16 \times 10^{-19} \text{ J}$ 5. (a) 2.38 Å, (b) 0.705 Å6. 107. $1.052 \times 10^{15} \text{ Hz}$ 8. $13.15 \times 10^{15} \text{ Hz}$; $2.28 \times 10^{-8} \text{ m}$, $8.7 \times 10^{-18} \text{ J}$ 9. 6.57×10^{15} 10. $2.193 \times 10^6 \text{ m sec}^{-1}$

Daily Practice Problems - 07

1.	2.	22.8 nm	3.	chromium	
4.	$\overline{v} = 9.75 \times 10^4 \mathrm{cm}^{-1}$				
5.	IE per hydrogen atom	$n = 2.182 \times 10^{-18}$	J, IE per mole	$= 1314 \text{ kJ mol}^{-1}$	
6.	(a) 19.638×10^{-18} J (b) 1.118×10^4 k.	I mol ⁻¹		

7. $2.186 \times 10^6 \text{ ms}^{-1}$; 7.29×10^{-3} 8. 8×10^6

9. $2.43 \times 10^5 \,\mathrm{cm}^{-1}$ 10. $\left| \frac{u_2}{u_1} = \frac{1}{2} \right|$

9. 5; 340 ev, -680 eV 10. $r_n = \frac{n^2 h^2}{4\pi^2 \times 3e^2 \times 208m_e}$ n = 25; 55.2 pm

Daily Practice Problems - 08

1.	$\frac{1}{2}$ n (n - 1)	2.	$1.095 \times 10^5 \ cm^{-1}$	3.	1 and 2	
4.	1.14×10^{-6} cm	5.	(a) $\Delta E_{3 \rightarrow 1} = \Delta E_{3 \rightarrow 2}$	+ $\Delta E_{2 \rightarrow 1}$ (b) no	t additive	
6.		7.		8.	4.059×10^{-8}	m
9.	$\lambda = 1.216 imes 10^{-7}$ m	m, $v = 2.4$	7×10^{15} cycle sec ⁻¹ , E	$= 16.36 \times 10^{-19}$	J,	
	$E_{Li^{2+}} = Z^2 \times E_{_H}$	= 9 × 16.3	$6 \times 10^{-19} \text{ J} = 147.27 \times$	10 ⁻¹⁹ 10.	Li ²⁺	
	Da	aily Pr	actice Proble	ems - 09]	
1	03972 Å	2.	3 3.	$\lambda_{\rm next} = 397.1$	6 nm; IE = 3.4	0 eV
1.				IICAL		
4 .	Hydrogen $2 \rightarrow 1$,	$3 \rightarrow 1, 4$	$\rightarrow 1$, Helium - 4 $\rightarrow 2$.	$, 6 \rightarrow 2, 8 \rightarrow 1$		

Daily Practice Problems - 10

11.

5th

1.	122.4 eV	2.	(a) 3.4 eV (b) -6.8 eV	(c) poten	tial energy will change
3.	3,1023 Å	4.	113.74 Å	5.	n = 5

(a) z = 4 , (b) $\lambda_{min} = 40441 \text{ \AA}$ 6. (a) 15.6 Volt (b) 2335 $\,\mathring{A}$ (c) 12.52 V (d) $1.01\times 10^7\,m^{-1}$ 7. Z = 5 16.53 eV 10. 36.56 eV 8. 9. **11.** 0.106 Å

			Dai	ly Pr	acti	ce P	robl	ems	- 11		
1. 4. 6.	(a) 2	21 (b) 8,	(c) 12 (2. (d) 1 (e) 7.	$2a_0 + 2$ and	+3 (f) 1		3. 5. 8.	32 C ¹³ i	sotpes	
9.	23V4	+: 1s ² , 2	$s^2 2p^6$,	3s ² 3p ⁶ 3	\mathbf{d}^{1}		10.	(a) 0	, (b) $\frac{1}{\sqrt{2}}$	$\frac{h}{2\pi}$ (c)	$\frac{2h}{\pi}$
		F							V	2 <i>1</i> .	π
			Dai	ly Pr	acti	ce P	robl	ems	- 12		
1.	С	2.	С	3.	В	4.	D	5.	С	6.	В
7.	С	8.	В	9.	A	10.	С	11.	D	12.	С
13.	В	14.	С	15.	В						
		Г	Dai		acti		rohl	ome	_ 13	7	
		L	Dai	IY FI	acti	LE P		CIII3	- 13		
1.	В	2.	С	3.	В	4.	А	5.	А	6.	В
7.	В	8.	В	9.	С	10.	А	11.	А	12.	С
13.	D	14.	С	15.	D						
		Г								7	
			Dai	ly Pr	acti	ce P	robl	ems	- 14		
1	А	2	в	3	С	4	А	5	B	6	D
7.	C	2. 8.	C	9.	A	10.	B	11.	A	0. 12.	D
13.	Ă	14.	D	15.	D	16.	Ā	17.	A	18.	Ā
		-								_	
			Dai	ly Pr	acti	ce P	robl	ems	- 15		
		-									

1.	12421Å
4.	2.5×10^{-7} metre
7.	2.553 eV
10	$2.0 \times 10^{10} \text{ cm sec}^{-1}$

300Å 0.119 J

 7.27×10^{-7} metre

2.

5.

8.

56.3 kcal per mol

3.

6.

9.

 $2.9 \times 10^{10} \,\mathrm{cm \ sec^{-1}}$ 10.

 $2.01 \times 10^{-24} \text{ kg m sec}^{-1}$ 9.69 n 10⁻¹⁸ g cm sec⁻¹ (a) K₂ = 4 K₁ (b) E₂ = 2E₁ 11.

Solved Example Subjective

Problem 1:

Which is larger, an He^+ ion with an electron in an orbit with n = 3 or Li^{2+} ion with an electron in an orbit with n = 5?

Solution:

Radius of the nth Bohr's orbit of the species of atomic number Z is given by

$$r_{n} = \frac{n^{2}a_{0}}{Z}$$
Where $a_{0} (= 0.529 \text{ Å})$ is called Bohr's radius.
 $r_{3}(\text{He}^{+}, Z = 2) = \frac{9a_{0}}{2} = 4.5a_{0}$
(ii) $r_{5}(\text{Li}^{2+}, Z = 3) = \frac{25a_{0}}{3} = 8.33a_{0}$

$$r_3(He^+, Z=2) = \frac{9a_0}{2} = 4.5a_0$$
 (ii) $r_5(Li^{2+}, Z=3) = \frac{2}{2}$

Problem 2:

(i)

How many elements would be in the second period of the periodic table if the spin

quantum number
$$m_s$$
 could have the value $-\frac{1}{2}, 0, \frac{1}{2}$?

Solution:

For second period n = 2, hence,

1 m m_s
0 0 +
$$\frac{1}{2}$$
, 0, $-\frac{1}{2}$
1 -1 + $\frac{1}{2}$, 0, $-\frac{1}{2}$
0 + $\frac{1}{2}$, 0, $-\frac{1}{2}$
+1 + $\frac{1}{2}$, 0, $-\frac{1}{2}$ Hence, total number of electrons = 12

(= total values of spin quantum number)

Problem 3:

Calculate the wavelength of a soft ball of mass of 100 g traveling at a velocity of 35 m s⁻¹.

Solution:

Using de-Broglie's equation

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J s}^{-1}}{\left(\frac{100}{1000}\right) \text{ kg} \times 35 \text{ m s}^{-1}} = 1.893 \times 10^{-34} \text{ m}$$

Problem 4:

O, undergoes photochemical dissociation into 1 normal oxygen atom (O) and more energetic oxygen atom O*. If (O*) has 1.967 eV more energy (O) and normal dissociation energy of O_2 , is 498 kJ mol⁻¹, what is the maximum wavelength effective for the photochemical dissociation of O₂?

 $0_2 \rightarrow 0 + 0^*$ Solution:

Dissociation energy = 498 kJ mol⁻¹ =
$$\frac{498 \times 1000}{6.02 \times 10^{23}}$$
 J molecule⁻¹

$$= 8.27 \times 10^{-19} \text{ J molecule}^{-1}$$

Excitation energy to form O^*

$$= 1.967 \text{ eV atom}^{-1} = 1.967 \times 1.6 \times 10^{-19} \text{ J atom}^{-1}$$
$$= 3.15 \times 10^{-19} \text{ J atom}^{-1}$$
$$= 11.42 \times 10^{-19} \text{ J} \qquad \text{E} = \frac{\text{hc}}{\lambda} \qquad \lambda = \frac{\text{hc}}{\text{E}}$$
$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{11.42 \times 10^{-19}} = 174 \times 10^{-9} \text{ m}$$
$$= 174 \text{ nm}$$

Problem 5:

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 the n = 2 orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition?

Solution:

$$\Delta E = E_{\infty} - E_2 = [0] - \left[-\frac{21.7 \times 10^{-12}}{4} \right]$$

Since $E_n = -\frac{21.7 \times 10^{-12}}{n^2}$ ergs, $= \frac{21.7 \times 10^{-12}}{4}$
 $\Delta E = hv$ $\Delta E = \frac{c}{\lambda}$
 $\frac{21.7 \times 10^{-12}}{4} = 6.627 \times 10^{-27} \times \frac{3 \times 10^{10}}{\lambda}$
whence $\lambda = 3.67 \times 10^{-5}$ cm ·

Problem 6:

The wave number of the first line in the Balmer series of hydrogen is 15200 cm⁻¹. What is the wave number of the first line in the Balmer series of Be^{3+} ?

Solution:

$$\overline{\nu}_{H} = R_{H} \left[\frac{1}{2^{2}} - \frac{1}{3^{2}} \right]; Z = 1 \text{ for H-atom}$$

$$\overline{\nu}_{Be^{3+}} = R_{H} \times 16 \left[\frac{1}{2^{2}} - \frac{1}{3^{2}} \right]; Z = 4 \text{ for } Be^{3+}$$
Thus, $\overline{\nu}_{Be^{3+}} = 16 \nu_{H} = 16 \times 152000 \text{ cm}^{-1}$

$$= 2.432 \times 10^{5} \text{ cm}^{-1} = 4.16 \times 10^{-14}.$$

Problem 7:

Two 1.0 g carbon disks 1.00 cm apart have equal and opposite charges. If force of attraction between them is $1.00 \times 10^{-5}N$, calculate the ratio of excess electrons to total atoms on the negatively charged disk. (permittivity) constant is $9.0 \times 10^9 N m^2 C^{-2}$).

Solution:

$$q_{1} = \sqrt{\frac{Fr^{2}}{k}} = \sqrt{\frac{1.00 \times 10^{-5} \times (1.0 \times 10^{-2})^{2}}{9.0 \times 10^{9}}} = 3.33 \times 10^{-10} \text{ C on each disk,}$$

Since charge on one electron $= 1.6 \times 10^{-19}$ C

hence, number of electron on the disk
$$=\frac{3.33 \times 10^{-10}}{1.6 \times 10^{-19}} = 2.08 \times 10^{9}$$

number of atoms in 1.0 g carbon $=\frac{1}{12} \times 6.02 \times 10^{23} = 5.0 \times 10^{22}$ atoms Hence, ratio of electron to atoms $=\frac{2.08 \times 10^9}{5.00 \times 10^{22}}$

10

Problem 8:

When a certain metal was irradiated with light of frequency 1.6×10^{16} Hz, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 1.0×10^{16} Hz. Calculate v_0 (threshold frequency) for the metal.

Solution:

$$KE_1 = h(v_1 - v_0)$$
 ... (i)

$$KE_2 = h(v_2 - v_0)$$
 ... (ii)

Dividing Eqs. (ii) by (i) we have

$$\therefore \qquad \frac{\nu_2 - \nu_0}{\nu_1 - \nu_0} = \frac{1}{2} \qquad \qquad \frac{1.0 \times 10^{16} - \nu_0}{1.6 \times 10^{16} - \nu_0} = \frac{1}{2}$$
$$2.0 \times 10^{16} - 2\nu_0 = 1.6 \times 10^{16} - \nu_0$$
$$\nu_0 = 4 \times 10^{15} \text{ Hz}$$

Problem 9:

One mole of He^+ ion is excited. Spectral analysis showed the existence of 50% ions in 3^{rd} level, 25% in 2^{nd} level and remaining 25% in ground state. ionization energy of He^+ is 54.4 eV; calculate total energy evolved when all the ions return to ground state.

Solution:

$$(\Delta E)_{3\to 1} = (54.4) \frac{N_0}{2} \left[\frac{1}{1^2} - \frac{1}{3^2} \right], \text{ for } \frac{N_0}{2} \text{ ions falling to ground state } = 54.4 \times \frac{4 \times N_0}{9} \text{ eV}$$

and $(\Delta E)_{3\to 1} = (54.4) \frac{N_0}{4} \left[\frac{1}{1^1} - \frac{1}{2^2} \right], \text{ for } \frac{N_0}{4} \text{ ions falling to ground state } = 54.4 \times \frac{3 \times N_0}{16} \text{ eV}$
Hence, total energy $= 54.4 \times N_0 \left[\frac{4}{9} + \frac{3}{16} \right] = 54.4 \times 6.02 \times 10^{23} \times \frac{91}{144} \text{ eV}$
 $= 54.4 \times 6.02 \times 10^{23} \times \frac{91}{144} \times 1.6 \times 10^{-19} \text{ J}$
 $= 3.31 \times 10^6 \text{ J}$

Problem 10:

Consider the following two electronic transition possibilities in a hydrogen atom as pictured below:

- (1) The electron drops from third Bohr's orbit to Second Bohr's orbit followed with the next transition from second to first Bohr's orbit.
- (2) The electron drops from third Bohr's orbit to first Bohr's orbit directly. Show that:
 - (a) The sum of the energies for the transitions n = 3 to n = 2 to n = 2 and n = 2 to n = 1 is equal to the energy of transition for n = 3 to n = 1.
 - (b) Are wavelengths and frequencies of the emitted spectrum are also additive in the same ways as their energies are ?

Solution:

(a)
$$\Delta E = R_{\rm H} \left[\frac{1}{n^2} - \frac{1}{n^2} \right]$$
 for 3 to 2 $\Delta E_{3\to 2} = R_{\rm H} \left[\frac{1}{2^2} - \frac{1}{3^2} \right]$

for 2 to 1 $\Delta E_{2\rightarrow 1} = R_{H} \left[\frac{1}{1^{1}} - \frac{1}{2^{2}} \right]$ for 3 to 1 $\Delta E_{3\rightarrow 1} = R_{H} \left[\frac{1}{1^{2}} - \frac{1}{3^{2}} \right]$ It is evident from Eqs. (1), (2) and (3), that

$$\Delta E_{3 \to 1} = \Delta E_{3 \to 2} + \Delta E_{2 \to 3}$$

(b) Also E = hv; thus frequencies are also additive

but $E = \frac{hc}{\lambda}$ and thus wavelengths are not additive.

Problem 11:

Ultraviolet light of wavelength 800Å and 700Å when allowed to fall on hydrogen atoms in their ground state is found to liberate electrons with kinetic energy 1.8 eV and 4.0 eV respectively. Find the value of Planck's constant.

Solution:

$$KE_1 = hv_1 - W = h \cdot \frac{c}{\lambda_1} - W \qquad \dots (i)$$

$$KE_2 = hv_2 - W = h \cdot \frac{c}{\lambda_2} - W \qquad \dots (ii)$$

Substracting equation (i) from equation (ii),

$$(KE_{2} - KE_{1}) = hc \left(\frac{1}{\lambda_{2}} - \frac{1}{\lambda_{1}}\right) = hc \left(\frac{\lambda_{1}}{\lambda_{1}} - \frac{\lambda_{2}}{\lambda_{2}}\right) \qquad \text{or} \qquad h = \frac{(KE_{2} - KE_{1}) \times \lambda_{1}\lambda_{2}}{c \times (\lambda_{1} - \lambda_{2})} \\ = \frac{(4.0eV - 1.8eV) \times 800 \times 10^{-10} \times 700 \times 10^{-10}}{3 \times 10^{8} \times (800 - 700) \times 10^{-10}} \qquad = \frac{(2.2 \times 1.6 \times 10^{-19} \text{ J}) \times (56 \times 10^{-16} \times \text{m}^{2})}{(3 \times 10^{8} \text{ ms}^{-1}) \times (100 \times 10^{-10} \text{ m})} \\ = \frac{2.2 \times 1.6 \times 56 \times 10^{-35}}{3} \text{ J} - \text{s} \qquad = 6.57 \times 10^{-34} \text{ J} - \text{s}$$

Problem 12:

The λ of H_{α} line of Balmer series is 6500Å. What is the λ of H_{β} line of Balmer series? Solution:

For H_a lines of Balmer series $n_1 = 2, n_2 = 3$

For H_{β} line of Balmer series $n_1 = 2, n_2 = 4$

$$\therefore \qquad \frac{1}{\lambda_{H_{\alpha}}} = R_{H} \left[\frac{1}{2^{2}} - \frac{1}{3^{2}} \right] \qquad \dots (1)$$

and
$$\frac{1}{\lambda_{H_{\beta}}} = R_{H} \left[\frac{1}{2^{2}} - \frac{1}{4^{2}} \right] \qquad \dots (2)$$

By Eqs. (1) and (2)

$$\therefore \qquad \frac{\lambda_{\beta}}{\lambda_{\alpha}} = \frac{\frac{1}{4} - \frac{1}{9}}{\frac{1}{4} - \frac{1}{16}} \qquad \qquad \qquad \lambda_{\beta} = \lambda_{\alpha} \times \left[\frac{80}{108}\right] = 6500 \times \frac{80}{108} = 4814.8\text{\AA}$$

Problem 13:

The IP_1 of H is 13.6 eV. It is exposed to electromagnetic waves of 1028Å and gives out induced radiations. Find the wavelength of these induced radiations.

Solution:

 E_1 of H atom = -13.6 eV Energy given to H atom = $\frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{1028 \times 10^{-10}}$ = 1.933×10⁻¹⁸ J = 12.07eV Energy of H atom after excitation = -13.6 + 12.07÷. = -1.53 eV \therefore $n^2 = \frac{-13.6}{-1.53} = 9$ $E_n = \frac{E_1}{n^2}$ ÷. *.*.. n = 3Thus, electron in H atom is excited to 3rd shell I induced $\lambda_1 = \frac{hc}{E_3 - E_1}$ \therefore $E_1 = -13.6 \text{ eV}; E_3 = -1.53 \text{ eV}$ $\lambda_1 = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{(-1.53 + 13.6) \times 1.602) \times 10^{-19}} = 1028 \times 10^{-10} \text{ m}$ ÷. Ŀ. \therefore II induced $\lambda_2 = \frac{hc}{(E_2 - E_1)}$ $\lambda = 1028 \text{ Å}$ *.*.. $E_1 = -13.6 \text{ eV}; E_2 = -\frac{13.6}{4} \text{ eV} \qquad \therefore \qquad \lambda_2 = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{\left(-\frac{13.6}{4} + 13.6\right) \times 1.602 \times 10^{-19}}$ ··. $=1216 \times 10^{-10} \text{ m} = 1216 \text{ Å}$:. III induced $\lambda_3 = \frac{hc}{E_3 - E_2}$:. $E_1 = -13.6 \text{ eV}; E_2 = -\frac{13.6}{4} \text{ eV}; E_3 = -\frac{13.6}{9} \text{ eV}$ $\lambda_{3} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{\left(-\frac{13.6}{9} + \frac{13.6}{4}\right) \times 1.602 \times 10^{-19}} = 6568 \times 10^{-10} \,\mathrm{m} = 6568 \,\mathrm{\AA}$

Problem 14:

Calculate the wavelength in angstrom of the photon that is emitted when an electron in Bohr orbit n = 2 returns to the orbit n = 1 in the hydrogen atom. The ionization potential of the ground state of hydrogen atom is 2.17×10^{-11} erg per atom.

Solution:

In the ground state of H-atom the solitary electron occupies the firs orbit and hence, the ionization potential of the ground state of the hydrogen atom is the energy of the electron of the first orbit, with sign reversed.

E₁ = −2.17×10⁻¹¹ erg
Thus, E₂ =
$$\frac{E}{n^2}$$
 = $-\frac{2.17 \times 10^{11}}{2^2}$
∴ Energy of the radiation emitted, $\Delta E = E_2 - E_1$
= $-\frac{2.17 \times 10^{-11}}{2^2} - (-2.17 \times 10^{-11})$ = 1.627×10⁻¹¹ erg
We know $\Delta E = hv = \frac{c}{\lambda}$ Thus $\frac{hc}{\lambda} = 1.627 \times 10^{-11}$
 $\lambda = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{1.627 \times 10^{-11}} = 1.22 \times 10^{-5}$ cm = 1220 Å (1Å = 10⁻⁸ cm)

Problem 15:

Infrared lamps are used in restaurants and cafeterias to keep food warm. The infrared radiation is strongly absorbed by water raising its temperature and that of the food in which it is incorporated. How many photons per second of infrared radiation are produced by an infrared lamp that consumes energy at the rate of 100 watt (100 Js⁻¹) and is 12% efficient in converting this energy to infrared radiation? Assume that the radiation has a wavelength of 1500 nm.

Solution:
$$E = Nh \nu = \frac{Nhc}{\lambda}$$

 $= \frac{N \times 6.626 \times 10^{-34} \times 3 \times 10^8}{1500 \times 10^{-9}}$
 $E = \frac{100 \times 12}{100} \text{ watt } (\text{Js}^{-1})$
 $\therefore \quad 100 \times \frac{12}{100} = \frac{N \times 6.626 \times 10^{-34} \times 3 \times 10^8}{1500 \times 10^{-9}}$ $\therefore \quad N = 9.06 \times 10^6 \text{ photons s}^{-1}$

Solved Example Objective

Problem 1:

Bohr's atomic model can explain

- (a) the spectrum of hydrogen atom only
- (b) the spectrum of an atom or ion containing one electron only
- (c) the spectrum of hydrogen molecule
- (d) the solar spectrum

Solution: (b)

In Bohr's theory while calculating the energy of electron, the potential energy has been found out by considering only the attraction between the electron and nucleus. If there is another electron in the orbit, the potential energy would change due electron-electron repulsion. Therefore the Bohr's model is meant for all one-electron systems.

Problem 2:

The orbital angular momentum of an electron in 2s orbital is

(a) 4 (b) 1 (c) zero (d) $\frac{h}{2\pi}$

Solution: (c)

The orbital angular momentum of an electron is calculated as $\sqrt{\ell(\ell+1)} \frac{h}{2\pi}$, $\sqrt{0(0+1)} \frac{h}{2\pi} = 0$

Problem 3:

The ratio of the energies of photons of 2000Å to that of 4000Å is

(a) 2 (b) 4 (c)
$$\frac{1}{2}$$
 (d) $\frac{1}{4}$

Solution: (a)

$$\mathbf{E} = \frac{\mathbf{hc}}{\lambda}, \quad \therefore \quad \frac{\mathbf{E}_1}{\mathbf{E}_2} = \frac{\lambda_2}{\lambda_1} = \frac{4000}{2000} = 2$$

Problem 4:

Which of the following postulates does not belong to Bohr's model of the atom?

- (a) Angular momentum is an integral multiple of $\frac{h}{2\pi}$
- (b) The electron stationed in the orbit is stable
- (c) The path of an electron is circular
- (d) The change in the energy levels of electron is continuous

Solution: (D)

In Bohr's model, the energy are discrete and not continuous

Problem 5:

The wave number of the first Balmer line of Li^{2+} ion is 1,36,800 cm⁻¹ the wave numberof the first line of Balmer series of hydrogen atom is (in cm⁻¹)(a) 68,400(b) 15,200(c) 76,000(d)30,800.

Solution: (b)

Atomic number of
$$\operatorname{Li}^{2+}$$
 is 3 $\frac{1}{\lambda} = \operatorname{R}_{H} Z^{2} \left[\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}} \right]$

$$1,36,800 = R_{\rm H} \times 9 \left[\frac{1}{2^2} - \frac{1}{3^2} \right] \qquad \qquad R_{\rm H} \left[\frac{1}{2^2} - \frac{1}{3^2} \right] = \frac{1,36,800}{9} = 15,200$$

Problem 6:

If uncertainty in the position of an electron is zero the uncertainty in its momentum will be

(a)
$$< \frac{h}{4\pi}$$
 (b) $> \frac{h}{4\pi}$ (c) zero (d) infinite

Solution: (d)

 $\Delta x \times \Delta p \ge h/4\pi$ if $\Delta x = 0$, then ΔP will be infinite

Problem 7:

The principle quantum number represents		
(a) shape of an orbital	<i>(b)</i>	number of electrons in an orbit
(c) distance of an electron from the nucleus	(d)	orientation of orbitals in space.
Solution: (c)		

Problem 8:

The energy of an electron of $2p_y$ orb	ital is
(a) greater than 2p orbital	(b) less than 2p, orbital
(c) equal to 2s orbital	(d) same as that of $2p_x$ and $2p_z$ orbitals
Solution: (d)	~ · ·

All the 2p orbitals are degenerate

Problem 9:

If the following matter waves travel with equal velocity, the longest wavelength is that of a/an.

(a) electron	(b) proton	(c) neutron	(d) α – particle
Solution: (a)			

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

 λ will be large if m is small

Problem 10:

Number of nodal planes (planes of zero electron density) in the d_{xy} orbital is

(a) 1 (b) 2 (c) 0 (d) 4

Solution: (b)

xz and yz are planes with zero electron density for d_{xy} orbital.

Problem 11:

If the speed of electron in the Bohr's first orbit of hydrogen atom is x the speed of the electron in the third Bohr's orbit is

(a)
$$x/9$$
 (b) $x/3$ (c) $3x$ (d) $9x$

Solution: (b)

According to Bohr's model for hydrogen and hydrogen like atoms the velocity of an electron in an atom is quantized and is given by $v = \frac{2\pi k ze^2}{nh}$

Problem 12:

Which set of quantum number is not consistent with the quantum mechanical theory? (a) $n = 2, l = 1, m = 1, s = \frac{1}{2}$ (b) n = 4, l = 3, m = 2, s = -1/2(c) n = 3, l = 2, m = 3, s = +1/2(d) n = 4, l = 3, m = 3, s = +1/2.

Solution: (c)

The e is a well defined co-relation between n, l, m and s quantum numbers in an atom. l =(n-1), m will be $\pm \frac{1}{2}$, for n = 3 there cannot be m = 3. Highest value m will be 2.

Problem 13:

If the radius of first Bohr orbit be a_0 , then the radius of third Bohr orbit would be (c) $9 \times a_{a}$ (b) $6 \times a_{a}$ (d) $1/9 \times a_{a}$ (a) $3 \times a_{a}$ **Solution:** (c)

The radius as per Bohr's model $r \propto n^2$

Problem 14:

The quantum numbers of most energetic electron in Ne atom when it is in first excited state is

(a) 2, 1, 0, $\pm 1/2$ (b) 3, 1, 1, $+ \frac{1}{2}$ (c) 3, 0, 0, +1/2 (d) 3, 1, 0, +1/2. **Solution:** (c)

The electronic configuration of Ne atom is $1s^2 2s^2 2p^6$. In its first excitation state the electron from 2p will unpair and shift to 3s where its quantum numbers will be 3, 0, 0, $+\frac{1}{2}$.

Problem 15:

Of the following transitions in hydrogen atom, the one which gives an absorption line of lowest frequency is

(a) n = 1 to n = 2 (b) n = 3 to n = 8 (c) n = 2 to n = 1 (d) n = 8 to n = 3**Solution:** (b)

Absorption line in the spectra arise when energy is absorbed i.e., electron shifts from lower to higher orbit, out of a and b, b will have the lowest frequency as this falls in the Paschen series.