

2

Structure of Atom



Cameras are ubiquitous in our daily lives. And you know what, their sensors are made up of atoms! A digital camera collects light and focuses it through a lens onto a silicon sensor. It is made up of a grid of tiny photosites that are light-sensitive. Each photosite is commonly referred to as a pixel, which is an abbreviation for "picture element." A DSLR camera's sensor contains millions of these individual pixels.

Topic Notes

- *Discovery of Subatomic Particles*
- *Dual Behaviour of Matter and Quantum Mechanical Model of Atom*

DISCOVERY OF SUBATOMIC PARTICLES

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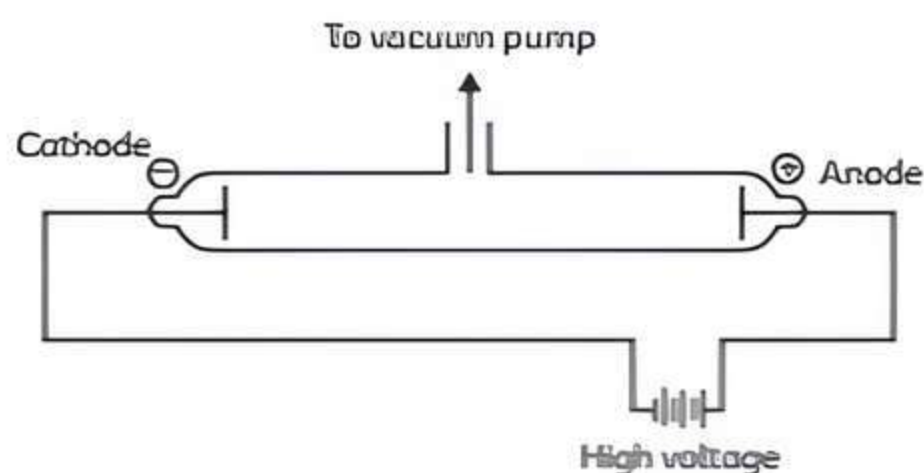
TOPIC 1

DISCOVERY OF ELECTRON

Atom is composed of three subatomic particles which are electrons, protons and neutrons. The experiments were done using discharge tubes to know the structure of atoms. The basis of this is 'Like charges repel each other and unlike charges attract each other.' The discovery of electrons is discussed below:

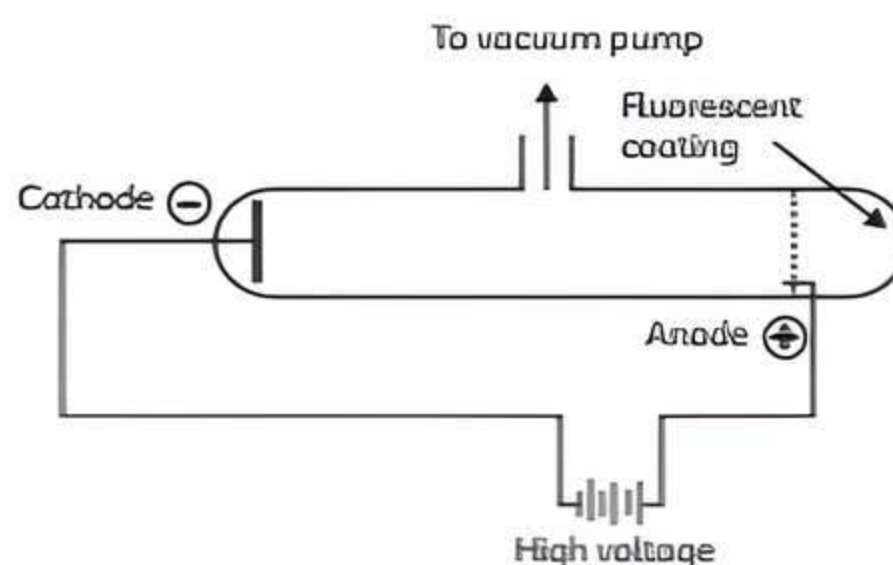
In 1830, Michael Faraday showed that when the electricity is passed through an electrolytic solution that contains electrodes, chemical reactions occurred at the electrodes which resulted in the liberation and deposition of matter at their respective electrodes which provided us with the evidence of particulate nature of electricity.

In the mid 1850s, many scientists worked on this especially, Faraday. He worked on the cathode ray discharge tubes that are made up of glass containing two thin pieces of metal, called electrodes sealed in it. The gases will get electrically discharged at very low pressure and high voltage. By evacuating the glass tubes the pressure of various gases can be changed. When a high voltage is applied between the electrodes, then the current will be flowing as a stream of particles travels through the tube from the negative electrode (cathode) to the positive electrode (anode). These particles are referred to as cathode ray particles or cathode rays.



Cathode ray discharge tube

The flow of current from these two electrodes can be verified by making a hole in the anode and the phosphorescent material (zinc sulphide) is coated inside the tube behind the anode. The cathode rays pass through the anode and hit the coating of zinc sulphide, leading to the appearance of a bright spot.



A cathode discharge tube with a perforated anode

From the above experiment following characteristics of cathode rays have been drawn:

- (1) The cathode rays travel from cathode to anode.
- (2) The behaviour of the cathode rays cannot be observed in normal conditions. Specific glowing materials like fluorescent or phosphorescent are required to study their behaviour which makes the material glow when the rays hit it.
- (3) The cathode rays travel in a linear path in absence of an electric or magnetic field.
- (4) The cathode rays consist of negatively charged particles called electrons which was confirmed by the experimental observation. As in the presence of an electrical or magnetic field the cathode rays exhibit similar behaviour to that of negatively charged particles.
- (5) The characteristics of cathode rays (electrons) don't depend on the electrode's material and the nature of gases present inside the cathode ray tube.
- (6) It confirms that the basic constituent of atoms is electrons.



Important

➤ The television picture tubes which are made up of coated phosphorescent or fluorescent materials are nothing but cathode ray tubes.

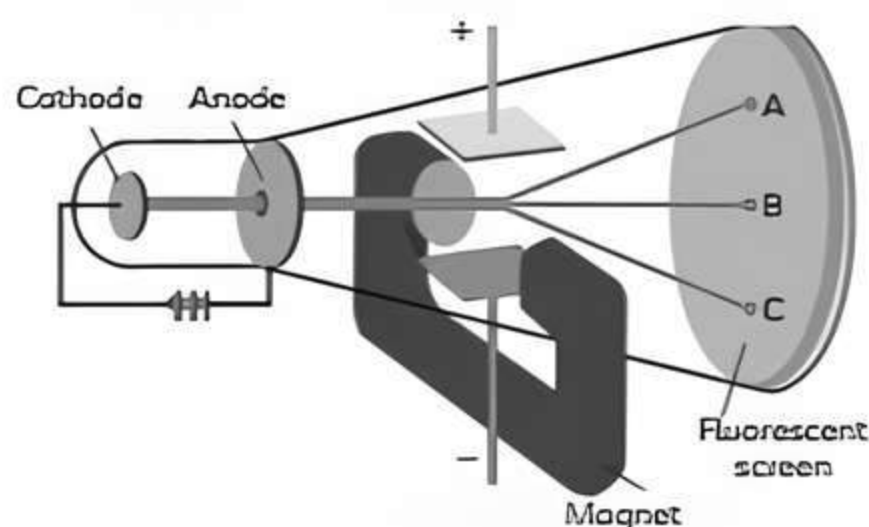
The Charge-to-Mass Ratio of Electrons

In 1897, J.J. Thomson established the ratio of an electrical charge (e) and electron's mass m_e by using a cathode ray tube under the influence of the electric

and magnetic fields. He applied electric and magnetic fields perpendicular to each other as well as to the path of the electron.

The following observations are recorded by Thomson during the experiment:

- (1) The electrons divert from their actual path and hit at point A of the cathode ray tube when only an electric field is applied.
- (2) When only the magnetic field is applied, the electron strikes at point C in the cathode ray tube.
- (3) When both the electrical and the magnetic field are applied equally, the electrons return to the original path.
- (4) The electrons hit the screen at point B in case of the absence of an electrical or magnetic field.



The setup for determining the ratio of charge and mass of an electron

Thomson proposed that the amount of deflection of the particles from their path is dependent on these factors:

- (1) **Magnitude of negative charge on the particle:** When the negative charge's magnitude on the particle is more significant, its interaction with the electric or magnetic field corresponds to a more significant deflection.

- (2) **The mass of the particle:** Lesser the mass of the particle, the more significant is the deflection.
- (3) **Strength of electrical and magnetic field:** There is an increase in the deflection of electrons from their original path when the magnetic field strength increases or there is an increase in the voltage.

By measuring the deflection of electrons on the magnetic field strength or electric field strength.

Thomson determined the value of $\frac{e}{m_e}$ as

$$\frac{e}{m_e} = 1.758820 \times 10^{11} \text{ C kg}^{-1}$$

Where the electron's mass is m_e expressed in kg, e is the magnitude of electron's charge expressed in coulomb (C). The electrons are expressed as e^- as they are negatively charged particles.

Charge on the Electron

To express the charge on the electron R.A. Millikan (1868–1953) devised the oil drop experiment (1906–1914). He discovered that the charge on the electron is $-1.6 \times 10^{-19} \text{ C}$. The presently accepted value of the electrical charge is $1.602176 \times 10^{-19} \text{ C}$. Combining these

results with Thomson's value of $\frac{e}{m_e}$ ratio the mass of the electron m_e can be determined as

$$\begin{aligned} m_e &= \frac{e}{\frac{e}{m_e}} \\ &= \frac{1.6022 \times 10^{-19} \text{ C}}{1.758820 \times 10^{11} \text{ C kg}^{-1}} \\ &= 9.1094 \times 10^{-31} \text{ kg} \end{aligned}$$

TOPIC 2

DISCOVERY OF PROTONS AND NEUTRONS

In 1886 Goldstein modified the discharge tube by using a perforated cathode. He observed a new type of luminous rays passing through the holes of the cathode when the pressure is reduced. These rays are moving in the direction opposite to cathode rays and are called canal rays. Canal rays have the following properties:

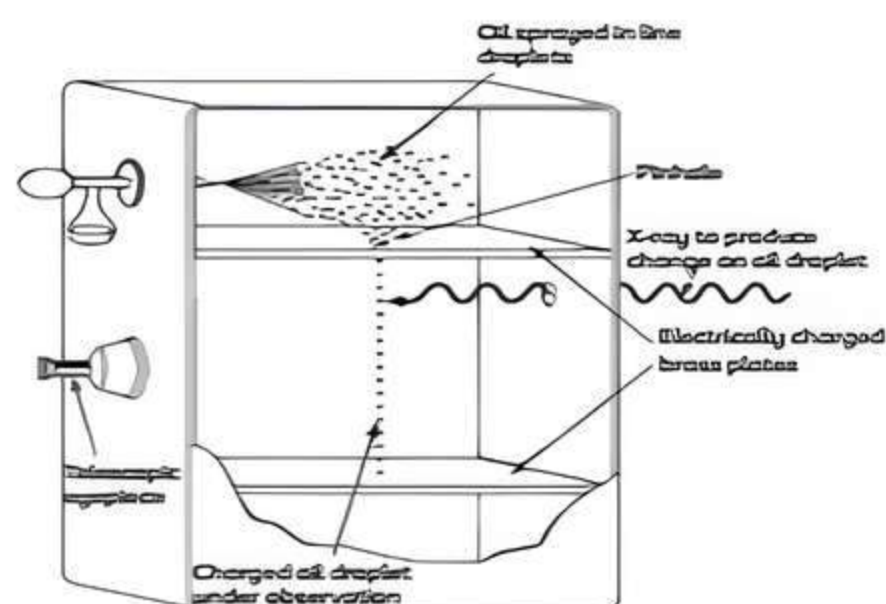
- (1) These rays are positively charged particles, gaseous ions and are dependent upon the nature of gas present in the cathode ray tube.
- (2) The particle's charge-to-mass ratio is affected by the gas from which they originate.
- (3) A few positively charged particles carry a multiple of fundamental electrical charge units.
- (4) Canal rays behave in an opposite manner in a magnetic or electrical field than cathode rays.

The protons are the smallest and lightest positive ion that was discovered in which is obtained from hydrogen, which is lighter in mass. When a thin sheet of beryllium was bombarded with particles, electrically neutral particles with a mass somewhat higher than protons were emitted. Chadwick named these particles as neutrons.

Millikan's Oil Drop Method

A tiny hole was made to permit the oil drops, in the form of mist, to enter into the upper plate of an electrical condenser, which was created by an atomizer. With a micrometre eyepiece, the motion of these droplets was observed through the telescope. The mass of

the oil droplets was estimated by monitoring the fall rate of these droplets. The air inside the chamber is ionized by the X-ray beam. Collisions with gaseous ions gave oil droplets their electrical charge. Based on the charge on the droplet, polarity, and strength of voltage given to the plate, the rate of falling of these charged droplets can be slowed, accelerated, or made immobile. Measuring the effects of the strength of electrical field strength, the motion of oil droplets, electrical charge's magnitude, on the droplets is found to be an integral multiple of the electrical charge 'e', i.e. $q = ne$ where n is 1, 2, 3, ...



Millikan's oil drop experiment

TOPIC 3

ATOMIC MODELS

The major problems after finding the subatomic particles were:

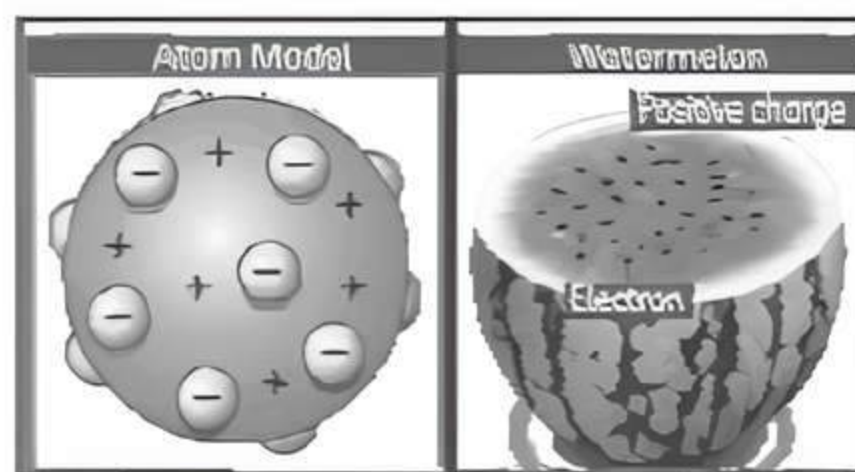
- (1) The atom's stability.
- (2) To compare the physical and chemical properties of elements.
- (3) About the formation of various molecules by the combination of various atoms.
- (4) Source and nature of characteristics of electromagnetic radiation which are absorbed or emitted by atoms.

This led to the requirement for atomic models that could account for the stability of all atoms and molecules and could also provide a comparison between the differences in the physical and chemical properties of different elements. Some atomic models are discussed below:

Thomson Model of Atom

J.J. Thomson proposed that an atom has a spherical shape in which positive charge is equally distributed, and electrons are enclosed into it that provides a

stable electrostatic arrangement. This type of model is also known as plum pudding, raisin pudding, or the fruit watermelon. The seeds of the watermelon are considered as electrons that are embedded in them. The major characteristic observed in this model is that the atom's mass is considered to be equally distributed over the atom and the atom's overall neutrality is explained. Thomson won the Nobel prize for his work on the conduction of electricity by gases in the area of physics.



A real-life example explaining the Thomson atomic model

Particle	Symbol	Absolute Charge/C	Charge	Mass/kg	Mass/u	Approx. Mass/u
Electron	e	$-1.602176 \times 10^{-19}$	-1	9.109382×10^{-31}	0.00054	0
Proton	P	$+1.602176 \times 10^{-19}$	+1	$1.6726216 \times 10^{-27}$	1.00727	1
Neutron	n	0	0	1.674927×10^{-27}	1.00867	1

Other Discoveries

X-ray: In 1895, Wilhelm Roentgen noticed that X-rays were produced when the anode made of metal is struck by the electrons. Since he didn't know about the nature of the ray, he named it X-ray. The X-rays are rays that consist of shorter wavelengths (~ 0.1 nm) of higher penetration power and these rays

are not deflected by electric and magnetic fields. It is used to study the internal structure of the matter through an X-ray scan.

Radioactivity: In 1852–1908, Henri Becquerel observed a phenomenon that certain elements are able to emit radiation by themselves, which is called radioactivity. The elements which show this phenomenon are called radioactive elements.

Radioactive Rays: Marie Curie, Pierre Curie and Rutherford and Fredrick soddy developed this field by observing α -rays consisting of high-energy particles. The alpha particles carry two units of +ve charge and four atomic mass units. α particles are Helium nuclei. β rays are particles that possess a negative charge that is similar to electrons & rays are high-energy radiations; they are neutral. The penetrating power of the particles is as follows:

$$\gamma \text{ (1000 times)} > \beta \text{ (100 times)} > \alpha \text{ (least)}$$

Rutherford's Nuclear Model of Atom

A thin gold foil was bombarded with particles by Rutherford and his students (Hans Geiger and Ernest Marsden). A stream of high-energy particles from the radiation source was directed towards a thin gold foil (thickness) which has a fluorescent zinc sulphide screen around it. A tiny flash of light was produced at a point where the particle hits the screen. This experiment is known as α -particle scattering experiment.

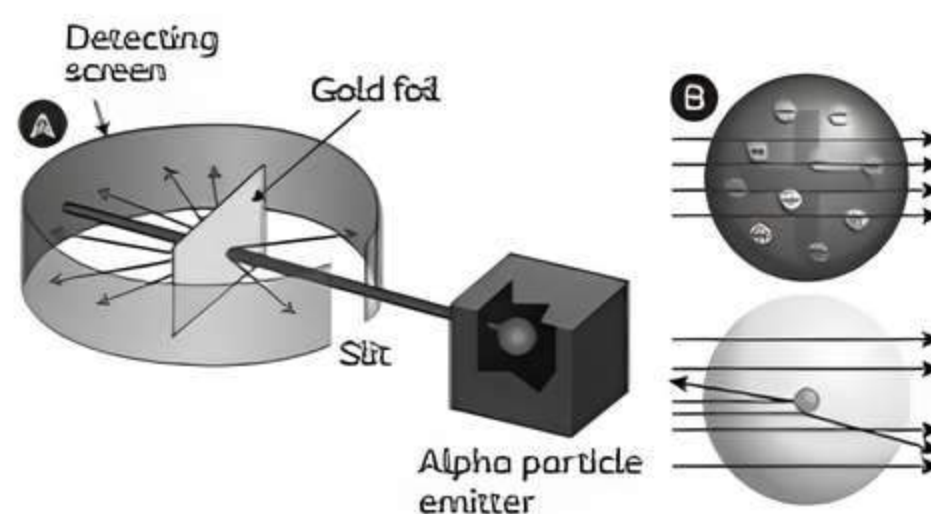
Some observations of this experiment were as follows:

- (1) The majority of the α particles went through the gold foil without being deflected.
- (2) Small angles of deflection happen by a small fraction of α -particles.
- (3) Only a few (~1 in 20,000) α -particles are deflected nearly 180° and bounced back.

From the above observations, Rutherford concluded that:

- (1) Most of the space in the atom is empty, due to which most of the α -particles passed through gold foil undeflected.
- (2) The deflection of a few positively charged α -particles occurred due to enormous repulsive force, indicating that the charge on the atom is not evenly distributed. But it may be concentrated in a small region where the positively charged α -particles were repelled and got deflected.
- (3) Compared to the entire volume of an atom, the nucleus takes up very little space. The atom's

radius is about 10^{-10} m while that for a nucleus is 10^{-15} m.



A-Rutherford Scattering experiment and
B-Molecular view of gold foil

It can be understood by considering when a cricket ball represents a nucleus, then the radius of an atom would be about 5 km. Based on these observations, Rutherford proposed the nuclear model of an atom. According to this model:

- (1) Most of the atom's mass was tightly concentrated in a very small region. This very small portion is called the nucleus, where the positively charged protons are present.
- (2) The nucleus is a very small component surrounded by electrons that move around the nucleus at high speed in a circular path known as orbit. It is similar to the solar system, where the sun serves as the nucleus, and the planets serve as electrons orbiting around the nucleus, i.e., the Sun.
- (3) The force that is responsible for holding the electron and the nucleus together is called electrostatic force.

Drawbacks of the Rutherford Model

This model failed to explain the stability of electrons in a circular path. According to Rutherford, electrons revolve around the nucleus in a circular path, but particles in motion would undergo acceleration and cause energy radiation. Eventually, electrons should lose energy and fall into the nucleus.

TOPIC 4

PROPERTIES OF ATOMS AND PLANCK'S QUANTUM THEORY

Atomic Number and Atomic Mass

Atomic number (Z)

The number of protons count that is present in the nucleus is called the atomic number (Z).

Eg. The hydrogen nucleus has 1 proton and the proton number in sodium is 11.

For a neutral atom, the number of electrons will equal the number of protons.



Important

➤ Atomic number (Z) = Number of protons present in the nucleus of an atom = Number of electrons in a neutral atom.

Atomic mass or Mass number (A)

The mass of the nucleus is due to the protons and neutrons. The protons and neutrons are collectively called nucleons. The total number of nucleons in an atom is known as mass number (A).

Important

➤ **Mass number (A) = Number of protons (Z) + Number of neutrons (n).**

Representation of an element

The normal element can be represented as X and the mass number (A) on the superscript of the left-hand side and the atomic number (Z) on the subscript of the left-hand side A_ZX

Mass number
(Number of protons
and neutrons in the atom)



Atomic symbol
(Abbreviation used
to represent atom
in chemical formulas)

Atomic number
(Number of
protons in the atom)

Mass Number and Atomic Number

Isotopes and Isobars

Isobars

Isobars are the atoms of the different elements. They have the same atomic mass but different atomic numbers. Eg: ${}^{14}_6\text{C}$ and ${}^{14}_7\text{N}$.

Isotopes

Isotopes are the atoms that have different mass numbers or neutron numbers but have the same atomic number.

Eg: ${}^{12}_6\text{C}$, ${}^{13}_6\text{C}$ and ${}^{14}_6\text{C}$

Hydrogen isotopes	Symbol	Isotopic abundance
Protium	${}^1_1\text{H}$ (1 proton and 0 neutrons)	99.985%
Deuterium	${}^2_1\text{D}$ (1 proton and 1 neutron)	0.015%
Tritium	${}^3_1\text{T}$ (1 proton and 2 neutrons)	10^{-15}

Isotopes of carbon	Number of protons and neutrons
${}^{12}_6\text{C}$	6 protons + 6 neutrons
${}^{13}_6\text{C}$	6 protons + 7 neutrons
${}^{14}_6\text{C}$	6 protons + 8 neutrons
${}^{35}_{17}\text{Cl}$	17 protons + 18 neutrons
${}^{37}_{17}\text{Cl}$	17 protons + 20 neutrons

Generally, the number of electrons determines the chemical property of an element. Therefore, all the isotopes should have the same chemical properties.

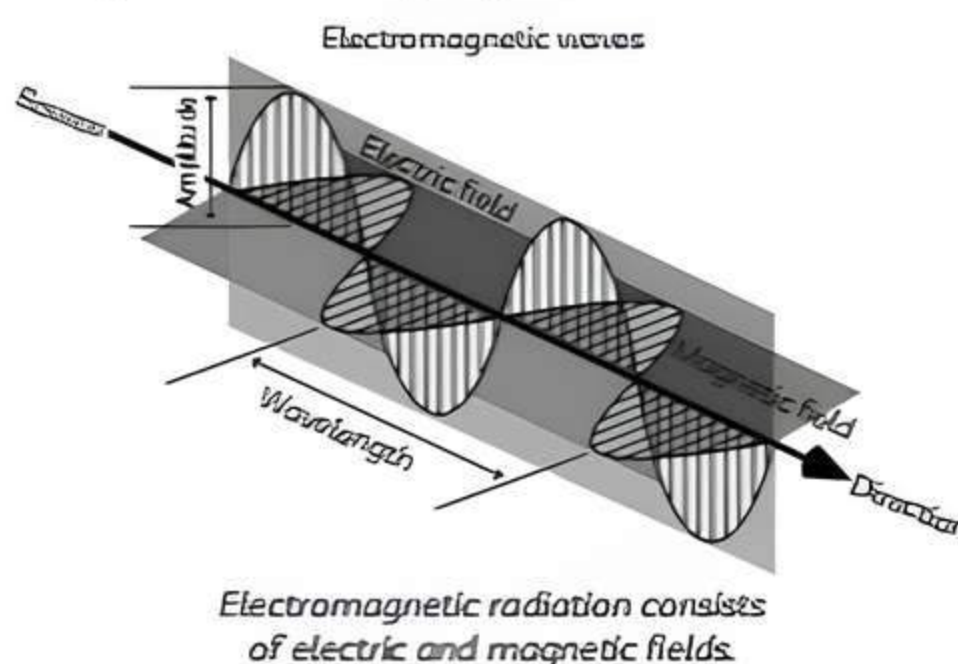
Developing leading to the Bohr's Model of Atom

The two major developments which played a major role in the formulation of Bohr's model were:

- (1) Dual character of electromagnetic radiation means that radiation possesses both wave and particle-like properties.
- (2) The atomic spectra experimental results were explained by assuming quantised electronic energy levels in the atom.

Wave nature of electromagnetic radiation

Physicists examined the absorption and emission of radiation by heating the objects. These are called Thermal radiations. James Clerk Maxwell explained the interaction between charged particles and the electrical & magnetic fields. When electrically charged particles travel under acceleration, altering electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves known as electromagnetic waves or electromagnetic radiation. Light is a type of radiation that has been recognized since the dawn of time. The light was once thought to be made up of particles.



Maxwell was the first to discover that light waves have oscillating electric and magnetic properties. A few basic properties of electromagnetic radiation are discussed here.

- (1) The charged particles produce electric and magnetic fields, these are perpendicular to one another, and they are perpendicular to the wave's direction of propagation.
- (2) In contrast to sound waves or water waves, electromagnetic waves do not require a medium and can travel in a vacuum.

Electromagnetic radiations come in various wavelengths that differ from one another (or frequency). This is referred to as the Electromagnetic spectrum. Different names

have been given to different regions of electromagnetic spectrum. Eg. Broadcasting utilises the radiofrequency region around 10^6 Hz, the microwave region around 10^{10} Hz is used for radar, and infrared region around 10^{13} Hz is used for heating. The component of the sun's radiation is around which is 10^{15} Hz shown by UV region. The small portion around 10^{15} Hz is called ordinary visible light.

Characteristics of electromagnetic radiation:

To examine the radiation that is not visible to our eyes needs advanced special instruments. Electromagnetic radiation is represented using a variety of units. These radiations are characterized by properties, namely: frequency and wavelength λ , velocity & wave number.

Frequency: Frequency is the number of waves that pass through a certain place in one second. Its SI units are cycles per second or reciprocal of seconds (s^{-1}), Hertz (Hz) named after the scientist Heinrich Hertz.

1 Hz = 1 cycle per second



Important

→ **Wavelength:** This is the distance between two successive crests or troughs of a wave. The meter is its SI unit (m). Smaller units are employed because electromagnetic waves are made up of many smaller wavelengths.

Velocity: In a vacuum, Electromagnetic radiations of all sorts travel at the same speed, regardless of wavelength, known as the speed of light $3 \times 10^8 \text{ ms}^{-1}$ ($2.997925 \times 10^8 \text{ ms}^{-1}$). The equation which relates the frequency, wavelength and light's velocity (c) is: $c = \lambda \times \nu$

Wavenumber: (ν) The number of wavelengths per unit length is known as the wavenumber. Its unit is inverse to the wavelength unit, the most widely used unit is m^{-1} (not SI unit). This value is very useful in spectroscopy.

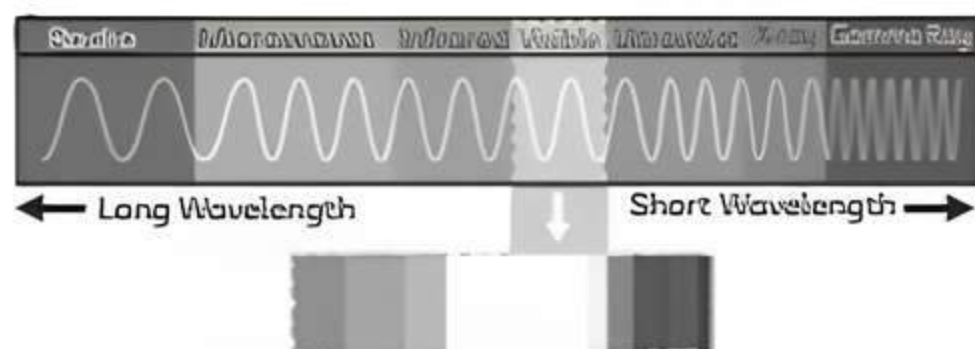
Relation between wavelength, wave number, frequency and velocity is given as

$$c = \lambda \times \nu$$

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

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

$$\nu = c\bar{\nu}$$



The Spectrum of Electromagnetic Radiation

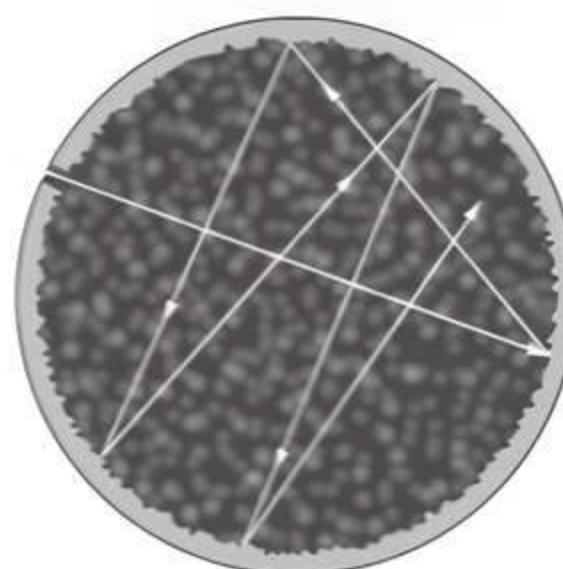
The wave nature of electromagnetic radiation is useful in explaining phenomena such as diffraction and interference. However, some of the concepts are not even explained by the wave nature of electromagnetic radiation, such as.

- (1) The nature of a heated body's radiation emission (Black body radiation).
- (2) When a metal surface is struck by electromagnetic radiation, electrons are ejected (photoelectric effect).
- (3) Thermal variation of the solid Heat capacity is considered in terms of the function of temperature.
- (4) Atomic line spectra with a particular focus on hydrogen.

These occurrences suggest that the system can only take energy in discrete amounts. It is impossible to absorb or radiate all potential energies.

Black body radiation: A black body is an ideal body that emits and absorbs radiation of all uniform frequencies, and the radiation emitted by these bodies is known as black body radiation.

Note: But in the real world, there is no such body. But Carbon black fairly resembles a black body.

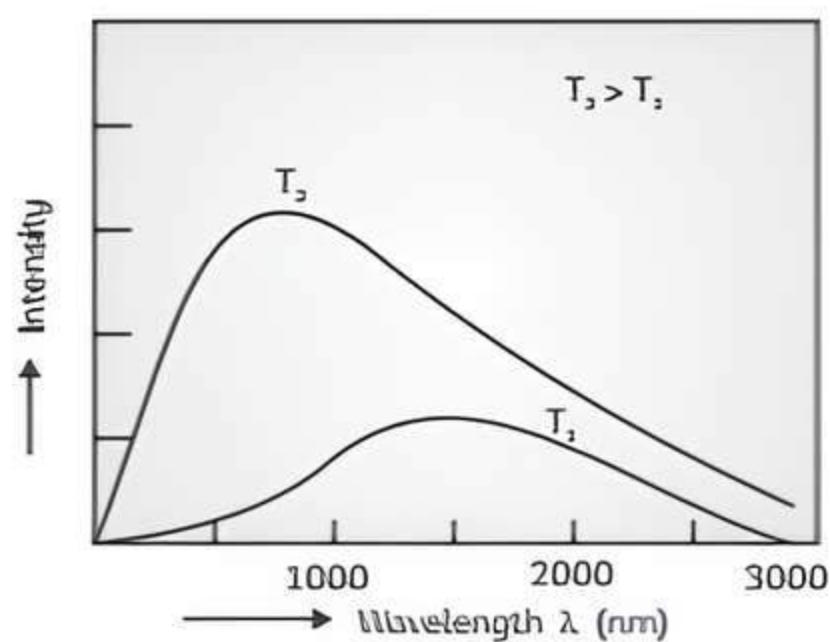


Black body

Characteristics of a good black body:

- (1) A good black body is a cavity that has a small hole and no other holes. The walls will reflect any ray that enters the hole before being absorbed by them.
- (2) A black body acts as an excellent radiant energy radiator, and it will maintain thermal balance with its surroundings.
- (3) The black body radiates the same amount of energy per unit area that it collects from its surroundings in a given amount of time.
- (4) The amount of light emitted by a black body and its spectral distribution is only affected by its temperature.

At a specific temperature, the intensity of emitted radiation increases with increasing wavelength, reaches a maximum at a particular wavelength and then decreases with increasing wavelength. As the temperature rises, the curve maxima shift to a shorter wavelength.



Wavelength Intensity relationship graph

The wave theory of light was used to predict radiation's intensity as a function of wavelength, but the results were insufficient. Thus, Planck suggested

that atoms and molecules could emit (or absorb) energy only in discrete quantities known as quantum. The energy of a quantum of radiation is related proportionally to its frequency and is expressed by the equation

$$E = h\nu$$

The constant of proportionality h is known as Planck's constant which has a value of $6.626 \times 10^{-34} \text{ Js}$.

He stated, the intensity distribution in the radiation from the black body is a function of frequency or wavelength at different temperatures. Quantization was demonstrated using the example of a man standing on a staircase. A man who can stand on the staircase, but not between two steps. Likewise, energy can take any of the following values, but not any of the values in between.

$$E = 0, h\nu, 2h\nu, 3h\nu, \dots, nh\nu$$

TOPIC 5

DUAL BEHAVIOUR OF ELECTROMAGNETIC RADIATION

The particle nature of light has described the photoelectric effect and black body radiation well. However, it was incompatible with the wave behaviour of light, which explains interference and diffraction. As a result, scientists agreed that light had both a particle and a wave nature, implying that it exhibits dual behaviour. When radiation interacts with matter, it exhibits particle-like properties instead of wave-like properties that it shows when propagating. Scientists were unfamiliar with this notion, but after a long time, they were convinced of its reality when they discovered some particles like electrons also exhibit the dual behaviour.

Example 1.1: Calculate the energy of a mole of photons with a frequency of $5 \times 10^{14} \text{ Hz}$. [NCERT]

Ans. The expression gives the energy of one photon

$$E = h\nu$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\nu = 5 \times 10^{14} \text{ s}^{-1}$$

$$E = (6.626 \times 10^{-34} \text{ Js}) \times (5 \times 10^{14} \text{ s}^{-1}) \\ = 3.313 \times 10^{-19} \text{ J}$$

The energy of one mole of photons

$$= (3.313 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \\ = 199.51 \text{ kJmol}^{-1}$$

Example 1.2: A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb. [NCERT]

Ans. Power of the bulb = 100 Watt = 100 Js^{-1}

$$E = h\nu$$

$$= \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{ Js}^{-1} \times 3 \times 10^8 \text{ ms}^{-1}}{400 \times 10^{-9} \text{ m}}$$

$$= 4.969 \times 10^{-19} \text{ J}$$

Number of photon emitted

$$= \frac{100 \text{ Js}^{-1}}{4.969 \times 10^{-19} \text{ J}}$$

$$= 2.012 \times 10^{20} \text{ s}^{-1}$$

Evidence for the Quantized Electronic Energy Levels: Atomic Spectra

The type of medium through which light passes determines its speed. When a beam of light travels from one medium to another, it is diverted or refracted from its initial path. When a ray of white light is transmitted through a prism, it is seen that the wave with the shorter wavelength bends more than the wave with the longer wavelength. Because typical white light comprises waves of all wavelengths in the visible range, the white light ray is split out into a series of coloured bands called the spectrum. The wavelength of red light is the longest and deviated the least. The violet-coloured light has the shortest wavelength and is the most deviated. The spectrum of white light, that we can see ranges from violet at $7.50 \times 10^{14} \text{ Hz}$ to red at $4 \times 10^{14} \text{ Hz}$. Such a spectrum is called a continuous spectrum. Because violet blends into blue, blue into green, and so on, this is a continual process (rainbow). Electromagnetic radiation includes visible light, but only a small part of it. Atoms may absorb energy and achieve a higher energy state when electromagnetic radiation interacts with matter. These

are in an unstable state as their energy increases. Atoms and molecules emit radiation in various parts of the electromagnetic spectrum to return to their normal energy state (more stable, lower energy states).

Emission and Absorption Spectra

The absorbed energy of radiation emitted by a substance is called an emission spectrum. The atoms, molecules, or ions get excited when they absorb radiation, producing an emission spectrum. The sample is heated to produce an emission spectrum, and the wavelength of the radiation emitted, as the sample gives up absorbed energy, is recorded.

The absorption spectrum and emission spectrum are contrary to each other. A radiation continuum is passed through a sample that absorbs radiation of certain wavelengths. The missing wavelength corresponds to radiation absorbed by matter, it leaves a dark space in the bright continuous spectrum. The study of emission or absorption spectra is referred to as **spectroscopy**.

The visible light spectrum was continuous as all wavelengths of visible light are represented in spectra. The emission spectra do not show a continuous spread of wavelength from red to violet. Instead, they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra.

Line emission spectra are used to study the electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra are used to identify unknown atoms and to determine people's fingerprints. The exact matching of lines of the emission spectrum of the atoms of a known sample quickly establishes the identity of the latter.

German Chemist, Robert Bunsen (1811–1899) used line spectra to identify elements like rubidium, Cesium, Indium, Gallium, thallium and Scandium. The element Helium was discovered in the sun by the spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is transmitted over gaseous hydrogen, the H_2 molecules dissociate, and the hydrogen atoms get excited, emitting electromagnetic radiations of discrete frequencies. The hydrogen spectrum is divided into various lines, each named after its discovery. Balmer demonstrated that when spectral lines are represented in terms of wavenumber, the visible lines of the hydrogen spectrum obey the formula below:

$$\bar{\nu} = 109.677 \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

Where n is an integer greater than or equal to 3 (i.e. $n = 3, 4, 5, 6, \dots$) The Balmer series of lines are the only ones that appear visible to electromagnetic radiation.

The Rydberg constant for hydrogen was discovered by the Swedish spectroscopists Johannes Rydberg, who noted that the following expression could describe every series of lines in the hydrogen spectrum.

$$\bar{\nu} = 109.677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}$$

Where $n_1 = 1, 2, \dots$

$$n_2 = n_1 + 1, n_1 + 2, \dots$$

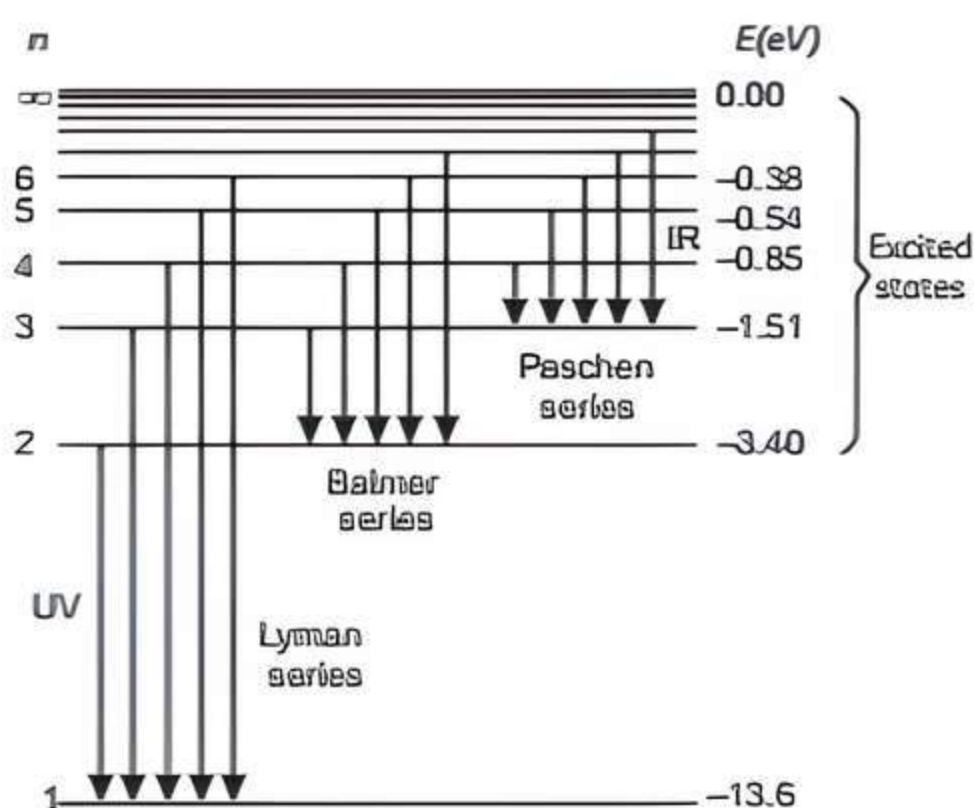
The value is called the Rydberg constant for Hydrogen. Lyman, Balmer, Paschen, Bracket and Pfund are the first five series of lines that correspond to $n_1 = 1, 2, 3, 4, 5, \dots$

Hydrogen has the most straightforward line spectrum of all the elements. For heavier atoms, the line spectrum becomes increasingly complicated. However, line spectra share several characteristics.

Each element's line spectrum has a predictable pattern. The line spectrum of features is unique.

Series	n_1	n_2	Spectral region
Lyman	1	2, 3, ...	UV
Balmer	2	3, 4, ...	Visible
Paschen	3	4, 5, ...	IR
Bracket	4	5, 6, ...	IR
Pfund	5	6, 7, ...	IR

Line spectrum of hydrogen



Energy level of the hydrogen atom with some of the transitions between them that give rise to the spectral line indicated
Spectral series of hydrogen

TOPIC 6

BOHR'S MODEL FOR HYDROGEN ATOM

In 1913, Niels Bohr quantified the general properties of the structure of the hydrogen atom and its spectrum. Even though Planck's concept of energy quantization is not the same as modern quantum mechanics, he used it to justify many points in the atomic structure and spectra. The postulates of Bohr's model are as follows:

- (1) The electron in a hydrogen atom can move in a circular path around the nucleus with a defined radius and energy. These paths are called orbits, allowed states, or stationary states. Around the nucleus, these orbits are organized concentrically.
- (2) An electron's energy in orbit does not change over time; however, an electron can travel from a lower to a higher stationary state by absorbing the needed amount of energy. This energy transformation does not happen continuously.
- (3) The frequency of radiation absorbed or emitted during the transition between two states, that differ in energy as ΔE , is given by

$$\begin{aligned} \nu &= \frac{\Delta E}{h} \\ &= \frac{E_2 - E_1}{h} \end{aligned}$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states. The frequency rule of Bohr is a well-known expression, which is called **Bohr's frequency rule**.

- (4) An electron's angular momentum is quantized i.e., an electron can move only in those orbits for which its angular momentum is an integral multiple of $\frac{nh}{2\pi}$. It can be stated in the equation

for a given stationary state as $\frac{nh}{2\pi}$

According to Bohr's theory for Hydrogen atoms:

- (1) The electron's stationary states are numbered. These integral multiples are known as **principal quantum numbers**.
- (2) The radii of the stationary states are expressed as $r_n = n^2 a_0$
Where $a_0 = 52.9 \text{ pm}$. Thus, the radius of the first stationary state is called the Bohr orbit. In the hydrogen atom, electrons are usually found in this orbit. The value of r will increase as n increases (i.e., the distance between the nucleus and electron is significant).
- (3) The energy of its stationary state is given by the equation:

$$\begin{aligned} E_n &= -R_H \frac{1}{n^2} \\ n &= 1, 2, 3, \dots \end{aligned}$$

Where R_H is called the Rydberg constant, and its value is $2.18 \times 10^{-18} \text{ J}$. The energy of the lowest state also called the ground state, is

$$\begin{aligned} E_1 &= -2.18 \times 10^{-18} \times \frac{1}{1^2} \\ &= -2.18 \times 10^{-18} \text{ J} \end{aligned}$$

- (4) For $n = 2$, the energy of the stationary state will be

$$\begin{aligned} E_2 &= -2.18 \times 10^{-18} \times \frac{1}{2^2} \\ &= -0.545 \times 10^{-18} \text{ J} \end{aligned}$$

- (5) The energy of an electron is 0 when it is free from the effect of the nucleus. The electron in this state is now known as an ionized hydrogen atom because it is associated with the stationary state of principal quantum number, $n = \infty$. The energy is emitted, and the electron's energy is diminished when the electron is attracted by the nucleus and is present in orbit. That is the explanation for the negative sign in the equation and its stability in comparison to the zero-energy reference state i.e., $n = \infty$.

The theory of Bohr can also be applied to ions with only one electron, such as hydrogen atoms.

E.g., He^+ , Li^{2+} , Be^{3+} and so on. The expression gives the energies of hydrogen-like ions.

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J}$$

And the radii by the expression,

$$r_n = \frac{529(n^2)}{Z} \text{ pm}$$

Where Z is the atomic number, which is 2, 3 for helium and lithium atoms. It is clear from the above equation that as Z increases, the value of energy decreases (becomes more negative), and the radius decreases. The electrons will be tightly bound to the nucleus due to this.

- (6) It is also feasible to determine the velocities of electrons passing through these orbits, but no precise equation is provided. Quantitatively, the magnitude of electron velocity grows as the principal quantum number decreases (n).

Example 1.3: Case Based:

Bohr proposed the following three postulates of Bohr's model:

- (1) The negative electron moves around the positive nucleus (proton) in a circular orbit. All electron orbits are centred at the nucleus. Not all classically possible orbits are available to an electron bound to the nucleus.
- (2) The allowed electron orbits satisfy the first quantization condition: In the n^{th} orbit, the angular momentum L_n of the electron can take only discrete values:

$$L_n = \frac{nh}{2\pi}, \text{ where } n = 1, 2, 3, \dots$$

This postulate says that the electron's angular momentum is quantized. Denoted by r_n and v_n respectively, the radius of the n^{th} orbit and the electron's speed in it, the first quantization condition can be expressed explicitly as:

$$m_e v_n r_n = \frac{nh}{2\pi}$$

- (3) An electron is allowed to make transitions from one orbit where its energy is E_n to another orbit where its energy is E_m . When an atom absorbs a photon, the electron makes a transition to a higher-energy orbit. When an atom emits a photon, the electron transits to a lower-energy orbit. Electron transitions with the simultaneous photon absorption or photon emission take place instantaneously. The allowed electron transitions satisfy the second quantization condition:

$$= |E_n - E_m|$$

where hf is the energy of either an emitted or an absorbed photon with frequency f . The second quantization condition states that an electron's change in energy in the hydrogen atom is quantized.

- (A) When an electron jumps from n_i orbital to n_f orbital, energy is given as:

$$(a) \Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (b) \Delta E = -R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$(c) \Delta E = R_H \left(\frac{1}{n_i} - \frac{1}{n_f} \right) \quad (d) \Delta E = -R_H \left(\frac{1}{n_i} - \frac{1}{n_f} \right)$$

- (B) When the n value (principal quantum number) increases, then the radius will:
- (a) decrease
 - (b) increase
 - (c) does not change
 - (d) cannot be predicted
- (C) Find the energy value for the second stationary state.
- (D) Using Bohr's frequency rule calculate the energy of radiation where the frequency of the radiation is $5 \times 10^{14} \text{ s}^{-1}$.

- (E) Assertion (A): Zero energy reference state corresponds to $n = \infty$

Reason (R): The energy of the electron is zero in this state.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

Ans. (A) (a) $\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$

Explanation: $\Delta E = \left(-\frac{R_H}{n_i^2} \right) - \left(-\frac{R_H}{n_f^2} \right)$ (where n_i and n_f stand for initial orbit and final orbits)

$$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

- (B) (b) increase

Explanation: When n increases, the radius also increases. This can be understood by this equation:

$$r_n = n^2 a_0$$

- (C) The energy of the stationary state equation is given by

$$E_n = -R_H \left(\frac{1}{n^2} \right)$$

For $n = 2$, the energy of the stationary state will be

$$E_2 = -2.18 \times 10^{-18} \times \frac{1}{2^2} \\ = -0.545 \times 10^{-18} \text{ J}$$

- (D) According to Bohr frequency rule

$$\Delta E = h\nu \\ = 6.626 \times 10^{-34} \text{ Js} \times 5 \times 10^{14} \text{ s}^{-1} \\ = 33.13 \times 10^{-20} \text{ J}$$

- (E) (a) Both (A) and (R) are true and (R) is the correct explanation of (A).

Explanation: The energy of an electron is 0 when it is free of the effect of the nucleus. The electron in this state is now known as an ionised hydrogen atom because it is associated with the stationary state of the principal quantum number $n = \infty$.

Explanation of Line Spectrum of Hydrogen

The hydrogen atom's line spectrum may be quantitatively explained using Bohr's model. According to assumption 2 in Bohr's model of an atom:

If an electron goes from a lower principal quantum number orbit to a higher principal quantum number orbit, radiation is absorbed. If an electron goes from a higher to a lower orbit, radiation is emitted. This energy difference between two orbits is determined by

$$\Delta E = E_f - E_i$$

Combining equations

$$\Delta E = \left(-\frac{R_H}{n_i^2} \right) - \left(-\frac{R_H}{n_f^2} \right)$$

Where n_i and n_f are for initial orbit and final orbits.

$$\begin{aligned} \Delta E &= R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \end{aligned}$$

The frequency associated with the absorption and emission of the photon can be calculated by the equation

$$\begin{aligned} \nu &= \frac{\Delta E}{h} \\ &= \frac{R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ &= 3.29 \times 10^{15} \frac{R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ Hz} \end{aligned}$$

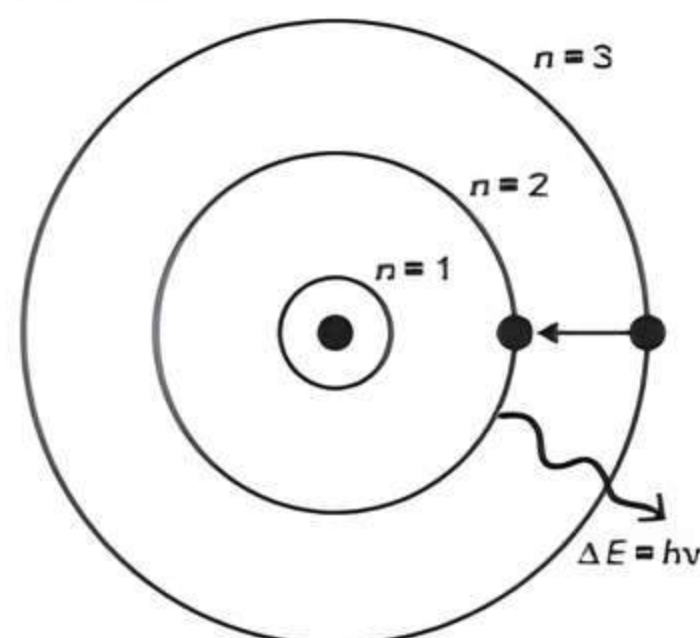
And in terms of wavenumbers

$$\begin{aligned} \bar{\nu} &= \frac{\nu}{c} \\ &= \frac{R_H}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ \bar{\nu} &= \frac{3.29 \times 10^{15} \text{ s}^{-1}}{3 \times 10^8 \text{ ms}^{-1}} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \\ \bar{\nu} &= 1.09677 \times 10^7 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ m}^{-1} \end{aligned}$$

- (1) In the absorption spectrum, the term in the parentheses is positive, indicating that energy is absorbed $n_f > n_i$.
- (2) Whereas, in the emission spectrum, E is negative, indicating that energy is emitted. $n_f < n_i$, E is negative, and energy is released.
- (3) The expression is comparable to Rydberg's, which was derived empirically using experimental data at the time.
- (4) Each spectral line (emission or absorption) can be interlinked to a specific hydrogen atom transition.

- (5) Different conceivable transitions can be observed in the presence of a large number of hydrogen atoms, leading to large spectral lines, depending on the number of photons of the same wavelength or frequency absorbed or emitted.

Example 1.4: Case Based:



Bohr's model of the atom: Electron is shown transitioning from the ($n=3$) energy level to the ($n=2$) energy level. The photon of light that is emitted has a frequency that corresponds to the difference in energy between the two levels.

Bohr's model explains the spectral lines of the hydrogen atomic emission spectrum. While the electron of the atom remains in the ground state, its energy is unchanged. When the atom absorbs one or more quanta of energy, the electron moves from the ground state orbit to an excited state orbit that is further away. Energy levels are designated with the variable n . The ground state is $n = 1$, the first excited state is $n = 2$, and so on. When the atom relaxes back to a lower energy state, it releases energy that is again equal to the difference in energy of the two orbits.

- (A) The electron is moving from the $n = 3$ to $n = 5$ quantum number during this transition of electrons. What will happen?
 - (a) Energy is released
 - (b) Energy is absorbed
 - (c) Energy becomes zero
 - (d) Energy becomes infinite
- (B) When will the energy value become negative?
 - (a) Absorption
 - (b) Emission
 - (c) Diffraction
 - (d) Scattering
- (C) Calculate the wave number when the electron is moving from the $n = 2$ to $n = 6$.
- (D) Calculate the frequency of the electron moving from the $n_i = 4 \rightarrow n_f = 6$
- (E) Assertion (A): The absorption spectrum is obtained during transition from smaller to higher quantum numbers $n_f > n_i$.
Reason (R): Energy is emitted during this transition.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
 (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
 (c) (A) is true but (R) is false.
 (d) (A) is false but (R) is true.

Ans. (A) (b) Energy is absorbed

Explanation: If an electron goes from a smaller principal quantum number orbit to a higher principal quantum number orbit, radiation is absorbed. If an electron goes from a higher to a smaller orbit, radiation is emitted. Here, the electron is moving from $n = 3$ to $n = 5$ smaller to the higher quantum numbers. So, the energy is absorbed.

(B) (b) Emission

Explanation: During the emission of radiation, the energy value becomes negative. The emission process corresponds when the electron is moving from the higher to smaller quantum number. So, it will have a negative value. This can be understood by this equation, $\Delta E = E_f - E_i$

The final energy value is lower and the initial value is higher means it would have a negative sign.

$$\begin{aligned}
 \text{(C)} \quad v &= \frac{R_H}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\
 &= \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\
 &= \frac{3.29 \times 10^{15} \text{ s}^{-1}}{3 \times 10^8 \text{ ms}^{-1}} \left(\frac{1}{2^2} - \frac{1}{6^2} \right) \quad n=2 \text{ to } n=6 \\
 &= 1.09677 \times 10^7 \left(\frac{1}{4} - \frac{1}{36} \right) \text{ m}^{-1} \\
 &= 1.09677 \times 10^7 \left(\frac{9-1}{36} \right) \\
 &= 1.09677 \times 10^7 \times 0.222 \\
 &= 0.24372 \times 10^7 \text{ m}^{-1}
 \end{aligned}$$

$$\text{(D)} \quad n_1 = 4 \rightarrow n_2 = 6$$

$$\begin{aligned}
 v &= \frac{\Delta E}{h} \\
 &= \frac{R_H}{h} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\
 &= \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\
 &= 3.29 \times 10^{15} \left(\frac{1}{4^2} - \frac{1}{6^2} \right) \\
 &= 3.29 \times 10^{15} \left(\frac{1}{16} - \frac{1}{36} \right) \\
 &= 3.29 \times 10^{15} \left(\frac{9-4}{144} \right) \\
 &= 3.29 \times 10^{15} \times 0.03472 \text{ s}^{-1} \\
 &= 0.11423 \times 10^{15} \text{ Hz}
 \end{aligned}$$

(E) (c) (A) is true but (R) is false.

Explanation: Energy is absorbed when electrons move from a lower to a higher energy level.

Limitations of Bohr's Model

Bohr's nuclear model is superior to Rutherford's in that it explains the stability and line spectra of hydrogen atoms and hydrogen-like ions. It does, however, have some restrictions.

- (1) It doesn't explain the finer details about a doublet, which is two closely spaced lines in the spectrum of hydrogen atoms seen using sophisticated spectroscopic techniques. The Bohr's model doesn't explain the finer spectral lines.
- (2) Rather than the Hydrogen spectrum, this model cannot describe the spectrum of other atoms which are having more than one electron. Example: the He atom, which has only two electrons but the spectrum of this is not explained by him.
- (3) Furthermore, Bohr's theory could not account for spectral line splitting in the presence of a magnetic field (Zeeman Effect) or an electric field (Stark effect).
- (4) It couldn't explain atoms' abilities to form molecules by chemical bonds.

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. Which of the following statement is not correct about the characteristics of cathode rays?

- (a) They start from the cathode and move towards the anode.
 (b) They travel in a straight line in the absence of an external electrical or magnetic field.

- (c) Characteristics of cathode rays do not depend upon the material of electrodes in the cathode ray tube.
- (d) Characteristics of cathode rays depend upon the nature of gas present in the cathode ray tube. [NCERT Exemplar]

Ans. (d) Characteristics of cathode rays depend upon the nature of gas present in the cathode ray tube.

Explanation: Characteristics of cathode rays do not depend on the nature of gas present in the cathode ray tube.

2. The absorption spectrum appears as:

- (a) A set of coloured lines on a black background.
- (b) Black lines on a coloured background.
- (c) Series of lines with white coloured.
- (d) Single line appears on a white background.

Ans. (b) Black lines on a coloured background.

Explanation: The absorption spectrum exhibits black lines on a coloured background. Because, when light with all wavelengths is passed, the matter absorbs the particular wavelength of light and gives a spectrum. This particular missing wavelength appears as a dark line or gap in the absorption spectrum.

3. Which of the following atomic properties could be appropriately explained by Thomson's model of an atom?

- (a) Overall neutrality of atom
- (b) Spectra of the hydrogen atom
- (c) Position of Electrons, Protons and Neutrons in atom
- (d) Stability of atom [NCERT Exemplar]

Ans. (a) Overall neutrality of atom

Explanation: According to Thomson atomic model:

- (1) An atom is spherical and has a radius of 10^{-10} meters.
- (2) The positive charge in the atom is evenly distributed.
- (3) The electrons are embedded in such a way that the atom's electrostatic configuration is the most stable. As a result, the model was able to explain the atom's overall neutrality.

4. Two atoms are said to be isobar if:

- (a) They have the same atomic number but different mass numbers.
- (b) They have the same number of electrons, but a different number of neutrons.
- (c) They have the same number of neutrons but different numbers of electrons.

- (d) Sum of the number of protons and neutrons is the same, but the element is different. [NCERT Exemplar]

Ans. (d) Sum of the number of protons and neutrons is the same, but the element is different.

Explanation: Isobars are the different elements having the same mass number but a different atomic number.



Caution

The student may confuse the term atomic mass and the mass number. Both are the same concepts but are used with different scientific names. Atomic mass is nothing but a mass of the nucleus including the number of protons and the number of neutrons.

5. Which ions do not represent the Hydrogen atom?

- (a) He^0 (b) Li^+
- (c) Be^{3+} (d) B^{4+}

Ans. (b) Li^+

Explanation: We know that a hydrogen atom has one electron in its orbital. Hence Li^+ do not represent the hydrogen atom. Because it has 2 electrons. While options a, c and d are having one electron in their orbits which resembles a hydrogen atom.

6. The n_1 and n_2 values corresponding to the Paschen series:

- (a) $n_1 = 1$ and $n_2 = 2, 3, \dots$
- (b) $n_1 = 2$ and $n_2 = 3, 4, \dots$
- (c) $n_1 = 3$ and $n_2 = 4, 5, \dots$
- (d) $n_1 = 4$ and $n_2 = 5, 6, \dots$

Ans. (c) $n_1 = 3$ and $n_2 = 4, 5, \dots$

Explanation: The Paschen series is the third series of the hydrogen absorption spectrum so, it has a value of $n_1 = 3$ and $n_2 = 4, 5, \dots$



Related Theory

The values of n_1 and n_2 in different series of hydrogen absorption spectra.

Series	n_1	n_2	Spectral region
Lyman	1	2, 3, ...	UV
Balmer	2	3, 4, ...	Visible
Paschen	3	4, 5, ...	IR
Brackett	4	5, 6, ...	IR
Pfund	5	6, 7, ...	IR

Spectrum lines of hydrogen

7. Match the following:

(A) IR	(i) 10^{13} Hz
(B) UV	(ii) 10^{10} Hz
(C) Radio waves	(iii) 10^{16} Hz
(D) Microwave	(iv) 10^6 Hz

Options:

- (a) (A) — (ii) (b) (B) — (i)
(c) (C) — (iv) (d) (D) — (iii)

Ans. (c) (C) — (iv)

Explanation:

Type of Radiation	Frequency Range (Hz)	Wavelength Range
Gamma-rays	$10^{20} - 10^{24}$	$< 10^{-12} \text{ m}$
X-rays	$10^{17} - 10^{20}$	$1 \text{ nm} - 1 \text{ pm}$
Ultraviolet	$10^{15} - 10^{17}$	$400 \text{ nm} - 1 \text{ nm}$
Visible	$4 - 7.5 \times 10^{14}$	$750 \text{ nm} - 400 \text{ nm}$
Near-infrared	$1 \times 10^{14} - 4 \times 10^{14}$	$25 \mu\text{m} - 750 \text{ nm}$
Infrared	$10^{13} - 10^{14}$	$25 \mu\text{m} - 2.5 \mu\text{m}$
Microwaves	$3 \times 10^{11} - 10^{13}$	$1 \text{ mm} - 25 \mu\text{m}$
Radio waves	$< 3 \times 10^{11}$	$> 1 \text{ mm}$

8. Name the metals used in commercial photoelectric cells.

- (a) Helium (b) Phosphorous
(c) Caesium (d) Polonium [Diksha]

Ans. (c) Caesium

Explanation: Hertz conducted the photoelectric experiment on Potassium, Rubidium and Caesium in which electrons were released from particular metals when they were exposed to light. Other elements are not used in the photoelectric cells. The caesium can easily convert sunlight into electricity and has low ionization enthalpy.

Helium is an inert gas, so it is incorrect. Phosphorus is not suitable for the photoelectric experiment. So it is incorrect. Polonium is a radioactive element which is also not suitable for the experiment. So, this is incorrect.



Related Theory

- The ionisation enthalpy is nothing but the energy required to remove an electron from the isolated atom. The elements having lower ionization enthalpy can easily emit photoelectrons. So, such elements are used in the photoelectric experiment.

9. The angular momentum of an electron is an integral multiple of:

- (a) $\frac{h}{2\pi}$ (b) $\frac{h}{4\pi}$
(c) $\frac{hc}{4\pi}$ (d) $\frac{\lambda}{2\pi}$

Ans. (a) $\frac{h}{2\pi}$

Explanation: According to the Bohr model of an atom an electron's angular momentum is quantized. It can be stated in equation form "In a given stationary condition, it is an integral multiple of $\frac{h}{2\pi}$."

$$m_e v r = n \frac{h}{2\pi}$$

10. The Paschen series occurs in which region of the electromagnetic spectrum:

- (a) Ultraviolet region
(b) Infrared region
(c) Visible region
(d) Radio wave region

Ans. (b) Infrared region

Explanation: The Paschen series is observed in the infrared region. It would require lower energy for the transition to occur.

11. The wavenumber of the first line of the Balmer series of hydrogen is 15200 cm^{-1} . The wave number of the first Balmer line of Li^{2+} ion is :

- (a) 15200 cm^{-1} (b) 60800 cm^{-1}
(c) 76000 cm^{-1} (d) 136800 cm^{-1}

Ans. (d) 136800 cm^{-1}

Explanation: Formula for wavenumber:

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

For hydrogen, $Z = 1$, for the first line of the Balmer series, $n_1 = 2$ and $n_2 = 3$

$$\begin{aligned} \bar{\nu}_H &= \frac{1}{\lambda_H} = R_H \times 1^2 \left[\frac{1}{2^2} - \frac{1}{3^2} \right] \\ &= 15200 \text{ cm}^{-1} \end{aligned}$$

For Li^{2+} ion

$$\begin{aligned} \bar{\nu}_{\text{Li}^{2+}} &= \frac{1}{\lambda_{\text{Li}^{2+}}} = R_H \times 3^2 \left[\frac{1}{2^2} - \frac{1}{3^2} \right] \\ &= 9 \times 15200 \text{ cm}^{-1} \\ &= 136800 \text{ cm}^{-1} \end{aligned}$$

Assertion-Reason (A-R)

In the following question no. (12-15), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices:

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).

- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
 (c) (A) is true but (R) is false.
 (d) (A) is false but (R) is true.

12. Assertion (A): Violet colour is the most deviated one.

Reason (R): The shorter is the wavelength, the greater is the deviation.

[NCERT Exemplar]

Ans. (a) Both (A) and (R) are true and (R) is the correct explanation of (A).

Explanation: The violet colour is having a shorter wavelength λ of 400nm. So when it travels from one medium to another, it will have a maximum value of angle of incidence. Also, the frequency is inversely proportional to the wavelength. When the wavelength is greater, the frequency will be lower. So the colour violet is most deviated.

13. Assertion (A): Value of work function for a few metals are given here: The work function value for alkali metals are decreasing down an alkali metal group.

Metal	Li	Na	K
W_0 / eV	2.42	2.3	2.25

Reason (R): The size of the atom increases down a group

Ans. (a) Both (A) and (R) are true and (R) is the correct explanation of (A).

Explanation: Work function is nothing but the minimum energy required to liberate or eject an electron from a substance. As in the given elements, the size of the atom keeps increasing down a group therefore the electrons are free from the influence of the nucleus. So on moving down a group, the energy required to eject the electron from the surface decreases.

14. Assertion (A): Circular orbit can be calculated by $r_n = 0.529 \text{ \AA} \left(\frac{n^2}{Z} \right)$, where Z = atomic number and $n = 1, 2, 3, \dots$

Reason (R): The radius of the helium atom is 0.149 \text{ \AA}

Ans. (c) (A) is true but (R) is false

Explanation: $r_n = 0.529 \text{ \AA} \left(\frac{n^2}{Z} \right)$

where Z = atomic number & $n = 1, 2, 3, \dots$

For Helium $Z = 2$ and $n = 1$

$$= 0.529 \text{ \AA} \left(\frac{n^2}{Z} \right) \\ = 0.2645 \text{ \AA}$$

15. Assertion (A): An ideal black body emits and absorbs radiation of all frequencies.

Reason (R): The frequency of radiation emitted by a body moves from a lower to a higher frequency with increased temperature.

Ans. (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

Explanation: The ideal body, which emits and absorb radiation of all frequency is called a black body. The exact frequency distribution of the emitted radiation from a black body depends only on its temperature. At a given temperature, Intensity of radiation emitted increases with decreases of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with decrease of wavelength.

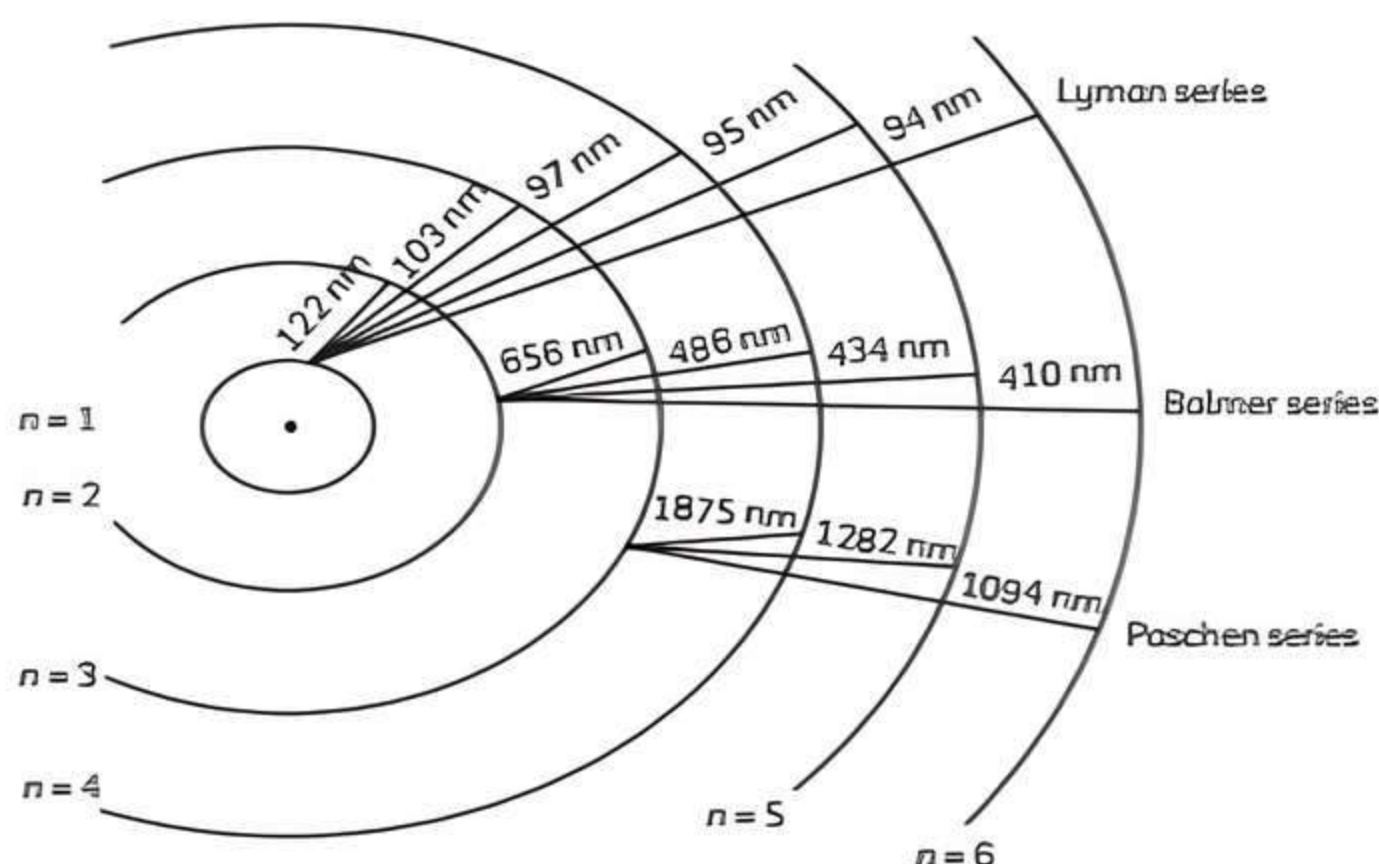
CASE BASED Questions (CBQs)

[4 & 5 marks]

Read the following passages and answer the questions that follow:

16. A hydrogen atom consists of an electron orbiting its nucleus. The electromagnetic force between the electron and the nuclear proton leads to a set of quantum states for the electron, each with its own energy. These states were visualised by the Bohr model of the hydrogen atom as being

distinct orbits around the nucleus. Each energy state, or orbit, is designated by an integer, n as shown in the figure. The Bohr's model was later replaced by quantum mechanics in which the electron occupies an atomic orbital rather than an orbit, but the allowed energy levels of the hydrogen atom remained the same as in the earlier theory.



(A) Which series of lines of the hydrogen spectrum lies in the visible region?

(B) Wavelengths of different radiations are given below:

- (I) $\lambda = 300 \text{ nm}$ (II) $\lambda = 300 \mu\text{m}$
 (III) $\lambda = 3 \text{ nm}$ (IV) $\lambda = 30 \text{ \AA}$

Arrange these radiations in the increasing order of their energies.

(C) What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum?

Ans. (A) Balmer series

(B) (IV) > (III) > (I) > (II)

The lower the wavelength the higher the energy.

(C) For the Balmer transition $n = 4$ to $n = 2$ in a He^+ ion, we can write

$$\begin{aligned} \frac{1}{\lambda} &= Z^2 R_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= Z^2 R_{\infty} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \\ &= \frac{3}{4} R_{\infty} \quad \text{---(i)} \end{aligned}$$

For a hydrogen atom

$$\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{---(ii)}$$

Equating equations (i) and (ii), we get

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

This equation gives $n_1 = 1$ and $n_2 = 2$. Thus, the transition $n = 2$ to $n = 1$ in hydrogen atom will have the same wavelength as the transition $n = 4$ to $n = 2$ in He^+ .

17. Based on the wave model of light, physicists predicted that increasing light amplitude would increase the kinetic energy of emitted photoelectrons, while increasing the frequency would increase measured current.

Contrary to the predictions, experiments showed that increasing the light frequency increased the kinetic energy of the photoelectrons, and increasing the light amplitude increased the current.

Based on these findings, Einstein proposed that light behaved like a stream of particles called photons with an energy of $E = h\nu$.

The work function, Φ , is the minimum amount of energy required to induce photoemission of electrons from a metal surface, and the value of Φ depends on the metal.

The energy of the incident photon must be equal to the sum of the metal's work function and the photoelectron kinetic energy:

$$E_{\text{photon}} = K E_{\text{electron}} + \Phi$$

(A) Radiation of 2500 \AA falls on a metal with a work function of 4 eV . The kinetic energy of the fastest photoelectron will be:

- (a) $3.22 \times 10^{-19} \text{ J}$ (b) $1.55 \times 10^{-19} \text{ J}$
 (c) $4 \times 10^{-19} \text{ J}$ (d) $2.5 \times 10^{-19} \text{ J}$

(B) When a photoelectric experiment is conducted, the number of electrons released is proportional to the:

- (a) Intensity of light
 (b) Brightness of light
 (c) Both (a) and (b)
 (d) None of the above

- (C) For an ejected electron, kinetic energy is:
- same as the frequency of the radiation from electromagnetic fields.
 - proportional to the frequency of the radiation from electromagnetic fields.
 - greater than the frequency of the radiation from electromagnetic fields.
 - inversely proportional to the frequency of the radiation from electromagnetic fields.
- (D) In an orbit, magnitude of kinetic energy is equal to:
- half of the potential energy
 - twice of the potential energy
 - one-fourth of the potential energy
 - none of the above
- (E) The minimum energy required to remove an electron is called:
- Stopping potential
 - Kinetic energy
 - Work function
 - None of these

Ans. (A) (b) $1.55 \times 10^{-19} \text{ J}$

Explanation:

Given $E_0 = 4 \text{ eV} = 4 \times 1.60 \times 10^{-19} \text{ J}$

We know that $c = 3 \times 10^8 \text{ m/s}$ [$1 \text{ \AA} = 10^{-10} \text{ m}$]

$$\therefore E = h\nu = \frac{hc}{\lambda}$$

$$\therefore E = \frac{6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{2500 \times 10^{-10} \text{ m}}$$

$$= 7.95 \times 10^{-19} \text{ J}$$

\therefore Kinetic energy of electron emitted

$$= (7.95 - 6.4) \times 10^{-19} \text{ J}$$

$$= 1.55 \times 10^{-19} \text{ J}$$

(B) (c) Both (a) and (b)

Explanation: Intensity and brightness of light decide the number of ejected electrons.

(C) (b) proportional to the frequency of the radiation from electromagnetic fields.

Explanation: Kinetic energy of ejected electron is proportional to frequency of the radiation from electromagnetic fields.

(D) (a) half of the potential energy

Explanation: We know that the Kinetic

$$\text{energy in an orbit} = \frac{Ze^2}{8\pi\epsilon_0 r}$$

Also the Potential energy in an orbit

$$= -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\text{From these two we have } KE = \frac{1}{2} PE$$

So, the magnitude of kinetic energy in an orbit is equal to half of the potential energy.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

18. The emission spectrum has a negative value for energy. Why?

Ans. In the emission spectrum, E is negative, indicating that energy is emitted (i.e., $n_f < n_i$) because the electron goes from a higher to a smaller energy level.

19. What is a black body? Give an example.

Ans. An ideal body which emits and absorbs radiations of all uniform frequencies is called a black body, and the radiation emitted by these bodies is called black body radiation.

Eg. Carbon black reasonably resembles a black body.

20. Which of the following particles will not show deflection from the path on passing through an electric field? Proton, cathode rays, electron and neutron. [NCERT Exemplar]

Ans. The electric field will not deflect neutrons as it has no charge (neutral).

21. What is meant by quantization of angular momentum? [Diksha]

Ans. As angular momentum becomes quantized, the orbit's radius and energy become quantized as well. Bohr believed that transitions of an electron from one permitted orbit / energy to another were the cause of the definite lines seen in the spectrum of hydrogen atom.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

22. Derive an equation to explain the relationship between wave number and velocity of a particle. [Diksha]

Ans. Relation between wavelength wave number. Frequency and Velocity is $c = \lambda \times v$

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

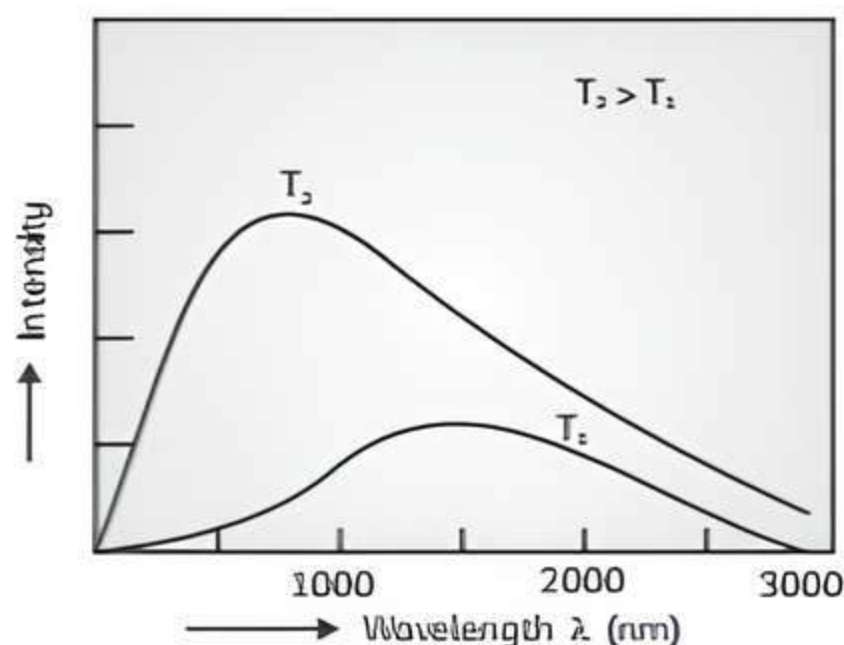
$$\frac{1}{\lambda} = \bar{\nu}$$

$$v = c\bar{\nu}$$

23. Explain the limitations of Bohr's atom model. [NCERT Exemplar]

- Ans.** (1) It doesn't explain the finer details (a doublet, which is two closely spaced lines in the spectrum of hydrogen atoms seen using sophisticated spectroscopic techniques).
- (2) Furthermore, Bohr's theory could not account for spectral line splitting in the presence of a magnetic field (Zeeman effect) or an electric field (Stark effect).

24. What do you understand from the below graph?



Wavelength-Intensity relationship

Ans. The intensity of emitted radiation increases with increasing wavelength reaches a maximum at a particular wavelength and then starts decreasing with increasing wavelength. As the temperature rises, the curve maxima shifts to a shorter wavelength.

25. Write the expression for the Bohr frequency rule.

Ans. The frequency of radiation absorbed or emitted during the transition between two states, depending on the energy difference between them, is given by

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

26. A bulb emits light of wavelength 4500\AA . The bulb is rated as 150 watts and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second? [Delhi Gov. QB 2022]

Ans. Energy of one photon

$$E = h\nu$$

$$= \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4500 \times 10^{-10}}$$

$$= 4.42 \times 10^{-19} \text{ J}$$

$$\text{Energy emitted by bulb} = \frac{150 \times 8}{100} \text{ J}$$

$$\therefore n \times 4.42 \times 10^{-19} = \frac{150 \times 8}{100}$$

$$\therefore n = 27.2 \times 10^{18} \text{ photons}$$

27. Chlorine exists in two isotopic forms Cl-37 and Cl-35, the atomic mass is 35.5. Then what will be the ratio of Cl-37 and Cl-35 approximately? [NCERT Exemplar]

Ans. Let the relative abundance of

$$\text{Cl-37} = x\%$$

And the relative abundance of

$$\text{Cl-35} = (100 - x)\%$$

$$\text{Average atomic mass} = \frac{x \times 37 + (100 - x) \times 35}{100}$$

$$35.5 = \frac{37x + 3500 - 35x}{100}$$

$$x = 25$$

$$100 - x = 75$$

Thus, the ratio of Cl-37 and Cl-35 is

$$= x : (100 - x)$$

$$= 25 : 75 = 1 : 3$$

28. Chlorophyll present in green leaves of plants absorbs light at 4.620×10^{14} Hz. Calculate the wavelength of radiation in nanometres. Which part of the electromagnetic spectrum does it belong to? [NCERT Exemplar]

Ans.

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ ms}^{-1}}{4.620 \times 10^{14} \text{ Hz}}$$

$$= 0.6494 \times 10^{-6} \text{ m}$$

$$= 649.4 \text{ nm}$$

Thus it belongs to visible region.

LONG ANSWER Type Questions (LA)

[5 & 6 marks]

29. Write about emission and absorption spectra.

Ans. The absorbed energy of radiation emitted by a substance is called an emission spectrum. The atoms, molecules, or ions get excited when they absorb radiation, producing an emission spectrum. The sample is heated to produce an emission spectrum and the wavelength of the radiation emitted, as the sample gives up absorbed energy, is recorded.

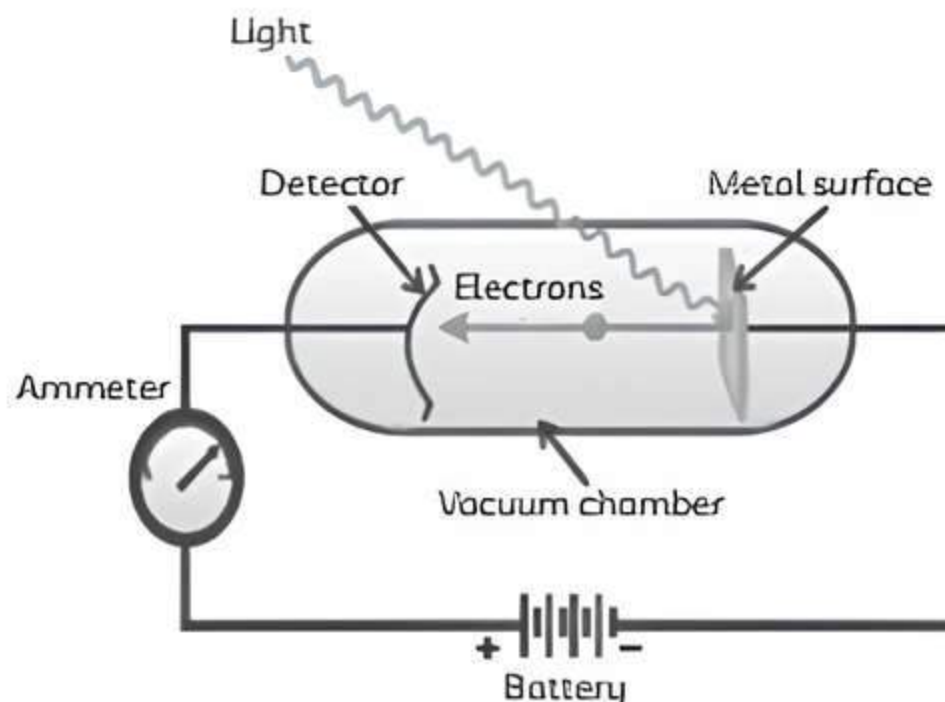
The absorption spectrum and emission spectrum are contrary to each other. A radiation continuum is passed through a sample that absorbs radiation of certain wavelengths. The missing wavelength corresponds to radiation absorbed by matter, it leaves a dark space in the bright continuous spectrum. The study of emission or absorption spectra is referred to as spectroscopy.

The visible light spectrum was continuous as all wavelengths of visible light are represented in spectra. The emission spectra do not show a continuous spread of wavelength from red to violet. Instead, they emit light only at specific wavelengths with dark spaces between them. Such spectra are called line or atomic spectra because the emitted radiation is identified by the appearance of bright lines in the spectra.

Line emission spectra are used to study the electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra identify unknown atoms and determine people's fingerprints. The exact matching of lines of the emission spectrum of the atoms of a known sample quickly establishes the identity of the latter.

30. Explain the photoelectric effect in detail.

Ans. In 1887, H. Hertz conducted an experiment in which electrons were released from particular metals when they were exposed to light (Potassium, Rubidium, Caesium, etc.). This phenomenon is called the photoelectric effect.



Experiment for studying the Photoelectric effect

The following observations were drawn by the photoelectric effect:

- (1) When a light beam strikes a metal surface, the electrons are rapidly expelled from the surface (there is no time delay between the striking of the light beam and the ejection of electrons from the metal surface).
- (2) The number of electrons ejected is proportional to the intensity or brightness of the light.
- (3) There is a particular minimum frequency for each metal called the threshold frequency, below which there is no photoelectric effect. At a frequency, $\nu > \nu_0$. The ejected electrons come out with certain kinetic energy, this kinetic energy of electrons increases with an increase in frequency of light used.

Einstein's observation:

- (1) When a photon of sufficient energy collides with an atom of metal-containing electrons, the photon instantly transmits its energy to the electron, releasing electrons without delay.
- (2) The higher the photon's energy, the more energy is imparted to the electron and the higher the kinetic energy of the expelled electron.

- (3) In simple terms, an expelled electron's kinetic energy is proportional to the frequency of electromagnetic radiation. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function W_0 , then the difference in energy is transferred as the kinetic energy of the photoelectron). The equation gives the kinetic energy of the ejected electrons:

$$h\nu = h\nu_0 + \frac{1}{2}m_0v^2$$

Where m_0 is the mass of the electron and v is the ejected electron's velocity.

- (4) A more intense beam of light consists of a large number of photons and the number of electrons ejected is also more significant than that in the experiment in which weaker intensity of light is employed.

31. Explain the Bohr's atom model.

[NCERT Exemplar]

Ans. Bohr proposed the following postulates:

- (1) The electron in a hydrogen atom can move in a circular path around the nucleus with a defined radius and energy. These paths are referred to as orbits, allowed states, or stationary states. Around the nucleus, these orbits are organised concentrically.
- (2) An electron's energy in orbit does not change over time; however, an electron can travel from a lower to a higher stationary state by absorbing the needed amount of energy. This energy transformation does not happen continuously.
- (3) The frequency of radiation absorbed or emitted during the transition between two states is given by

$$\begin{aligned} \nu &= \frac{\Delta E}{h} \\ &= \frac{E_2 - E_1}{h} \end{aligned}$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states.

- (4) An electron's angular momentum is quantized. It can be stated in equation form in a given stationary condition, it is an integral multiple of $\frac{h}{2\pi}$

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

- (5) According to Bohr's theory for Hydrogen atoms:

The electron's stationary states are numbered. $n = 1, 2, 3, \dots$. These integral multiples are known as principal quantum numbers.

- (6) The radii of the stationary states are expressed as $r_n = n^2 a_0$

Where $a_0 = 52.9$ pm. Thus the radius of the first stationary state is called the Bohr orbit. In the hydrogen atom, electrons are normally found in this orbit. The energy of its stationary state is given by the expression:

$$E_n = -R_H \left(\frac{1}{n^2} \right)$$

Where R_H is called the Rydberg constant and its value is 2.18×10^{-18} J. The energy of the lowest state also called the ground state, is $E_1 = -2.18 \times 10^{-18}$ J

- (7) The theory of Bohr can also be applied to ions with only one electron, such as hydrogen atoms.

Eg. He^+ , Li^{2+} , Be^{3+} , and so on. The energies of ions hydrogen-like are given by the expression:

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{J}$$

And the radii by the expression,

$$r_n = \frac{529(n^2)}{Z} \text{pm}$$

NUMERICAL Type Questions

32. In the hydrogen spectrum of the Balmer series which corresponds to the transition from $n_1 = 2$ to $n_2 = 3, 4, \dots$. The Balmer series lies in the visible region. Calculate the wavenumber of the line corresponding to the transition when the electron moves to $n = 4$.

($R_H = 109677 \text{ cm}^{-1}$). [NCERT Exemplar](2m)

Ans.

$$\begin{aligned} \bar{\nu} &= 109677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1} \\ &= 109677 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \text{cm}^{-1} \\ &= 109677 \left(\frac{1}{4} - \frac{1}{16} \right) \text{cm}^{-1} \\ &= 20564.44 \text{ cm}^{-1} \end{aligned}$$

33. Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 7800\AA . Calculate the metal's threshold frequency (ν_0) and work function (W_0). (3m)

Ans. Threshold frequency (ν_0) = $\frac{c}{\lambda}$

$$= \frac{3 \times 10^8 \text{ ms}^{-1}}{78 \times 10^{-9} \text{ m}}$$

$$= 3.84 \times 10^{14} \text{ s}^{-1}$$

Work function (W_0) = $h\nu_0$

$$= (6.626 \times 10^{-34} \text{ Js}) \times (3.8 \times 10^{14} \text{ s}^{-1})$$

$$= 25.1788 \times 10^{-20}$$

$$= 2.51788 \times 10^{-19} \text{ J}$$

34. Calculate the wavelength and frequency, if the period of the light wave is $8 \times 10^{-10} \text{ s}$.

Ans. Frequency = $\frac{1}{\text{Time period}}$

$$= \frac{1}{8.0 \times 10^{-10} \text{ s}}$$

$$= 1.25 \times 10^9 \text{ s}^{-1}$$

Wavelength (λ) = $\frac{c}{\nu}$

$$= \frac{3 \times 10^8 \text{ ms}^{-1}}{1.25 \times 10^9 \text{ s}^{-1}}$$

$$= 0.24 \text{ m}$$

35. What is the amount of energy emitted when electrons of 1 mole of hydrogen atom undergo a transition to give spectral lines in Balmer's series of lowest energy ($R_H = 1.1 \times 10^7 \text{ m}^{-1}$)? (2m)

Ans. The line of lowest energy of the Balmer series will be observed when the transition occurs from 3rd orbit to 2nd orbit i.e. $n_1 = 2$ and $n_2 = 3$

$$\bar{\nu}_w = \frac{1}{\lambda_w}$$

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

$$= \frac{5}{36} R$$

$$E = \frac{hc}{\lambda}$$

$$= \frac{6.6 \times 10^{-34} \times 3 \times 10^8 \times 1.1 \times 10^7 \times 5}{36}$$

$$= 3.025 \times 10^{-19} \text{ J per atom}$$

Energy corresponding to 1.0 g atom of hydrogen

$$= 3.025 \times 10^{-19} \times \text{Avogadro's number}$$

$$= 3.025 \times 10^{-19} \times 6 \times 10^{23} \text{ J}$$

$$= 18.15 \times 10^4 \text{ J}$$



DUAL BEHAVIOUR OF MATTER AND QUANTUM MECHANICAL MODEL OF ATOM

2

TOPIC 1

DUAL BEHAVIOUR OF MATTER

In 1924, de Broglie discovered that just like light, matter also shows dual nature, i.e. particle and wave nature. Thus an electron possesses a wave nature during its motion. It has a specific momentum and wavelength. This theory is popularly known as the **wave mechanical model of matter**.

de Broglie gave the relation for calculating the wavelength and momentum of particle/electron which is as follows:

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

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

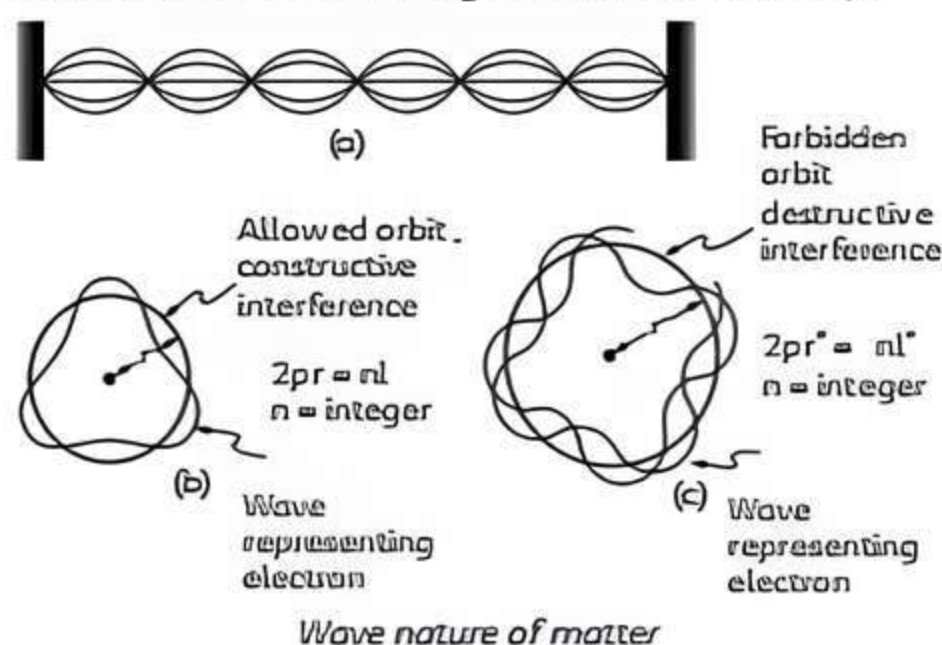
Here, m = the mass of the particle

v = the velocity of the particle

h = Planck's constant = 6.626×10^{-34} joule-seconds

p = momentum of the particle

de Broglie's theory was confirmed experimentally when it was discovered that the electron beam undergoes diffraction (characteristic of waves), which was considered for making the electron telescope.



Example 2.1: The mass of an electron is 9.1×10^{-31} kg. If its kinetic energy is 3.0×10^{-25} J, calculate its wavelength. [NCERT]

Ans.

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

Since

$$v = \left(\frac{2KE}{m} \right)^{1/2}$$

$$= \left(\frac{2 \times 3.0 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \right)^{1/2}$$

$$= 812 \text{ ms}^{-1}$$

Now the wavelength can be calculated as:

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

$$= \frac{6.626 \times 10^{-34} \text{ Js}}{9.1 \times 10^{-31} \text{ kg} \times 812 \text{ ms}^{-1}}$$

$$= 8967 \times 10^{-10} \text{ m}$$

$$= 896.7 \text{ nm}$$

Example 2.2: Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wavenumber ($\bar{\nu}$) of yellow light. [NCERT]

Ans. $\nu = \frac{c}{\lambda}$

Given here:

$$c = 3 \times 10^8 \text{ ms}^{-1}$$

$$\lambda = 580 \times 10^{-9} \text{ m}$$

$$\nu = \frac{3 \times 10^8 \text{ ms}^{-1}}{580 \times 10^{-9} \text{ m}}$$

$$= 5.17 \times 10^{14} \text{ s}^{-1}$$

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

$$= \frac{1}{580 \times 10^{-9} \text{ m}}$$

$$= 1.72 \times 10^6 \text{ m}^{-1}$$

Heisenberg Uncertainty Principle

According to the Werner Heisenberg theory, "it is impossible to measure the exact position and momentum (or velocity) of the small body like an electron simultaneously."

The relation gives the uncertainty in the measurement of position and momentum:

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

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

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

If $\Delta x = 0$, $\Delta v = \infty$

If $\Delta v = 0$, $\Delta x = \infty$

So, if the position of an electron is known accurately, i.e. Δx is small, then Δv becomes prominent and vice versa.

Significance of the Uncertainty principle

The Heisenberg uncertainty principle rules out the existence of definite paths or trajectories of electrons and other similar particles. But the effect of the Heisenberg uncertainty principle is significant only for the motion of microscopic objects and is negligible for that of macroscopic objects.

In the case of a microscopic object like an electron, mass is 9.11×10^{-31} kg, the uncertainty principle will be

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

$$= \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 9.11 \times 10^{-31} \text{ kg}}$$

$$= 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

It means that if we want to find the exact location of an electron with an uncertainty of only 10^{-9} then the uncertainty in velocity will be

$$\frac{10^{-4} \text{ m}^2 \text{ s}^{-1}}{10^{-9} \text{ m}} = 10^5 \text{ m s}^{-1}$$

The value obtained is very large. So, based on this principle, Bohr's theory, which gives the electron's fixed orbit and definite velocity, is no longer applicable. Thus, in place of precise terms, we should use probability through which we can locate the electron in a three-dimensional region around the nucleus. This is what happens in the quantum mechanical model of the atom.

Example 2.3: A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 angstrom. What is the uncertainty involved in the measurement of its velocity?

[NCERT]

Ans.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

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

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

According to Heisenberg's uncertainty principle

$$\Delta x = \frac{6.6 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times (0.1 \times 10^{-10} \text{ m}) \times (9.1 \times 10^{-31} \text{ kg})}$$

$$= 5.79 \times 10^6 \text{ m s}^{-1}$$

Example 2.4: A golf ball has a mass of 40 g, and a speed of 45 m/s. If the speed can be measured with an accuracy of 2%, calculate the uncertainty in the position.

Ans. The uncertainty in the speed is 2%, i.e.

$$45 \times \frac{2}{100} = 0.9 \text{ m s}^{-1}$$

From equation $\Delta x = \frac{h}{4\pi m \Delta v}$

$$\Delta x = \frac{6.6 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 0.9 \text{ m s}^{-1} \times 40 \times 10^{-3} \text{ kg}}$$

$$= 1.46 \times 10^{-33} \text{ m}$$

This is near 10^{-18} times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements.

Reasons for the failure of the Bohr's Model

The reasons for the failure of the Bohr's model are

- (1) According to the Bohr's model, an electron is considered as a charged particle moving in a well-defined circular orbit around the nucleus. Its wave character is not considered in the Bohr's model. Hence dual behaviour of matter is not considered.
- (2) Bohr's model considered that an orbit is a clearly defined path and it can be completely defined only if both the position and velocity of the electron are known exactly at the same time. But this contradicts with the Heisenberg uncertainty principle.

Because of these two weaknesses in the Bohr model, there was no point in extending the Bohr model to other atoms. In fact, there is a need for a theory which could deal with the wave-particle duality and be consistent with the Heisenberg uncertainty principle. So, quantum mechanics came into consideration for dealing with these facts.

QUANTUM MECHANICAL MODEL OF ATOM

The branch of science which deals with the dual behaviour of matter is known as quantum mechanics. When the quantum mechanical concept is applied to macroscopic objects (for which wave-like properties are insignificant) the results are the same as those from classical mechanics. Quantum mechanics is the theoretical science that deals with the study of the motion of microscopic objects.

Schrodinger Wave Equation

Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrodinger. Schrodinger developed a new model known as the Quantum mechanical wave model of the atom with the help of de Broglie and Heisenberg's uncertainty principle.

For a system (such as an atom or molecule whose energy does not change with time), the Schrodinger equation is written as:

$$\hat{H}\Psi = E\Psi$$

Here, \hat{H} is Hamiltonian operator (energy operator)

E is energy eigenvalue

Ψ is a wavefunction

The total energy of the system takes account of the kinetic energies of all the subatomic particles, attractive potential between electrons and nuclei and repulsive potential among the electrons and nuclei individually.

Hydrogen atom and Schrodinger equation

When the Schrödinger equation is solved for the hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave functions, Ψ of the electron associated with each energy level. These quantized energy states and corresponding to wave functions which are characterized by a set of three quantum numbers principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m) arise as a natural consequence in the solution of the Schrödinger equation. The wave function contains all the information about the electron corresponding to any energy state. It is a mathematical function and does not have any physical significance. It is possible to find the region around the nucleus with a maximum probability of locating electrons of specific energy for hydrogen or hydrogen-like species. This region is called the atomic orbital. The probability of finding an electron at a point within an atom is proportional to Ψ^2 . The quantum mechanical results of the hydrogen atom successfully predict the aspects of the hydrogen atom spectrum including the phenomenon which were not explained by the Bohr model.

The Schrodinger equation cannot be solved for the multi-electron atoms. The energies of the orbitals in the multi-electron atoms depend on quantum numbers n and l .



Important

➤ **Significance of Ψ** : It represents the amplitude of wave or wave function, but it has no significance.

➤ **Significance of Ψ^2** : It represents the probability of finding the electron in 3D space.

Important features of quantum mechanical model of the atom

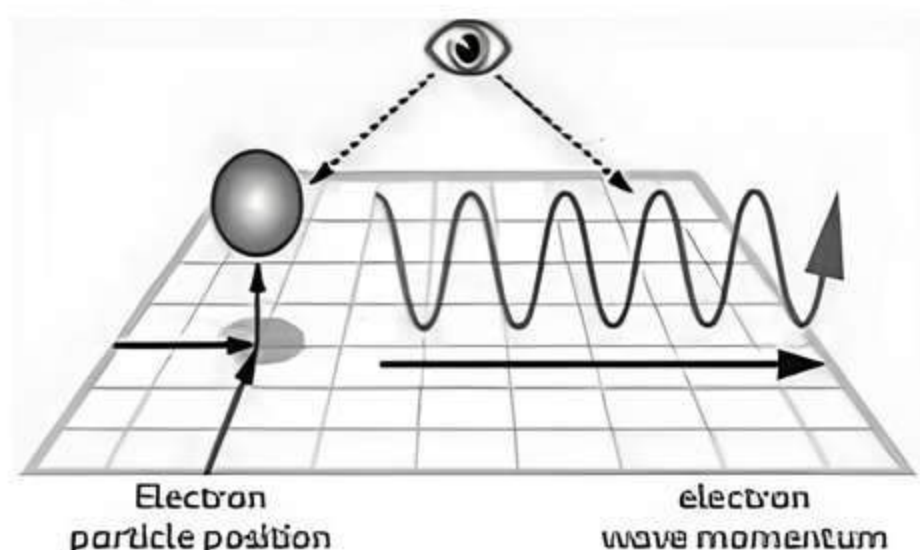
The important features of quantum mechanical model of an atom are as follows:

- (1) The energy of an electron in an atom is quantized (i.e., they can only have certain specific values).
- (2) The existence of quantized electron energy levels is a direct outcome of the wave-like properties of electrons and are allowed solutions of the Schrodinger wave equation.
- (3) The exact position and velocity of an electron cannot be determined simultaneously. Only the probability of finding the electron at different points in an atom can be determined.
- (4) The wave function Ψ for an electron in an atom represents the atomic orbital. The orbital can acquire a maximum of two electrons and electrons in each orbital have a definite energy. In a multi-electron atom, the electrons are filled in various orbitals in increasing order of energy.
- (5) The probability of finding the electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\Psi|^2$ at that point. From the value of $|\Psi|^2$ at different points within an atom it is possible to predict the region around the nucleus where the electron will most probably be found.

Example 2.5: Case Based:

In 1927, the German physicist Werner Heisenberg said that the more precisely the position of some particle is determined, the less precisely its momentum can be predicted from initial conditions, and vice versa. This was called the uncertainty principle. Heisenberg's uncertainty principle states that for particles exhibiting both particle and wave nature, it will not be possible to accurately determine both the position and velocity at the same time. Heisenberg's principle applies to all matter waves. The measurement error of any two conjugate properties, whose dimensions happen to be joule sec, like position-momentum and time-energy

will be guided by Heisenberg's value. But it will be noticeable and of significance only for small particles like an electron with very low mass. A bigger particle with a heavy mass will show the error to be very small or negligible.



(A) The error in measurement of the lifetime of an atom is 4×10^{-2} sec. What is the minimum uncertainty in its energy in eV?

(B) How will you represent the uncertainty in velocity, if the uncertainty in position and momentum are equal?

(C) Which one is the correct statement?

- (a) The uncertainty principle is $\Delta E \Delta t \geq \frac{h}{4\pi}$
- (b) de Broglie wavelength is given by $\lambda = \frac{h}{4\pi}$ where h is Planck's constant.
- (c) The uncertainty principle states that it is very possible to determine the exact position and momentum of the electron.
- (d) The effect of Heisenberg's uncertainty principle is significant for the motion of macroscopic objects.

(D) Which of the following is an incorrect expression for Heisenberg's uncertainty principle?

- (a) $\Delta E \Delta t \geq \frac{h}{4\pi}$
- (b) $\Delta x \Delta p \geq \frac{h}{4\pi}$
- (c) $\Delta x \Delta m \geq \frac{h}{4\pi}$
- (d) $\Delta x \Delta v \geq \frac{h}{4\pi m}$

(E) Assertion (A): Angular momentum of the electron in the orbit which has four subshells is $\frac{2h}{\pi}$.

Reason (R): Angular momentum of an electron is quantized.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

Ans. (A) According to the Heisenberg uncertainty principle:

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

$$\Delta E = \frac{h}{4\pi \Delta t}$$

$$= \frac{6.62 \times 10^{-34}}{4 \times \pi \times 4 \times 10^{-2}} = 1.31 \times 10^{-33} \text{ J}$$

Therefore, minimum uncertainty in energy is

$$\begin{aligned} \text{eV} &= \frac{1.31 \times 10^{-33}}{1.6 \times 10^{-19}} \\ &= 8.2 \times 10^{-15} \text{ eV} \end{aligned}$$

(B) If the uncertainty in position and momentum are equal then the uncertainty in velocity will be

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x = \Delta p$$

$$(\Delta p)^2 = \frac{h}{4\pi}$$

$$\Delta p = \frac{1}{2} \sqrt{\frac{h}{\pi}}$$

$$m \Delta v = \frac{1}{2} \sqrt{\frac{h}{\pi}}$$

$$\Rightarrow \Delta v = \frac{1}{2m} \sqrt{\frac{h}{\pi}}$$

(C) (a) The uncertainty principle is $\Delta E \Delta t \geq \frac{h}{4\pi}$

Explanation: The uncertainty principle is represented by:

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$$\text{or } \Delta E \Delta t \geq \frac{h}{4\pi}$$

de Broglie wavelength is given by $\lambda = \frac{h}{mv}$ where h is Planck's constant.

The uncertainty principle states that it is impossible to determine the exact position and momentum of the electron. The effect of the Heisenberg's uncertainty principle is significant for the motion of microscopic objects and is negligible for macroscopic objects.

(D) (c) $\Delta x \Delta m > \frac{h}{4\pi}$

Explanation: The relation gives the uncertainty in the measurement of position and momentum:

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

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

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

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

(E) (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

Explanation: Angular momentum of an electron is determined by the formula

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

For a shell with four sub-shells is fourth shell i.e., $n = 4$

$$\text{Therefore } mvr = \frac{4h}{2\pi} = \frac{2h}{\pi}$$

According to the Bohr's theory, the angular momentum (mvr) is quantised. So both the assertion and reason are true but the reason is not explaining the assertion.



Related Theory

→ According to de Broglie, the movement of an electron flows in a circular orbit around the nucleus.

According to Bohr's theory

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

If the circular orbit radius is r , then the circumference is

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

According to de Broglie equation $\lambda = \frac{h}{mvr}$. Thus $2\pi r = n\lambda$

where n = total number of waves 1, 2, 3, ... ∞

mvr = angular momentum, which is the integral multiple of

$\frac{h}{2\pi}$. Therefore, there is a similarity between the wave

and Bohr's theories.

Orbitals and Quantum Numbers

Suppose you are fond of reading books and you have read almost all the books in your college library. You spend most of your time in the library. Now, here the college in which you are studying is an atom and you as a student are an electron who is studying in a college and attending the lectures, visiting the library,

canteen, labs, etc. But you spend most of your time by reading the books in the library and that may be considered as an orbital because the possibility of finding you (electron) is maximum there. So, we can say that the region around the nucleus where the probability of finding electrons is maximum is called **atomic orbital**.

Four identification numbers are required to describe and identify the electron in an atomic orbital, these are called quantum numbers.

- (1) Principal quantum number (n) → Shell
- (2) Azimuthal quantum number (l) → Sub shell
- (3) Magnetic quantum number (m) → Orbital
- (4) Spin quantum number (s) → Spin of electron

Principal quantum number (n)

- (1) It determines the size, name and energy of the orbital.
- (2) Value of n is a positive integer, i.e., 1, 2, 3, ...
- (3) Size of the orbital increases with an increase in the number of n .
- (4) Energy of the shell increases with the increases in the value of n .
- (5) The number of electrons in a particular shell is $= n^2$.
Shell = K, L, M, N, ... $n = 1, 2, 3, \dots$

Azimuthal quantum number (l)

- (1) It determines the shape of subshell and orbital.
- (2) Value of l lies between 0 to $n - 1$.
 $l = 0$ (s-subshell)
 $l = 1$ (p-subshell)
 $l = 2$ (d-subshell)
 $l = 3$ (f-subshell)
- (3) Example:
If $n = 2, l = 0, 1$
here $n = 2$ means 2 shells and 0, 1 means 2 subshell (s and p)
If $n = 3, l = 0, 1, 2$
Here $n = 3$ means 3 shells and 0, 1, 2 means 3 subshells (s, p, and d)
- (4) Energy of subshells: $s < p < d < f$



Important

→ Orbital angular momentum is calculated by $\sqrt{l(l+1)} \frac{h}{2\pi}$
Orbital angular momentum for subshell $s = 0$

$$\text{for } p\text{-subshell} = \sqrt{2} \frac{h}{2\pi}$$

Maximum number of orbitals in any subshell $= 2l + 1$

Maximum number of electrons in any subshell $= 2(2l + 1)$

Magnetic quantum number (m)

- (1) It denotes the orientation of electron clouds (known as orbitals) and the shape of different orbitals.

- (2) Each subshell is further divided into orbitals under the influence of a magnetic field.
- (3) For any sub-shell $(2l + 1)$ values of m are possible.
- (4) Values of m are from $-l$ to $+l$ including zero.

Spin quantum number(s)

- (1) It represents the spin of the electrons around its own axis.

- (2) For clockwise / up spin (\uparrow) of the electron: $+\frac{1}{2}$
- (3) For anticlockwise / down spin (\downarrow) of the electron: $-\frac{1}{2}$
- (4) Each orbital containing two electrons always has opposite spins.

TOPIC 3

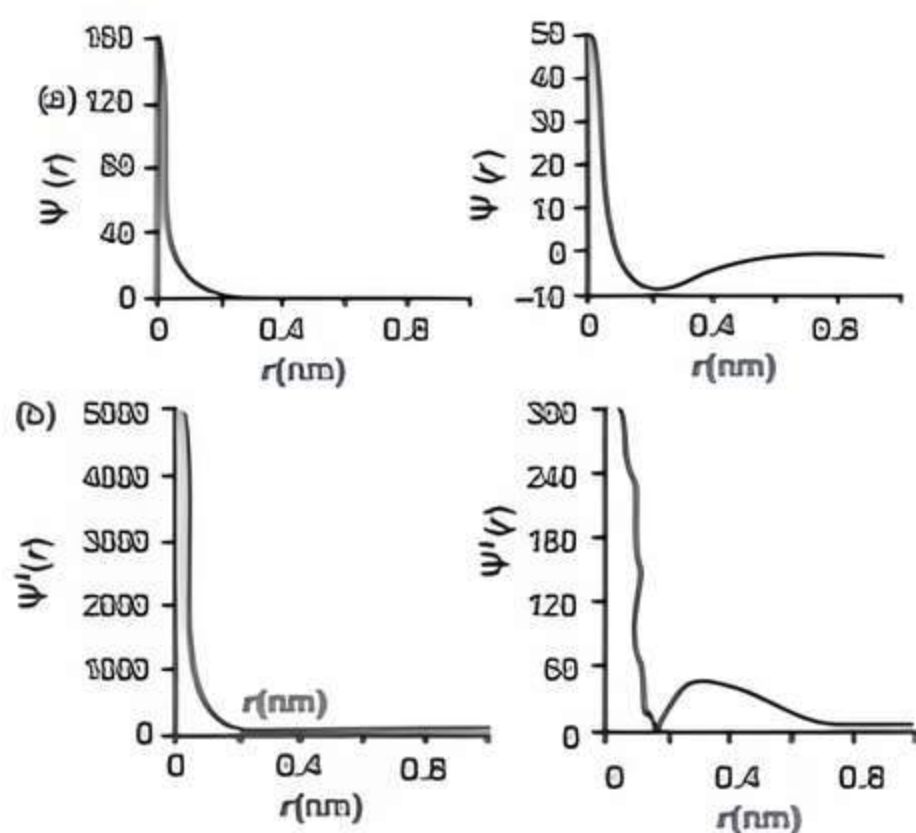
SHAPES OF ATOMIC ORBITALS

The orbital wave function or ψ has no physical meaning. It is a mathematical function of the coordinates of the electron. For different orbitals the plot of corresponding wave functions as a function of radius is different. It can be seen in the plots given below that $1s$ orbital has the maximum probability density (ψ^2) at the nucleus and decreases sharply as we move away from it. Similarly, for $2s$ orbital the probability density decreases sharply to zero and again starts increasing. After reaching the maxima it again approaches zero as the value of r (distance from the nucleus) increases. The region where the probability density is zero is called **nodal surface or nodes**.



Important

- Total number of nodes = $n - 1$
- Radial nodes = $n - l - 1$
- Angular nodes = l



The plots of an orbital wave function $\psi(r)$ and (b) variation of probability density $\psi^2(r)$ as a function of distance r of the electron from the nucleus for $1s$ and $2s$ orbitals.

Boundary surface diagrams: The probability density variation can be visualized in the terms of a charge cloud diagram, called the boundary surface diagram. In this representation the boundary surface or contour surface is drawn in space for an orbital on which the value of probability is constant. However, several such

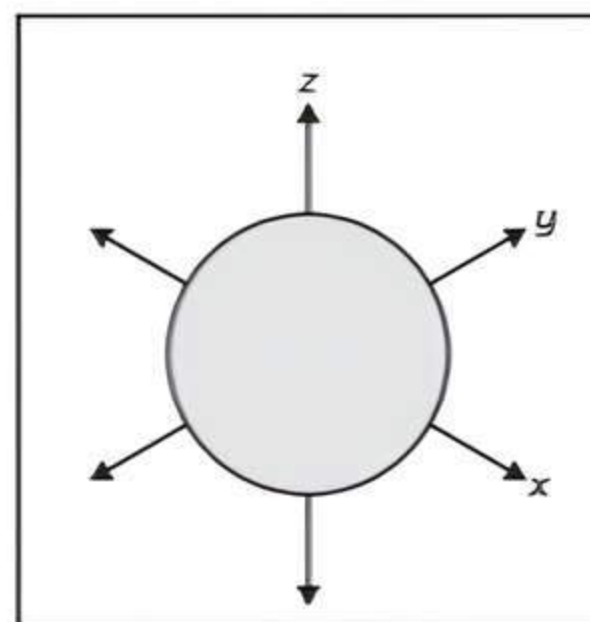
boundary surface diagrams may be possible. The shape of the orbital is given by, only that boundary surface diagram where the probability density is constant or say the most probable region.

The shapes of orbitals are discussed below:

If, $l = 0$ and $m = 0$.

s-subshell

- (1) It implies that s subshell has only one orbital.
- (2) s -orbitals are spherically symmetrical about the nucleus, so the probability of finding electrons is the same in all directions.
- (3) The electron cloud is maximum near the nucleus and decreases with the distance. The intermediate region is zero electron density, called nodal surface or nodes.
- (4) The size of the orbital depends on the principal quantum number. It increases with an increase in n , i.e., $5s > 4s > 3s > 2s > 1s$.

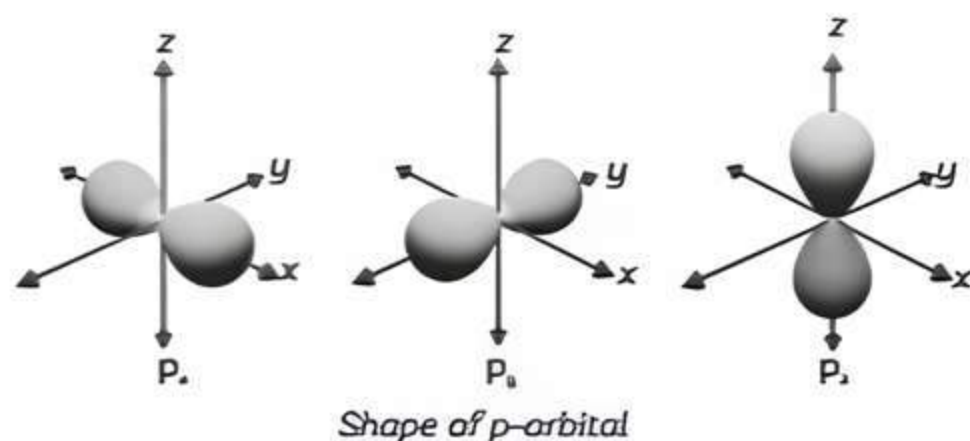


Shape of s -orbital

If $l = 1$ and $m = -1, 0, +1$

p-subshell

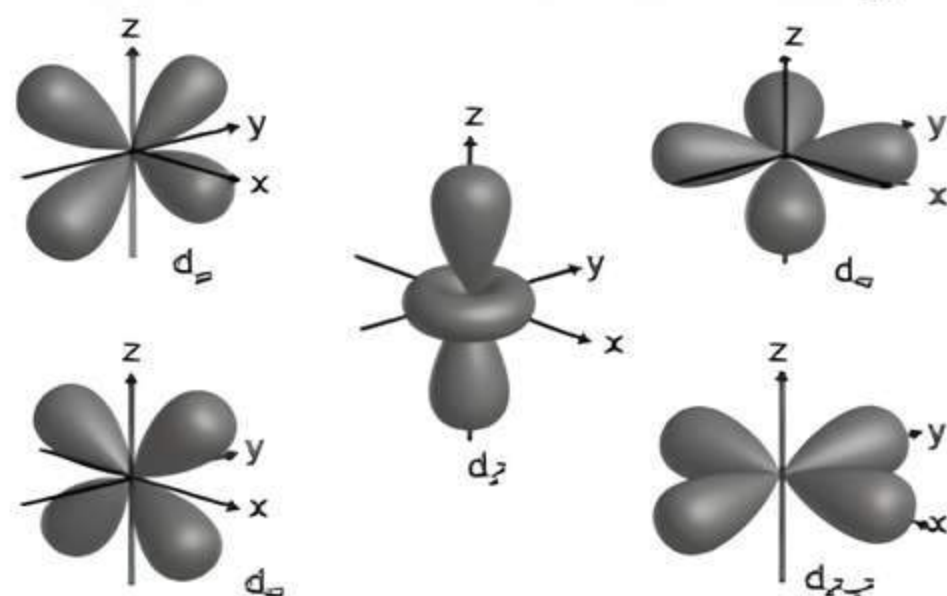
- (1) Namely, three p orbitals are there p_x , p_y and p_z whose axes are mutually perpendicular.
- (2) They differ in their distribution of charge and direction, but they have the same energy and the same relation with the nucleus.
- (3) The p -orbital has a dumbbell shape.



If $l = 2$ and $m = -2, -1, 0, +1, +2$

d-subshell

- (1) Namely, five d orbitals are present d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2}
- (2) d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ have four lobes while d_{z^2} has two lobes. All five d orbitals have equivalent energies.
- (3) The d-orbital has a double dumbbell shape.
- (4) The shapes of 4d and 5d-orbitals are equivalent to that 3d-orbital but differ in size and energy.



Shape of d-orbitals

Energies of Orbitals

The energy of an electron in a hydrogen atom is determined by the principal quantum number, but in the case of a multi-electron atom it is determined by an azimuthal quantum number.

In the case of the hydrogen atom, the energy of orbitals increases as follows

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$$

Although the shapes of 2s and 2p are different but the electron has the same energy when it is in orbital 2s and 2p orbital. The orbitals having the same energy are called degenerate orbitals. The orbital in a hydrogen atom is in the most stable condition and is called the ground state. There is only one electron in the hydrogen atom and therefore no shielding effect is present. The only interaction is the attraction between the negatively charged electron and the positively charged nucleus.

In the case of multi-electron atoms, the energy is different for different subshells. The electrons of the valence shell are attracted toward the nucleus or repelled by the electrons present in the inner shell.

The actual force of attraction between the nucleus and outer shell is somewhat decreased by repulsive forces acting in opposite directions. Thus, the shielding of the outer shell electrons from the nucleus by the inner shell electron is called the **shielding or screening effect**. This effect is different in different types of the orbitals. The net positive charge experienced by electrons from the nucleus is called an effective nuclear charge (Z_{eff}). The order of shielding is $s > p > d > f$. The electron present in s-orbital will be more tightly bounded with the nucleus as compared to p-orbital and vice versa.

(n + l) Rule

According to this rule, lower the value of $(n + l)$ for an orbital the lower is its energy. If two orbitals have the same $(n + l)$ value, the orbital with the lower value of n will have lower energy. The table given below depicts the energy level of multielectron atoms.

Orbital	Value of n	Value of l	Value of $(n + l)$	
1s	1	0	1+0=1	2p ($n=2$) has lower energy than 3s ($n=3$) 3p ($n=3$) has lower energy than 4s ($n=4$) 3d ($n=3$) has lower energy than 4p ($n=4$)
2s	2	0	2+0=2	
2p	2	1	2+1=3	
3s	3	0	3+0=3	
3p	3	1	3+1=4	
4s	4	0	4+0=4	
3d	3	2	3+2=5	
4p	4	1	4+1=5	

Arrangement of orbital with an increasing energy on the basis of $(n + l)$ rule.

Thus, the energies of the orbitals in the same subshell decrease with increase in the atomic number (Z_{eff}). For example, energy of the 2s orbital of a hydrogen atom is greater than that of the 2s orbital of a lithium and that of lithium is greater than that of sodium and so on that is, $E_{2s}(\text{H}) > E_{2s}(\text{Li}) > E_{2s}(\text{Na}) > E_{2s}(\text{K})$.

Example 2.6: The bromine atom possesses 35 electrons. It contains 6 electrons in 2p orbital, 6 electrons in 3p orbital and 5 electrons in 4p orbital. Which of these electrons experiences the lowest effective nuclear charge? [NCERT]

Ans. The effective nuclear charge is the net charge an electron experiences in an atom with multiple electrons. The greater the distance of electrons from the nucleus, the lower the effective nuclear charge. Among p-orbitals, 4p-orbitals are the farthest from the nucleus of the bromine atom. Hence, the electrons that reside in the 4p orbital are the ones to experience the lowest effective nuclear charge. These electrons are also shielded by electrons that are present in the 2p and 3p-orbitals along with the s-orbitals.

Example 2.7: What is the total number of orbitals associated with the principal quantum number $n=3$? [NCERT]

Ans. For $n=3$, the possible values of l are 0, 1, 2

Thus, there is one 3s-orbital ($n = 3, l = 0, m = 0$);

There are three p-orbitals ($n = 3, l = 1, m = -1, 0, +1$);

There are five 3d-orbitals ($n = 3, l = 2, m = -2, -1, 0, +1, +2$);

Therefore, the total number of orbitals is $1 + 3 + 5 = 9$.

Example 2.8: The quantum numbers of six electrons are given below. Arrange them in order of increasing energies.

(A) $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$

(B) $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

(C) $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

(D) $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$

(E) $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$

(F) $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$

Ans. (A) The quantum numbers $n = 4, l = 2$.

$m_l = -2, m_s = -\frac{1}{2}$ represents 4d-orbital.

(B) The quantum numbers $n = 3, l = 2, m_l = 1$.

$m_s = +\frac{1}{2}$ represents 3d-orbital.

(C) The quantum numbers $n = 4, l = 1, m_l = 0$.

$m_s = +\frac{1}{2}$ represents 4p-orbital.

(D) The quantum numbers $n = 3, l = 2, m_l = -2$.

$m_s = -\frac{1}{2}$ represents 3d-orbital.

(E) The quantum numbers $n = 3, l = 1, m_l = -1$.

$m_s = +\frac{1}{2}$ represents 3p-orbital.

(F) The quantum numbers $n = 4, l = 1, m_l = 0$.

$m_s = +\frac{1}{2}$ represents 4p-orbital.

The order of increasing energies is (E) < (B) = (D) < (F) = (C) < (A)

Example 2.9: Case Based:

Neha is in search of her ten-year-old friend. To locate her address, the first step she will do is to find the state in which she is living. After that she will look for the district and then the city, area and house number, to reach out to her friend. Similarly, to locate an electron, quantum numbers are needed. The four quantum numbers are required to give the complete

address of the location of electrons. These quantum numbers are: principal quantum number (n), azimuthal quantum number (l), magnetic quantum number (m), and spin quantum number (s). ' n ' represents the shell and it determines the size of the orbital. ' l ' represents the subshell and determines the shape of the orbital. ' m ' denotes the orientation of the electron cloud and ' s ' represents the spin of the electron in the orbital.



Quantum numbers

- (A) How will you determine the maximum number of electrons having the same value of the spin quantum number in any subshell?
- (B) What will be the shape of the orbital when the azimuthal quantum number has a value of 1?
- (C) Two electrons occupying the same orbital can be distinguished by:

- (a) Azimuthal quantum number
(b) Principal quantum number
(c) Spin quantum number
(d) Magnetic quantum number

- (D) The degeneracy of the first excited state ($n=2$) of the H-atom is (do not consider the electron spin):

- (a) 2 (b) 4
(c) 8 (d) 7

- (E) Assertion (A): The energy of an electron is largely determined by the principal quantum number.

Reason (R): The principal quantum number is a measure of the most probable distance of finding electrons around the nucleus.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

Ans. (A) In any sub-shell, the maximum number of electrons having the same value of a spin quantum number is equal to the number of orbitals. The value of orbitals can be determined by the formula: $2l + 1$.

- (B) The value of $l = 1$ is for the p-orbitals. The p-orbital has a dumb-bell shape. Namely, three p orbitals are there p_x, p_y and p_z .

whose axes are mutually perpendicular. They differ in their distribution of charge and direction, but they have the same energy and the same relation with the nucleus.

(C) (c) Spin quantum number

Explanation: The two electrons occupying the same orbital can be differentiated by the spin quantum number. The value of n, l, m is the same but the value of 's' is different i.e., $+\frac{1}{2}$ and $-\frac{1}{2}$

(D) (b) 4

Explanation: For the H-atom, the energy of 2s orbital = energy of 2p orbital so the degeneracy is $1 + 3 = 4$.

(E) (a) Both (A) and (R) are true and (R) is the correct explanation of (A).

Explanation: The principal quantum number represents the main energy level or the energy shell. Since each energy level is associated with a definite amount of energy, this quantum number determines to a large extent the energy of an electron. It also determines the average distance of the electrons from the nucleus. So, both the statements are true and the reason is the correct explanation of the assertion.

Rules of Filling Electrons in the Orbitals

The filling of electrons into the orbitals of different atoms takes place according to the Aufbau principle which is based on the Pauli exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals.

Aufbau principle

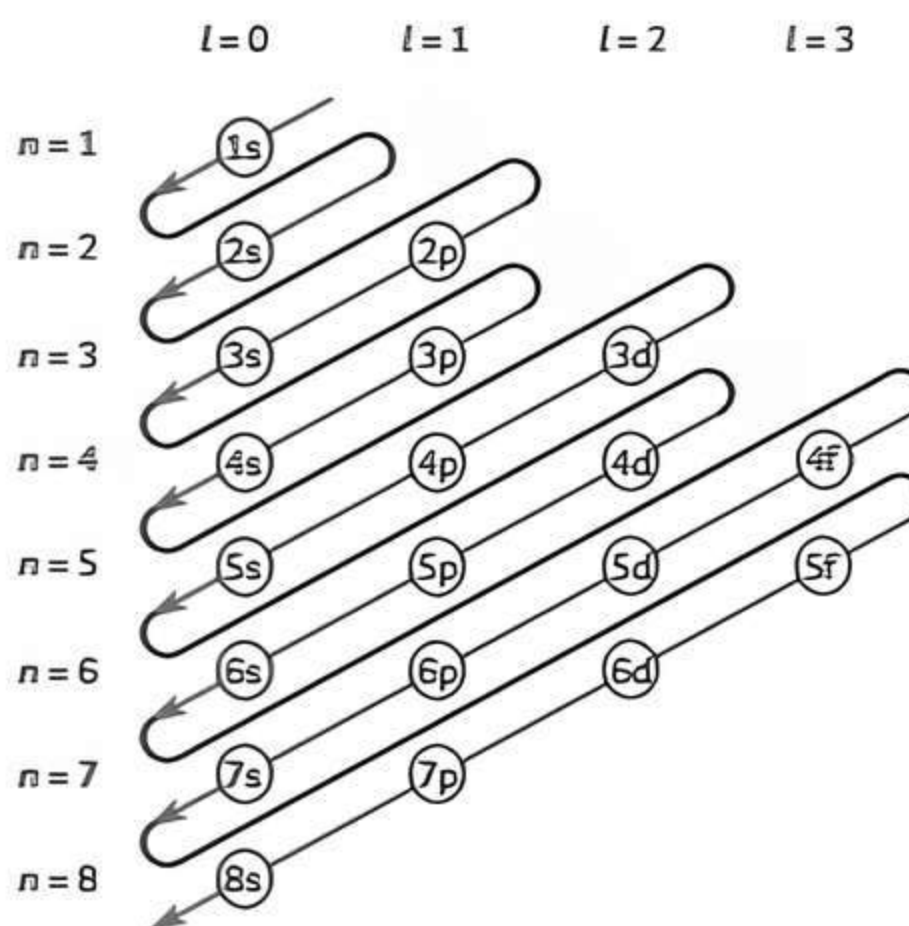
According to the Aufbau principle, in the atom's ground state, the orbitals are filled in order of their increasing energy value ($n+l$). The electrons first occupy the lowest energy orbital and then enter to the higher energy orbital only after the lower energy orbitals are filled.

As per the Aufbau principle, the filling of electrons is in the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s.

So, the right filling sequence of the sub-shell is $f > d > p > s$

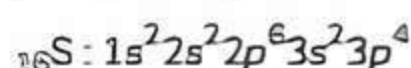
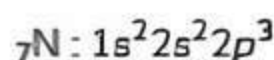
Important

- The less the $n+l$ value of an orbital, the less the energy and thus electrons are filled first in these orbitals.
- More the $n+l$ value of an orbital, the more the energy and thus electrons are filled last in these orbitals.
- If the $n+l$ value is the same for different orbital, then whoever has the lesser n value will be filled first with the electrons.



Order of filling of orbitals

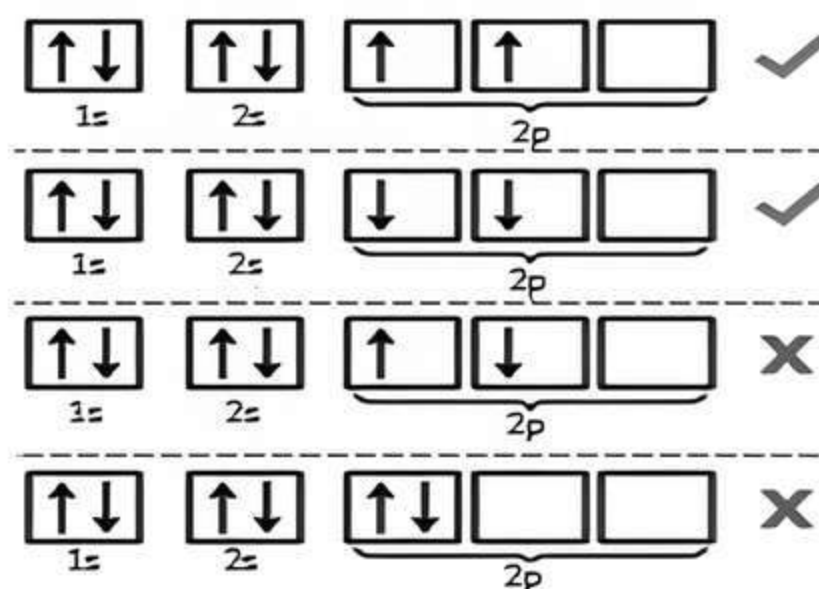
Examples of Aufbau principle:



Hund's rule

Let's take an example of people getting on an empty bus. When people enter the two-seater empty bus, they always want to grab the window seat. They rush towards the window seats and when all the window seats get occupied by one-one person each, the others have to sit together. This happens in Hund's rule also, where the electron is first singly filled before it gets paired up. Hund's rule is applicable for the degenerate orbital (equal energy orbitals) of the same subshell. According to this rule, pairing of electrons in the orbitals belonging to the same subshell does not occur until each orbital belonging to that subshell has got one electron each i.e., electrons filling in the orbital is first singly with parallel spin electron and then they begin to pair up.

Example: Carbon Electron Configuration

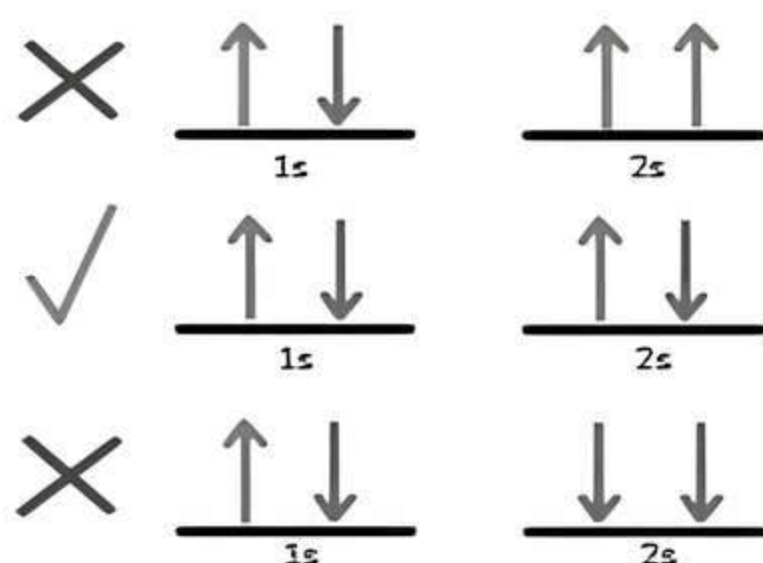


Filling of an electron according to Hund's rule

Pauli's exclusion principle

According to Pauli's exclusion principle, no two electrons in an atom have the same set of four quantum numbers. An orbital can have a maximum of two electrons with an opposite spin.

Example:



Representation of Pauli's exclusion principle

Electronic Configuration of Atoms

The sequential distribution of electrons in an atomic orbital is called electronic configuration. The electronic configuration helps in determining an atom's valency, group, and period.

The electronic configuration is represented in two ways:

(1) $s^a p^b d^c$ notation

(2) Orbital diagram

It is written in the terms of $n l^x$.

Where, n represents the order of shell, l represents the subshell and x indicates the number of electrons present in the sub-shell.

The electrons with completely filled shells are known as core electrons and the electrons with the highest principal quantum number are called valence electrons. For example: the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons.

Some examples representing the electronic configuration of different atoms are shown in the figure.

Table: Ground State Electronic Configuration of Elements

Z	Element	Electronic configuration	Z	Element	Electronic configuration
1	H	$1s^1$	21	Sc	$[\text{Ar}]3d^1 4s^2$
2	He	$1s^2$	22	Ti	$[\text{Ar}]3d^2 4s^2$
3	Li	$[\text{He}]2s^1$	23	V	$[\text{Ar}]3d^3 4s^2$
4	Be	$[\text{He}]2s^2$	24	Cr	$[\text{Ar}]3d^5 4s^1$
5	B	$[\text{He}]2s^2 2p^1$	25	Mn	$[\text{Ar}]3d^5 4s^2$
6	C	$[\text{He}]2s^2 2p^2$	26	Fe	$[\text{Ar}]3d^6 4s^2$
7	N	$[\text{He}]2s^2 2p^3$	27	Co	$[\text{Ar}]3d^7 4s^2$
8	O	$[\text{He}]2s^2 2p^4$	28	Ni	$[\text{Ar}]3d^8 4s^2$
9	F	$[\text{He}]2s^2 2p^5$	29	Cu	$[\text{Ar}]3d^{10} 4s^1$
10	Ne	$[\text{He}]2s^2 2p^6$	30	Zn	$[\text{Ar}]3d^{10} 4s^2$
11	Na	$[\text{Ne}]3s^1$	31	Ga	$[\text{Ar}]3d^{10} 4s^2 4p^1$
12	Mg	$[\text{Ne}]3s^2$	32	Ge	$[\text{Ar}]3d^{10} 4s^2 4p^2$
13	Al	$[\text{Ne}]3s^2 3p^1$	33	As	$[\text{Ar}]3d^{10} 4s^2 4p^3$
14	Si	$[\text{Ne}]3s^2 3p^2$	34	Se	$[\text{Ar}]3d^{10} 4s^2 4p^4$
15	P	$[\text{Ne}]3s^2 3p^3$	35	Br	$[\text{Ar}]3d^{10} 4s^2 4p^5$
16	S	$[\text{Ne}]3s^2 3p^4$	36	Kr	$[\text{Ar}]3d^{10} 4s^2 4p^6$
17	Cl	$[\text{Ne}]3s^2 3p^5$	37	Rb	$[\text{Kr}]5s^1$
18	Ar	$[\text{Ne}]3s^2 3p^6$	38	Sr	$[\text{Kr}]5s^2$
19	K	$[\text{Ar}]4s^1$	39	Y	$[\text{Kr}]4d^1 5s^2$
20	Ca	$[\text{Ar}]4s^2$	40	Zr	$[\text{Kr}]4d^2 5s^2$

Stability of the Half-filled and Completely Filled Subshell

The ground state electronic configuration of the atom of an element always corresponds to the lowest energy state to give higher stability. The electronic configuration of most of the atoms follows basic rules. But in some cases, like in chromium and copper, the rules are violated.

Chromium and copper have electron configurations $[\text{Ar}]3d^5 4s^1$ instead of $[\text{Ar}]3d^4 4s^2$ and $[\text{Ar}]3d^{10} 4s^1$ instead of $[\text{Ar}] 3d^9 4s^2$ respectively. This exception is caused due to increase in the stability caused by half-filled and fully filled subshells and a comparatively low energy gap between the 3d and 4s subshells. Causes of stability of completely filled and half-filled subshells are symmetric distribution of electrons and exchange energy. Therefore, the configuration of electrons in certain atoms doesn't obey the Aufbau principle.

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. Which of the following options does not represent an atom's ground state electronic configuration?

- (a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$
- (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
- (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$
- (d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

[NCERT Exemplar]

Ans. (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$

Explanation: According to the Aufbau principle, "atoms in the ground state are filled according to the order of their increasing energies". But in the case of copper configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ due to the high stability of the full filled orbital of the d-subshell. Since the energies of both 4s and 3d are almost the same, that's why full-filled d-orbitals in the case of copper attain the state of stability. So, it is not represented in the ground state.



Cautlon

Students may get confused here because of the general tendency of the electronic configuration in which electrons tend to be filled in 4s before entering in 3d but in copper's, it is considered as an exception because of stability of fully filled d orbital.

2. The de Broglie wavelength for particles with the same kinetic energy is:

- (a) directly proportional to its velocity
- (b) inversely proportional to its velocity
- (c) independent of velocity and mass
- (d) unpredictable

[Diksha]

Ans. (a) directly proportional to its velocity

Explanation:

$$\frac{\lambda_1}{\lambda_2} = \frac{m_2 v_2}{m_1 v_1} = \frac{\frac{1}{2} m_2^2 v_2^2}{\frac{1}{2} m_1^2 v_1^2} \cdot \frac{v_1}{v_2}$$

$$= \frac{KE_1}{KE_2} \cdot \frac{v_1}{v_2}$$

As $KE_1 = KE_2$

$$\therefore \frac{\lambda_1}{\lambda_2} = \frac{v_1}{v_2} \text{ or } \lambda \propto v$$

3. "The exact path of an electron in 2p-orbital cannot be determined." This statement is based upon:

- (a) Aufbau principle
- (b) Heisenberg's uncertainty principle
- (c) Hund's rule
- (d) Pauli exclusion principle

Ans. (b) Heisenberg's uncertainty principle

Explanation: According to Heisenberg's uncertainty principle it is impossible to determine the actual position and momentum of electrons at the same time. Thus, the exact path of the electron in 2p-orbital cannot be determined according to this principle.

4. An electron is moving in Bohr's orbit. Its de Broglie wavelength is λ . What is the circumference of the fourth orbit?

- (a) 2λ
- (b) 2λ
- (c) 4λ
- (d) 4λ

Ans. (d) 4λ

Explanation: According to the Bohr's model

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

and According to the de Broglie,

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

Therefore, $2\pi r = \frac{nh}{mv} = n\lambda$

de Broglie's Wavelength of an electron in the 4th orbit = 4λ

Therefore circumference of the 4th orbit = 4λ

5. In a subshell all three orbitals are degenerate.

What does this sentence mean?

- (a) All the orbitals have the same shape.
- (b) All the orbitals have the same energy.
- (c) All the orbitals have the same orientation.
- (d) All the orbitals are unoccupied.

Ans. (b) All the orbitals have the same energy.

Explanation: The degenerate orbitals are those orbitals which have the same energy. The $3p_x$, $3p_y$ and $3p_z$ are the three orbitals of the subshell and all of them have the same energy.

6. Number of angular nodes for 3d orbital is:

- (a) 4
- (b) 3
- (c) 2
- (d) 1

Ans. (c) 2

Explanation: Total nodes = $n-1$

Here, $n = 3$ and $l = 2$

$$= 3 - 1$$

$$= 2$$

$$\text{Radial nodes} = n - l - 1 = 0$$

$$\text{Total angular nodes} = \text{total nodes} - \text{radial nodes}$$

$$= 2 - 0 = 2$$

Thus, the number of angular nodes in 3d orbital is 2.

7. Orbital angular momentum depends on:

- (a) l
- (b) n and l
- (c) l and m
- (d) m and n

[NCERT Exemplar]

Ans. (a) l

Explanation: Orbital angular momentum is calculated by:

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

Hence, according to the formula, orbital angular momentum depends on l only.

8. Which of the following sets of quantum numbers is correct?

	n	l	m
(a)	1	1	± 2
(b)	2	1	± 1
(c)	4	2	-3
(d)	3	4	-2

Ans. (b) $n : 2, l : 1, m : \pm 1$

Explanation: According to formula, $l = 0$ to $(n-1)$ and $m = -l$ to $+l$

If $n = 2, l = 0, 1$

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

So, (b) is correct.

9. What is the uncertainty in the momentum of an electron, provided that the uncertainty in the position of the electron is zero?

- (a) $< \frac{h}{2\pi}$
- (b) Infinite
- (c) zero
- (d) None of these

Ans. (b) Infinite

Explanation: We know,

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

when $\Delta x = 0$

$\Rightarrow \Delta p$ becomes infinite.

That means the uncertainty in the momentum of the electron will be infinite when uncertainty in the position of the electron will be zero.

Assertion-Reason (A-R)

In the following question no. (10-13) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices:

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

10. Assertion (A): The p-orbital has a dumb-bell shape.

Reason (R): Electrons present in the p-orbital can have any one of three values of magnetic quantum number, i.e. $\pm 1, 0, -1$.

Ans. (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

Explanation: The electrons present in p-orbitals have a dumb-bell shape. The 3p-orbitals lie along the three different mutually perpendicular axes that differ in orientation. The three subshells are namely p_x, p_y and p_z . They have a magnetic quantum number equal to $\pm 1, 0$ and -1 .

11. Assertion (A): Angular momentum of d-orbitals are $\frac{6h}{\pi}$.

Reason (R): $\sqrt{l(l+1)} \frac{h}{2\pi}$ is the angular momentum of the orbit.

Ans. (d) (A) is false but (R) is true.

Explanation: The angular momentum of

d -orbital is $\sqrt{6} \frac{h}{2\pi}$.

The angular momentum of the orbit is determined by the equation:

$$\begin{aligned} & \sqrt{l(l+1)} \frac{h}{2\pi} \\ &= \sqrt{2(2+1)} \frac{h}{2\pi} \\ &= \sqrt{6} \frac{h}{2\pi} \end{aligned}$$

12. Assertion (A): s -orbitals do not accommodate more than two electrons.

Reason (R): s -orbitals have a poor shielding effect as compared to d and f -orbitals.

Ans. (c) (A) is true but (R) is false.

Explanation: Magnetic fields occur in electrons as they are considered as magnets. There are only two possible orientations that exist in those fields and a single orbital can be occupied by two electrons only if the two orientations

are mutually opposed. Because the distance between the s -orbital and the nucleus is less than the orbital, the shielding depends on the electron density in an orbital. Hence, we can say that since d and f -orbitals are farther away from the nucleus, so they have a less shielding effect than s -orbital.

13. Assertion (A): It is impossible to determine the exact position and exact momentum of an electron simultaneously.

Reason (R): The path of an electron in an atom is clearly defined.

[NCERT Exemplar]

Ans. (c) (A) is true but (R) is false.

Explanation: According to the Heisenberg uncertainty principle, it is impossible to determine the exact position and momentum of an electron simultaneously. Thus, the path of an electron in an atom is not clearly defined as its position cannot be measured with absolute accuracy. The effect of the Heisenberg uncertainty principle is considerable for microscopic objects' motion and is negligible for the macroscopic objects.

CASE BASED Questions (CBQs)

[4 & 5 marks]

Read the following passages and answer the questions that follow:

14. In 1924, de Broglie suggested that if the light is known to consist of waves and under certain situations assume the aspect of a particle then the particle should also behave like a wave. He based his reasoning on the assumption that nature possesses symmetry and that the two physical entities matter and waves must be symmetrical also. de Broglie took the quantum idea of emission of energy of a photon of radiation of a certain frequency which can be obtained using the equation given by him. That equation is called de Broglie's equation and this wavelength is called de Broglie's wavelength. The novel idea of this equation is the wave-particle nature of matter with the relative motion of particles and certain wave links with it. This idea leads to the dual nature of light also.

(A) de Broglie equation is obtained by a combination of:

- (a) Interference
- (b) Diffraction
- (c) Einstein's theory of mass-energy equivalence
- (d) Photoelectric effect

(B) Wave nature of the electron is shown by:

- (a) Photoelectric effect
- (b) Compton effect
- (c) Diffraction experiment
- (d) None of the above

(C) de Broglie wavelength of a particle is:

- (a) Proportional to mass
- (b) Inversely proportional to momentum
- (c) Inversely proportional to plank constant
- (d) Proportional to velocity

(D) A 0.66 kg ball is moving with a speed of 100 m/s. the associated wavelength will be ($h = 6.6 \times 10^{-34}$ Js):

- (a) 6.6×10^{-34}
- (b) 6.6×10^{-36}
- (c) 1.6×10^{-34}
- (d) 1×10^{-35}

(E) The position of both the electron and the Helium atom is known within 1 nm and the momentum of the electron is known within 50×10^{-26} kg ms⁻¹. The minimum uncertainty in the measurement of the momentum of the helium atom is:

- (a) 50×10^{-26} kg ms⁻¹
- (b) 50 kg ms⁻¹

(c) 80 kg ms^{-1}

(d) $60 \times 10^{-28} \text{ kg ms}^{-1}$

Ans. (A) (c) Einstein's theory of mass-energy equivalence

Explanation: Einstein's theory of mass equation and Planck's constant contributes to the de Broglie equation.

$$E = h\nu = \frac{hc}{\lambda}$$

$$E = mc^2$$

As the smaller particle exhibits dual nature, and energy being the same, de Broglie equated both these relations for the particle moving with velocity 'v'. From these two equations:

$$E = \frac{hc}{\lambda} = mv^2$$

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

(B) (c) Diffraction experiment

Explanation: According to de Broglie, the wave nature is shown by diffraction experiments. Louis de Broglie in his thesis suggested that any moving particle, whether microscopic or macroscopic will be associated with a wave character. It was called 'Matter Waves'. He further proposed a relation between the velocity and momentum of a particle with the wavelength, if the particle had to behave as a wave.

(C) (b) Inversely proportional to momentum

Explanation: According to the de Broglie equation, the wavelength is inversely proportional to the mass and the velocity. de broglie equation: $\lambda = \frac{h}{mv}$

(D) (d) 1×10^{-35}

Explanation: According to the de Broglie

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

$$\lambda = \frac{6.6 \times 10^{-34}}{0.66 \times 100} = 1 \times 10^{-35} \text{ m}$$

(E) (a) $50 \times 10^{-28} \text{ kg ms}^{-1}$

Explanation: The product of uncertainties in the momentum and position of a subatomic particle $= \frac{h}{4\pi}$. Since position (Δx)

is the same for both electron and the Helium atom so Δp must be the same for both the particles i.e. $50 \times 10^{-28} \text{ kg ms}^{-1}$.

15. A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom. The combination of all quantum numbers of all electrons in an atom is described by a wave function that complies with the Schrödinger equation. Each electron in an atom has a unique set of quantum numbers; according to the Pauli Exclusion Principle, no two electrons can share the same combination of four quantum numbers. Quantum numbers are important because they can be used to determine the electron configuration of an atom and the probable location of the atom's electrons. Quantum numbers are also used to understand other characteristics of atoms, such as ionisation energy and the atomic radius.

In atoms, there are a total of four quantum numbers: the principal quantum number (n), the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the electron spin quantum number (m_s). The principal quantum number, n, describes the energy of an electron and the most probable distance of the electron from the nucleus. In other words, it refers to the size of the orbital and the energy level at which an electron is placed. The number of subshells, or l, describes the shape of the orbital. It can also be used to determine the number of angular nodes. The magnetic quantum number, m_l , describes the energy levels in a subshell, and m_s refers to the spin on the electron, which can either be up or down.

(A) Answer the following questions:

(i) What do the quantum numbers $+\frac{1}{2}$

and $-\frac{1}{2}$ for electron spin represent?

(ii) Which quantum number represents the size and shape of the subshell?

(B) In which order, the energy of different subshells can be arranged for the given value of n?

(C) In d_{xy} subshell, at what angle there is the probability of finding an electron?

Ans. (A) (i) The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$

electron spin represents the clockwise and anti-clockwise spin with no significant similarities.

(ii) The primary quantum number 'n' represents the size of an orbital. The comparative distance from the nucleus as well as the energy levels is shown by the primary quantum number.

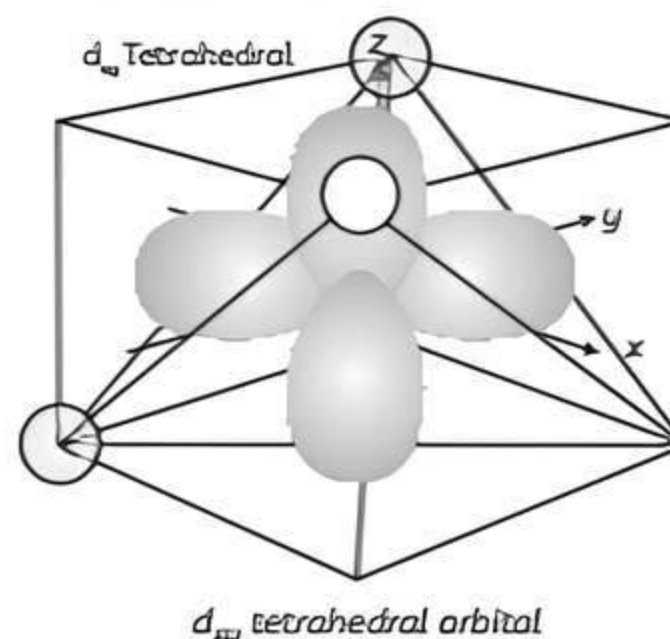
The azimuthal quantum number ' l ' represents the shape of an orbital and also determines its angular momentum.

- (B) For the given value of n , the energy of different subshells can be arranged according to Aufbau's principle. As per the Aufbau principle, the filling of electrons is in the order $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s$.

So, the right filling sequence of the subshell is $f > d > p > s$.

- (C) According to the d -orbital subshell representation, the probability of finding

the electrons in d_{xy} orbital is along the X -axis at an angle of 45° .



VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

16. What is a nodal plane? [Diksha]

Ans. The plane on which the possibility of finding the electron is zero.



Related Theory

- There are nodal planes around the atomic nucleus where electrons are highly unlikely to be found. The Schrödinger wave equation is used to identify the shape of atomic or molecular orbitals, which in turn determines the coordinates of these planes. Depending on the density of the electron cloud around a molecule or atom, it is more likely for electrons to be found in those areas. An electron is more likely to be found in a dense cloud. The electron cloud density in nodal planes is totally absent, so it is unlikely that electrons are found in these planes.

17. Why did Heisenberg's uncertainty principle replace the concept of definite orbit by the concept of probability? [Delhi Gov. QB 2022]

Ans. An electron in an atom has both velocity and some specific coordinate in 3-dimensional space. But it is experimentally proved that both velocity and stamp can not be determined simultaneously.

Thus, the values obtained are very inaccurate and uncertain using Bohr's model of the atom. Hence, Heisenberg's uncertainty principle replaces the concept of definite orbit by the concept of probability.

18. Why does s -orbital not show the directional property?

Ans. s -orbital does not have directional characteristics because orbital is a spherically shaped orbital and has spherical symmetry. So, the wave function depends only on the distance from the nucleus and not on the direction.

19. Which of the following orbitals are degenerate?

$3d_{xy}, 4d_{xy}, 3d_{z^2}, 3d_{yz}, 4d_{yz}, 4d_{z^2}$

[NCERT Exemplar]

Ans. Degenerate orbitals are those orbitals which have the same value of energy.

$3d_{xy}, 3d_{z^2}$ and $3d_{yz}$ are degenerate.

$4d_{xy}, 4d_{yz}$ and $4d_{z^2}$ are degenerate.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

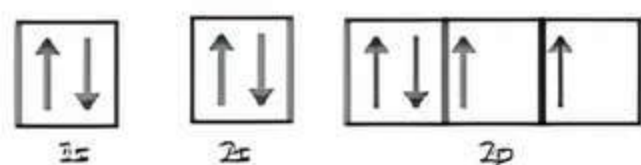
20. Why is it difficult to measure the position and velocity of a subatomic particle simultaneously with accuracy?

Ans. According to the Werner Heisenberg theory, "it is impossible to measure the exact position and momentum of the small body like an electron simultaneously." In microscopic

particles, the impact of a striking photon causes a large displacement from the normal path due to a change in both the velocity and momentum of the particle. That's why it is difficult to measure the position and velocity of a subatomic particle simultaneously with accuracy.

21. Explain the rule which is used for filling an electron in a degenerate orbital.

Ans. Degenerate orbitals have the same energy for all the subshells. Hund's rule is used to explain the filling of an electron in a degenerate orbital very well. According to Hund's rule, the pairing of electrons in degenerate orbitals does not occur until all the degenerate orbitals are singly occupied. For example: In the case of an oxygen atom its configuration is $1s^2 2s^2 2p^4$. It can be represented by Hund's rule as follows:



Electronic configuration of oxygen

22. Arrange s, p, and d sub-shells of a shell in the increasing order of effective nuclear charge experienced by the electron present in them. [NCERT Exemplar]

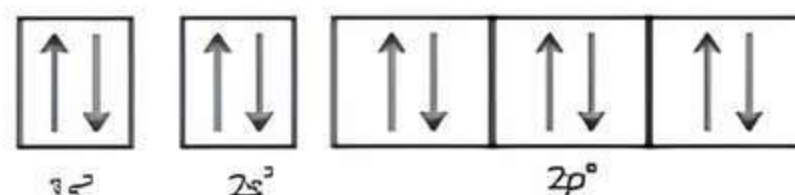
Ans. The s-orbital does have a spherical shape. It is more effective in shielding electrons from the nucleus than p-orbitals, which in turn shields more effectively than d-orbitals. As a result, the subshells are organised in increasing order of effective nuclear charge:

$$d < p < s$$

23. Show the distribution of electrons in the neon atom (atomic number 10) using an orbital diagram.

Ans. Electronic configuration for atomic no 10 will be: $1s^2 2s^2 2p^6$.

The orbital diagram is shown below:



Electronic configuration of neon

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

24. What do you understand by the $n+l$ rule, explain with an example?

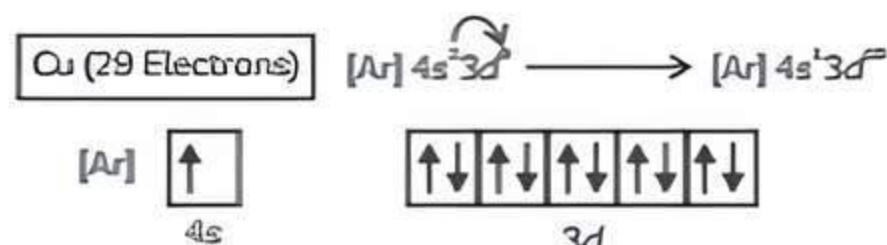
Ans. According to this rule, the lower the value of $(n + l)$ for an orbital the lower is its energy. If two orbitals have the same $(n + l)$ value, the orbital with the lower value of n will have lower energy.

For example, the $(n + l)$ value for 3s and 3p orbital will be:

Orbital	n	l	$n + l$
3s	3	0	$3 + 0 = 3$
3p	3	1	$3 + 1 = 4$

25. The electronic configuration of the valence shell of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ and is not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$. How is this configuration explained? [NCERT Exemplar]

Ans. The electronic configuration of the valence shell of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ and is not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$ because configurations with full-filled and half-filled orbitals offer more stability due to the symmetric distribution of electrons. In the configuration of copper, the s-orbital is half-filled, while the d-orbital is completely filled. As a result, copper is more stable due to the full-filled configuration.



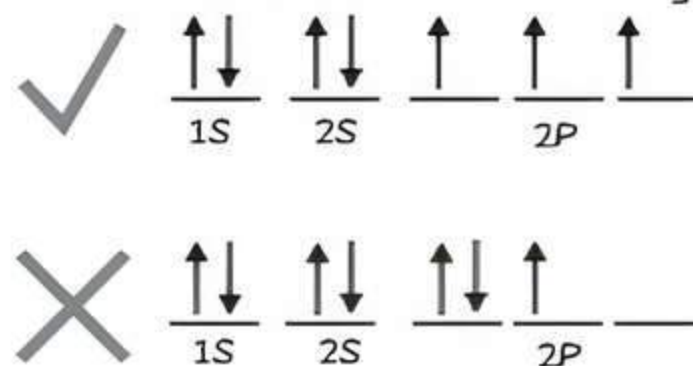
Orbital diagram of copper

26. Explain the difference between the Aufbau principle and the Pauli exclusion principle.

Ans. According to Pauli's exclusion principle, two electrons cannot have the same quantum numbers. This means that two electrons in a single orbital must have opposite spins, while the Aufbau Principle states that the electrons are filled according to the increasing energy level.

As per the Aufbau principle, the filling of electrons is in the order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s.

As per the Pauli exclusion principle, filling of electrons is shown in the figure:



Filling of electrons

LONG ANSWER Type Questions (LA)

[4 & 5 marks]

27. How are orbits different from orbitals?

Ans.	Orbits	Orbitals
	Orbits are well-defined circular paths around the nucleus in which the electron revolves.	Orbital is a 3-D space around the nucleus with a maximum probability of finding an electron.
	All orbits are circular and disc-like.	Different orbitals have different shapes.
	It represents the planar motion of the electron not according to Heisenberg's uncertainty principle.	It represents the 3-D motion of the electron in accordance with Heisenberg's uncertainty principle.
	They do not have any direction.	All orbitals except 's' have directional properties.
	The maximum electron in any orbit is given by $2n^2$.	The maximum number of electrons in any orbital is two.

28. Explain the significance of various quantum numbers.

Ans. The significance of quantum number are as follows:

(1) Principal quantum numbers (n)

- It describes the energy of an electron from the nucleus.
- It represents the distance of the electron from the nucleus.
- It determines the size of the orbit.

(2) Azimuthal quantum number (l)

- It is the number of subshells present in any main shell.
- It represents the relative energies of the subshells.
- It determines the 3-D shapes of orbitals.

(3) Magnetic quantum number (m)

- It represents the number of orbitals present in any subshell.
- It explains the Zeeman effect (splitting of spectral lines in several components in a strong magnetic field).
- It determines the orientation of the electron cloud in a subshell.

(4) Spin quantum number(s)

- It represents the anticlockwise and clockwise direction of electron spin.

29. Why was a change in the Bohr's model of the atom required? Due to this important development(s), the concept of the movement of an electron in orbit was replaced by the concept of probability of finding an electron in an orbital. What is the name given to the changed model of an atom? [NCERT Exemplar]

Ans. The electrons according to the Bohr model are charged particles that move in a well-defined circular orbital. The position and velocity of an orbit should be known to characterize it, but the Bohr's model did not illustrate this. Few attempts were made to construct a more appropriate and comprehensive model for atoms to address this limitation. Two major developments made a significant impact on the outcome.

(1) Dual behaviour of matter.

(2) Heisenberg uncertainty principle.

Werner Heisenberg stated the uncertainty principle, which is the consequence of the dual behaviour of matter and radiation. One of the important implications of the Heisenberg Uncertainty Principle is that it rules out the existence of definite paths or trajectories of electrons and other similar particles. Therefore, the concept of movement of an electron in orbit was replaced by the concept of finding an electron in an orbital because of its wave-like and particle-like properties. Thus, the name of the changed model of the atom is the Quantum Mechanical Model of the atom.

NUMERICAL Type Questions

30. $2.50 \times 10^{-27} \text{ kg m/s}$ is the momentum of a certain photon. What will be the de Broglie wavelength of a photon? (1m)

Ans. $p = 2.50 \times 10^{-27} \text{ kg m/s}$

Planck's constant $h = 6.626 \times 10^{-34} \text{ Js}$

The de Broglie wavelength of the photon can be calculated using:

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

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{2.5 \times 10^{-27} \text{ kg m/s}}$$

$$= 265 \times 10^{-9} \text{ m}$$

$$= 265 \text{ nm}$$

31. 10 g is the mass of a table-tennis ball and has a speed of 90 m/s. If speed can be measured with an accuracy of 4%, what will be the uncertainty in speed and position? (2m)

Ans. Uncertainty in the speed of the ball
= 4% of 90 m/s

$$= 90 \times \frac{4}{100} = 3.6 \text{ m/s}$$

From Heisenberg relation

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

$$\Delta x = \frac{6.626 \times 10^{-34} \text{ Js}}{(4 \times 3.14 \times 10 \times 10^{-3} \times 3.6)}$$

$$= 1.46 \times 10^{-33} \text{ m}$$

32. What is the minimum uncertainty in the position of an electron moving with a speed of $4 \times 10^6 \text{ m/s}$? The mass of an electron is $9.11 \times 10^{-31} \text{ kg}$. (2m)

Ans. The equation for Heisenberg's uncertainty principle is

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

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

Given:

$$\Delta v = 4 \times 10^6 \text{ m/s}$$

$$m = 9.11 \times 10^{-31} \text{ kg}$$

Putting the value in the equation:

$$\Delta x \geq \frac{6.62 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 9.11 \times 10^{-31} \times 4 \times 10^6}$$

$$\Delta x \geq 1.45 \times 10^{-11} \text{ m}$$

33. Calculate the mass of the photon with a wavelength of 3.6 \AA .

[Delhi Gov. QB 2022](1m)

Ans. According to de Broglie, wavelength $\lambda = \frac{h}{mv}$

$$m = \frac{h}{\lambda v}$$

$$\lambda = 3.6 \text{ \AA} = 3.6 \times 10^{-10} \text{ m}$$

$$= \frac{6.626 \times 10^{-34}}{(3.6 \times 10^{-10})(3 \times 10^8)}$$

$$= 6.135 \times 10^{-33} \text{ kg}$$

