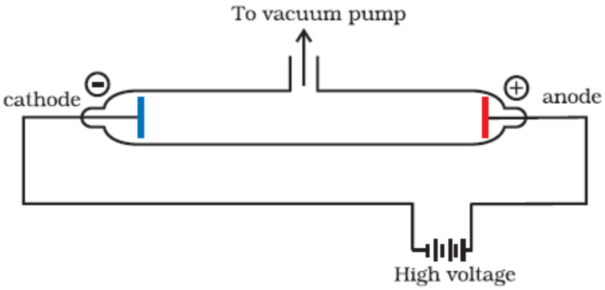
2. STRUCTURE OF ATOM

The word ‘atom’ has been derived from the Greek word ‘a-tomio’ means ‘uncutable’ or ‘non-divisible’. The first atomic theory of matter was proposed by John Dalton in 1808. Dalton’s atomic theory was able to explain the law of conservation of mass, law of constant proportion and law of multiple proportion very successfully. However, it failed to explain many experimental results.

Discovery of Sub-atomic particles

1. Discovery of Electron

Electron was discovered by J J Thomson through *Cathode ray discharge tube experiment*. A cathode ray tube is made of glass containing two thin metal pieces (called electrodes) sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages.



When a very high voltage (about 10,000 volts) is applied between the two electrodes, no electric discharge occurs at normal pressure. When the pressure of the gas inside the tube is less than 1 mm of mercury, a dark space appears near the cathode. When the pressure is reduced to 0.01 mm Hg, it fills the whole tube. When the pressure is further reduced (10^{-4} mm Hg), the electric discharge passes between the electrodes and the tube begins to glow. This is due to the striking of some invisible rays from the cathode. These *rays which start from the cathode and move away from it, in straight lines are called* ***cathode rays or cathode ray particles***.

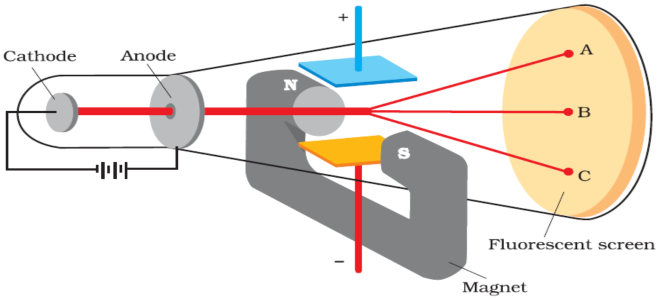
These rays can be further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material like zinc sulphide. When these rays strike the zinc sulphide coating, a bright spot on the coating is developed.

Properties of Cathode Rays

i. The cathode rays start from cathode and move towards the anode.
ii. They are invisible, but their behaviour can be observed with the help of fluorescent or phosphorescent materials.
iii. In the absence of electrical or magnetic field, these rays travel in straight lines.
iv. In the presence of electrical or magnetic field, the cathode rays behave similar to that of negatively charged particles. From this, it is clear that the cathode rays consist of negatively charged particles called electrons.
v. The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.
vi. These rays possess kinetic energy and hence can do mechanical work.
vii. They can produce x-rays when incident on metals with high atomic mass.

Charge to Mass (e/m_e) Ratio of Electron

J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons. There is a fluorescent screen on one side of the discharge tube. When these rays strike the fluorescent screen, a bright spot is developed.



In the absence of electric or magnetic field, the cathode rays hit the screen at point B. When only electrical field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly, when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron beam to the point B. From the strength of electrical and magnetic field, Thomson was able to calculate the value of e/m_e as:

$$e/m_e = \mathbf{1.7588 \times 10^{11}\ C\ kg^{-1}}$$

Where, m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C).

Charge on the Electron (e)

R.A. Millikan determined the charge on the electrons by a method known as 'oil drop experiment'. He found that the charge on the electron to be $-\mathbf{1.6022 \times 10^{-19}}$ **C**.

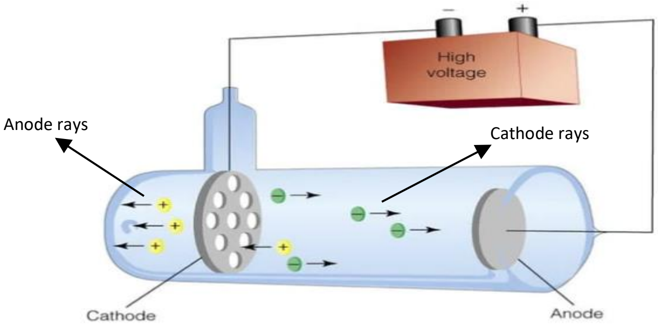
Mass of electron (m_e)

The mass of the electron (m_e) was determined as follows:

$$\text{Mass of electron } (m_e) = \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19}}{1.7588 \times 10^{11}}$$
$$= \mathbf{9.1 \times 10^{-31}\ kg}$$

2. Discovery of Protons

E. Goldstein modified the discharge tube experiment by perforated (with small holes) cathode. After evacuating the tube and on applying high voltage, he found that some rays were emitting behind the cathode and moving in the opposite direction of cathode rays. These rays deflect to the negative plate of electric field. So they carry positive charge and were called **anode rays or canal rays**.



Properties of Canal rays

The characteristics of canal rays are:

i. They depend on the nature of gas present in the cathode ray tube. These are positively charged gaseous ions.
ii. The charge to mass ratio of anode rays depends on the nature of the gas.
iii. Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

iv. They also travel in straight lines, in the absence of electrical or magnetic field.

v. The behaviour of these particles in the magnetic or electrical field is opposite to that observed for cathode rays.

vi. They can produce heating effect and can do mechanical work.

vii. They are invisible and can be observed with the help of fluorescent or phosphorescent materials.

The smallest and lightest positive ion was obtained from hydrogen and was called ***proton****.*

3. Discovery of Neutrons

Neutrons were discovered by James Chadwick by bombarding a thin sheet of beryllium by α-particles.

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

They are electrically neutral particles having mass slightly greater than that of the protons.

Characteristics of sub-atomic particles

Sub-atomic particle	Symbol	Discoverer	Absolute Charge (in Coulomb)	Relative charge	Mass (in kg)
Electron	e	J J Thomson	-1.6022×10^{-19}	-1	9.01×10^{-31}
Proton	p	E Goldstein	$+1.6022\times10^{-19}$	+1	1.6726×10^{-27}
Neutron	n	James Chadwick	0	0	1.675×10^{-27}

Some important terms relating to Atomic structure

Atomic Number: It is the number of protons present in the nucleus or number of electrons present outside the nucleus.

It is denoted by the symbol 'Z'.

Atomic number (Z) = nuclear charge or number of protons (p)

= number of electrons (e)

Mass Number: It is the total number of protons and neutrons in atom. Or, it is the total number of nucleons in an atom. [Protons and neutrons are together called nucleons].

It is denoted by 'A'.

i.e. Mass number (A) = no. of protons (p) + no. of neutrons (n)

or, **A = p + n**

By knowing the atomic number and mass number, we can calculate the number of neutrons as: **n = A – Z**

If an element 'X' has the atomic number Z and the mass number A, it is denoted as: $^{A}_{Z}\mathrm{X}$ or $_{Z}\mathrm{X}^{A}$

Isotopes, Isobars and Isotones

Isotopes are atoms with same atomic number but different mass number. That is, they contain same number of protons but different number of neutrons.

Hydrogen has three isotopes: Protium ($^{1}_{1}\mathrm{H}$), Deuterium ($^{2}_{1}\mathrm{H}$ or $^{2}_{1}\mathrm{D}$) and Tritium ($^{3}_{1}\mathrm{H}$ or $^{3}_{1}\mathrm{T}$). Among these, Protium is the ordinary hydrogen and Tritium is the radioactive isotope of Hydrogen.

The number of protons, neutrons and electrons present in the 3 types of hydrogen are:

Isotope	Number of protons	Number of electrons	Number of neutrons
Protium	1	1	0
Deuterium	1	1	1
Tritium	1	1	2

Almost all the elements have isotopes. All the isotopes of a given element have same chemical properties, but they differ in their physical properties.

Isobars are atoms of different elements having same mass number but different atomic number. i.e. they have different number of protons but have equal sum of the protons and neutrons (nucleons).

e.g. $^{14}_{6}\mathrm{C}$ and $^{14}_{7}\mathrm{N}$ $^{40}_{18}\mathrm{Ar}$ and $^{40}_{20}\mathrm{Ca}$

Isotones are atoms having same number of neutrons but have different atomic numbers. Some examples are:

Isotones	p	e	N
$^{14}_{6}\mathrm{C}$	6	6	8
$^{15}_{7}\mathrm{N}$	7	7	8
$^{16}_{8}\mathrm{O}$	8	8	8

ATOM MODELS

1. Thomson's Model of Atom

J. J. Thomson proposed the first atom model, which is known as ***the plum pudding or raisin pudding or watermelon model***.

According to this model:

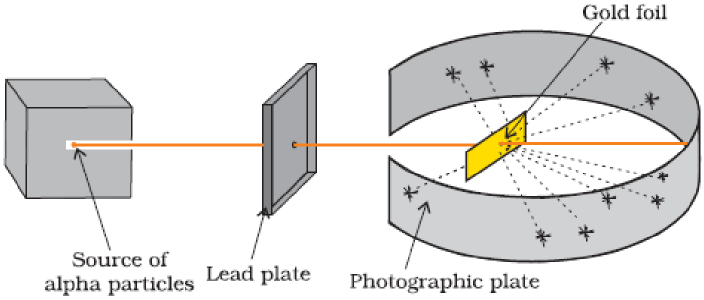
- an atom has a spherical shape in which the positive charge is uniformly distributed.
- The electrons are distributed in it, just like the seeds are distributed in a water melon or plums are distributed in a pudding.
- The mass of the atom is uniformly distributed over the atom.
- The total positive charge in an atom is equal to the total negative charge and hence the atom is electrically neutral.

This model was able to explain the electrical neutrality of the atom. But it failed to explain the experimental observations made by Rutherford and others.

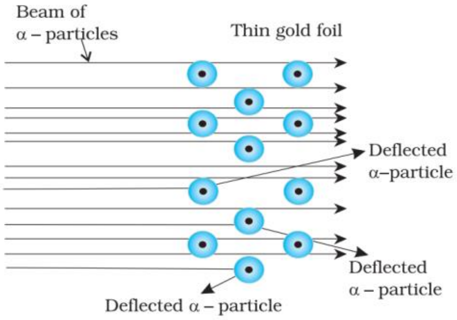
1. Rutherford's Nuclear Model of Atom

Earnest Rutherford proposed an atom model based on α–particle scattering experiment. He bombarded a very thin gold foil [approximately 10^{-7}m or 100 nm thickness] with α–particles.

The Experiment: A stream of high energy α–particles from a radioactive source was directed at a thin gold foil. The thin gold foil had a circular fluorescent zinc sulphide screen (photographic plate) around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point.



[Rutherford's scattering experiment]



[Schematic molecular view of the gold foil]

Observations and conclusions of α–particle scattering experiment are:

Observations	Conclusions
1. Most of the α- particles passed through the gold foil without any deviation.	1. Most space in the atom is empty.
2. A small fraction of the α-particles was deflected by small angles.	2. The positive charge of the atom is concentrated in a very small volume at the centre called nucleus.

3. A very few α– particles (approximately 1 out of 20,000) bounced back [i.e. deflected by nearly 180°].	3. The volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. [The radius of the atom is about 10^{-10} m, while that of the nucleus is 10^{-15} m].

On the basis of above observations and conclusions, Rutherford proposed ***the nuclear model of atom*** or ***Planetary model of atom.*** According to this model:

1. The positive charge and most of the mass of the atom are concentrated in an extremely small region called nucleus.
2. Electrons are revolving round the nucleus with a very high speed in circular paths called orbits.
3. Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks or Limitations of Rutherford's atom model

1. Rutherford's model could not explain the stability of the atom.
2. It could not explain the electronic structure of atom.

Wave nature of Electromagnetic Radiation

James Clerk Maxwell suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called e***lectromagnetic waves or electromagnetic radiation (emr)***. These are the radiations associated with electrical and magnetic fields.

The important characteristics of these radiations are:

1. The oscillating electrical and magnetic fields are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
2. The electromagnetic waves do not require a medium for propagation and can move in vacuum.
3. There are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute electromagnetic spectrum. The important electromagnetic radiations in the increasing order of wavelength are:
   Cosmic rays, Gamma rays, X-rays, Ultra-violet rays, Visible light, Infra-red rays, Microwaves, Radio waves.
4. All electromagnetic radiations travel with a constant speed of 3×10^8 m/s through vacuum.

Some important terms relating to electromagnetic radiations

1. **Frequency (ν):** It is defined as the number of waves that pass through a given point in one second. The SI unit for frequency is hertz (Hz) or s^{-1}.
2. **Wavelength (λ)** : It is the distance between two adjacent crusts or troughs. Its unit is m or cm. Commonly the wavelength of electromagnetic radiations are expressed in nanometer (nm) or Angstrom unit (A^0). $1 nm = 10^{-9} m = 10^{-7} cm$ $1A^0 = 10^{-10} m = 10^{-8} cm$.
3. **Speed of light (c)**: It is the distance travelled by an electromagnetic radiation in one second. $c = 3 \times 10^8$ m/s in vacuum.

The frequency (ν), speed of light (c) and the wave length (λ) are related to each other as: $\mathbf{c = \nu \lambda}$

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

4. **Wave number ($\bar{\nu}$)**: It is defined as the number of wavelengths per unit length. Or, it is the reciprocal of wavelength. i.e. $\bar{\nu} = 1/\lambda$. Its SI unit is m^{-1}. But it is commonly expressed in cm^{-1}.

Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon like diffraction and interference can be explained by the wave nature of the electromagnetic radiation. But some phenomena like black body radiation, photoelectric effect, variation of heat capacity of solids with temperature, line spectra of atoms etc. could not be explained by the wave nature of electromagnetic radiation.

Black body radiation

An ideal body which emits and absorbs all frequencies of radiations is called a *black body* and the radiation emitted by such a body is called *black body radiation*.

A perfect black body is rare. But carbon black behaves nearly like a black body.

The amount of light emitted (intensity of radiation) *from a black body* and its spectral distribution *depends only on its temperature*. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value and then decreases.

The phenomenon of black body radiation was first explained by ***Max Planck*** by his ***Quantum theory***. According to this theory:

1. Atoms and molecules could emit (or absorb) energy not in a continuous manner, but discontinuously in small packets of energy called quanta or photons.
2. The energy (E) of a quantum of radiation is proportional to its frequency (ν). i.e. **$E = h\nu$.** Where 'h' is known as Planck's constant ($h = 6.626\times10^{-34}$ Js).

Photoelectric effect

It is the phenomenon of ejection of electrons by certain metals (like potassium, rubidium, caesium etc.) when light of suitable frequency incident on them. The electrons ejected are called photoelectrons.

This phenomenon was first observed by Heinrich Hertz.

The important results observed in photoelectric effect are:

1. The electrons are ejected from the metal surface as soon as the beam of light strikes the surface. i.e., there is no time lag between the striking of 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 light.
3. For each metal, there is a minimum frequency (known as threshold frequency [ν_0]) below which photoelectric effect is not observed.
4. The kinetic energy of the ejected electrons is directly proportional to the frequency of the incident light.

Explanation of photoelectric effect by Einstein

A satisfactory explanation to photoelectric effect was first given by Albert Einstein using Planck's quantum theory.

According to him, when a photon of sufficient energy strikes the metal surface, it suddenly transfers its energy to the electron of the metal atom and the electron is ejected without any time lag. A part of this energy is used to eject the electron from the metal surface (i.e. to overcome the attractive force of the nucleus). This energy is called work function [$h\nu_0$]. The other part of this energy is given to the ejected electron in the form of kinetic energy. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron.

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 ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron.

Applying the law of conservation of energy principle, the kinetic energy of the ejected electron is given by $K.E = h\nu - h\nu_0$

Or, $h\nu = h\nu_0 + \frac{1}{2} m_e v^2$

Where m_e is the mass of the electron and v is the velocity of the ejected electron.

A more intense beam of light contains larger number of photons, so the number of electrons ejected is also larger.

Q1) The threshold frequency for a metal is $7.0 \times 10^{14}\ s^{-1}$. Calculate the kinetic energy of an emitted electron when radiation of frequency (ν) $1.0 \times 10^{15}\ s^{-1}$ hits the metal.

Ans: Here threshold frequency (ν_0) = $7.0 \times 10^{14}\ s^{-1}$ and frequency of radiation (ν) = $1.0 \times 10^{15}\ s^{-1}$

K.E of emitted electron = $h\nu - h\nu_0 = h(\nu - \nu_0) = 6.626 \times 10^{-34} (1.0 \times 10^{15} - 7.0 \times 10^{14})$ = ***19.878×10^{-20} J***

Dual Behaviour of Electromagnetic Radiation

Some phenomena of electromagnetic radiations can be explained by the wave nature of emr, but some others can be explained by its particle nature. So electromagnetic radiations possess both particle and wave nature. This is known as dual nature of Electromagnetic Radiation. When radiation interacts with matter, it shows particle like nature.

Atomic spectrum

When a ray of white light is passed through a prism, we get a series of coloured bands called spectrum. This spectrum is called continuous spectrum, because here violet merges into blue, blue into green and so on.

Similarly, when electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy unstable state. To attain stability, they emit radiations in the form of spectrum. Such a spectrum is called ***atomic spectrum***.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an ***emission spectrum***. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted is recorded.

An ***absorption spectrum*** is like the photographic negative of an emission spectrum. Here a continuum of radiation (like white light) is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelengths leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as ***spectroscopy***.

The emission spectra of atoms in the gas phase do not form a continuous spectrum. The excited atoms emit light only at specific wavelengths with dark spaces between them. Such spectra are called ***line spectra or atomic spectra.***

Line emission spectra are very useful in the study of electronic structure of atoms. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. So line emission spectra are also called ***finger print of atoms***.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. The first five series of lines are **Lyman, Balmer, Paschen, Brackett and Pfund series**. Among these lines, the Balmer series is the only series that we can be visible (since it lies in the visible region of emr).

Johannes Rydberg proposed an equation for finding the wave number of the different lines in Hydrogen spectrum. The expression is: $\bar{V} = \frac{1}{\lambda} = 109677\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\}$ cm^{-1}

Where $n_1 = 1, 2, 3, \ldots$ and $n_2 = n_1 + 1, n_1 + 2, \ldots$

The different spectral lines, their spectral region and their n_1 and n_2 values are as follows:

Series	Spectral region	n_1	n_2
Lyman series	Ultra violet	1	2,3,4….
Balmer series	Visible	2	3,4,5….
Paschen series	Infra-red	3	4,5,6…..
Brackett series	Infra-red	4	5,6,7….
Pfund series	Infra-red	5	6,7,8…..

3. BOHR'S MODEL FOR HYDROGEN ATOM

The general features of the structure of hydrogen atom and its spectrum were first explained by Niels Bohr. The important postulates of his theory are:

1. The electron in the hydrogen atom can move around the nucleus in circular paths of fixed radius and energy. These paths are called orbits or stationary states or allowed energy states. These energy levels are numbered as 1,2,3 etc or as K, L, M, N, etc. These numbers are known as **Principal quantum numbers**.
2. The energy of an electron in an orbit does not change with time. However, when an electron absorbs energy, it will move away from the nucleus (i.e. to a higher energy level) and when it loses energy, it will move towards the nucleus (i.e. to a lower energy level).
3. The radius of orbits can be given by the equation: $r_n = a_0 n^2$ where $a_0 = 52.9$ pm. Thus the radius of the first stationary state is 52.9 pm (called the Bohr radius). As n increases, the value of r will increase.
4. The energy of electron in an orbit is given by the expression: $E_n = -R_H.\frac{1}{n^2}$, where n = 1,2,3…… and R_H is a constant called Rydberg constant. Its value is 2.18×10^{-18} J. The energy of the lowest state (the ground state) is given by $E_1 = -2.18 \times 10^{-18}$J. As the value of n increases, the energy of the electron also increases.
5. The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by: $\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$

Where E_1 and E_2 are the energies of lower and higher energy levels respectively. This expression is commonly known as *Bohr's frequency rule.*

6. The angular momentum of an electron is quantized. i.e. it is an integer multiple of h/2π.

   Or, Angular momentum, $m_e vr = \frac{nh}{2\pi}$

Where m_e is the mass of electron, v is the velocity of electron and r is the radius of Bohr orbit. n = 1,2,3….. Thus an electron can move only in those orbits whose angular momentum is an integral multiple of h/2π. So only certain fixed orbits are allowed.

Significance of negative energy of electron

When the electron is free from the influence of nucleus, its energy is taken as zero. In this situation, the electron is at the orbit with $n = \infty$. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation.

Explanation of Line Spectrum of Hydrogen

According to Bohr atom model, radiation is absorbed if the electron moves from lower energy to higher energy level and radiation is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation:

$$\Delta E = E_2 - E_1$$

But $E_1 = \frac{R_H}{n_1^2}$ and $E_2 = \frac{R_H}{n_2^2}$

Therefore, $\Delta E = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$= 2.18 \times 10^{-18} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

The frequency associated with the absorption and emission of the photon can be given as:

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ Hz}$$

$$= \frac{2.18 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{Js}}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ Hz}$$

$$= 3.29 \times 10^{15}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ Hz}$$

The wave number $(\breve{V}) = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{R_H}{hc}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ m}^{-1}$

$$= \frac{3.29 \times 10^{15}}{3 \times 10^{8}}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ m}^{-1}$$

$$= 1.09677 \times 10^{7} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ m}^{-1}$$

$$= 109677 \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{ cm}^{-1}$$

In case of absorption spectrum, $n_2 > n_1$ and the term in the bracket is positive and energy is absorbed. On the other hand, in case of emission spectrum $n_1 > n_2$, ΔE is negative and energy is released.

Limitations of Bohr Atom Model:

Bohr atom model could explain the stability and line spectra of hydrogen atom and hydrogen like ions (e.g. He^+, Li^{2+}, Be^{3+} etc). But it has the following limitations:

1. It could not explain the fine spectrum of hydrogen atom.
2. It could not explain the spectrum of atoms other than hydrogen.
3. It was unable to explain the splitting of spectral lines in the presence of electric field (Stark effect) and in magnetic field (Zeeman effect).
4. It could not explain the ability of atoms to form molecules by chemical bonds.
5. It did not consider the wave character of matter and Heisenberg's uncertainty principle.

Dual Behaviour of Matter – de Broglie's equation

de Broglie proposed that like radiation, matter also exhibit dual behaviour i.e., both particle and wave like properties. This means that electrons should also have momentum as well as wavelength. He gave the following relation between wavelength (λ) and momentum (p) of a material particle.

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

Where m is the mass of the particle, v is the velocity and p is the momentum. The above equation is known as **de Broglie's equation**.

Like electromagnetic radiations, an electron beam also undergoes diffraction. This is an evidence for the wave nature of electrons. An electron microscope works on the principle of wave nature of electron.

According to de Broglie, every moving object has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can be detected experimentally.

Heisenberg's Uncertainty Principle

Werner Heisenberg proposed the uncertainty principle which is the consequence of dual behaviour of matter and radiation. It states that "*it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of a moving microscopic particle like electron*". Mathematically, it can be given as in equation:

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

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

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

Where Δx is the uncertainty in position and Δp (or, Δv) is the uncertainty in momentum (or velocity) of the particle.

If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [Δv is large] and vice versa.

Significance of Uncertainty Principle

Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is not applicable to macroscopic objects. According to this Principle, we cannot determine the exact position and momentum of an electron. Thus it rules out the existence of definite paths or orbits of electrons. We can only say the probability of finding an electron at a given point.

Reasons for the Failure of the Bohr Model

In Bohr model, electrons are moving in well-defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. Therefore, Bohr model of the hydrogen atom not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.

QUANTUM MECHANICAL MODEL OF ATOM

On the basis of dual nature of matter and the uncertainty principle, Erwin Schrodinger and Werner Heisenberg proposed a new model of atom called Quantum mechanics. The fundamental equation of quantum mechanics was developed by Schrödinger and is known as Schrödinger equation. It is written as: $\hat{H}\psi = E\psi$

where $\hat{H}$ is a mathematical operator called *Hamiltonian operator*, E is the total energy of the system (K.E + P.E) and ψ is called the wave function. On solving the above equation, we get different values for E and ψ.

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function (ψ). These quantized energy states and corresponding wave functions are characterized by a set of three quantum numbers.

Significance of ψ

The wave function (ψ) is a mathematical function and it has no physical meaning. Wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. All the information about the electron in an atom is stored in its orbital wave function ψ. It may be positive or negative.

But ψ^2 has some physical significance. It gives the probability of finding an electron at a point within an atom. So ψ^2 is known as **probability density** and is always positive. From the value of ψ^2, it is possible to predict the probability of finding the electron around the nucleus.

Quantum Numbers

These are certain numbers used to explain the size, shape and orientation of orbitals. Or, Quantum numbers are the address of an electron. There are four quantum numbers which describe the electron in an atom. They are Principal Quantum number (n), Azimuthal Quantum number (l), Magnetic Quantum number (m or m_l) and Spin Quantum number (s).

1. Principal Quantum Number (n)

The following information are obtained from n.

1. It gives the size of the orbit.
2. It gives the energy of electron in an orbit.
3. It gives the shell in which the electron is found.
4. It also gives the average distance between the electron and the nucleus. As the value of n increases, the distance between the electron and the nucleus also increases.

The possible values of n are 1, 2, 3, 4, 5 etc.

If n = 1 the electron is in K shell
n = 2 the electron is in L shell
n = 3 the electron is in M shell and so on.

2. Azimuthal Quantum Number [Subsidiary or orbital angular momentum ***Quantum number] (l)***

The following information are obtained from l .

1. It gives the shape of the orbital.
2. It gives the sub shell or sub level in which the electron is located.
3. It also gives the orbital angular momentum of the electron.

For a given value of n, l can have n values ranging from 0 to n – 1. That is, for a given value of n, the possible value of l are : l = 0, 1, 2, ... (n-1).

For example, when n = 1, value of l is only 0. For n = 2, the possible value of l can be 0 and 1. For n = 3, the possible l values are 0,1 and 2.

l= 0 represents s orbital, l = 1 represents p orbital, l = 2 represents d orbital and l = 3 represents f orbital

The number of sub shells in a principal shell is equal to the value of n. For example,

When n = 1, l= 0. i.e. K shell contains only one sub shell - s sub shell
when n = 2, l = 0 and1. i.e. L shell contains two sub shells - s and p sub shells
when n = 3, l = 0, 1 and 2. i.e. M shell contains three sub shells – s, p and d sub shells
when n = 4, l = 0, 1, 2 and 3. i.e. N shell contains four sub shells – s, p,d and f sub shells

3. Magnetic Quantum Number (m or m_l)

It gives information about the orientation of orbitals in space. *For a given 'l' value, there are $(2l+1)$ possible values for m* and these values are given by : m = – l to 0 to + l

Thus for $l = 0$, $m_l = 0$ [2 x 0+1 = 1]. i.e. s sub shell contains only one orbital called s orbital.

For $l = 1$, $m_l = –1$, 0 and +1 [2x1+1 = 3]. i.e. p subshell contains three orbitals called p orbitals (p_x, p_y and p_z).

For $l = 2$, $m_l = –2, –1, 0, +1$ and +2 [2x2+1 = 5]. i.e. d subshell contains five orbitals called d orbitals (d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2})

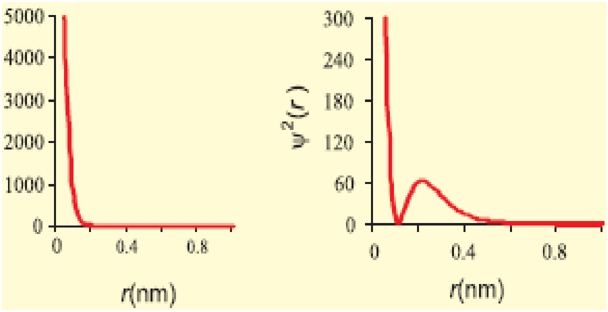
4. Spin Quantum Number (s or m_s)

It is the only experimental quantum number and it gives the spin orientation of electrons. This spin may be either clockwise or anticlockwise. So the values for s may be $+\frac{1}{2}$ or $-\frac{1}{2}$. $+\frac{1}{2}$ represents clock-wise spin and $-\frac{1}{2}$ represents anticlock-wise spin.

Shapes of orbitals

1. **s-orbitals**

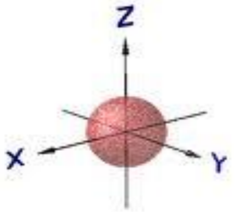
For s-orbitals, $l = 0$ and hence $m_l = 0$. So there is only one possible orientation for s orbitals. They are spherically symmetrical. The plots of probability density (ψ^2) against distance from the nucleus (r) for 1s and 2s atomic orbitals are as follows:

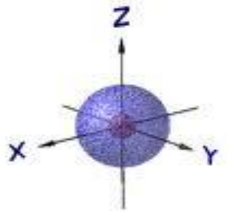


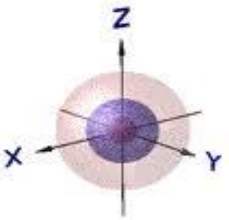
For 1s orbital the probability density is maximum at the nucleus and it decreases with increase in r. But for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maximum it decreases again and approaches zero as the value of r increases. The region where the probability density (ψ^2) reduces to zero is called **nodal surface** or **node**.

For 1s orbital, there is no node, for 2s orbital there is only one node, for 3s orbital there are 2 nodes and so on. In general, for an ns-orbital there are (n – 1) nodes.

All the s-orbitals are spherically symmetrical and their size increases with increase in n. The boundary surface diagrams for 1s, 2sand 3s orbitals are as follows:







2. **p-orbitals**

For p-orbitals, $l = 1$ and $m_l = -1, 0, +1$. i.e., there are three possible orientations for p orbitals. So there are 3 types of p-orbitals – p_x, p_y and p_z. Each p orbital consists of two lobes. The probability density function is zero on the plane where the two lobes touch each other.

The size, shape and energy of the three orbitals are identical. They differ only in the orientation of the lobes. For p_x orbital, the lobes are along the x-axis, for p_y, they are along the y-axis and for p_z, they are along the z-axis. All the p-orbitals have dumb-bell shape.

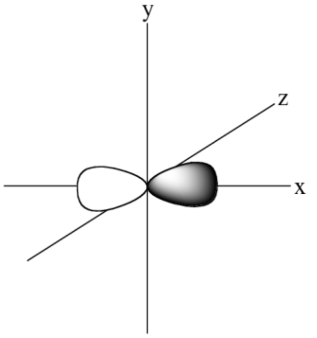
The number of radial nodes for p-orbitals are given by (n –2), that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on. Besides the radial nodes, the probability density functions for the np orbitals are zero at the plane, passing through the nucleus (origin). For example, in the case of p_z orbital, xy-plane is a nodal plane. These are called angular nodes and number of angular nodes is given by 'l'.

Number of radial nodes = n - l – 1

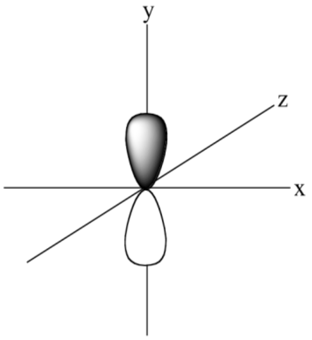
Number of angular nodes = l

Total number of nodes = n-1

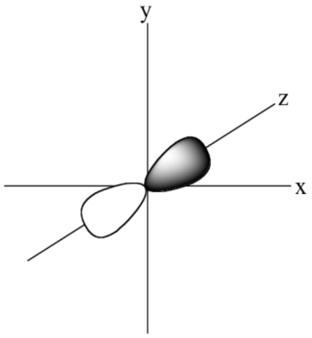
The boundary surface diagrams for three 2p orbitals are as follows:



$2p_x$ orbital



$2p_y$ orbital

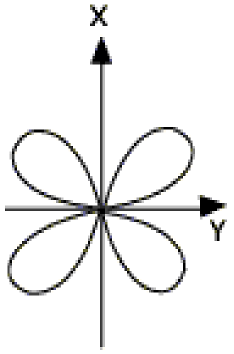


$2p_z$ orbital

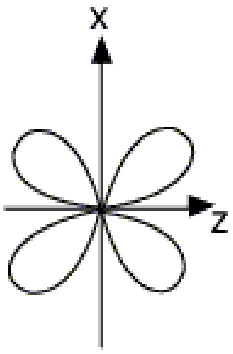
3. d-orbitals

For d-orbitals, l = 2 and m_l = -2, -1, 0, +1 and +2. i.e., there are five possible orientations for d orbitals. So there are 5 types of d-orbitals. They are d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}.

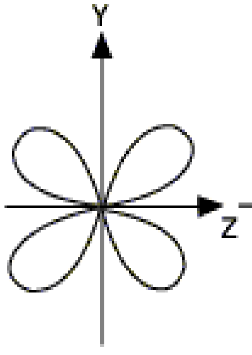
The shapes of the first four d-orbitals are double dumb-bell and that of the fifth one, d_{z^2}, is dumb-bell having a circular collar in the xy-plane. The five d-orbitals have equivalent energies. For d-orbitals the number of radial nodes is 2 and the total number of nodes is n-2. Boundary surface diagrams for d-orbitals are as follows:



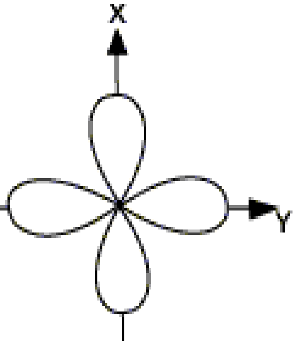
d_{XY}



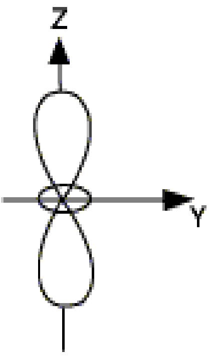
d_{zx}



d_{yz}



$d_{x^2} - d_{y^2}$



d_{z^2}

4. f-orbitals

For f-orbitals, l = 3 and m_l = -3, -2, -1, 0, +1, +2 and +3. i.e., there are seven possible orientations for f orbitals. So there are 7 types of f-orbitals.

They are fx^3, fy^3, fz^3, $fx(y^2-z^2)$, $fy(z^2-x^2)$, $fz(x^2-y^2)$ and fxyz. They have diffused shapes.

Rules for Filling of electrons in various orbitals

The filling of electrons into the orbitals of different atoms takes place according to the 3 rules - aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

1. **Aufbau principle**:

The German word aufbau means 'build up'. The building up of orbitals means the filling up of orbitals with electrons.

The principle states that *the orbitals are filled in the increasing order of their energies*. In other words, electrons first occupy the lowest energy orbital and then to higher energy orbitals.

This rule has two sub rules:

a) *The various orbitals are filled in the increasing order of their (n+l) value.*
b) *If two orbitals have the same (n+l) values, the orbital with the lower n value is filled first.*

The increasing order of orbitals is as follows:

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

2. **Pauli's Exclusion Principle**

It states that no two electrons in an atom can have the same set of four quantum numbers. i.e. an orbital can accommodate a maximum of only 2 electrons with opposite spin.

If 2 electrons have same values for n, l and m, they should have different values for s. i.e. if s = +½ for the first electron, it should be -½ for the second electron.

3. **Hund's rule of maximum multiplicity**

It states that electron pairing takes place only after partially filling all the degenerate orbitals. [Orbitals having same energies are called degenerate orbitals]. For example the electronic configuration of N is $1s^2\ 2s^2\ 2px^1py^1pz^1$ and not $1s^2\ 2s^2\ 2px^2py^1$.

Electronic Configuration of Atoms

The distribution of electrons into various orbitals of an atom is called its *electronic configuration*. The electronic configuration of different atoms can be represented in two ways.

(i) $s^a\ p^b\ d^c$ ...... notation

(ii) Orbital diagram

The electrons in the completely filled shells are known as *core electrons* and the electrons in the outer most shell are called *valence electrons*.

Stability of Completely Filled and Half Filled Subshells

Atoms having ***half filled or completely filled electronic configurations have extra stability*** compared to other atoms. This is ***due to their symmetrical distribution of electrons and greater exchange energy***.

For example, the electronic configuration of Cr is [Ar] $3d^5 4s^1$ and not $3d^4 4s^2$. This is because d^5 represents a half filled configuration and has extra stability. Similarly for Cu, the electronic configuration is [Ar] $3d^{10} 4s^1$ and not $3d^9 4s^2$. This is due to the greater stability of completely filled d^{10} configuration.

****