Structure of Atom

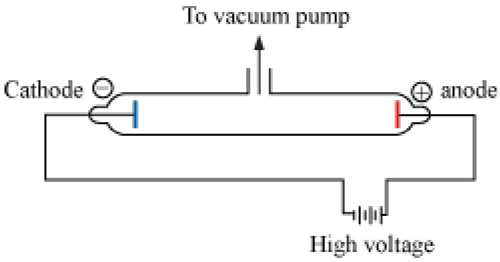
Subatomic Particles: Discovery and Characteristics

Subatomic Particles

Electrons, protons and neutrons are the three main subatomic particles that form an atom.

Discovery of Electron (Michael Faraday's Cathode Ray Discharge Tube Experiment)

Experimental Setup:



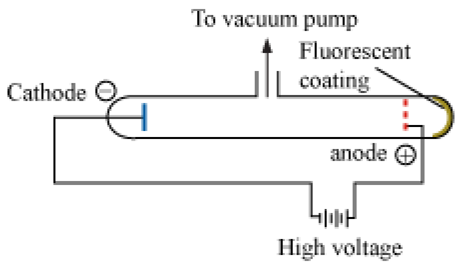
- Glass tube is partially evacuated (low pressure inside the tube).
- Very high voltage is applied across the electrodes.

Observation:

Stream of particles move from the cathode (−ve) to the anode (+ ve). These particles are known as cathode ray particles.

Results:

- Cathode rays move from the cathode to the anode.
- Cathode rays are not visible; they can be observed with the help of phosphorescent or fluorescent materials (such as zinc sulphide).



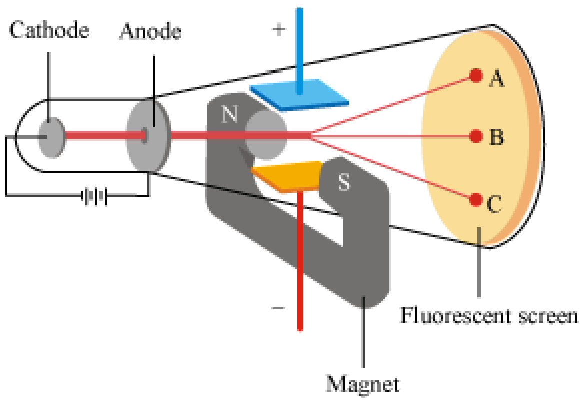
- These rays travel in a straight line in the absence of an electric or magnetic field.
- The behaviour of cathode rays is similar to that of the negatively charged particles (electrons) in the presence of an electrical or magnetic field.
- Characteristics of cathode rays do not depend upon the material of the electrodes and the nature of the gas present in the tube.

Conclusions:

- Cathode rays consist of electrons.
- Electrons are the basic units of all atoms.

Charge to Mass Ratio of Electrons (J. J. Thomson's Experiment)

- J. J. Thomson measured the ratio of charge (e) to the mass of an electron (m_e) by using the following apparatus.



- He determined $\frac{e}{m_e}$ by applying electric and magnetic fields perpendicular to each other as well as to the path of the electrons.
- The amount of deviation of the particles from their path in the presence of an electric or magnetic field depends upon:

1. the magnitude of the negative charge on the particle (greater the magnitude on the particle, greater the deflection)

2. the mass of the particle (lighter the particle, greater the deflection)

3. the strength of the electric or magnetic field (stronger the electric or magnetic field, greater the deflection)

Observations:

- When only electric field is applied, the electrons deviate to point A (as shown in the figure).
- When only magnetic field is applied, the electrons strike point C (as shown in the figure).
- On balancing the strength of electric and magnetic fields, the electrons hit the screen at point B (as shown in the figure) as in the absence of an electric or magnetic field.

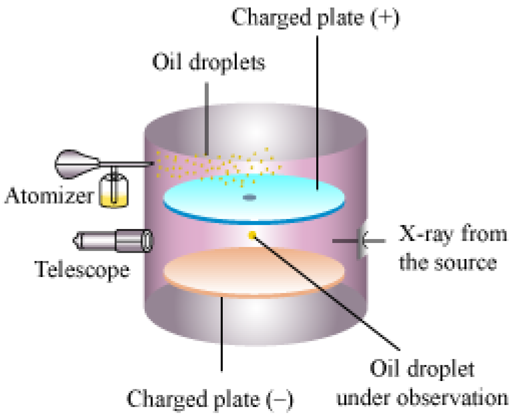
Result:

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

To test your knowledge of **this concept**, solve the following puzzle.

Charge on Electron (Millikan's Oil-Drop Experiment)

- **Millikan's Oil-Drop Apparatus**



- Atomiser forms oil droplets.
- The mass of the droplets is ascertained by calculating their falling rate.

- X-ray beam ionises the air.
- Oil droplets acquire charge by colliding with gaseous ions on passing through the ionised air.
- The falling rate of droplets can be controlled by controlling the voltage across the plate.
- Careful observation of the effects of electric field strength on the motion of droplets leads to the conclusion that $q = ne$. Here, q is the magnitude of electrical charge on the droplets, e is the electrical charge and n is 1, 2, 3,…

Results:

Charge on an electron = -1.6022×10^{-19} C

Mass of an electron

$$(m_e) = \frac{e}{\frac{e}{m_e}}$$

$$= \frac{1.6022 \times 10^{-19}\ \text{C}}{1.758820 \times 10^{11}\ \text{C kg}^{-1}}$$

$$= 9.1094 \times 10^{-31}\ \text{kg}$$

Discovery of Proton

- Electric discharge carried out in a modified cathode ray tube led to the discovery of particles carrying positive charge; these are known as canal rays.
- These positively charged particles depend upon the nature of gas present in them.
- The behaviour of these positively charged particles is opposite to that of the electrons or cathode rays in the presence of an electric or magnetic field.
- The smallest and lightest positive ion is called a **proton** (obtained from hydrogen).

Discovery of Neutron

- Neutrons are electrically neutral.
- They were discovered by Chadwick, by bombarding a thin sheet of beryllium with alpha particles.

The given table lists the properties of these fundamental particles.

Name	Symbol	Absolute Charge/C	Relative Charge	Mass/kg	Mass/*u*	Approx. Mass/u
Electron	e	-1.6022×10^{-19}	-1	9.10939×10^{-31}	0.00054	0
Proton	p	$+1.6022 \times 10^{-19}$	$+1$	1.67262×10^{-27}	1.00727	1
Neutron	n	0	0	1.67493×10^{-27}	1.00867	1

Thomson's Atomic Model

Atom Is Divisible

Do you recall **Dalton's atomic theory**? Dalton postulated in his theory that an **atom is indivisible**. However, the later discoveries of **protons** and **electrons** proved this to be erroneous.

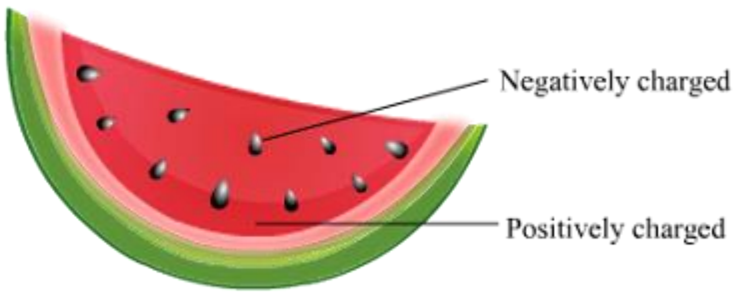
In 1886, while carrying out an experiment in a gas discharge tube, E. Goldstein discovered positively charged radiations which led to the discovery of the subatomic particles called protons. Later, in 1897, J. J. Thomson discovered another type of subatomic particle—the negatively charged electron. Consequent to these discoveries, an atom was no longer indivisible; rather, it became a sum total of differently charged subatomic particles.

We know that an atom is neutral. It is made up of an equal number of oppositely charged particles—protons and electrons. Now, the question that arises is this:

How are the subatomic particles arranged inside an atom?

Many scientists performed varied experiments to develop different models for the structure of an atom. The first such model was proposed by J. J. Thomson. His atomic model is compared to a plum pudding and a watermelon; hence, it is known by the names 'the plum-pudding model'.

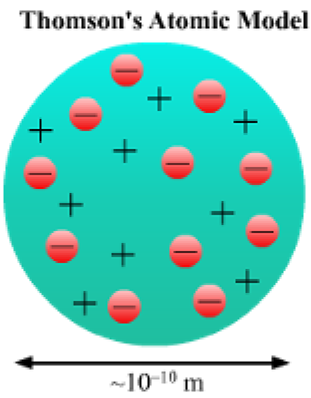
The Plum-Pudding Model of an Atom



Let us understand Thomson's atomic model with the help of a slice of a watermelon. The slice consists of a red edible portion with embedded black seeds. Now, if we liken this watermelon to an atom, then (as per Thomson's model) the positive charge in the atom is spread all over the red edible part; and the negatively charged particles, like the seeds, are embedded in this positively charged space.

In the same way, we can liken an atom to a plum pudding. In this case, the positive charge is spread all over the pudding, while the negatively charged particles are embedded like plums in this positively charged space.

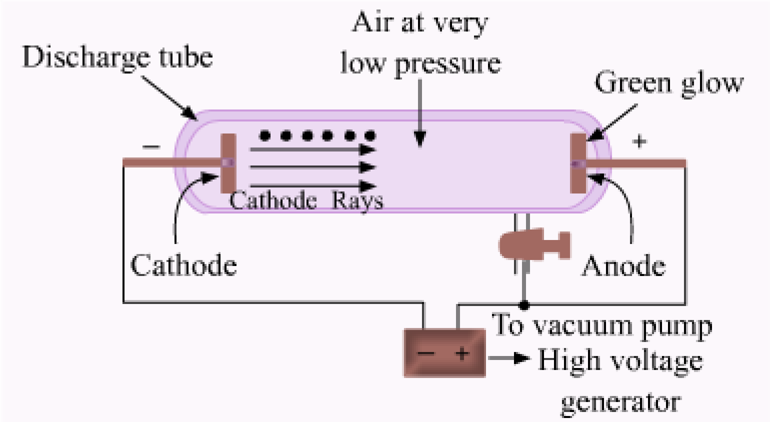
According to Thomson's atomic model:



1. An atom consists of a positively charged sphere with electrons embedded in it.

2. The negative and positive charges present inside an atom are equal in magnitude. Therefore, an atom as a whole is electrically neutral.

Cathode Rays

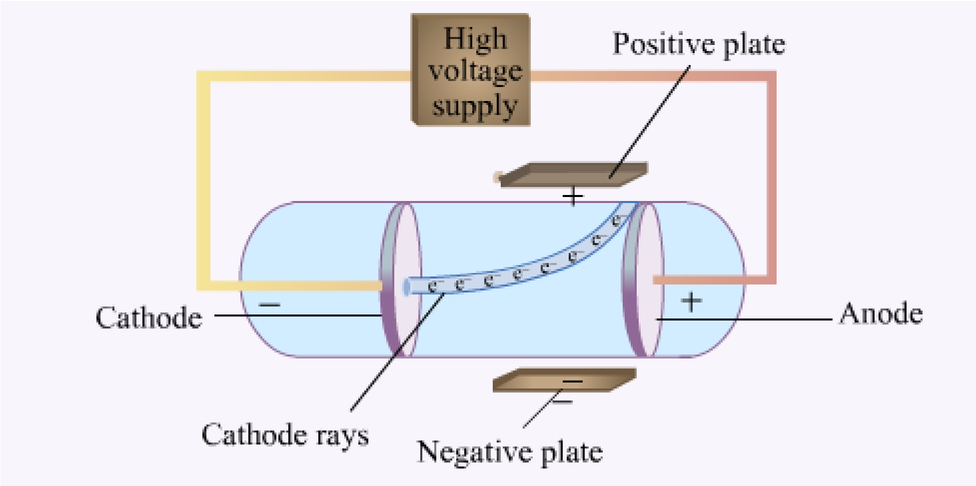


Production of Cathode Rays

J.J Thomson discovered that there are small particle present in the atom and that atom is divisible. J.J Thomson and his colleagues conducted experiments using discharge tube apparatus.
A discharge tube apparatus consists of a glass tube of about 15 cm length and 3 cm in diameter, filled with gas at low pressure. The tube is connected with the vacuum pump and two metal electrodes are fitted to the ends of the tube.

Low pressure was created inside the tube and high voltage was applied to the electrodes of the tube. This produced greenish glow at the anode end of the tube. The greenish glow at anode was produced due to the emission of the streams of rays from the cathode. These rays are known as cathode rays. Cathode rays will emit with blue glow.
When J.J Thomson placed a light paddle wheel inside the tube in the path of the cathode rays, the wheel started rotating. This led him to conclude that cathode rays are particulate in nature.

Properties of Cathode Rays



Experiment to demonstrate properties of cathode rays

When J.J Thomson applied an electric field in the direction parallel to the path of cathode rays , he observed that the rays were deflected towards the anode.

This observation led to the conclusion that cathode rays are negatively charged.

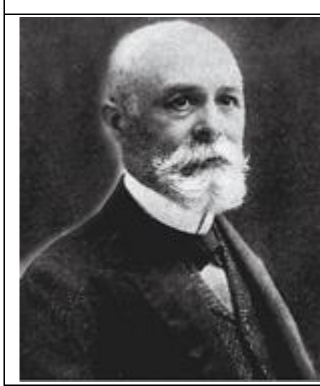
When the above experiment was conducted with different gases, same observation were made and he named these negatively charged particles as electrons.

An electron is lighter than hydrogen atom and has very small mass in comparison to the mass of an atom.

Thus, J.J Thomson's experiment and discovery of electron proved that atom is divisible and is made up of sub – atomic particles.

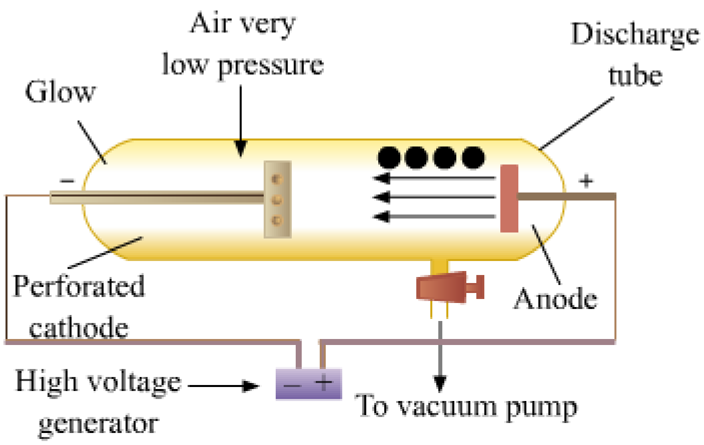
Know Your Scientist

Sir Joseph John Thomson (1856–1940) was a British physicist. He is known for the discovery of electrons and for his model of an atom, popularly known as 'the plum-pudding model'. He received the Nobel Prize in Physics in 1906 for discovering electrons and for his research on conduction in gases. In 1912, while working on the composition of canal rays, he and his colleague (F. W. Aston) found the first evidence for isotopes of neon.



Eugen Goldstein (1850–1930) was a German physicist. He is known for the discovery of canal rays which led to the discovery of protons. He also investigated comets using gas discharge tubes. His experiments established that a small object (like a ball) placed in the path of cathode rays produces emissions, flaring outward just like in case of a comet's tail.

Canal Rays



Production of anode rays

After J.J Thomson's discovery of atom another question arose that: if electrons are present inside the atom, then how is atom electrically neutral? Does this mean that there are positively charged particle also present inside the atom?

To find out the answers to such questions, Goldstein conducted an experiment similar to that of J.J Thomson's but with some modifications, for example he used perforated cathode in the discharge tube.

It was observed during the experiment that some rays were travelling in the direction opposite to that of cathode rays. Goldstein named these rays as anode rays.
When he applied an electric field in the direction parallel to that of the rays he observed that rays deflected towards cathode, thereby he concluded that anode rays are positively charged.
However, the deflection of anode rays in the discharge tube was found to be very less than that of cathode rays, because the emission of cathode rays was not dependent on the nature of the gas taken in the discharge tube. The deflection was seen highest for the hydrogen gas, when taken in the discharge tube.
The positive particles of hydrogen were found to be lightest and were named protons. Their mass is approximately equal to 1840 times that of electron. This mass is assumed as **1 atomic mass unit**. The charge on a proton (+1) is equal to charge on an electron in magnitude (-1).

Rutherford's Atomic Model

Why the Plum-Pudding Model Failed

The plum-pudding model of an atom was unable to explain the findings of Rutherford's experiment while studying radioactivity.

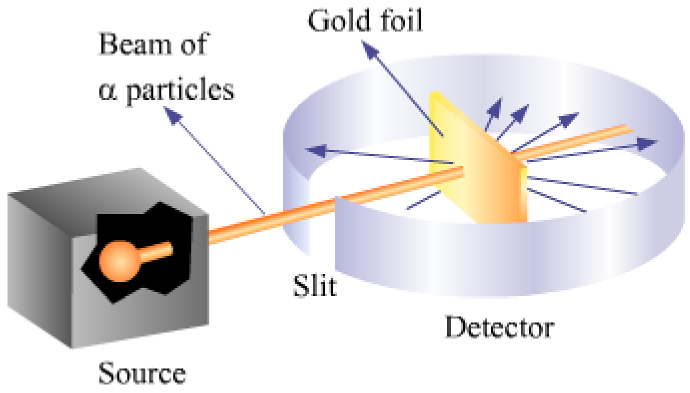
In an experiment with gold foil, Rutherford bombarded the gold foil with **alpha particles**. With Thomson's model as the basis, Rutherford expected small deviations; however, his findings were different from what was expected.

As we go further into this lesson, we will learn more about Rutherford's gold-foil experiment, his observations and his conclusions. We will also learn about the atomic model that he came up with on the basis of his conclusions.

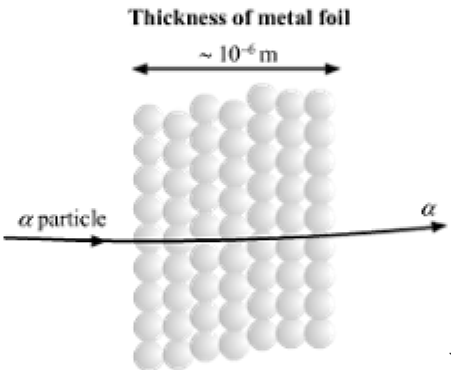
Set up for Rutherford's experiment:

1. A thin gold foil, approximately 1000 atoms thick, was taken. Gold was chosen for its high malleability.
2. A detector screen with a small slit (for emission of radiation from the atom) was placed around the foil.
3. A source of alpha particles was kept in front of the foil.
4. The foil was bombarded with fast-moving alpha particles.

The set-up for Rutherford's gold-foil experiment is shown in the figure.



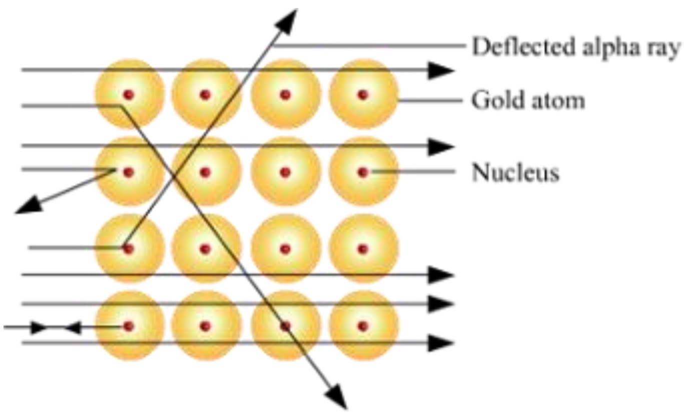
Rutherford's Expectations and Observations



What Rutherford expected?

Rutherford expected that the alpha particles would pass straight through the foil and only a small fraction of alpha particles would be deflected. This expectation was in compliance with Thomson's atomic model.

What Rutherford observed?



Rutherford's findings were contrary to his expectation. He observed that:

1. Most of the fast-moving alpha particles passed straight through the gold foil.

2. Some particles were deflected through the foil by small angles.

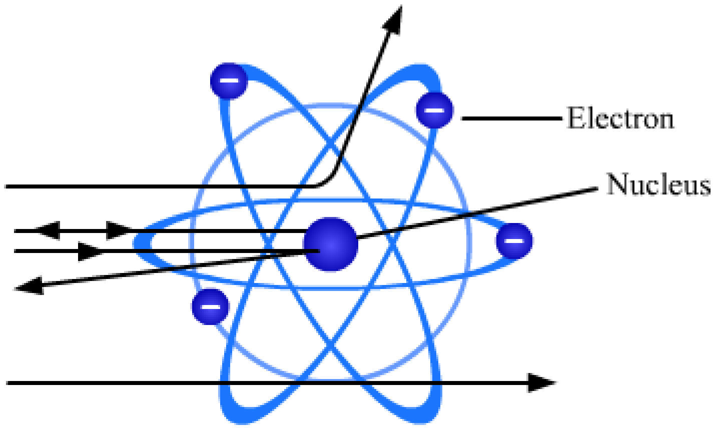
3. One out of every 12000 particles rebounded, i.e., they got deflected by an angle of 180°.

What Rutherford Concluded from His Observations

Rutherford then carefully studied his observations and made the following conclusions.

1. Most alpha particles passed through the gold foil without any deflection. This indicates that most of the space inside an atom is empty.
2. Very few particles suffered a deflection from their path. This means that positive charge occupies very little space inside an atom.

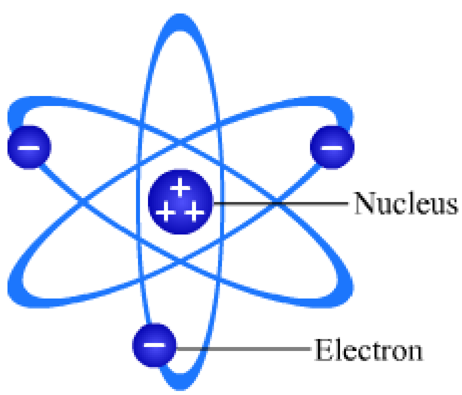
3. Only a small fraction of particles underwent a 180° deflection. This shows that the entire positive charge and mass of an atom are present within a very small volume inside the atom.



Rutherford's Atomic Model

Based on his conclusions in the gold-foil experiment, Rutherford devised his own atomic model. The major features of **Rutherford atomic model** or **the nuclear model of an atom** are as follows:

1. An atom consists of a nucleus at its centre and all the protons are present inside this nucleus.
2. Electrons reside outside the nucleus and revolve around the nucleus in well-defined orbits.
3. The size of the nucleus is very small as compared to the size of the atom. As per Rutherford's calculations, the nucleus is 10^5 times smaller than the atom.
4. Since the mass of the electrons is negligible as compared to the mass of the protons, almost all the mass of the atom is concentrated in its nucleus.



Know Your Scientist

Ernest Rutherford (1871–1937) was a British chemist and physicist. He is known as 'the father of nuclear physics'. He discovered radioactive half-life. He proved that alpha radiations are nothing but helium ions. He was awarded the Nobel Prize in Chemistry in 1908 for his work on 'the disintegration of elements' and 'the chemistry of radioactive substances'. He was the first scientist to split an atom in a nuclear reaction. The element 'rutherfordium' (atomic number 104) is named after him.

Solved Examples

Hard

Example 1: **What would have been observed if neutrons had been used to bombard the gold foil?**

1. **The observations of the experiment would have remained the same in spite of the change in the nature of the bombarding particles.**
2. **The neutrons would have suffered no deflection from the subatomic particles.**
3. **All the neutrons would have been absorbed by the gold atoms.**
4. **All the neutrons would have rebounded.**

Solution:

The correct answer is B.

Neutrons do not carry any charge; so, they do not suffer any repulsion. Hence, if neutrons had been used to bombard the gold foil, no deflection would have occurred. It is also possible that some neutrons would have been absorbed by the nucleus.

Medium

Example 2: **State whether the following statements are true (T) or false (F).**

1. **Increasing the energy of the alpha particles will lead to more deflection.____**
2. **Speed of the alpha particles can be increased by increasing their energy.____**

3. **Use of aluminium sheet will lead to the same result as in case of gold foil.____**

Solution:

1. **T**: Increasing the energy of the alpha particles will cause them to strike closer to the nucleus. Consequently, they will suffer greater deflection.
2. **T**: The kinetic energy of the alpha particles is directly related to their velocity. So, increasing their energy will result in an increase in the speed of the particles.
3. **F**: The positive charge on the nucleus in case of an aluminium foil is much smaller as compared to that on the gold nucleus. So, the result will vary.

Easy

Example 3:

One of the postulates of Rutherford's atomic model is that

1. **an atom consists of a positively charged sphere.**
2. **an atom has its mass concentrated in its nucleus.**
3. **the nucleus of an atom is composed of electrons and protons.**
4. **the mass of an atom is the sum of the masses of all electrons and protons.**

Solution:

The correct answer is B.

The postulates of Rutherford's atomic model are as follows:

1. An atom consists of a nucleus at its centre and all the protons are present inside this nucleus.
2. Electrons reside outside the nucleus and revolve around the nucleus in well-defined orbits.
3. The size of the nucleus is very small as compared to the size of the atom. As per Rutherford's calculations, the nucleus is 10^5 times smaller than the atom.
4. Since the mass of the electrons is negligible as compared to the mass of the protons, almost all the mass of the atom is concentrated in its nucleus.

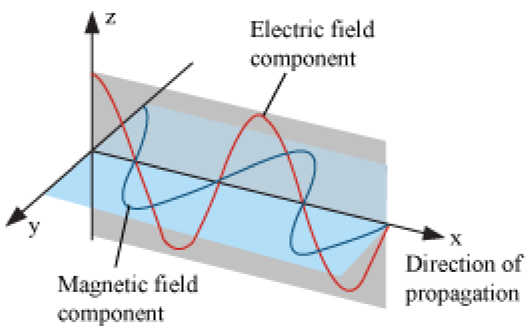
Rutherford also noticed that the actual mass of the nucleus was much more higher than the sum of the masses of protons and electrons. This lead him to predict that nucleus contains some kind of neutral particle whose mass must be equal to that of proton.

This was experimentally proved by James Chadwick in the year 1932. He proved that nucleus of atom contains an additional neutral particle and called them **neutrons.** The mass of these neutrons is equal to that of protons.

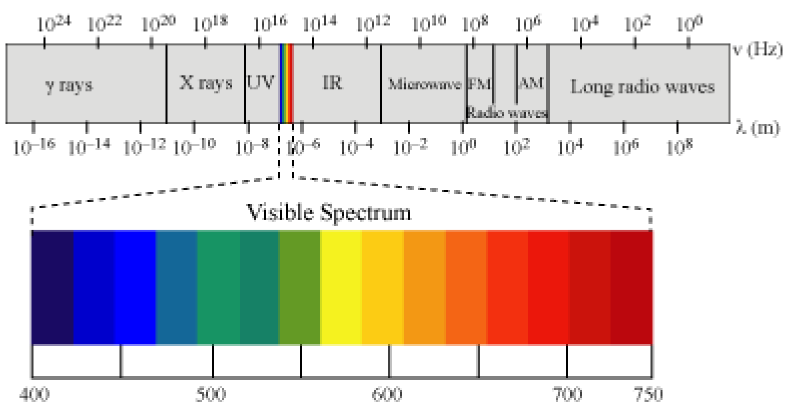
Wave Nature of EM Radiation, Particle Nature of EM Radiation, Dual Behaviour of EM Radiation

Wave Nature of Electromagnetic Radiations

- Radiations which are associated with electric and magnetic field are called electromagnetic radiations.
- **Properties of Electromagnetic Radiation**
- The oscillating electric and magnetic field produced by the oscillating charged particles are perpendicular to each other and also perpendicular to the direction of propagation of wave.



- Electromagnetic waves do not require any medium. They can move in vacuum.
- There are many types of electromagnetic waves which differ from one another in wavelength (or frequency). These electromagnetic radiations constitute *electromagnetic* spectrum.



- Different kinds of units are used for the representation of electromagnetic waves.
- Electromagnetic radiations are characterized by the properties – frequency (ν) and wave length (λ).

- **Frequency** – Number of waves that pass a given point in one second

  The S.I. unit of frequency (ν) is hertz (Hz, s^{-1}).

- The S.I. unit of wavelength is metre (m).

- Electromagnetic waves travel at the speed of 3.0×10^8 m/s, which is the speed of light (denoted by c).

- The relationship between frequency (ν), wavelength (λ), and velocity of light (c) is given by,

  $c = \nu\lambda$

- Wave number $(\bar{\nu})$ – It is defined as the number of wavelengths per unit length or it is the reciprocal of wavelength. The SI unit of wavenumber is m^{-1}.

Examples

(i) The Red FM radio station of India Today Network is broadcasted on a frequency range of 93.5 MHz.

The wavelength (λ) of the electromagnetic radiation emitted by the transmitter can be calculated as

$$\lambda = \frac{c}{\nu}$$
$$= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{93.5 \times 10^6 \text{ s}^{-1}}$$
$$\lambda = 3.2 \text{ m}$$

The radiation of wavelength 3.2 m belongs to radio wave region of the spectrum.

(ii) Wave number $(\bar{\nu})$ of red light having wave length 750 nm can be calculated as

$\lambda = 750$ nm

$= 750 \times 10^{-9}$ m

Wave number $(\bar{\nu}) = \frac{1}{\lambda}$

$$= \frac{1}{750 \times 10^{-9} \text{m}}$$
$$= 0.00133 \times 10^9 \text{ m}$$
$$= 1.33 \times 10^6 \text{m}^{-1}$$

$$\therefore \bar{\nu} = 1.33 \times 10^4 \text{ cm}^{-1}$$

Particle Nature of Electromagnetic Radiation

Wave nature of electromagnetic radiation failed to explain many phenomena such as *black body radiation* and *photoelectric effect*.

Black Body Radiation

- Solids on heating emit radiations over a wide range of wavelengths.

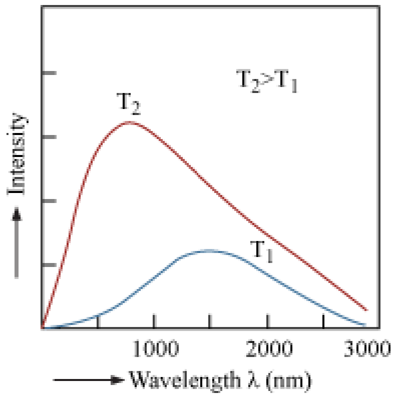
- Radiations emitted shift from lower frequency to a higher frequency as the temperature increases.

- An ideal body which absorbs and emits all radiation is called a black body and the radiation emitted by it is called black body radiation.

- An ideal black body is defined as a perfect absorber and a perfect emitter of radiations.

- The distribution of frequency of the emitted radiation from a black body depends upon temperature.

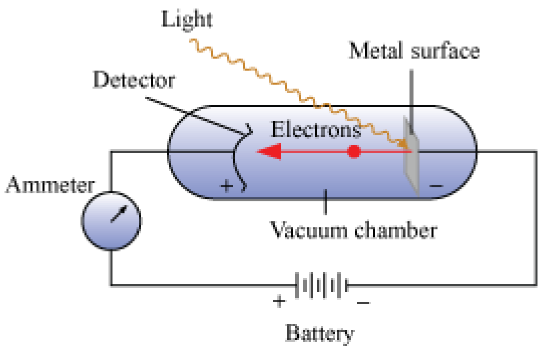
- The intensity of emitted radiation at a given temperature increases with the decrease in wavelength. It attains a maximum value at a given wavelength and then starts decreasing with further decrease of wavelength.



- These experimental results cannot be explained on the basis of wave theory of light.

Photoelectric Effect

- When certain metals such as potassium, rubidium, caesium, etc. are exposed to a beam light, the electrons are ejected from the surface of the metals as shown in the figure below.



- The phenomenon is called *Photoelectric effect*.

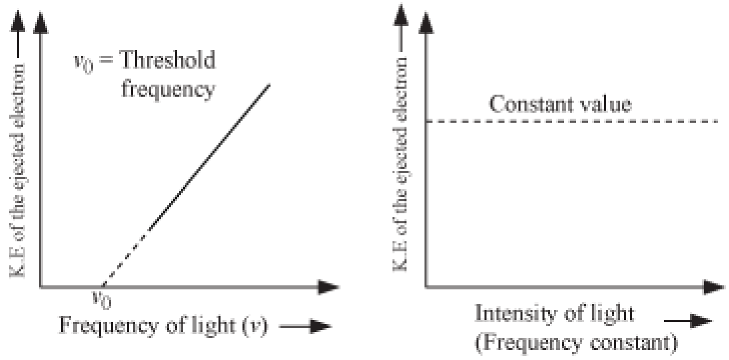
- **Results of the Experiment**

- The electrons are ejected from the surface of the metal as soon as the beam strikes the metal surface.

- The number of electrons ejected from the metal surface is directly proportional to the intensity of light.

- For each metal, there is a certain minimum frequency of light below which photoelectric effect is not observed. This minimum frequency is called threshold frequency (ν_0).

  When $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energy of the emitted electrons is directly proportional to the frequency of incident radiation and is independent of incident radiation.



- The results of photoelectric effect could not be explained by using law of classical physics.

  Planck's Quantum Theory of Radiation

  Main features of Planck's quantum theory of radiation are as follows:

- Radiant energy is not emitted or absorbed in continuous manner, but discontinuously in the form of small packets of energy called *quanta*.

- Each quantum of energy is associated with definite amount of energy.

- The amount of energy (E) associated with quantum of radiation is directly proportional to frequency of light (ν).

  i.e., $E \propto \nu$

  Or, $E = h\nu$

‘h’ is known as Planck’s constant and has the value 6.626×10^{-34} Js.

Example

Energy of one mole of photons of radiation whose frequency is $3.0 \times 10^{15}\ s^{-1}$ can be calculated as:

Energy (E) of one photon is given by,

$E = h\nu$

$h = 6.6.26 \times 10^{-34}$ Js

$\nu = 3.0 \times 10^{15}\ s^{-1}$

$\therefore E = (6.626 \times 10^{-34}\ Js) \times (3.0 \times 10^{15}\ s^{-1})$

$E = 1.99 \times 10^{-18}$ J

Energy of one mole of photons

$$= \left(1.99 \times 10^{-18}\ J\right) \times \left(6.022 \times 10^{23}\ mol^{-1}\right)$$
$$= 11.984 \times 10^{5}\ J\ mol^{-1}$$
$$= 1198.4\ kJ\ mol^{-1}$$

Explanation of Photoelectric Effect Using Quantum Theory

- According to Einstein,

  Energy of the striking photon = Binding energy + Kinetic energy of ejected electron

  Energy of the striking photon = $h\nu$

  Binding energy = $h\nu_0$ (also called work function or threshold energy)

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

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

$$\text{Or, } \frac{1}{2}mv^2 = h(\nu - \nu_0)$$

- If $\nu < \nu_0$, then no electrons will be ejected, no matter how high the intensity is.
- If $\nu > \nu_0$, then the excess energy is imported to the ejected electron as kinetic energy. As the frequency of radiation increases, the kinetic energy of the electron will increase.
- As the intensity increases, more electrons will be ejected, but their kinetic energy does not change.

Dual Behaviour of Electromagnetic Radiations

- Some phenomena (reflection, refraction, diffraction) were explained using wave nature of electromagnetic radiation and some phenomena (photoelectric effect and black body radiation) were explained by using particle nature of radiation.
- This suggests that microscopic particles exhibit wave-particle duality.

Atomic Spectra

- The spreading of a ray of white light into a series of coloured bands is called spectrum.
- The spectrum of white light which ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz is called **continuous spectrum**.

Emission and Absorption Spectra

- Emission spectrum is the spectrum of radiation emitted by a substance that has absorbed energy.
- Absorption spectrum is like the photographic negative of an emission spectrum.
- Spectroscopy is the study of emission or absorption spectra.
- Atoms in the gas phase do not show a continuous spread of wavelength from red to violet. They emit only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra.**

Line Spectrum of Hydrogen

- If an electric discharge is passed through gaseous hydrogen, then the H_2 molecules get dissociated to produce energetically excited hydrogen atoms. These atoms emit electromagnetic radiations of discrete frequencies.

- A spectrum of hydrogen consists of several series of lines.

- When the spectral lines are expressed in terms of wave number $(\bar{v})$, the visible lines of the hydrogen spectra obey the following formula:

  $$\bar{v} = 109,677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\text{cm}^{-1}$$

  Where, n is an integer equal to or greater than 3 (i.e., n = 3, 4, 5, ...)

- The series of lines that can be described by the formula is called Balmer series. It is the only series of line in the hydrogen spectrum which appears in the visible region of the electromagnetic spectrum.

- All the series of lines in the hydrogen spectrum can be described by the following expression:

  $$\bar{v} = 109,677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-1}$$

  Where, n_1 = 1, 2, ...

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

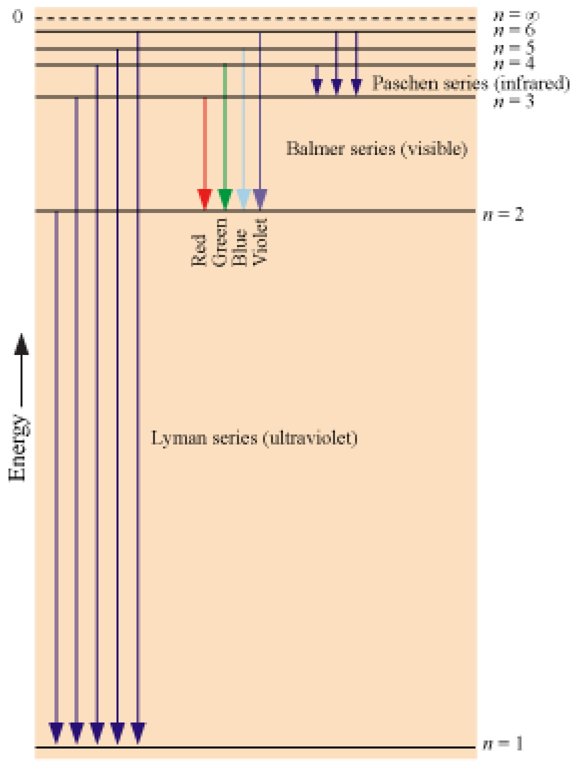
  109,677 is called Rydberg constant for hydrogen (R_H)

- The first five series of lines that correspond to n_1 = 1, 2, 3, 4, 5 are known as Lyman, Balmer, Paschen, Brackett and Pfund series.

Series	n_1	n_2	**Spectral Region**
Lyman	1	2,3...	Ultraviolet

Balmer	2	3,4…	Visible
Paschen	3	4,5,…	Infrared
Brackett	4	5,6…	Infrared
Pfund	5	6,7…	Infrared

- The Lyman, Balmer and Paschen series of transition for hydrogen atom are shown in the figure.



Bohr's Model for Hydrogen Atom

Postulates for Bohr's model for hydrogen Atom

- The electron in the hydrogen atom moves around the nucleus in a circular path of fixed radius and energy. These circular paths are called orbits, stationary states, or allowed energy states.

- Energy is absorbed when electron jumps from lower orbit to a higher orbit and is emitted when electron jumps from higher orbit to a lower orbit.

- Frequency (ν) of absorbed or emitted radiation is given by,

  $\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$ (Bohr's frequency rule)

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

- Angular momentum (L) of an electron in a stationary state is given by,

  $m_e vr = n \cdot \frac{h}{2\pi}$ $(n = 1, 2, 3 \ldots)$

  On the Basis of These Postulates, Bohr's Theory for Hydrogen Atom was Obtained

- The stationary states of electron are numbered as n = 1, 2, 3 … and these numbers are called principal quantum numbers.

- Radii of the stationary states (r_n) are given by,

  $r_n = n^2 a_0$

  Where, a_0 = 52.9 pm (called Bohr radius)

- Energy (E_n) of the stationary state is given by,

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

  R_H is called Rydberg constant (= 2.18×10^{-18} J)

- When electron is free from the influence of nucleus, the energy will be zero.

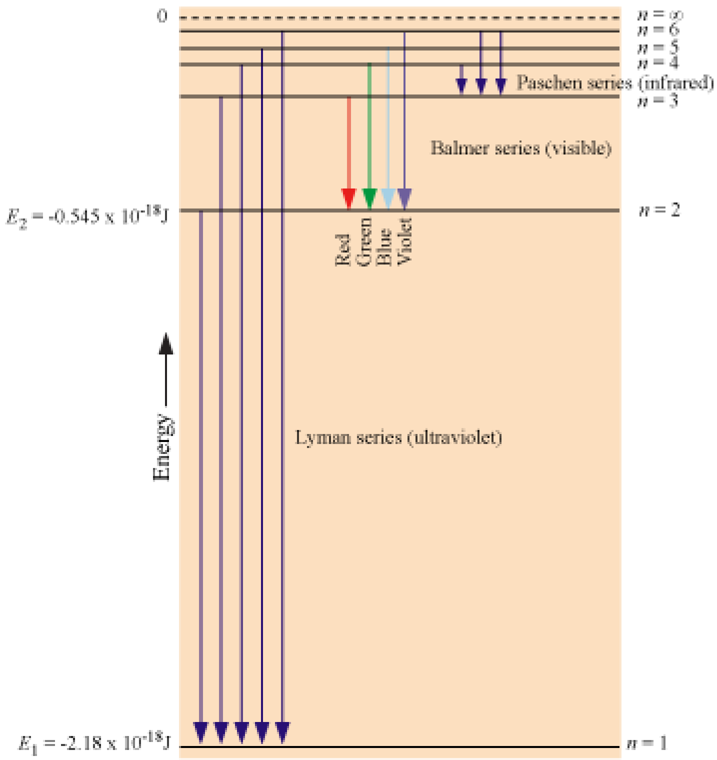
- When the energy is zero, the electron has principal quantum number,

  $n = \infty$ (It is called ionized hydrogen atom)

Thus, $E_1 = -2.18\times10^{-18}\left(\frac{1}{1^2}\right) = -2.18\times10^{-18}$ J

E_1 is the energy of the lower state (called as ground state).

$$E_2 = -2.18\times10^{-18}\left(\frac{1}{2^2}\right) = -0.545\times10^{-18} \text{ J}$$



(Energy of different energy levels of hydrogen atom)

This figure is called energy level diagram.

- Bohr's theory can be applied to the ions, which are similar to hydrogen atom (containing only one electron). For example – He^+, Li^{2+}, Be^{3+}, etc.

- Energies and radii of the stationary states for hydrogen-like species is given by,

$$E_n = -2.18\times10^{-18}\left(\frac{Z^2}{n^2}\right)\ \text{J}$$

$r_n = \frac{52.9(n^2)}{Z}$ pm = $r_n = \frac{0.0529(n^2)}{Z}$ nm; Z is the atomic number

Example:

Let us try to calculate the energy associated with the second orbit of Be^{3+} and the radius of this orbit.

Energy, $E_n = -\frac{(2.18\times10^{-18}\ \text{J})Z^2}{n^2}\text{atom}^{-1}$

For Be^{3+}, $n = 2$, $Z = 4$

$$E_2 = \frac{-(2.18\times10^{-18}\ \text{J})(4)^2}{2^2}$$

$$\therefore E_2 = -8.72\times10^{-18}\ \text{J}$$

Radius, $r_n = \frac{(0.0529\,\text{nm})n^2}{Z}$

$$r_2 = \frac{(0.0529\ \text{nm})\times2^2}{4}$$

$$\therefore r_2 = 0.0529\ \text{nm}$$

- Calculation of velocities of electrons moving in the orbits is possible by using Bohr's theory.
- Magnitude of velocity of electron decreases with the decrease in positive charge on the nucleus and increase of principal quantum number.

Line Spectrum of Hydrogen

- Energy difference between two stationary states is given by,

$$\Delta E = E_f - E_i$$

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

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

$$= 2.18\times10^{-18}\ \text{J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

(Where n_i and n_f stand for initial and final orbits respectively)

- The frequency (ν) for the absorption and emission of photon is given by,

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \frac{2.18\times10^{-18}\ \text{J}}{6.626\times10^{-34}\ \text{Js}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= 3.29\times10^{15}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\text{Hz}$$

- In terms of wave numbers $(\bar{\nu})$,

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \frac{3.29\times10^{15}\ \text{s}^{-1}}{3\times10^{8}\ \text{ms}^{-1}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= 1.09677\times10^{7}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\text{m}^{-1}$$

- When $n_f > n_i$, energy is absorbed (absorption spectra).
- When $n_i > n_f$, energy is released (emission spectra).
- Each spectral line is associated with particular transition in hydrogen atom.
- Intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

Example:

Let us try to calculate the frequency and wavelength of the photon emitted during the transition from n = 5 to n = 3 states in the hydrogen atom.

Since n_1 = 5 and n_2 = 3, this transition gives rise to spectral lines in the infrared region of the Paschen series.

$$\Delta E = \mathrm{R_H}\left[\frac{1}{n_f^2}-\frac{1}{n_i^2}\right] = -2.18\times10^{-18}\ \mathrm{J}\left[\frac{1}{(5)^2}-\frac{1}{(3)^2}\right]$$

$$\Rightarrow \Delta E = -2.18\times10^{-18}\ \mathrm{J}\ \left[-\frac{16}{225}\right]$$

$$\Rightarrow \Delta E = 1.55\times10^{-19}\ \mathrm{J}$$

$$\text{Frequency}\ (\nu) = \frac{\Delta E}{h}$$

$$= \frac{1.55\times10^{-19}\ \mathrm{J}}{6.626\times10^{-34}\ \mathrm{Js}}$$

$$\Rightarrow \nu = 2.34\times10^{14}\ \mathrm{Hz}$$

$$\text{Wavelength}\ (\lambda) = \frac{c}{v}$$

$$\Rightarrow \lambda = \frac{3\times10^{8}\ \mathrm{ms^{-1}}}{2.34\times10^{14}\ \mathrm{Hz}} = 1282\ \mathrm{nm}$$

$$\therefore \lambda = 1282\ \mathrm{nm}$$

Limitations of Bohr's Model of Atom

- Unable to explain the spectrum of multi-electron atoms (For example – helium atom which contains two electrons)
- Unable to explain splitting of spectral lines in electric field (Stark effect) or in magnetic field (Zeeman effect)

- Fails to explain finer details (doublet – two closely spaced lines) of hydrogen atom spectrum
- Fails to explain the ability of atoms to form molecules by chemical bonds

Dual Behaviour of Matter & Heisenbergs Uncertainty Principle

Dual Behaviour of Matter

- Matter, like radiation, exhibits dual behaviour (i.e., both particle and wave-like properties).
- Electrons should have momentum as well as wavelength, just as photon has momentum as well as wavelength.
- De Broglie gave the relationship between wavelength (λ) and momentum (*p*) of a material particle.

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

Where, *m* is the mass of the particle and *v* is its velocity

- According to de Broglie, every object in motion has a wave character.
- Wavelengths of objects having large masses are so short that their wave properties cannot be detected.

Example

Let us try to calculate the wavelength of a ball of mass 0.01 kg, moving with a velocity of 20 ms^{-1}.

Using de Broglie equation

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

$$= \frac{(6.626 \times 10^{-34}\ \text{Js})}{(0.01\ \text{kg})\ (20\ \text{ms}^{-1})}$$

$\therefore \lambda = 3.313 \times 10^{-33}$ m

The value of wavelength is so small that wave properties of the ball cannot be detected.

- Wavelengths of particles having very small masses (electron and other subatomic particles) can be detected experimentally.

Example

If an electron is moving with a velocity of 6.0×10^6 m/s, then the wavelength of the electron can be calculated as follows:

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

$$= \frac{6.62 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{9.1 \times 10^{-31}\ \text{kg} \times 6.0 \times 10^6\ \text{ms}^{-1}}$$

$\therefore \lambda = 1.21 \times 10^{-10}$ m

Thus, de Broglie's concept is more significant for microscopic particles whose wavelength can be measured.

Heisenberg's Uncertainty Principle

- Impossible to determine simultaneously the exact position and the exact momentum of an electron (microscopic particle) with absolute accuracy and certainty

- Mathematically, it can be represented as

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

$$\text{Or, } \Delta x \times \Delta(mv_x) \geq \frac{h}{4\pi}$$

$$\text{Or, } \Delta x \times \Delta v_x \geq \frac{h}{4\pi\ m}$$

Where,

Δx is the uncertainty in position

Δv_x is the uncertainty in velocity

Δp_x is the uncertainty in momentum

- If the uncertainty in position (Δx) is less, then the uncertainty in momentum (Δp_x) would be large. On the other hand, if the uncertainty in momentum (Δp) is less, the uncertainty in position (Δx) would be large.

Significance of Uncertainty Principle

- Heisenberg's uncertainty principle rejects the existence of definite paths or trajectories of electrons and other similar particles.

- The effect of Heisenberg's uncertainty principle on the motion of macroscopic objects is negligible.

Example

When an uncertainty principle is applied to an object of mass 10^{-6} kg,

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

$$= \frac{6.626\times10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4\times3.14\times10^{-6}\ \text{kg}}$$

$\approx 0.5275 \times 10^{-28}\ \text{m}^2\ \text{s}^{-1}$

The value of $\Delta v \cdot \Delta x$ is extremely small, and hence, is insignificant. Thus, Heisenberg's uncertainty principle has no significance for macroscopic bodies.

- However, this is not the case with the motion of microscopic objects.

Example

For an electron whose mass is 9.11×10^{-31} kg, the value of $\Delta v \cdot \Delta x$ can be calculated as follows:

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

$$= \frac{6.626\times10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4\times3.14\times9.11\times10^{-31}\text{kg}}$$

$\therefore \Delta v \cdot \Delta x \approx 0.0579 \times 10^{-4}\ \text{m}^2\ \text{s}^{-1}$

The value of $\Delta v \cdot \Delta x$ is quite large, and hence, cannot be neglected.

Reasons for the failure of the Bohr's Model

- **Bohr's model ignores the dual behaviour of matter –** In Bohr's model of hydrogen atom, electron is regarded as a charged particle moving around the nucleus in well-defined circular orbits. **It does not account for the wave character of an electron**.

- **Bohr's model contradicts Heisenberg's Principle –** In the Bohr's model, the electron moves in an orbit. An orbit by definition is a clearly defined path. However, such a completely-defined path can be obtained only if the position and velocity of the electron are known exactly at the same time. **This is not possible according to the Uncertainty Principle**.

Quantum Mechanical Model of Atom

- Macroscopic objects have particle character, so their motion can be described in terms of classical mechanics, based on Newton's laws of motion.

- Microscopic objects, such as electrons, have both wave-like and particle-like behaviour, so they cannot be described in terms of classical mechanics. To do so, a new branch of science called quantum mechanics was developed.

- Quantum mechanics was developed independently by Werner Heisenberg and Erwin Schrodinger in 1926.

- Quantum mechanics takes into account the dual nature (particle and wave) of matter.

- On the basis of quantum mechanics, a new model known as quantum mechanical model was developed.

- In the quantum mechanical model, the behaviour of microscopic particles (electrons) in a system (atom) is described by an equation known as Schrodinger equation, which is given below:

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

  Where,

  $\hat{H}$ = Mathematical operator known as Hamiltonian operator

  ψ = Wave function (amplitude of the electron wave)

  E = Total energy of the system (includes all sub-atomic particles such as electrons, nuclei)

- The solutions of Schrodinger equation are called wave functions.

Hydrogen atom and Schrodinger equation

- After solving Schrodinger equation for hydrogen atom, certain solutions are obtained which are permissible.

- Each permitted solution corresponds to a definite energy state, and each definite energy state is called an orbital. In the case of an atom, it is called atomic orbital, and in the case of a molecule, it is called a molecular orbital.

- Each orbital is characterised by a set of the following three quantum numbers:

- Principal quantum number (n)

- Azimuthal quantum number (l)
- Magnetic quantum number (m_l)
- For a multi-electron atom, Schrodinger equation cannot be solved exactly.

Important Features of the Quantum Mechanical Model of an Atom

- The energy of electrons in an atom is quantised (i.e., electrons can only have certain specific values of energy).
- The existence of quantised electronic energy states is a direct result of the wave-like property of electrons.
- The exact position and the exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle).
- An atomic orbital is represented by the wave function ψ, for an electron in an atom, and is associated with a certain amount of energy.
- There can be many orbitals in an atom, but an orbital cannot contain more than two electrons.
- The orbital wave function ψ gives all the information about an electron.
- $|\psi|^2$ is known as probability density, and from its value at different points within an atom, the probable region for finding an electron around the nucleus can be predicted.

Orbitals and Quantum Numbers

Smaller the size of an orbital, greater is the chance of finding an electron near the nucleus.

Each orbital is characterised by a set of the following three quantum numbers:

- The principal quantum number (n)

- Positive integers (n = 1, 2, 3,.........)
- Determines the size and energy of the orbital
- Identifies the shell
- n = 1, 2, 3, 4, ...

Shell = K, L, M, N, ...

With an increase in the value of n, there is an increase in the number of allowed orbitals (n^2), the size of an orbital and the energy of an orbital.

- The Azimuthal quantum number (l)

- Also known as orbital angular momentum or subsidiary quantum number
- Defines the three-dimensional shape of an orbital
- For a given value of n, l can have n values, ranging from 0 to $n - 1$.

For $n = 1$, $l = 0$

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

For $n = 3$, $l = 0, 1, 2$

For $n = 4$, $l = 0, 1, 2, 3$, ...and so on

- Each shell consists of one or more sub-shells or sub-levels. The number of sub-shells is equal to n, and each sub-shell corresponds to different values of l.

For $n = 1$, there is only one sub-shell ($l = 0$)

For $n = 2$, there are two sub-shells ($l = 0, 1$)

For $n = 3$, there are three sub-shells (l = 0, 1, 2)........ and so on

Value for l	0	1	2	3	4	5 ......
Notation for sub-shell	s	p	d	f	g	h ......

Sub-shell notations corresponding to the given principal quantum numbers and azimuthal quantum numbers are listed in the given table.

Principal quantum number (n)	**Azimuthal quantum number (l)**	**Sub-shell notations**
1	0	1s
2	0	2s

2	1	2p
3	0	3s
3	1	3p
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4f

- The magnetic orbital quantum number (m_l):

- Gives information about the spatial orientation of the orbital with respect to the standard set of co-ordinate axis
- For a given value of l (i.e., for a given sub-shell), $2l + 1$ values of m_l are possible.

  $m_l = -l, -(l-1), -(l-2), \ldots 0, 1, \ldots (l-2), (l-1), l$

  Example:

  For $l = 0$, $m_l = 0$ (one *s*-orbital)

  For $l = 1$, $m_l = -1, 0 + 1$ (three *p*-orbitals)

  For $l = 2$, $m_l = -2, -1, 0, +1, +2$ (five *d*-orbitals)

  For $l = 3$, $m_l = -3, -2, -1, 0, + 1, +2, + 3$ (seven *f*-orbitals)

The relation between the sub-shell and the number of orbitals is given in the following table:

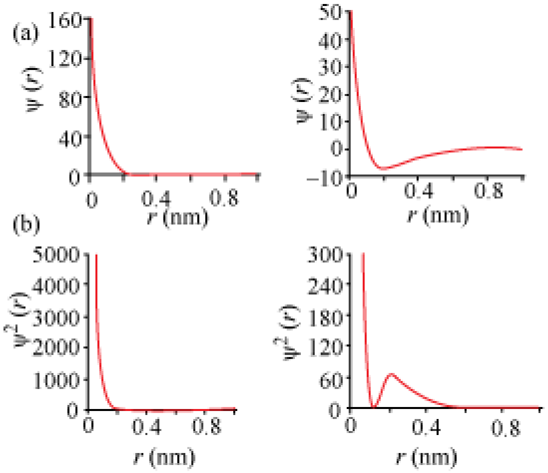
Sub-shell notation	**Number of orbitals**

s	1
p	3
d	5
f	7
g	9
h	11

- There is a fourth quantum number known as the electron spin quantum number (m_s).
- It designates the orientation of the spin of an electron. There are two orientations of an electron, known as the two spin states of an electron: $+\frac{1}{2}$ and $-\frac{1}{2}$ or ↑(spin up) and ↓(spin down)
- An orbital cannot hold more than two electrons.

Shapes of Atomic Orbitals; Energies of Atomic Orbitals

- Ψ^2 (i.e, square of the wave function) at a point gives the probability density of the electron at that point.
- The variations of $\Psi^2$and Ψ with r for 1s and 2s orbitals are shown in the figure below.



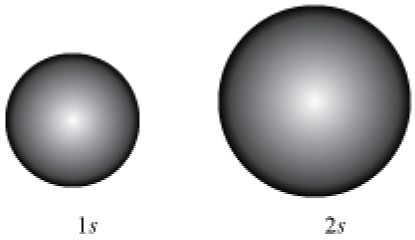
- For 1s orbital, the probability density is maximum at the nucleus and it decreases sharply as we move away from it.

- For 2*s* orbital, the probability density first decreases sharply to zero and then again starts increasing.
- The region where the probability density function reduces to zero is called nodal surface or node.
- For *ns*-orbital, there are (n -1) nodes.

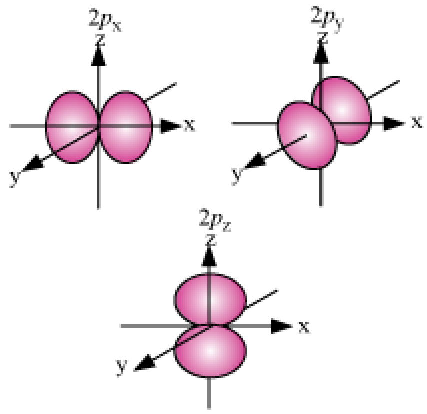
  For 2*s*-orbital, there is one node; and for 3*s*-orbitals, there are two nodes.

  Boundary Surface Diagrams

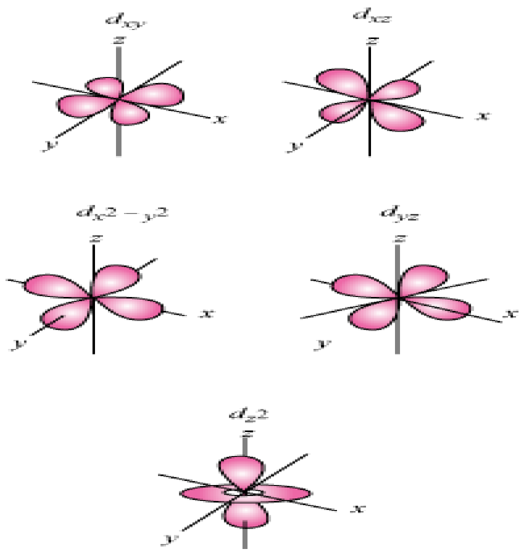
- Give a fairly good representation of the shape of the orbitals
- Boundary surface diagrams for 1*s* and 2*s* orbitals are:



- 1*s* and 2*s* are spherical in shape.
- Boundary surface diagram for three 2p orbitals (l = 1) are shown in the figure below.



- Boundary diagrams for the five 3*d* orbitals are shown in the figure below.



- The total number of nodes is given by (n-1) i.e, sum of l angular nodes and (n-l-1) radial nodes.

Energy of Orbitals:

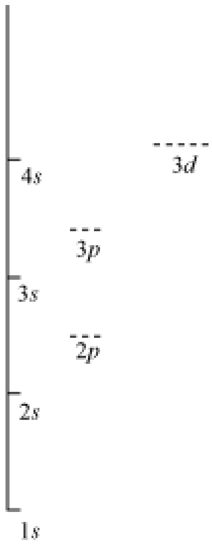
- The energy of the orbitals increases as follows:

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

- Lower the value of (n + l) for an orbital, lower is its energy.

- When two orbitals have the same value of (n + l), the orbital with lower value of n will have lower energy.

- Energy level diagram:



- Effective nuclear charge ($Z_{eff}\,e$): Net positive charge experienced by the electrons from the nucleus

- Energies of the orbitals in the same subshell decrease with the increase in the atomic number (Z).

Filling of Orbitals in Atom & Electronic Configuration of Atoms

Aufbau Principle

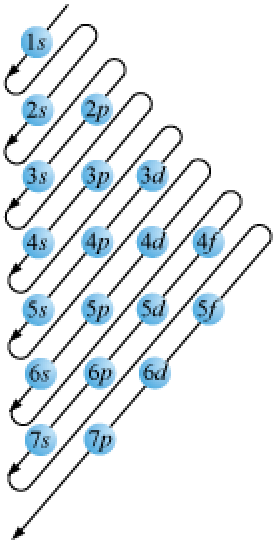
- In the ground state of atoms, the orbitals are filled in the increasing order of their energy.

- The given table shows the arrangement of orbitals with increasing energy on the basis of ($n + l$) rule.

Orbitals	Value of n	Value of l	Value of ($n + 1$)	
1s	1	0	1 + 0 = 1	
2s	2	0	2 + 0 = 2	

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

- Increasing order of the energy of the orbitals and hence, the order of the filling of orbitals: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, ...



Pauli Exclusion Principle

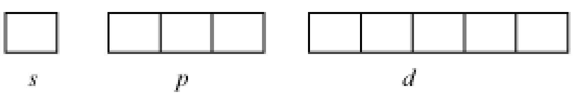
- No two electrons in an atom can have the same set of all the four quantum numbers.
- Two electrons can have the same value of three quantum numbers n, l, and m_e, but must have the opposite spin quantum number (s).
- The maximum number of electrons in the shell with the principal quantum number n is equal to $2n^2$.

Hund's Rule of Maximum Multiplicity

- Pairing of electrons in the orbitals belonging to the same sub-shell (p, d, or f) does not take place until each orbital belonging to that sub-shell has got one electron each (i.e., singly occupied).
- Orbitals of equal energy (i.e., same sub-shell) are called degenerate orbitals.

Electronic Configuration of Atoms

- Can be represented in two ways:
- $s^a\, p^b\, d^c$ …
- Orbital diagram



- a, b, c, …, etc. represent the number of electrons present in the sub-shell. In an orbital diagram, an electron is represented by an up arrow (↑) indicating a positive spin, or a down arrow (↓) indicating a negative spin.
- For example,

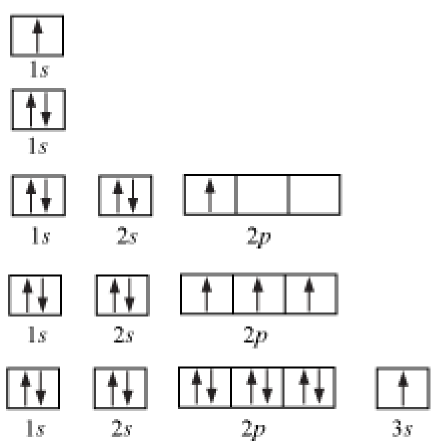
$H \rightarrow 1s^1$;

$He \rightarrow 1s^2$;

$B \rightarrow 1s^2\, 2s^2\, 2p^1$;

$N \rightarrow 1s^2\, 2s^2\, 2p^3$;

$Na \rightarrow 1s^2\, 2s^2\, 2p^6\, 3s^1$;



Stability of completely filled and half-filled sub-shells

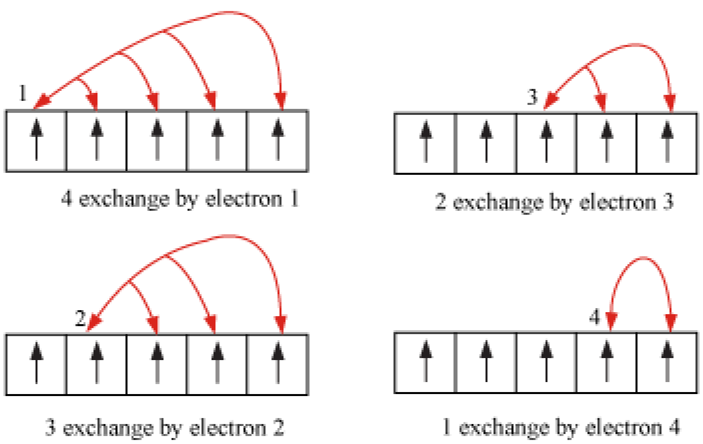
- p^3, p^6, d^5, d^{10}, f^7, f^{14}, etc. configurations, which are either half-filled or fully filled, are more stable.

- **Symmetrical Distribution of Electrons**

- Symmetry leads to stability.
- The completely filled or half-filled sub-shells have symmetrical distribution of electrons in them. Hence, they are stable.

- **Exchange Energy**

- Whenever two or more electrons with the same spin are present in the degenerate orbitals of a sub-shell, the stabilising effect arises.
- Such electrons tend to exchange their positions and the energy released due to the exchange is called exchange energy.
- If the exchange energy is maximum, then the stability is also maximum.
- The number of exchanges that can take place is maximum when the sub-shell is either half-filled or completely filled.
- Possible exchange for d^5 configuration:



Total number of exchanges = 4 + 3 + 2 + 1 = 10.