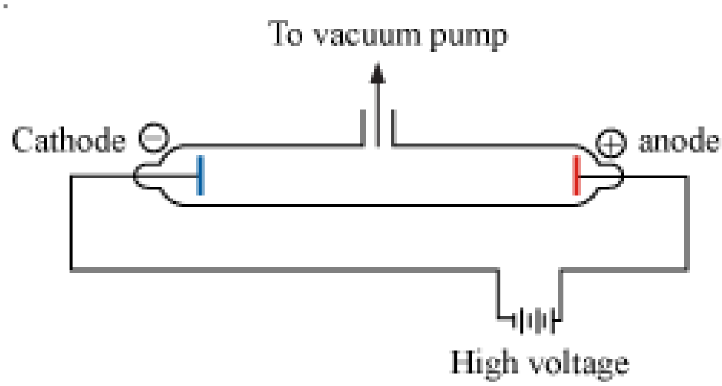
Atomic Structure-Notes

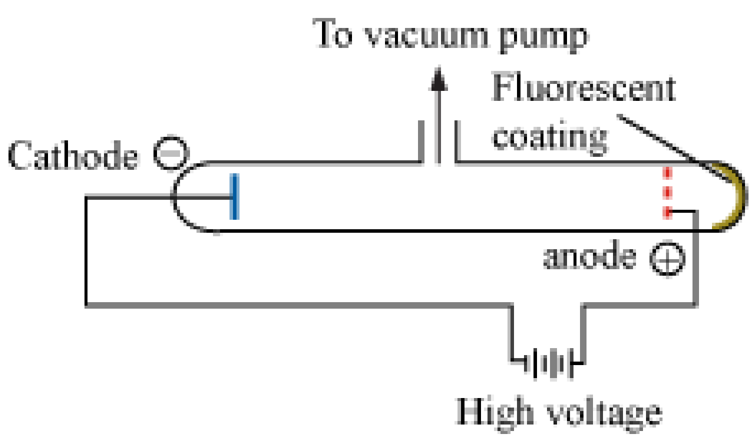
Subatomic Particles
Electron, proton and neutron

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

- **Experimental Setup:**



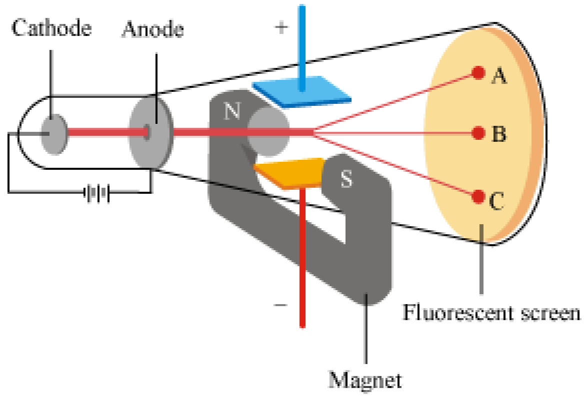
- Glass tube is partially evacuated (Low pressure inside the tube)
- Very high voltage is applied across the electrodes
- **Observation:**
  Stream of particles move from the cathode (− ve) to the anode (+ ve) −−− known as cathode rays or cathode ray particles
- **Results:**
- Cathode rays move from 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 electric and magnetic fields.
- The behaviour of cathode rays is similar to negatively charged particles (electrons) in the presence of an electrical or a 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.

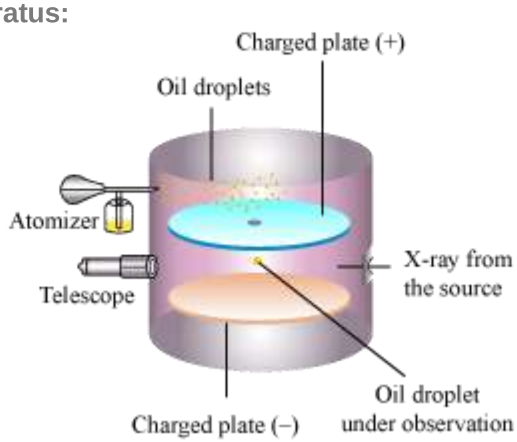


- He determined $\frac{e}{m_e}$ by applying electric and magnetic fields perpendicular to each other as well as to the path of the electrons.
- The amount of deviation of the particles from their path in the presence of an electric or a magnetic field depends upon:
- Magnitude of the negative charge on the particle (greater the magnitude on the particle, greater is the deflection)
- Mass of the particle (lighter the particle, greater is the deflection)
- Strength of the electric or magnetic field (stronger the electric or magnetic field, greater is the deflection)
- **Observations:**
- When only electric field is applied, the electrons deviate to point A (shown in the figure).
- When only magnetic field is applied, electrons strike point C (shown in the figure).
- On balancing the electric and magnetic field strength, the electrons hit the screen at point B (shown in the figure) as in the absence of an electric or a magnetic field.
- **Result:**

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

Charge on Electron (Millikan's Oil Drop Experiment)

- **The Millikan Oil Drop Apparatus:**



- Atomizer forms oil droplets.
- The mass of the droplets is measured by measuring 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 measurement of the effects of electric field strength on the motion of droplets leads to conclusion, $q = ne$ [Where, q is the magnitude of electrical charge on the droplets, e is electrical charge, n = 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 modified cathode ray tube led to the discovery of particles carrying positive charge (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 a magnetic field.
- The smallest and lightest positive ion is called proton (it was obtained from hydrogen).

Discovery of Neutron

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

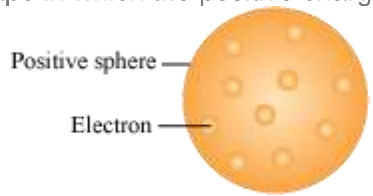
Example :

Explain why less pressure is maintained in the cathode ray experiment?

In the cathode ray experiment, low pressure is needed to increase the space between the atoms of the gas. By doing this, the ions can be accelerated to high speed as there will be no loss of kinetic energy of the ions due to collisions with the gas atoms. When the space between the atoms of the gas increases, the electrons travel more distance with higher speed. This produces the effect of fluorescence in the discharge tube.

Thomson's Model of Atom

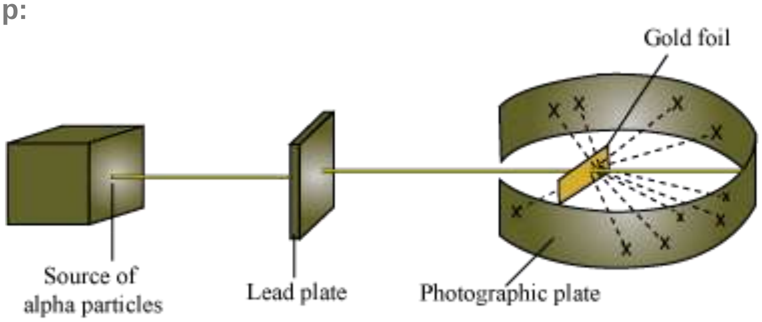
- An atom possesses a spherical shape in which the positive charge is uniformly distributed.



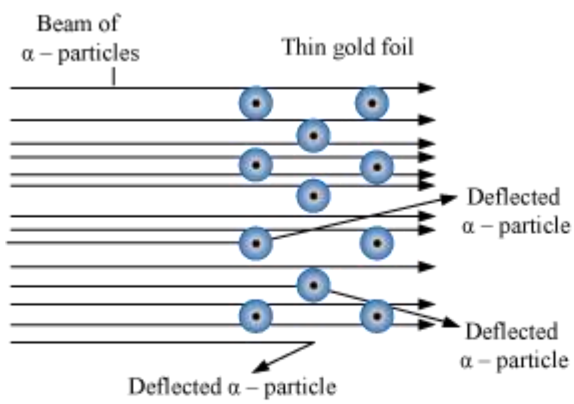
- Known as plum pudding, raisin pudding or watermelon model
- Feature: The mass of an atom is assumed to be uniformly distributed across the atom.

Rutherford's scattering experiment

- **Experimental Setup:**



- A stream of high-energy α-particles from a radioactive source was directed at the thin gold foil.
- Gold foil had a circular fluorescent screen (of zinc sulphide) around it.
- A tiny flash of light was observed at the point, whenever an α-particle struck the screen.
- **Observation:**



- Most of the alpha (α) particles passed through the gold foil without deflection.
- Some of the α-particles (a small fraction) were deflected by small angles.
- Very few of them were deflected nearly by 180°.
- **Conclusions:**
- Most of the space in an atom is empty as most of the α-particles passed through the gold foil un-deflected.
- The positive charge is concentrated in a very small volume that repelled and deflected few positively charged α-particles. This small volume of the atom is called nucleus.
- The volume of the nucleus is negligibly small as compared to the total volume of the atom.

Rutherford's Model of Atom

Based on his experiment, Rutherford proposed:

- Positive charge and most of the mass of an atom are densely concentrated in a small region (called nucleus).
- Electrons revolve around the nucleus, with very high speeds, in circular paths called orbits.
- Electrons and nucleus are held together in the atom by a strong electrostatic force of attraction.

Drawbacks of Rutherford's Model

- It cannot explain the stability of an atom on the basis of classical mechanics and electromagnetic theory.
- If the electrons were stationary, then the strong electrostatic force of attraction between the dense nucleus and the electrons would pull the electrons towards the nucleus. Thus, it cannot explain the stability of an atom.
- Rutherford's model does not give any idea about the distribution of electrons around the nucleus (i.e., the electronic structure of the atom), and about their energy.
- It cannot explain the atomic spectra.

Atomic Number and Mass Number

- Atomic number (*Z*) = Number of protons in the nucleus of an atom
  = Number of electrons in a neutral atom
- Mass number (*A*) = Number of protons (*Z*) + Number of neutrons (*n*)

Isotopes and Isobars

- Isotopes are the atoms with the same atomic number, but different mass numbers.
  For example, ${}^{1}_{1}H, {}^{2}_{1}D$ and ${}^{3}_{1}T$ are the isotopes of hydrogen.
- Isobars are the atoms with the same mass number, but different atomic numbers.
  For example, ${}^{14}_{6}C$ and ${}^{14}_{7}N$; ${}^{40}_{18}Ar$ and ${}^{40}_{20}Ca$

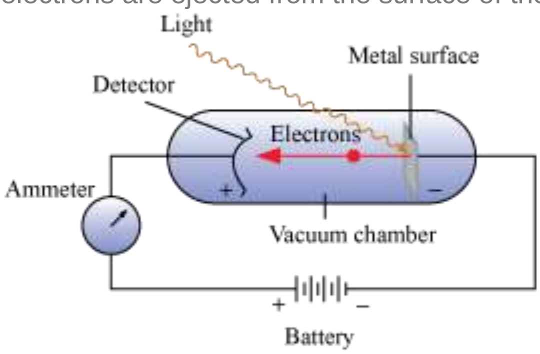
Example :

In Rutherford's scattering experiment, why a movable circular screen coated with zinc sulphide is placed around the gold foil?

To detect the α−particles after scattering, a movable circular screen coated with zinc sulphide is placed. When α−particles strike the zinc sulphide screen, they produce flashes of light or scintillations which can be detected. By examining different positions on the screen, it is possible to determine the proportions of the α−particles which got deflected through various angles.

Photoelectric Effect

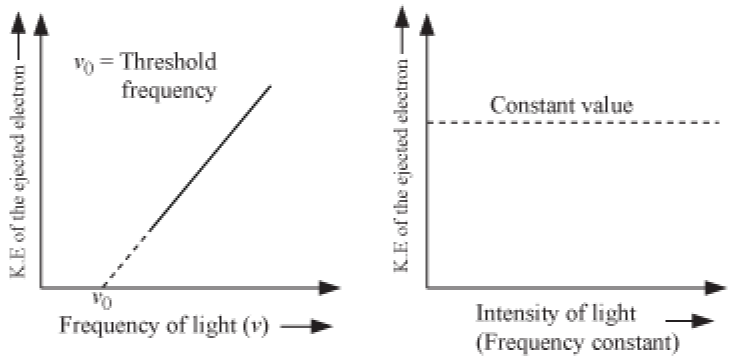
- When certain metals such as potassium, rubidium, caesium, etc. are exposed to a beam light, the electrons are ejected from the surface of the metals as shown in the figure below.



- 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 (v).

  i.e., $E \propto v$

  Or, $E = hv$

  '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,

$E = hv$

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

Example :

If the number of photons emitted by a 100 watt bulb is 4.01 × 10^{20}, then what is the wavelength of the electromagnetic radiation to be emitted?

Number of photons emitted by the bulb = 4.01 × 10^{20}
Energy of 1 photon = 100***/*** **(**4.01 × 10^{20}) = 24.938 × 10-^{20} J

$$\text{Now, energy of a photon, } E = \frac{hc}{\lambda}$$

$$\text{or, } \lambda = \frac{hc}{E} = \frac{6.62 \times 10^{-34}\ \text{Js} \times 3 \times 10^{8}\ \text{ms}^{-1}}{24.938 \times 10^{-20}\ \text{J}}$$

$$\text{or, } \lambda = 0.8 \times 10^{-6}\ \text{m} = 800\ \text{nm}$$

Example :

What will be the kinetic energy (in eV) of an electron with wavelength 0.7 nm?

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

$$mv = \frac{h}{\lambda} = \frac{6.625\times10^{-27}}{0.7\times10^{-7}}\,\text{g cm/s}$$

$$= 9.46\times10^{-20}\,\text{g cm/s}$$

$$\text{K.E.} = \frac{1}{2}mv^2 = \frac{1}{2m}(mv)^2$$

$$= \frac{1}{2\times9.1\times10^{-28}}\times(9.46\times10^{-20})^2$$

$$= 4.91\times10^{-12}\,\text{ergs}$$

$$\text{K.E.} = \frac{4.91\times10^{-12}}{1.602\times10^{-12}} \qquad \left[\because 1\,ev = 1.6\times10^{-12}\,\text{ergs}\right]$$

$$= 3.06\,ev$$

So, applied potential = 3 eV.

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 (v) 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,

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

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,

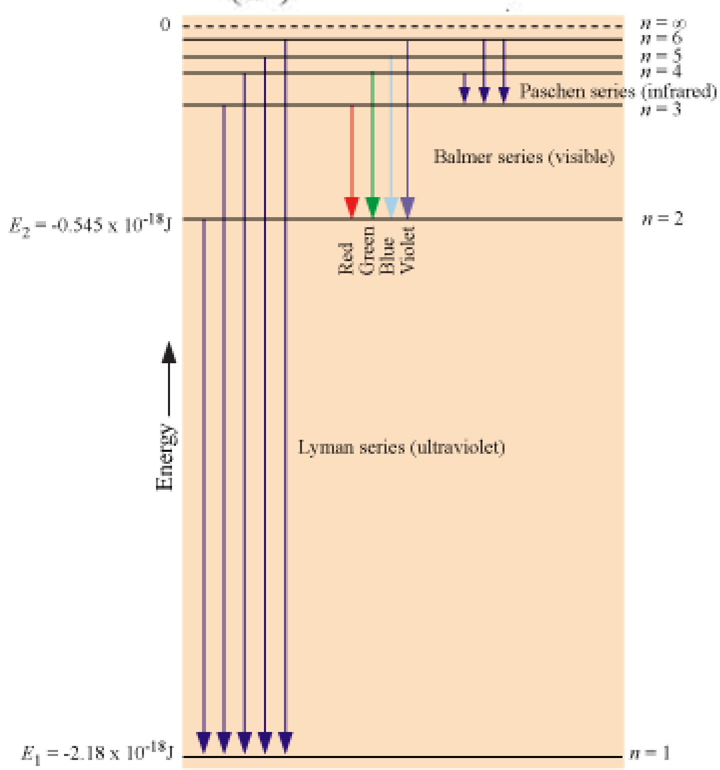
  $n = \infty$ (It is called ionized hydrogen atom)

$$E_1 = -2.18 \times 10^{-18}\left(\frac{1}{1^2}\right) = -2.18 \times 10^{-18}\ \text{J}$$

Thus,

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

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



(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,

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

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

- 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.

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

- 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

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

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

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,

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

$= \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 10^{-6}\ \text{kg}}$

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

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:

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

$= \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 9.11 \times 10^{-31}\text{kg}}$

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

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**.

Example :

Calculate the uncertainty in the position of a proton moving with a velocity of 400 ms^{-1}, accurate up to 0.001 %.

Uncertainty in velocity,

$$\Delta v = 400 \times \frac{0.001}{100} = 4 \times 10^{-3}\ \text{ms}^{-1}$$

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

where, Δx is the uncertainity in position.

Δv is the uncertainity in velocity.

m is the mass of the proton and.

h is the Planck's constant.

$$\text{Or, } \Delta x = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 1.67 \times 10^{-27} \times 4 \times 10^{-3}}$$

$$= 0.079 \times 10^{-4}\ \text{m}$$

$$= 7.9 \times 10^{-6}\ \text{m}$$

Hence, the uncertainty in the position of the proton is 7.9×10^{-6} m.

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

- 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.

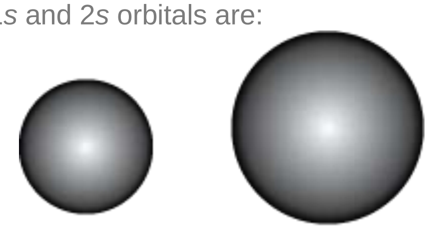
For 1*s* orbital, the probability density is maximum at the nucleus and it decreases sharply as we move away from it.

- 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.

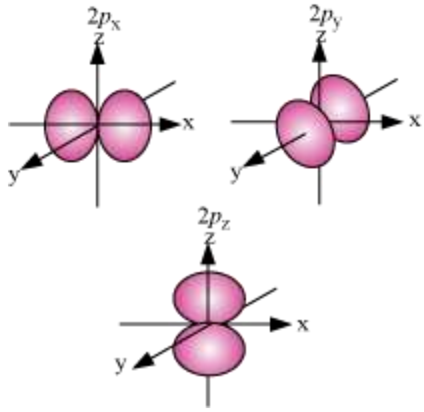
Boundary Surface Diagrams

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

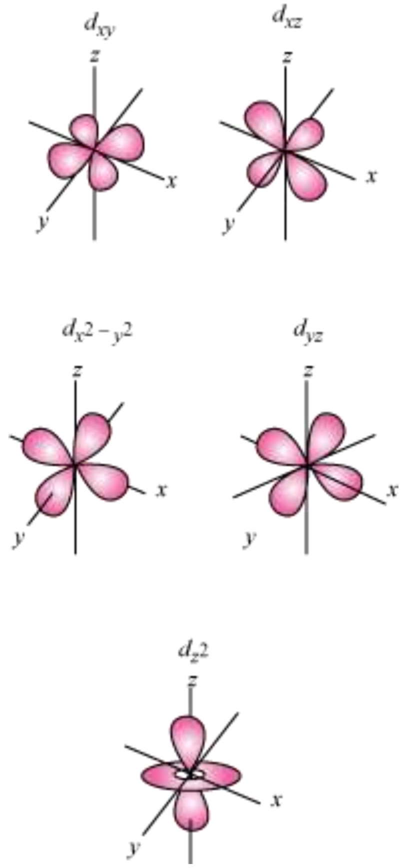


1*s* 2*s*

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



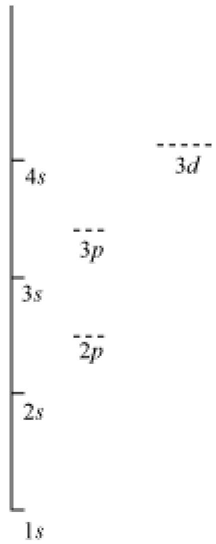
- Boundary diagrams for the five 3*d* orbitals are shown in the figure below.



-
- 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:
  1*s* < 2*s* = 2*p* < 3*s* = 3*p* = 3*d* < 4*s* = 4*p* = 4*d* = 4*f* < ….
- 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).

Example :
A non-metal forms a trinegative ion. It is present in 3rd period and 15th group of the periodic table. Calculate the number of neutrons present in the ion.

The element is phosphorus having atomic number 15 and mass number 31
Number of protons = Atomic number = 15
Number of electron = Atomic number + 3 = 18
Number of neutrons = Mass number − Atomic number = 31 − 15 = 16.

Example :
A monatomic cation with tripositive charge contains 23 electrons and 33 neutrons. The element is

- A) Al
- B) Co
- C) Fe
- D) Cr

The number of electrons in the atom
= 23 + 3
= 26

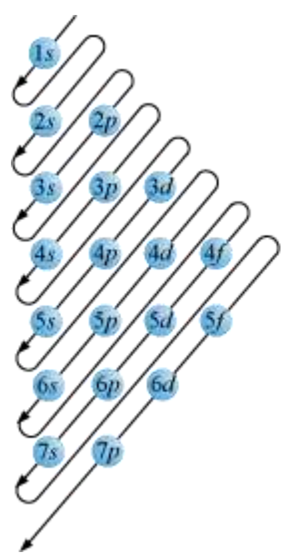
Number of electron = Number of protons = Atomic number of element = 26
So, the element is **iron**.

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

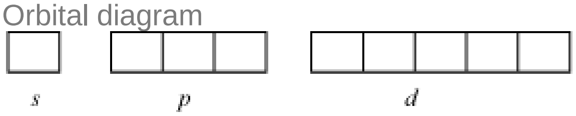
- No two electrons in an atom can have the same set of all the four quantum numbers.
- Two electrons can have the same value of three quantum numbers *n*, *l*, and m_e, but must have the opposite spin quantum number (*s*).
- The maximum number of electrons in the shell with the principal quantum number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

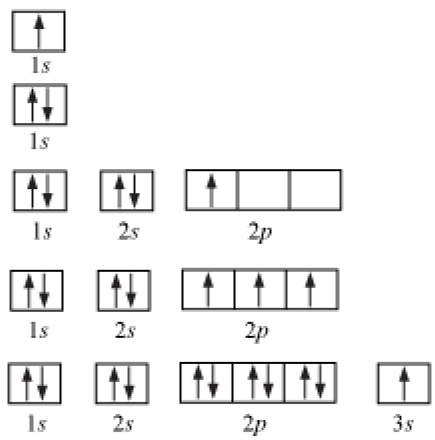
$H \rightarrow 1s^1$;

$He \rightarrow 1s^2$;

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

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

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



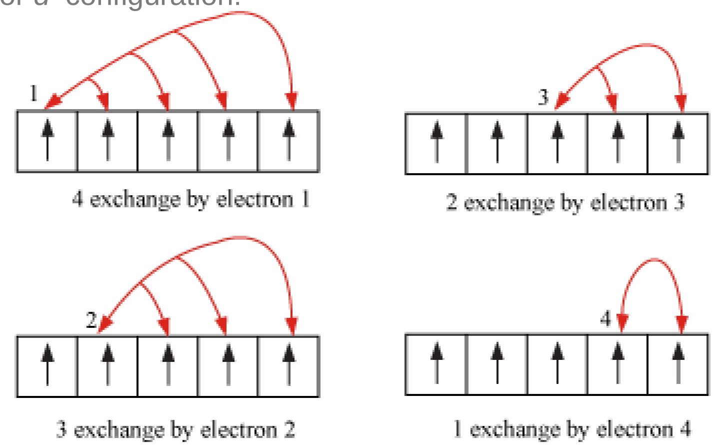
Stability of completely filled and half-filled sub-shells

- 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.

Example :
Number of unpaired electrons of an atom having electronic configuration 2K 8L 9M 2N are

- A) 4
- B) 3
- C) 2
- D) 1

Total number of electrons present in the atom is
2 + 8 + 9 + 2 = 21

Electronic configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$
∴ Number of unpaired electrons = 1

@@@