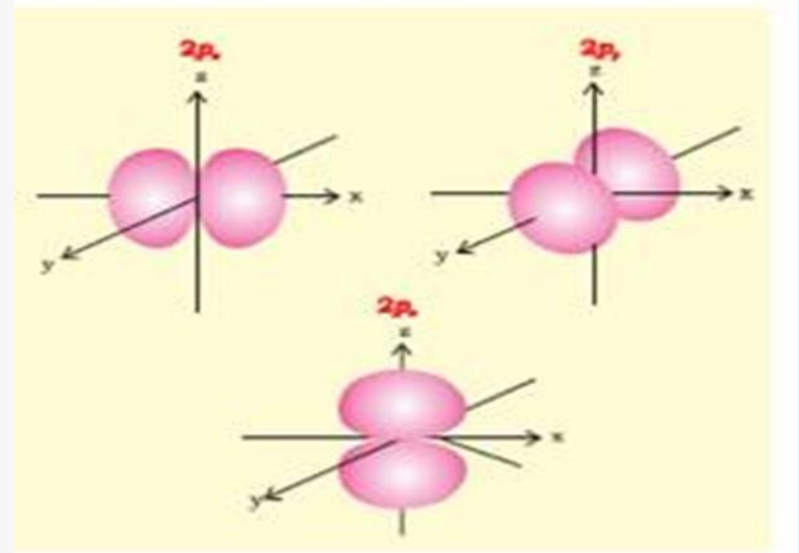
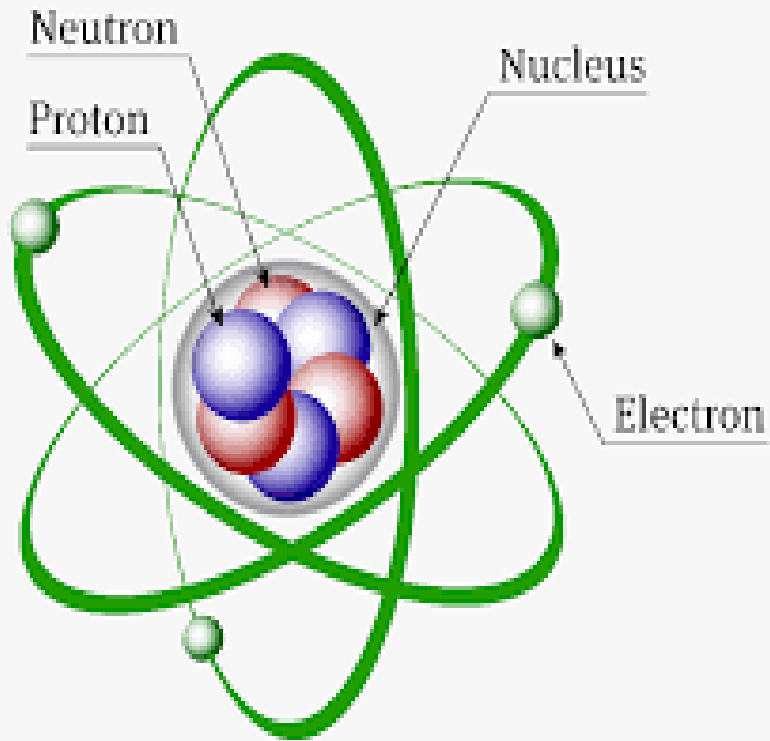


STRUCTURE OF ATOM



A HISTORY OF THE ATOM: THEORIES AND MODELS

How have our ideas about atoms changed over the years? This graphic looks at atomic models and how they developed

SOLID SPHERE MODEL

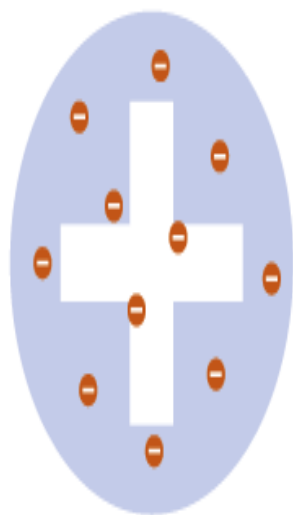


JOHN DALTON



1803

PLUM PUDDING MODEL



J.J. THOMSON



1904

NUCLEAR MODEL

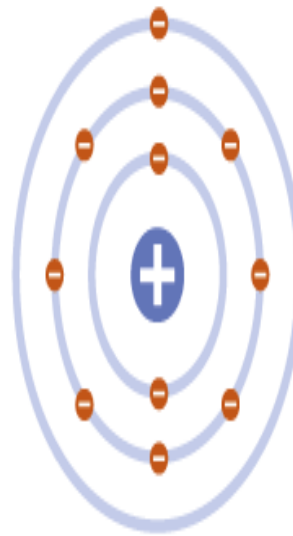


ERNEST RUTHERFORD



1911

PLANETARY MODEL



NIELS BOHR



1913

QUANTUM MODEL



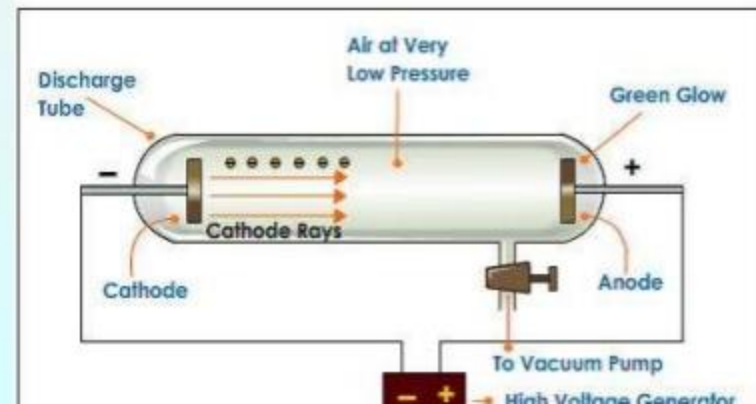
ERWIN SCHRÖDINGER



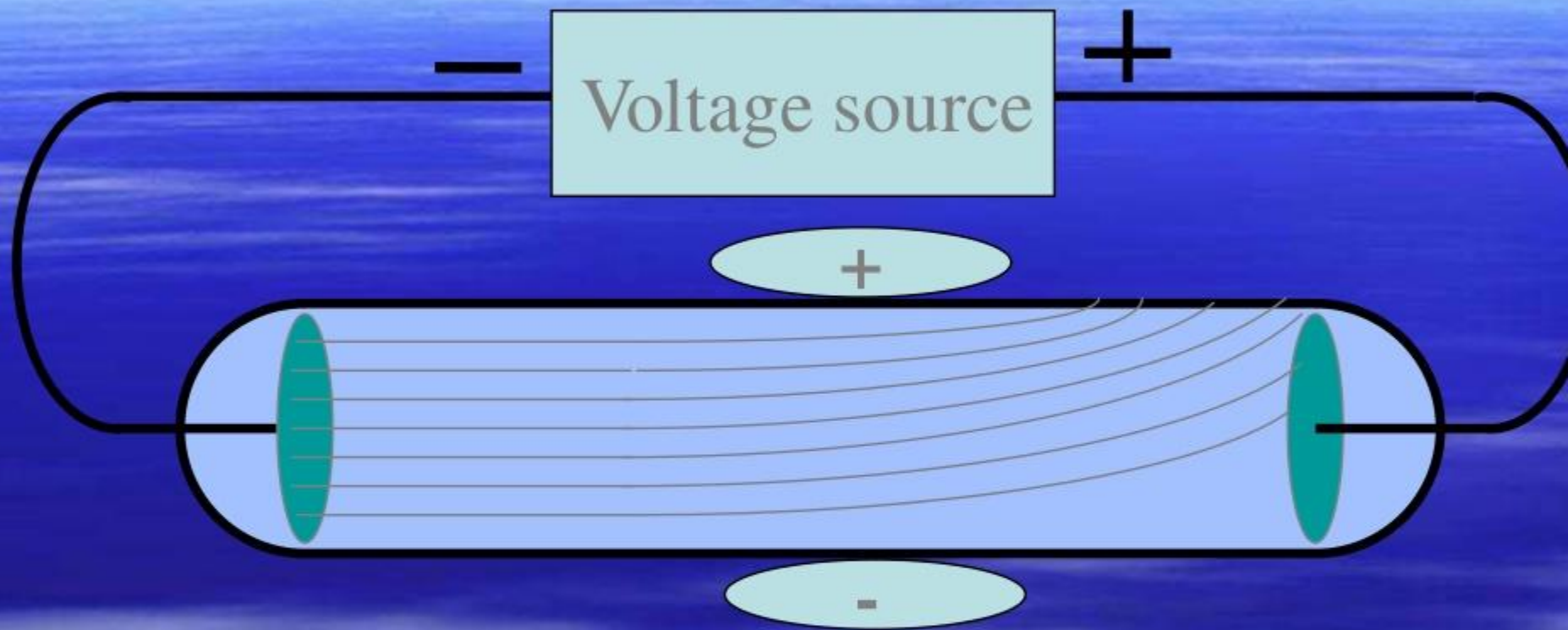
1926

DISCOVERY OF AN ELECTRON

- ◆ An electron was discovered by cathode ray discharge tubes experiment.
- ◆ A cathode ray tube is made of glass containing two thin pieces of metal called electrodes, sealed in it. The electrical discharge through the gas could be observed only at very low pressures and at very high voltage. The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, the current starts to flow through a stream of particles moving in the tube from the negative electrode to the positive one. These rays were called the cathode rays or cathode ray particles.
- ◆ The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material called zinc sulphide coating, a bright spot on the coating is developed.



Thomson's Experiment



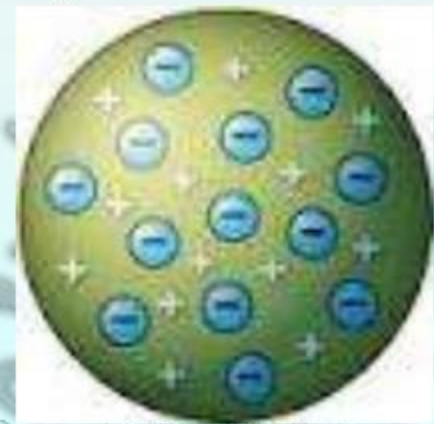
- By adding an electric field he found that the moving pieces were negative. He called these moving pieces “electron”

Discovery of protons and neutrons

- ◆ Electrical discharge carried out in the modified cathode rays tube led to the discovery of particles carrying positive charge also known as **canal rays**.
- ◆ The characteristics of these rays are:
 - Unlike cathode rays, the positively charged particles depend upon the nature of gas present in the cathode ray tube. These gases are simple positively charged ions.
 - The charge to mass ratio of the particles is found to depend on the gas from which they originate.
 - Some of the +vely charged particles carry a multiple of the fundamental unit of electrical charge.
 - The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

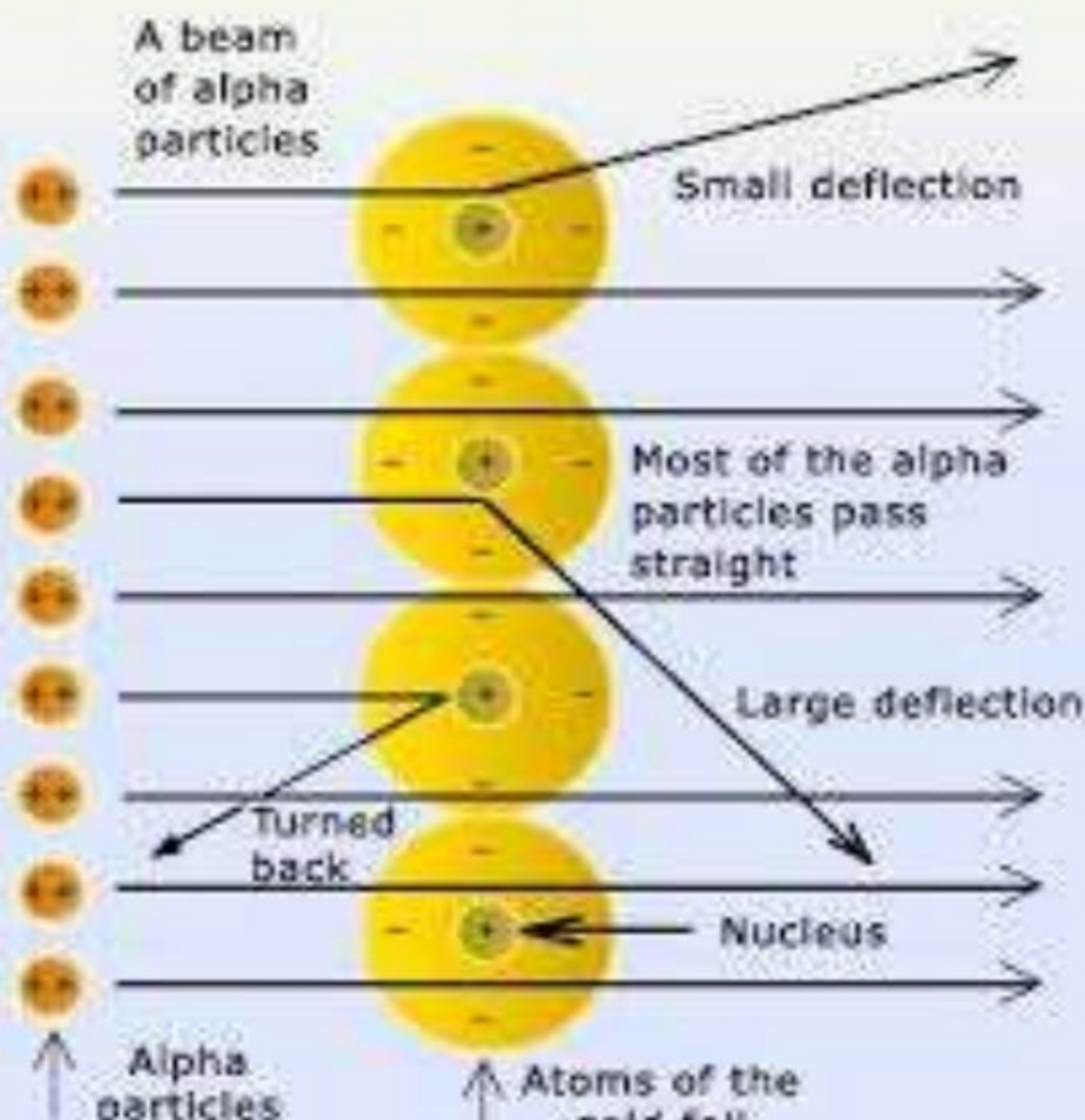
Thomson's model of an atom

- ◆ According to Thomson, atom was in a spherical in shape which had positive charged particle sand negative charged particles equally distribution and hence it was electrically neutral.
- ◆ Its observation could be called as a plum pudding model or a watermelon.



Rutherford's model of atom

- ▶ Famous experiment of Rutherford was the α -particle scattering experiment.
- ▶ A stream of high energy α particles from a radioactive source was directed at a thin foil of a gold metal. The thin foil had a circular fluorescent zinc sulphide screen around it. Whenever α -particles struck the screen, a tiny flash of light was produced at the point.



- The results of this experiment were unexpected.
- ◆ (1) most of the α -particles passed through the gold foil undeflected.
 - ◆ (2) a small fraction of α -particles was deflected by small angles
 - ◆ (3) a very few α -particles (-1 in 20,000) bounced back, that is were deflected by nearly 180 degree.

Observations:

- ◆ Most of the space in the atom is empty as most of the α -particles passed through the foil undeflected.
- ◆ A few +vely charged α -particles were deflected.
- ◆ The deflection must be due to enormous repulsive force showing the positive charge in the atom.
- ◆ The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α -particles.

Conclusions:

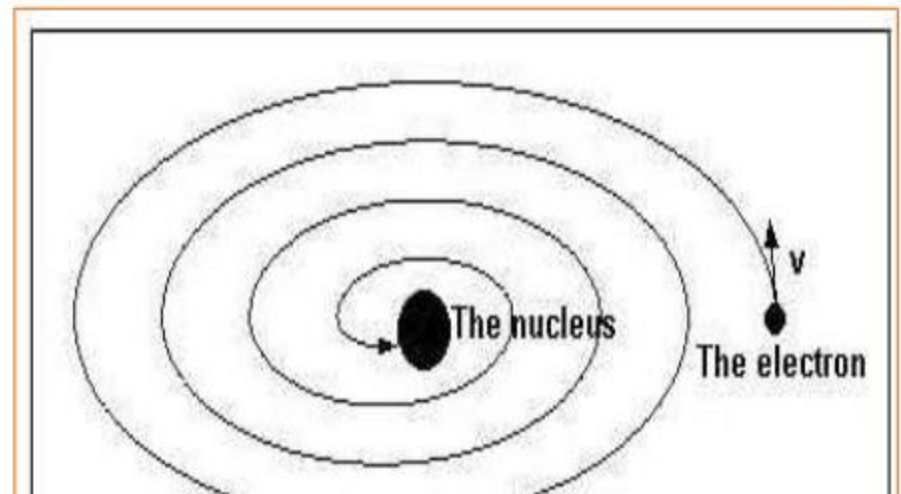
The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This concentrated region was called nucleus.

The nucleus was surrounded by electrons moving in a very high speed in circular paths called orbits.

Electrons and the nucleus are held together by the electrostatic forces of attraction.

The model created by [Rutherford](#) had still some serious discordance. According to the classic science, electron moving around the nucleus the planetary model of atom, is unstable. Because, in the planetary model of atom, the electron should radiate energy and finally fall into the nucleus.

The planetary model of atom



Electromagnetic radiations:

The radiations which are associated with electrical and magnetic fields are called electromagnetic radiations. When an electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves. These waves are called electromagnetic waves or electromagnetic radiations.

Properties of electromagnetic radiations:

- a. Oscillating electric and magnetic field are produced by oscillating charged particles. These fields are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
- b. They do not need a medium to travel. That means they can even travel in vacuum.

Characteristics of electromagnetic radiations:

a. **Wavelength:** It may be defined as the distance between two neighbouring crests or troughs of wave as shown. It is denoted by λ .

b. **Frequency (v):** It may be defined as the number of waves which pass through a particular point in one second.

c. **Velocity (v):** It is defined as the distance travelled by a wave in one second. In vacuum all types of electromagnetic radiations travel with the same velocity. Its value is $3 \times 10^8 \text{ m sec}^{-1}$. It is denoted by v

d. Wave number: Wave number is defined as the number of wavelengths per unit length.

Velocity = frequency \times wavelength $c = v\lambda$

Planck's Quantum Theory-

- o The radiant energy is emitted or absorbed not continuously but discontinuously in the form of small discrete packets of energy called 'quantum'. In case of light, the quantum of energy is called a 'photon'
 - o The energy of each quantum is directly proportional to the frequency of the radiation,
i.e. $E \propto \nu$ or $E = h\nu$ where $h =$ Planck's constant = 6.626×10^{-34} Js
 - o Energy is always emitted or absorbed as integral multiple of this quantum. $E = n h \nu$ Where $n = 1, 2, 3, 4, \dots$
- Black body:** An ideal body, which emits and absorbs all frequencies, is called a black body. The radiation emitted by such a body is called black body radiation.

Q: Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 \AA .

Q: The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz).

Q: Calculate energy of one mole of photons of radiation whose frequency is $5 \times 10^{14} \text{ Hz}$.

Q: A 100 watt bulb emits monochromatic light of wavelength 400 nm . Calculate the number of photons emitted per second by the bulb.

Photoelectric effect:

The phenomenon of ejection of electrons from the surface of metal when light of suitable frequency strikes it is called photoelectric effect. The ejected electrons are called photoelectrons.

- o Threshold frequency (ν_0): For each metal there is a characteristic minimum frequency below which photoelectric effect is not observed. This is called threshold frequency.

- o If frequency of light is less than the threshold frequency there is no ejection of electrons no matter how long it falls on surface or how high is its intensity.

Photoelectric work function (W_0):

The minimum energy required to eject electrons is called photoelectric work function. $W_0 = h\nu_0$

Kinetic Energy of the ejected electrons :

$$h(\nu - \nu_0) = \frac{1}{2} m_e v^2$$

Q: When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of $1.68 \times 10^5 \text{ J mol}^{-1}$. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause the photoelectron to be emitted?

Q: The threshold frequency ν_0 for a metal is $7.0 \times 10^{14} \text{ s}^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times 10^{15} \text{ s}^{-1}$ hits the metal.

Dual behavior of electromagnetic radiation

The light possesses both particle and wave like properties, i.e., light has dual behavior .

Whenever radiation interacts with matter, it displays particle like properties.(Black body radiation and photoelectric effect)

Wave like properties are exhibited when it propagates(interference and diffraction)

Spectrum :-

When a white light is passed through a prism, it splits into a series of coloured bands known as **spectrum**.

Spectrum is of two types:(a) Continuous and line spectrum The spectrum which consists of all the wavelengths is called continuous spectrum.

(b) line spectrum A spectrum in which only specific wavelengths are present is known as a line spectrum. It has bright lines with dark spaces between them.

Electromagnetic spectrum is a continuous spectrum. It consists of a range of electromagnetic radiations arranged in the order of increasing wavelengths or decreasing frequencies. It extends from radio waves to gamma rays.

Spectrum is also classified as emission and line spectrum.

o **Emission spectrum:** The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum.

o **Absorption spectrum** is the spectrum obtained when radiation is passed through a sample of material. The sample absorbs radiation of certain wavelengths. The wavelengths which are absorbed are missing and come as dark lines.

Hydrogen Spectrum

The emission spectrum of atomic hydrogen has been divided into a number of **spectral series**, with wavelengths given by the Rydberg formula. These observed spectral lines are due to the electron making transitions between two energy levels in an atom. The classification of the series by the Rydberg formula was important in the development of quantum mechanics. The spectral series are important in astronomical spectroscopy for detecting the presence of hydrogen and calculating red shifts.

Series

Series	n_1	n_2	Spectral Region
Lyman	1	2, 3, 4, 5 ...	Ultraviolet
Balmer	2	3, 4, 5 ...	Visible
Paschen	3	4, 5 ...	Infrared
Brackett	4	5, 6 ...	Infrared
Pfund	5	6, 7...	Infrared

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

Spectral Lines for atomic hydrogen:

Rydberg equation

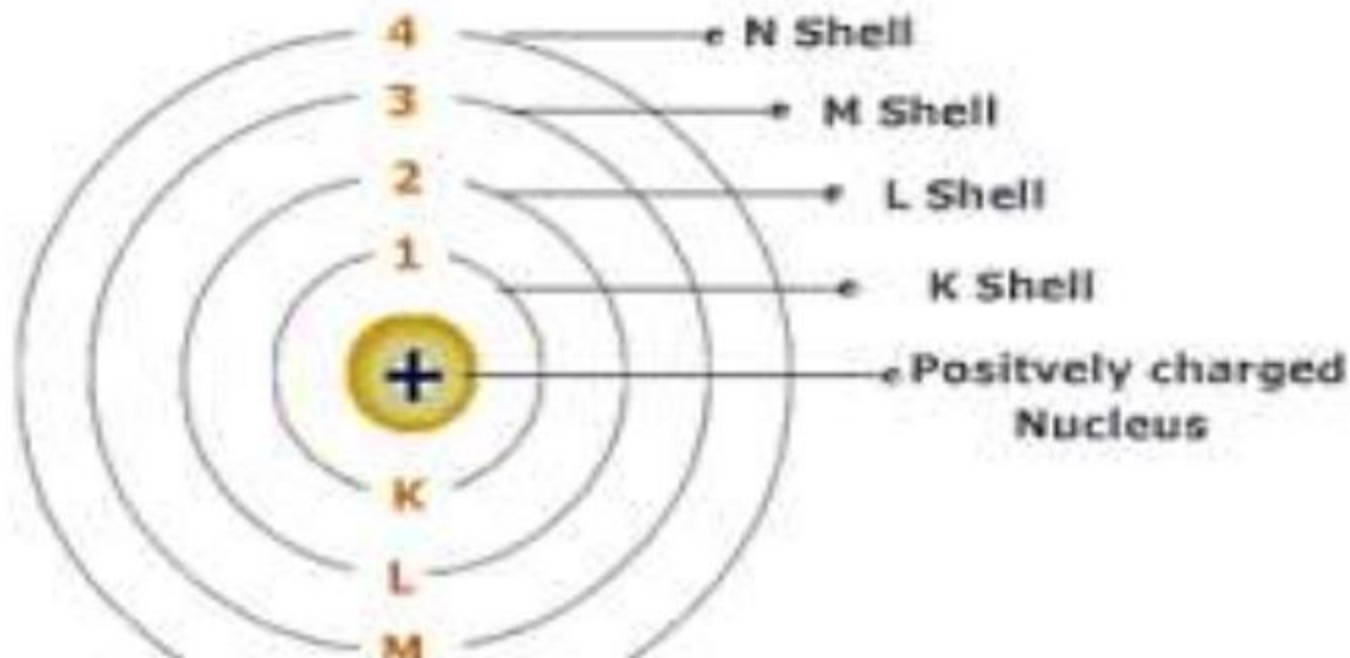
$$\bar{\nu} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$$

R = Rydberg's constant = 109677 cm^{-1}

Q: What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Bohr's Model of the Atom

- The special orbits known as discrete orbits of electron are allowed inside an atom. These orbits or shells are represented by the letters K,L,M,N,..... Or the numbers , $n=1,2,3,4,.....$



Bohr's model for hydrogen atom:

- a. An electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits or energy levels. These orbits are arranged concentrically around the nucleus
- b. As long as an electron remains in a particular orbit, it does not lose or gain energy and its energy remains constant.
- c. When transition occurs between two stationary states that differ in energy, the frequency of the radiation absorbed or emitted can be calculated

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

An electron can move only in those orbits for which its angular momentum is an integral multiple of $h/2\pi$

$$m_e v r = n \cdot \frac{h}{2\pi} \quad n = 1, 2, 3, \dots$$

The radius of the n th orbit is given by

$$r_n = 52.9 \times n^2 / Z \text{ pm}$$

Energy of electron in n th orbit is :

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

Q: Calculate the energy associated with the first orbit of He^+ . What is the radius of this orbit?

Q: How much energy is required to ionize a H atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from $n = 1$ orbit).

Q: The energy associated with the first orbit in the hydrogen atom is $-2.18 \times 10^{-18} \text{ J atom}^{-1}$. What is the energy associated with the fifth orbit?

Q: Calculate the radius of Bohr's fifth orbit for hydrogen atom.

Q: Calculate the wavenumber for the longest wavelength transition in the Balmer series of atomic hydrogen. 2.18 What is the energy in joules, required to shift the electron of the hydrogen atom

Limitations of Bohr's model of atom:

- a. Bohr's model failed to account for the finer details of the hydrogen spectrum.
- b. Bohr's model was also unable to explain spectrum of atoms containing more than one electron.

Dual behavior of matter:

de Broglie proposed that matter exhibits dual behavior i.e. matter shows both particle and wave nature. de Broglie's relation is

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

Q: What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s^{-1} ?

Q: Calculate the wavelength of an electron moving with a velocity of $2.05 \times 10^7 \text{ m s}^{-1}$.

Q: The mass of an electron is $9.1 \times 10^{-31} \text{ kg}$. If its K.E. is $3.0 \times 10^{-25} \text{ J}$, calculate its wavelength.

Heisenberg's uncertainty principle:

It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.

The product of their uncertainties is always equal to or greater than $h/4\pi$.

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

where $\Delta x =$ uncertainty in position,
 $\Delta p =$ uncertainty in momentum

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

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

Q. Using Heisenberg's uncertainty principle, show that an electron cannot exist inside the nucleus.

Failure of Bohr's model:

- a. It ignores the dual behavior of matter.
- b. It contradicts Heisenberg's uncertainty principle.

Quantum numbers:

There are a set of four quantum numbers which specify the energy, size, shape and orientation of an orbital. To specify an orbital only three quantum numbers are required while to specify an electron all four quantum numbers are required.

Principal quantum number (n): It identifies shell, determines sizes and energy of orbitals

N	1	2	3	4
Shell no.:	K	L	M	N
Total number of orbitals in a shell = n^2	1	4	9	16
Maximum number of electrons = $2n^2$	2	8	18	32

Azimuthal quantum number (l): Azimuthal quantum number. 'l' is also known as orbital angular momentum or subsidiary quantum number. l.

It identifies sub-shell, determines the shape of orbitals, energy of orbitals in multi-electron atoms along with principal quantum number and orbital angular momentum, *i.e.*, The number of orbitals in a subshell = $2l + 1$. For a given value of n , it can have n values ranging from 0 to $n-1$. Total number of subshells in a particular shell is equal to the value of n .

Subshell notation	s	p	d	f	g
Value of 'l'	0	1	2	3	4
Number of orbitals	1	3	5	7	

Magnetic quantum number or Magnetic orbital quantum number (m_l):

It gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis.

For any sub-shell (defined by 'l' value) $2l+1$ values of m_l are possible.

For each value of l , $m_l = -l, -(l-1), -(l-2)\dots 0, 1\dots(l-2), (l-1), l$

Electron spin quantum number (m_s): It refers to orientation of the spin of the electron. It can have two values $+1/2$ and $-1/2$. $+1/2$ identifies the clockwise spin and $-1/2$ identifies the anti-clockwise spin.

Nodal surfaces or simply nodes :

The region where this probability density function reduces to zero is called nodal surfaces or simply nodes.

Radial nodes:

Radial nodes occur when the probability density of wave function for the electron is zero on a spherical surface of a particular radius.

Number of radial nodes = $n - l - 1$

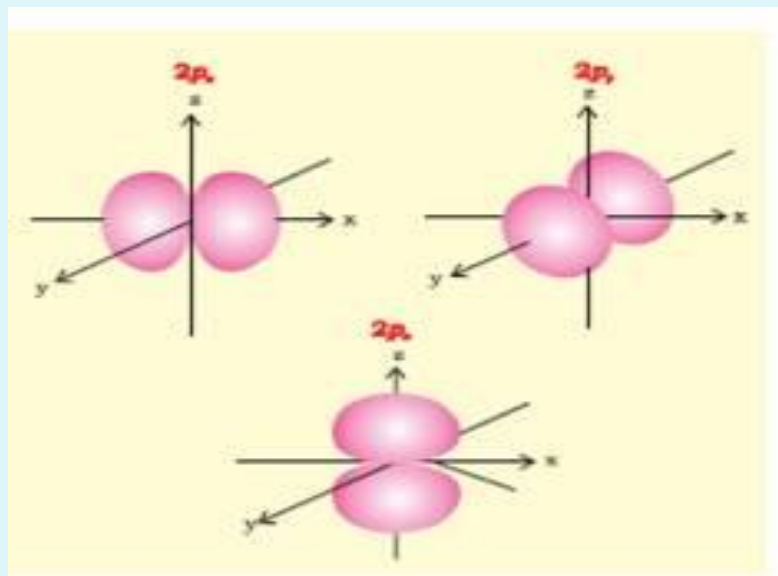
Angular nodes:

Angular nodes occur when the probability density wavefunction for the electron is zero along the directions specified by a particular angle.

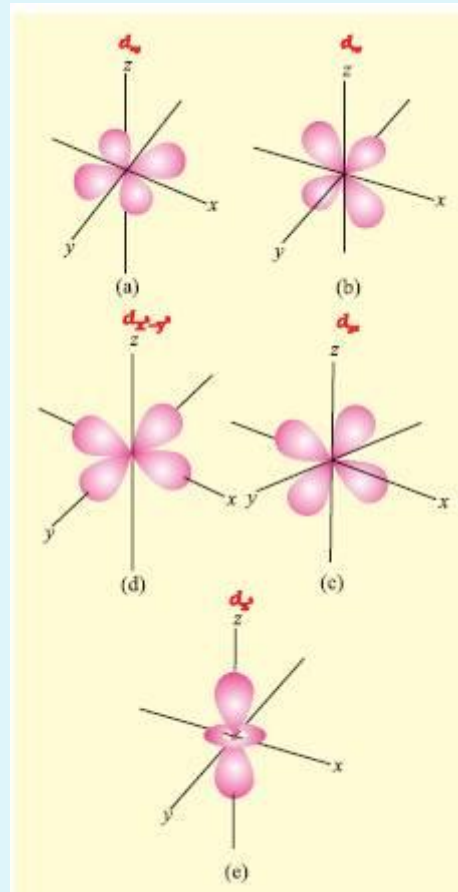
Number of angular nodes = l

Total number of nodes = $n - 1$

Degenerate orbitals: Orbitals having the same energy are called degenerate orbitals. Shape of p and d-orbitals



d Orbitals



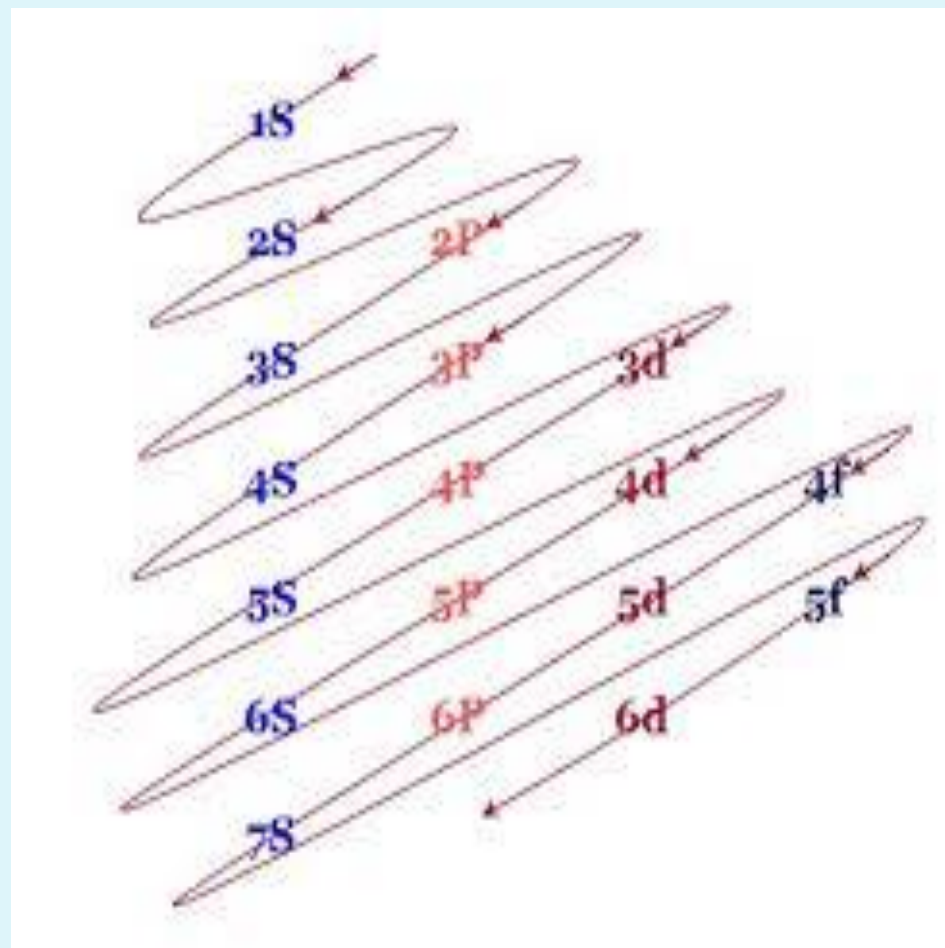
Aufbau Principle:

In the ground state of the atoms, the orbitals are filled in order of their increasing energies

$n+l$ rule-

Orbitals with lower value of $(n+l)$ have lower energy. If two orbitals have the same value of $(n+l)$ then orbital with lower value of n will have lower energy.

The order in which the orbitals are filled is as follows:
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s...



Pauli Exclusion Principle:

No two electrons in an atom can have the same set of four quantum numbers. Only two electrons may exist in the same orbital and these electrons must have opposite spin.

Hund's rule of maximum multiplicity:

Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

Stability of completely filled and half filled subshells:

- a. Symmetrical distribution of electrons- the completely filled or half filled sub-shells have symmetrical distribution of electrons in them and are more stable.

- b. Exchange energy-The two or more electrons with the same spin present in the degenerate orbitals of a sub-shell can exchange their position and the energy released due to this exchange is called exchange energy. The number of exchanges is maximum when the subshell is either half filled or completely filled. As a result the exchange energy is maximum and so is the stability.

Q: Using s, p, d notations, describe the orbital with the following quantum numbers.

(a) $n=1, l=0$; (b) $n = 3; l=1$ (c) $n = 4; l =2$; (d) $n=4; l=3$.

Q: An electron is in one of the 3d orbitals. Give the possible values of n , l and m_l for this electron.

Q: Indicate the number of unpaired electrons in : (a) P, (b) Si, (c) Cr, (d) Fe and (e) Kr. 2.67

Q: How many subshells are associated with $n = 4$? How many electrons will be present in the subshells having m_s value of $-1/2$ for $n = 4$?

Q: (i) An atomic orbital has $n = 3$. What are the possible values of l and m_l ?

(ii) List the quantum numbers (m_l and l) of electrons for 3d orbital.

(iii) Which of the following orbitals are possible?

1p, 2s, 2p and 3f

(iv) What is the lowest value of n that allows g orbitals to exist?