Welcome to

Aakash + BYJU'S LIVE

Atomic Structure

J.J. Thomson's Model

Rutherford's Model

Bohr's Model

Planck's Quantum Theory

de Broglie's hypothesis

SWE

Heisenberg's Uncertainty principle

Discovery of electron

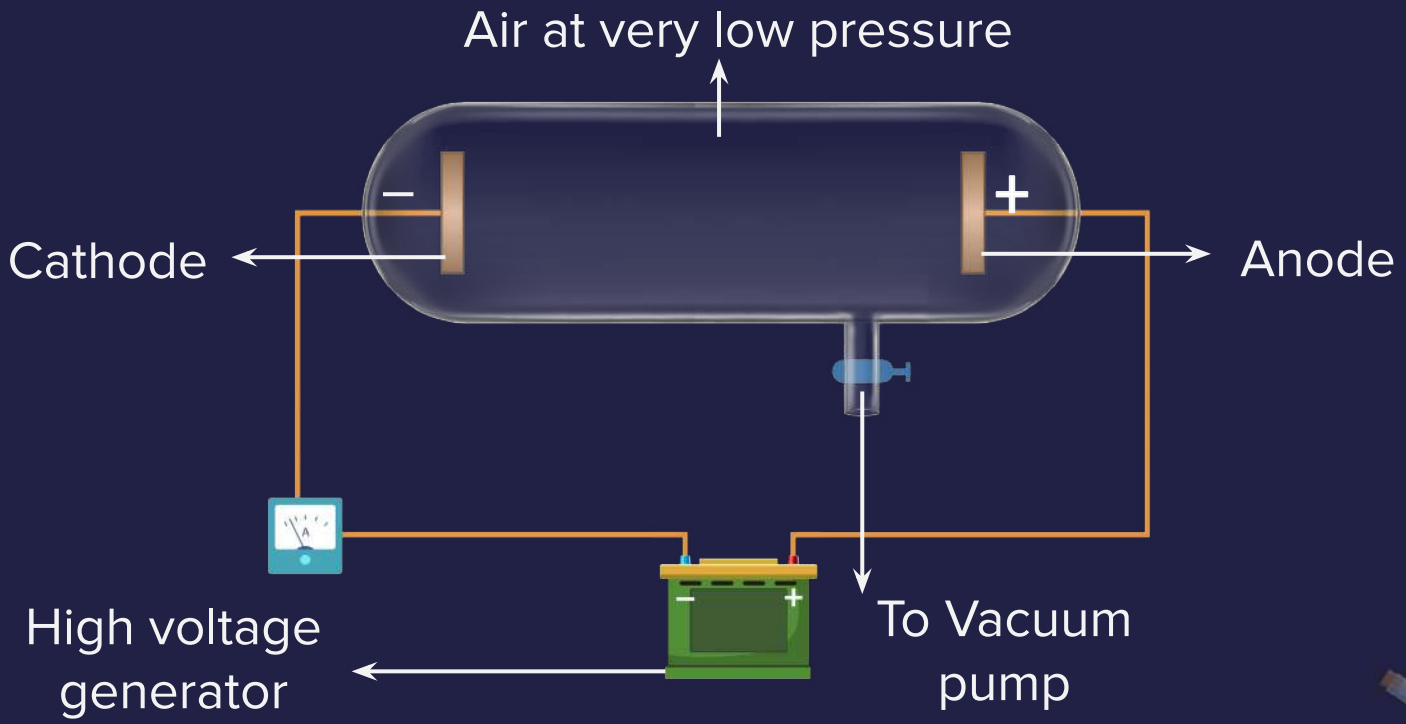
Cathode rays

In 1891, George Johnstone Stoney named the fundamental unit of electricity as 'electron'

J. J. Thomson and his team identified electron as a particle in 1897

Discovery of electron

Discharge tube: Cylindrical hard glass tube fitted with two metallic electrodes connected to a battery.

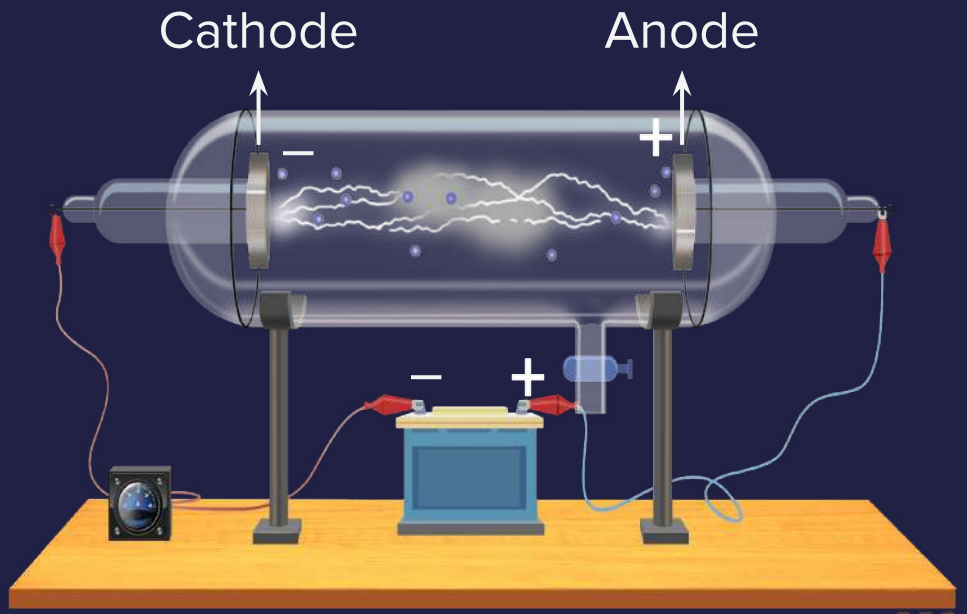


Discovery of electron

Observations

Readings of electric current was observed

Anode end of the tube showed a greenish glow on the ZnS screen



Discovery of electron

Why are Gases used under LOW pressure?

At high pressure, more number of gas molecules are present and so there is more obstructions in the paths of electrons which prevents electrons from reaching the anode.

Discovery of electron

Observation and Characteristics

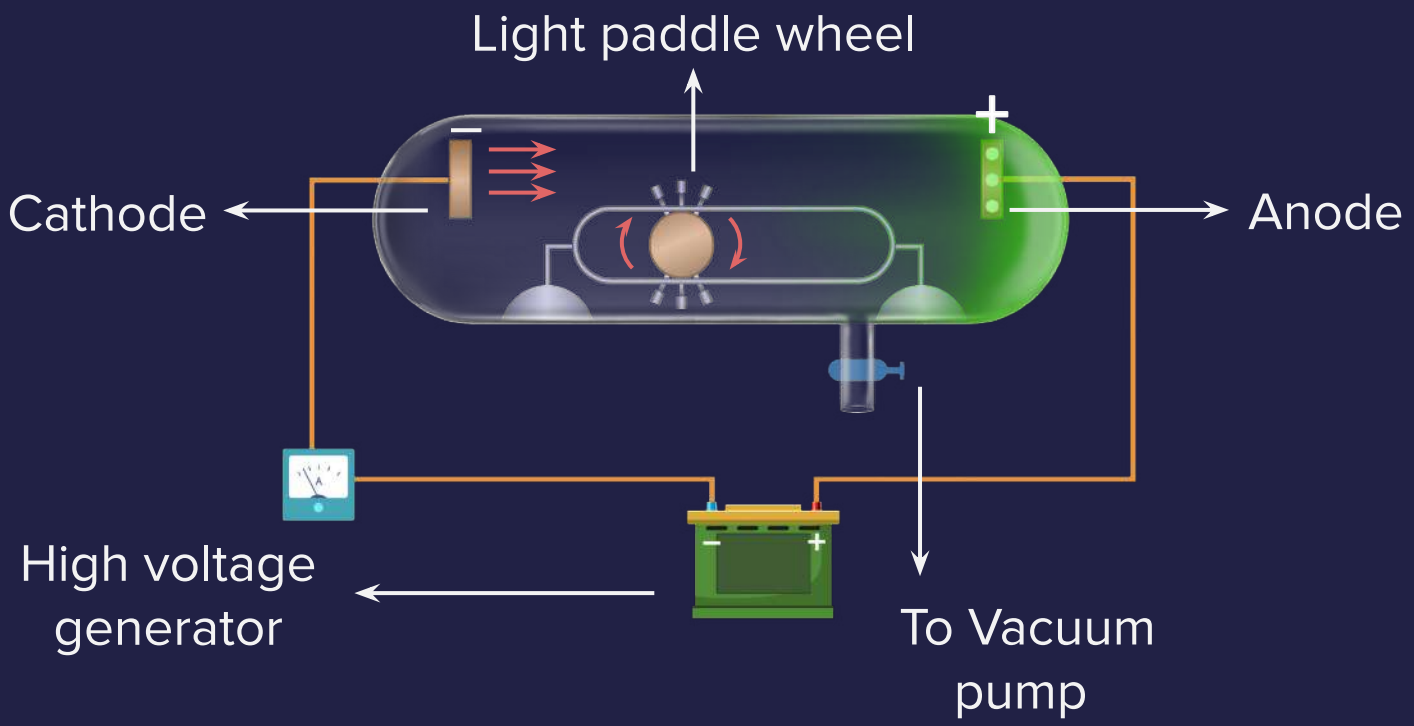
1. Cathode rays move from cathode to anode.

2. Cathode rays travel in a straight line with high velocity in the absence of electric & magnetic fields.

3. Cathode rays are more efficiently observed with the help of a fluorescent or phosphorescent material like ZnS.

4. Cathode rays rotate the light paddle wheel placed in their path. It shows that the particles of cathode ray particles are **material particles** which have **mass** and **velocity.**

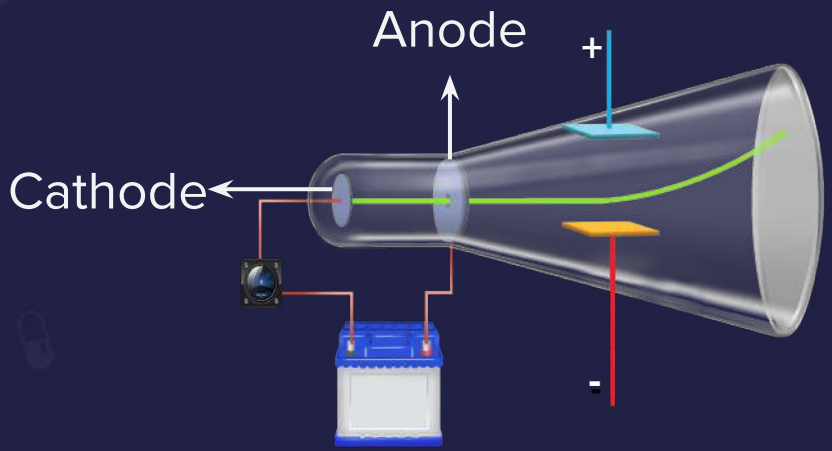
Discovery of electron



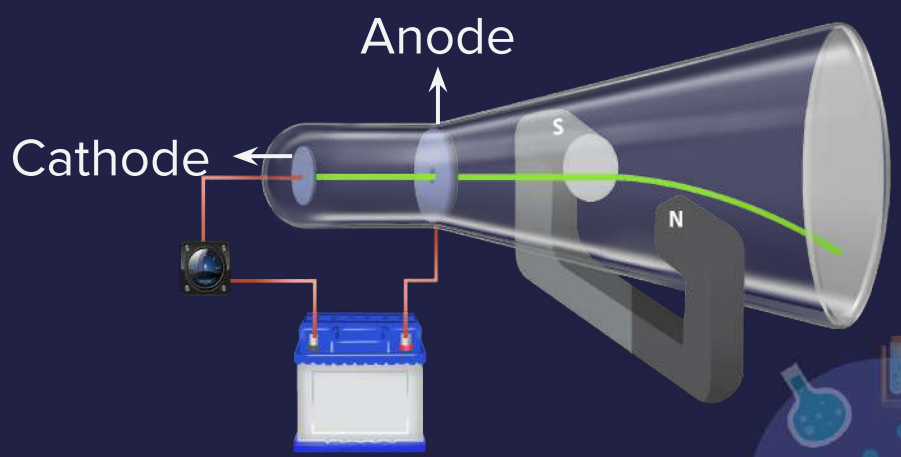
Discovery of electron

Observation and Characteristics

5. Cathode rays are deflected in the presence of an electric field.



6. Cathode rays are deflected in the presence of a magnetic field.



Discovery of electron

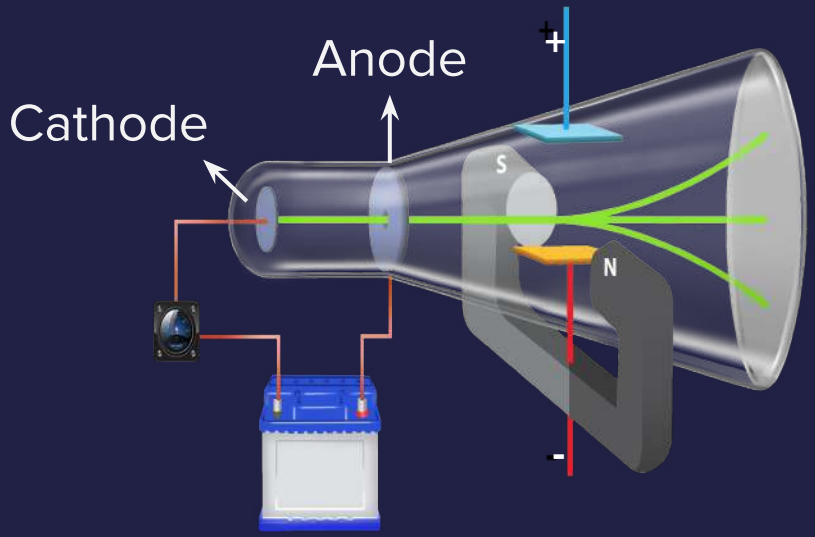
Conclusions

Cathode rays consist of negatively charged particles and identified as electrons.

Charge to mass ratio

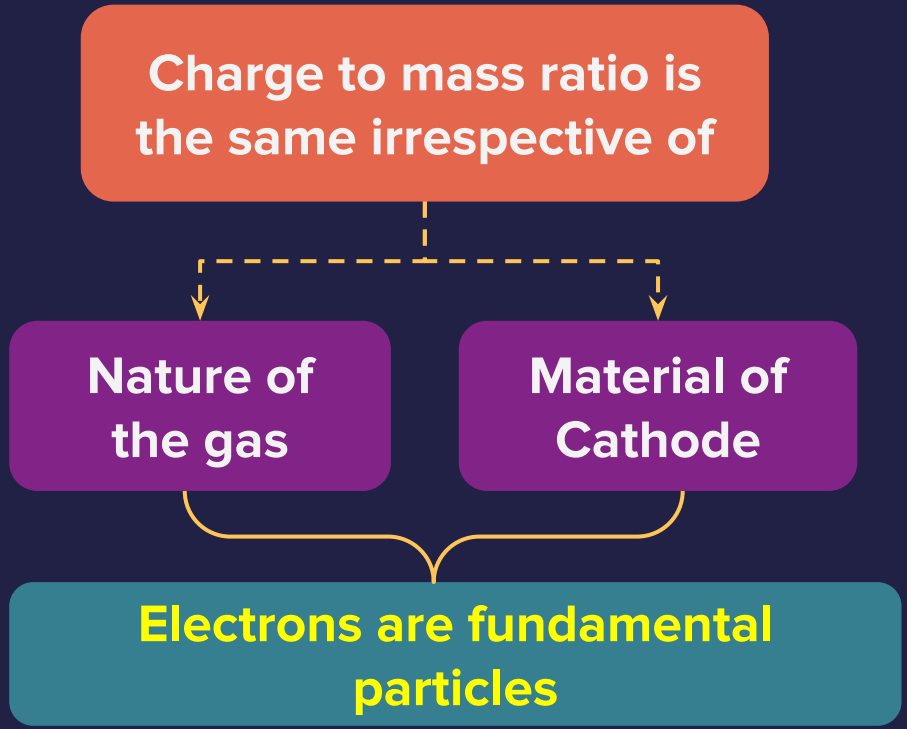
In 1897, J.J. Thomson

- Measured the charge (e) to mass (m) ratio of an electron.
- Electric & magnetic fields were applied perpendicular to each other & to the path of electrons



$$\frac{e}{m} = 1.758820 \times 10^{11}\ C/kg$$

Charge to mass ratio

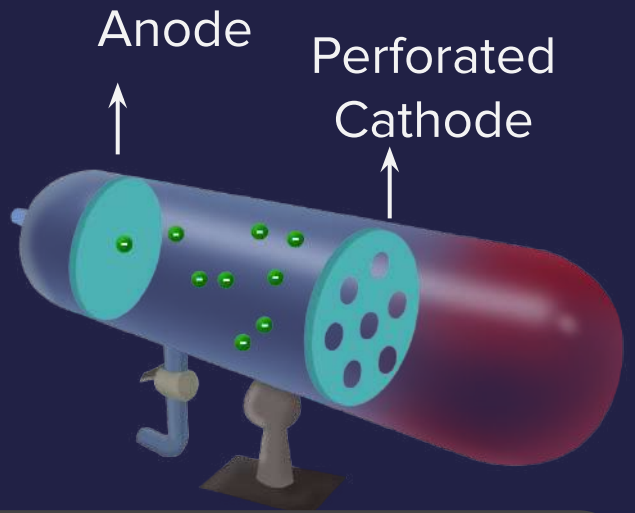


Discovery of Anode Rays

Discovered by Goldstein

He repeated experiment with a discharge tube by using a perforated cathode.

Existence of positively charged particles was shown using anode rays.



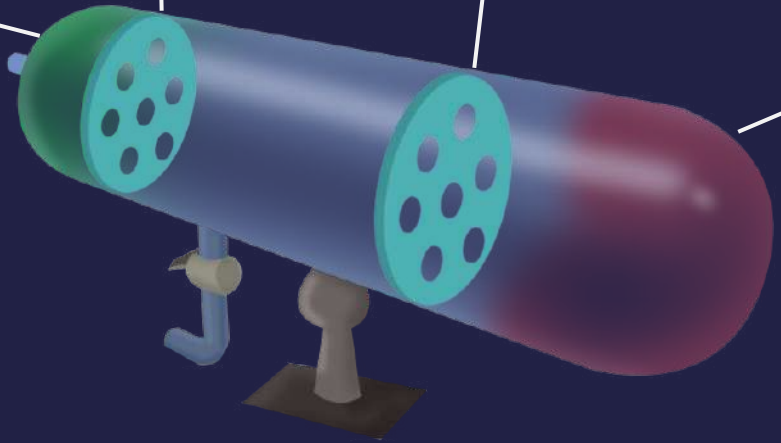
Red glow is due to anode particles which passes through perforated cathode and strikes the wall of the tube at the cathode side.

Discovery of Anode Rays

Green colour fluorescence observed due to Cathode rays

Perforated Anode

Perforated Cathode



Red colour fluorescence observed due to Anode rays

Observations and Characteristics

1. Anode rays possess positive charge

Concluded by their directions of deflections in the presence of electric & magnetic fields

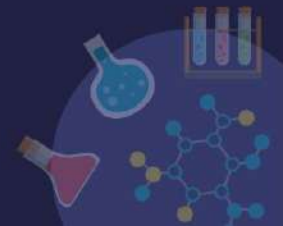
2. Anode rays travel in straight lines in the absence of both electric and magnetic fields.

Observations and Characteristics

3. e/m ratio of the canal rays is different for different gases

Properties of anode rays depends on nature of the gas taken in the discharge tube

In 1919, Rutherford discovered that the smallest and the lightest positive ions are obtained from hydrogen and called them protons



Discovery of Neutrons

James Chadwick

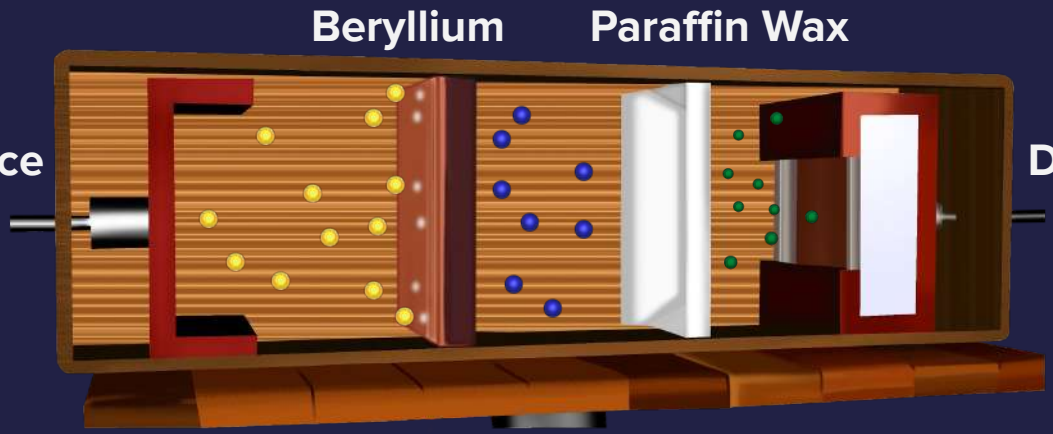
Named the electrically neutral particles emitted as neutrons

Discovered neutrons in 1932

Mass of neutrons is slightly greater than that of protons

Bombarded a thin sheet of beryllium ($^{9}_{4}Be$) with alpha particles ($^{4}_{2}He^{2+}$)

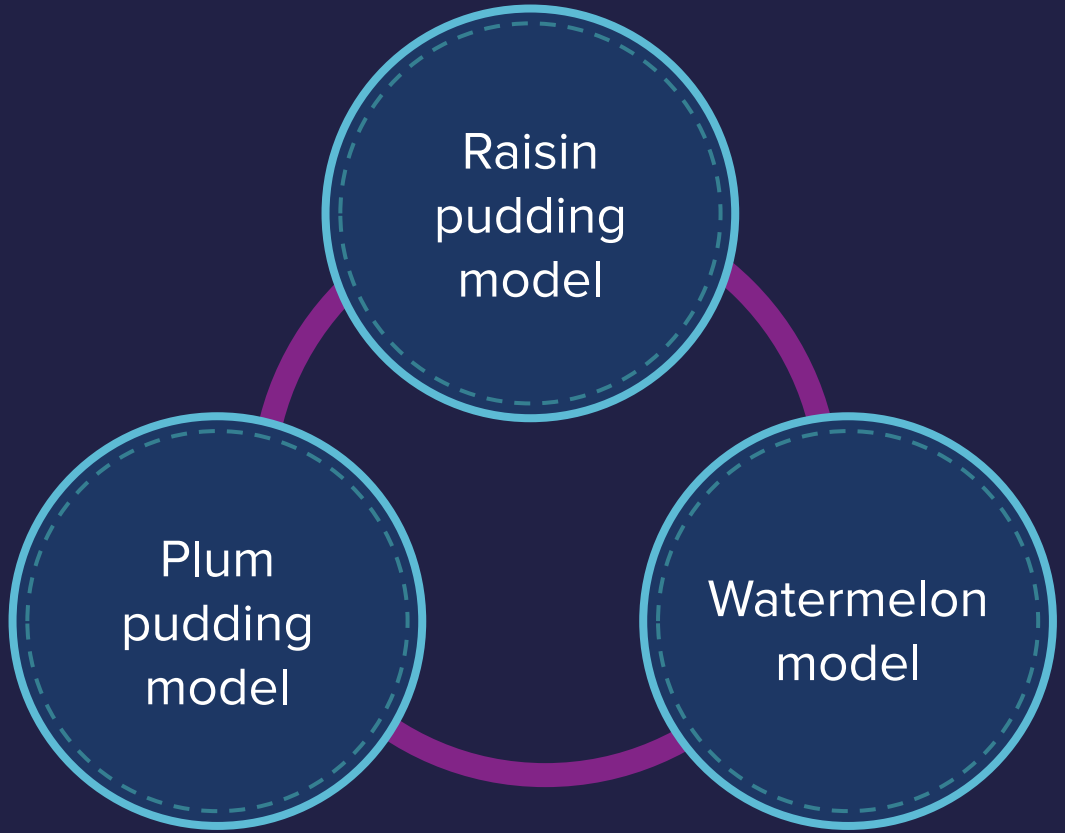
Discovery of Neutrons



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

$ {}^{4}_{2}He^{++} $	$ {}^{9}_{4}Be $	$ {}^{12}_{6}C $	$ {}^{1}_{0}n $
Z = 2 A = 4	Z = 4 A = 9	Z = 6 A = 12	q = 0 A = 1

Thomson's Model



Thomson's Model

1. An atom has a spherical shape (radius $\sim 10^{-10}$ m)

2. Positive charge is uniformly distributed throughout the sphere

3. Negatively charged electrons are embedded in it like raisins in a pudding

4. Mass of the atom is assumed to be uniformly distributed all over it

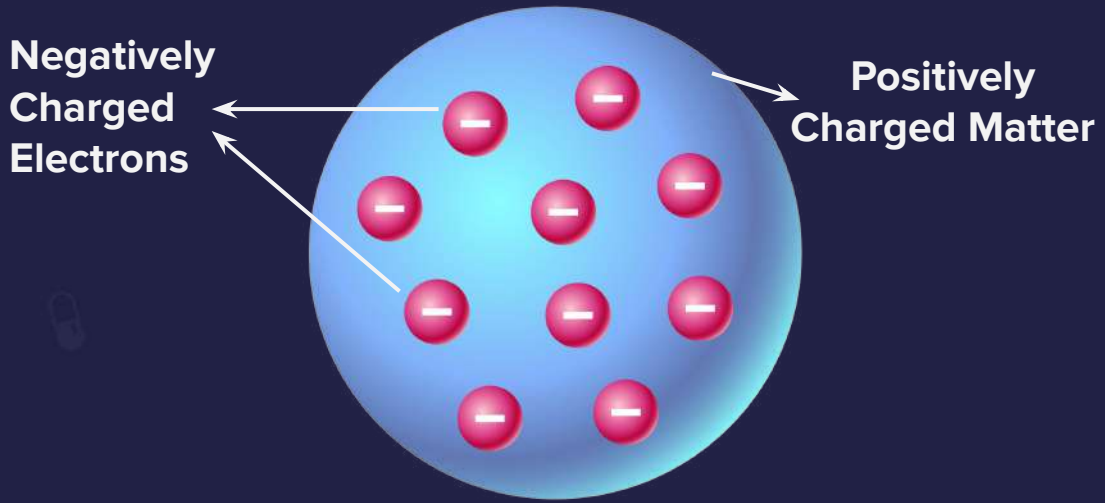
Plum Pudding

Watermelon

Thomson's Model

Electrons are embedded in an atom in such a way that the most stable electrostatic arrangement is achieved.

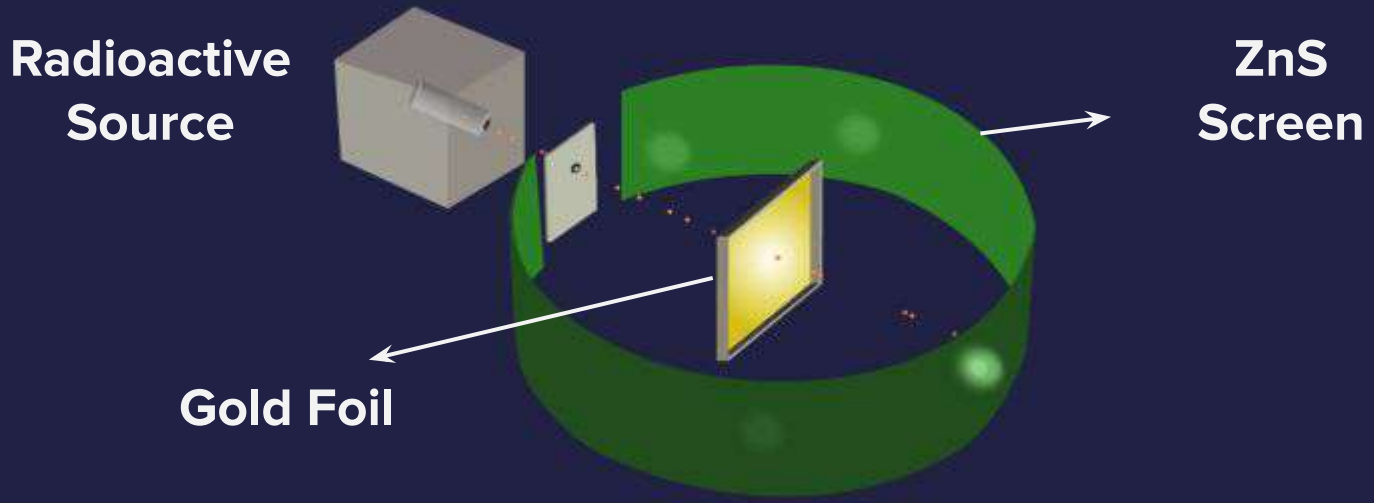
Explains the overall neutrality of an atom



Drawback:
Not consistent with the results of later experiments

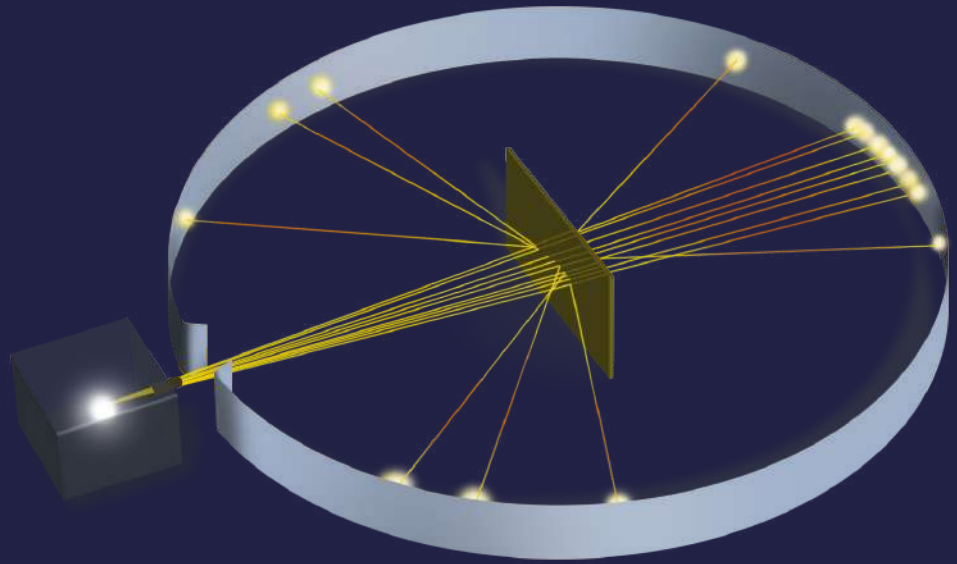
Rutherford's Experiment

A stream of high energy ***α***–particles was directed at a thin gold foil (thickness ~ 100 nm)

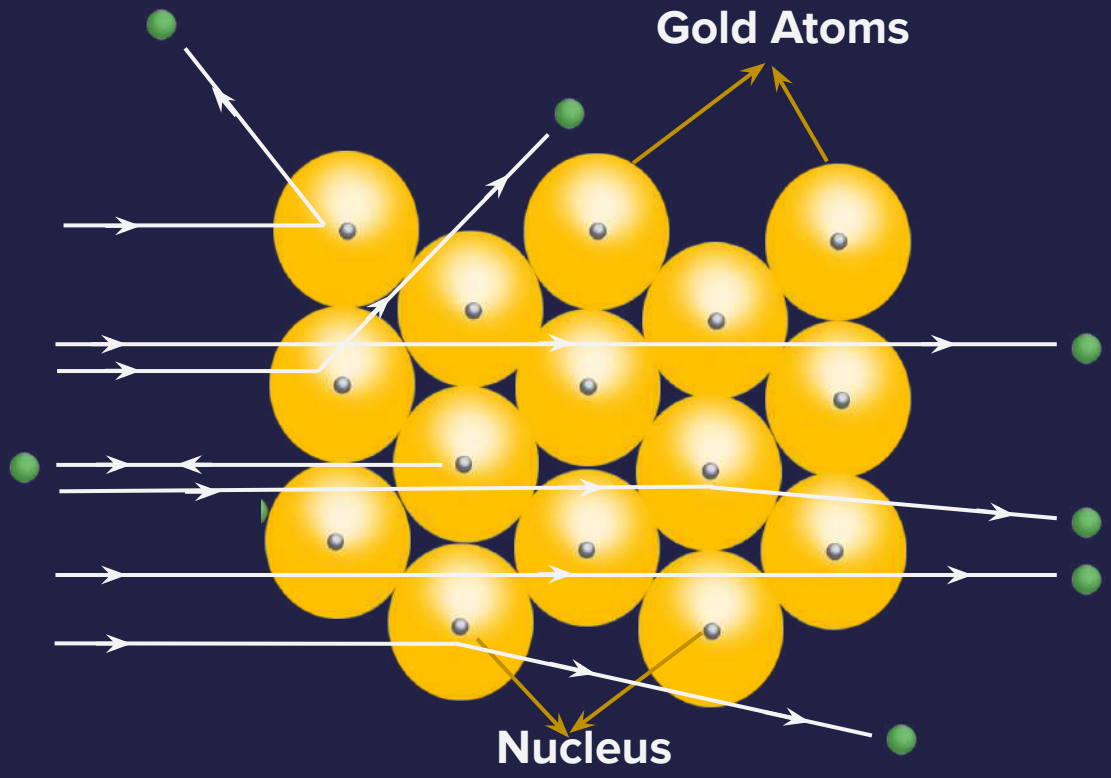


Observations of Rutherford's Experiment

When an ***α***–particle strikes the screen, a glow was produced at that point on the screen



Observations of Rutherford's Experiment



Observations of Rutherford's Experiment

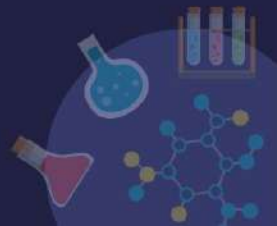
α–particles

1. Most of them passed undeflected

2.Very small fraction was deflected by large angles

3. Very few were deflected by 180° (~1 in 20,000)

4. Small fraction was deflected by small angles



Observation	Conclusion
Most ***α***-particles passed through the foil without deflection.	Presence of large empty space in the atom.
Few ***α***-particles were deflected by small angles.	Positive charge is concentrated in a very small region.
Very few ***α***-particles (~1 of 20,000) deflected at 180°.	Small positively charged core at the centre.

Nucleus

Atom consists of a small positively charged core at the center which carries almost the entire mass of the atom

It has negligible volume compared to the volume of the atom.

Nucleus

Both, protons and neutrons present in the nucleus are collectively called nucleons.

$$R = R_0 A^{\frac{1}{3}}$$

Radius of the atom ← $\sim 10^{-10}$ m

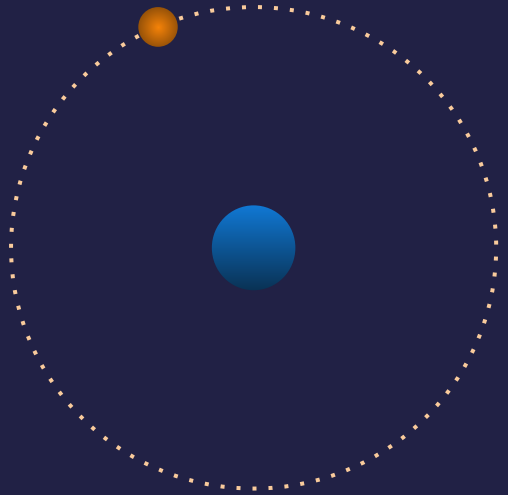
$\sim 10^{-15}$ m → Radius of the nucleus

R = Radius of nucleus of an element

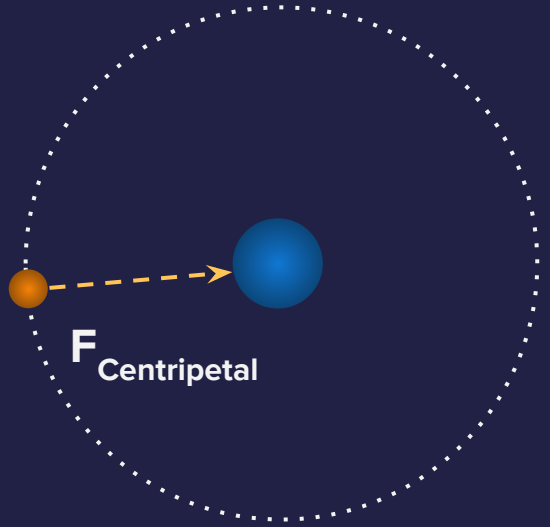
A = Mass number of element

R_0 = 1.11 x 10^{-15} m to 1.44 x 10^{-15} m

Extranuclear part



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



Nucleus is surrounded by revolving electrons.

$$F_{Electrostatic} = F_{Centripetal}$$

Drawbacks of Rutherford's Model

It could not explain stability of the atom.

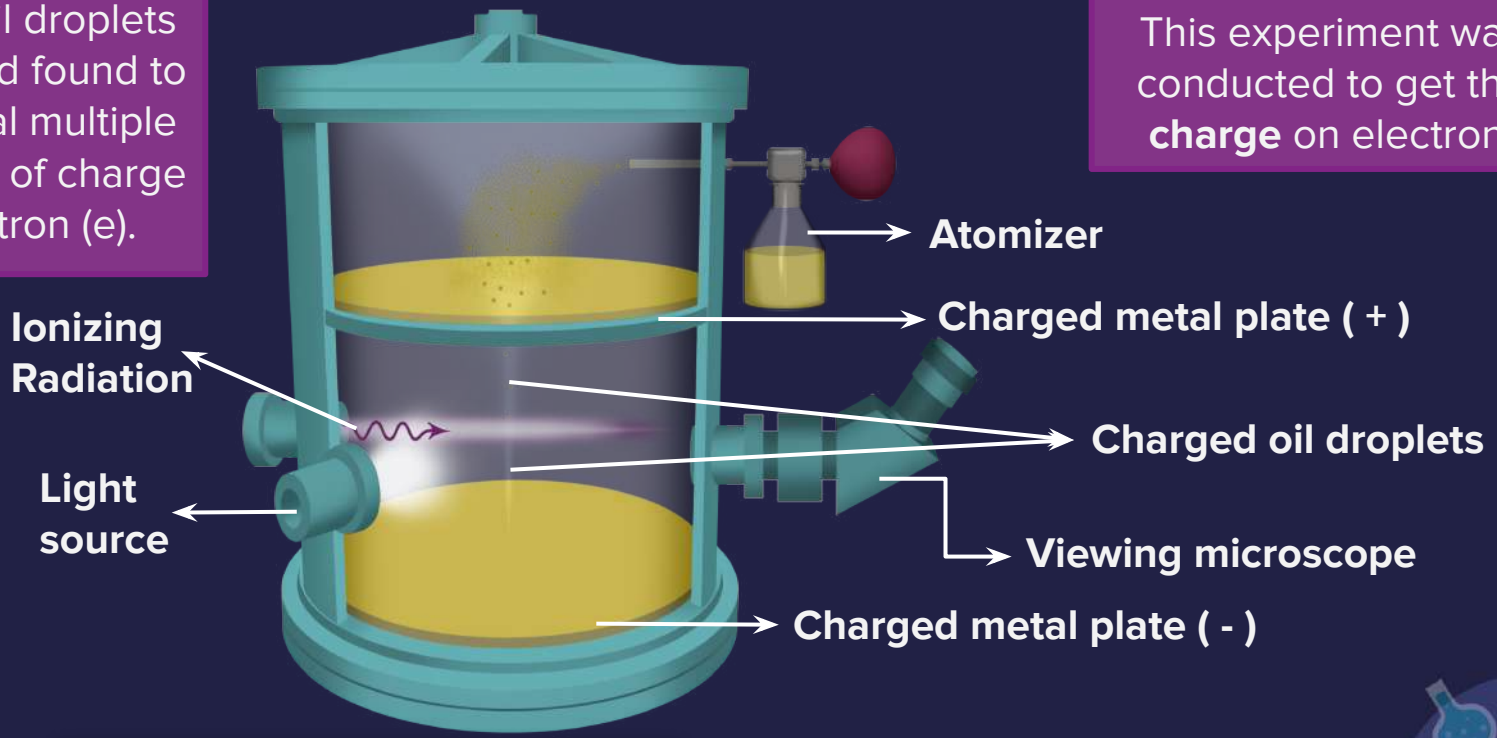
It could not explain line spectrum of the H atom.

It could not explain the electronic structure of the atom.

R.A. Millikan's Oil drop experiment

Charge on oil droplets measured and found to be an integral multiple of magnitude of charge on an electron (e).

This experiment was conducted to get the **charge** on electron.



Charge on electron $-1.602176 \times 10^{-19}$ C

Mass of the electron

Thomson's e/m ratio → 1.75882×10^{11} C kg^{-1}

Charge from Millikan's experiment → $-1.602176 \times 10^{-19}$ C

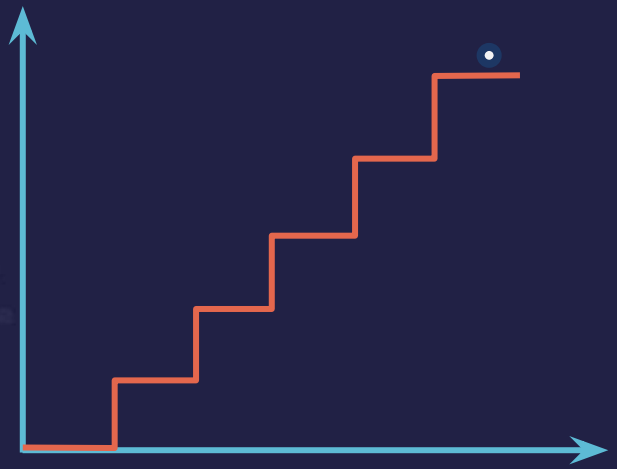
From Thomson's experiment, e/m ratio calculated and from Oil drop experiment, charge of electron calculated. Using the data from these two experiments, mass of the electron was determined.

Subatomic Particles

Subatomic Particles	Mass (u)	Absolute Mass (kg)
Electron	0.0005	9.1×10^{-31}
Proton	1.007	1.6722×10^{-27}
Neutron	1.008	1.6749×10^{-27}

Subatomic Particles	Relative Charge	Absolute Charge (C)
Electron	-1	-1.602×10^{-19}
Proton	+1	1.602×10^{-19}
Neutron	0	0

Quantization of Charge



$q = n\ (1.6 \times 10^{-19}\ C)$

$q = n\ (4.8 \times 10^{-10}\ esu)$

$n = 1, 2, 3 \ldots$

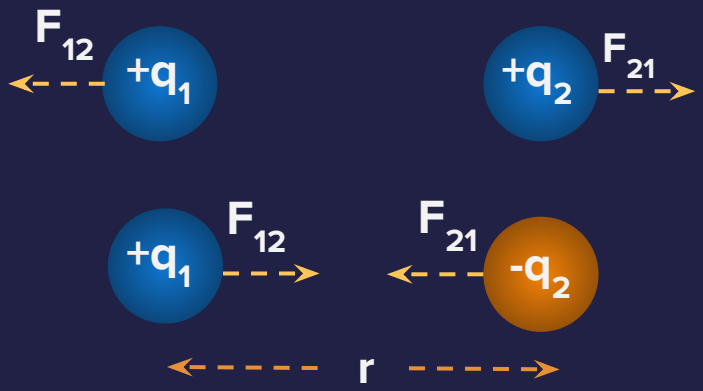
$q = n\ (e)$

The charge can't have continious range of values but only take values in multiple of charge on one electron. The magnitude of charge on an electron is the smallest unit and denoted as "e". Thus charge on an electron is -e and on a proton, it is +e.

Electrostatic Force

$$F_{12} = F_{21} = K\frac{q_1 q_2}{r^2}$$

$$K = \frac{1}{4\pi\varepsilon_0} = 9 \times 10^9 \frac{Nm^2}{C^2}$$



$$\varepsilon_0 = 8.854 \times 10^{-12} \frac{C}{Vm}$$

ε_0 = Permittivity of vacuum

Potential Energy

$$P.E. = q \times V$$

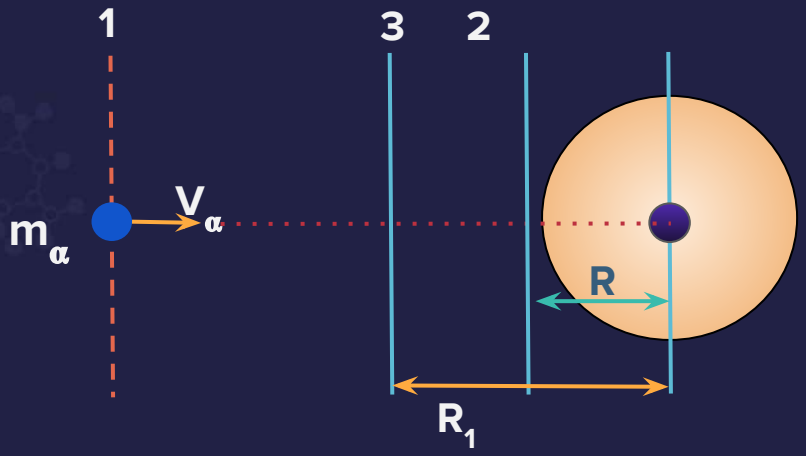
q = Charge of the particle

V = Potential of surface

$$P.E. = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r}$$

$$P.E. = K \frac{q_1 q_2}{r}$$

Closest Distance Of Approach

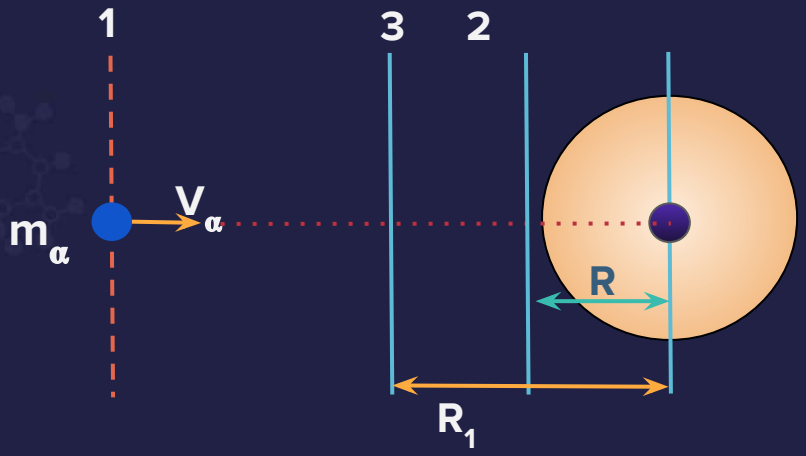


Closest distance of approach(in alpha particle scattering by gold nucleus),

$R = \sqrt{4KZe^2/m_\alpha V_\alpha}$

When two charged particles of similar nature approach each other, the repulsion between them increases but due to initial kinetic energy, the particles come closer to each other (Recall the bombarding of positively charged alpha particle on gold foil where the alpha particle approaching positively charged nucleus of gold atom).

Closest Distance Of Approach



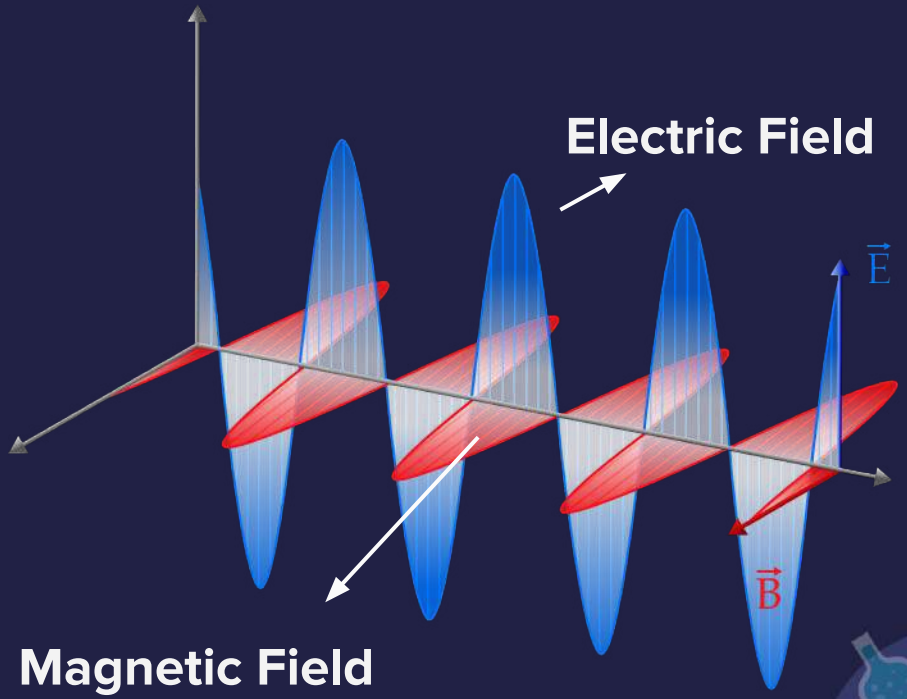
But at a certain distance between them, the relative velocity becomes zero and after that due to repulsion, the particles starts going away from each other. This distance between the particles where velocity once becomes zero is called Closest distance of approach and can easily be calculated using conservation of energy concept.

Closest distance of approach,

$R = \sqrt{4KZe^2/m_\alpha V_\alpha}$

Electromagnetic Waves

Oscillating Electric & Magnetic field



Properties of Electromagnetic Waves

Electric & magnetic field oscillate perpendicular to each other

Both oscillate perpendicular to the direction of propagation of wave

Do not require any medium for propagation

Can travel in vacuum

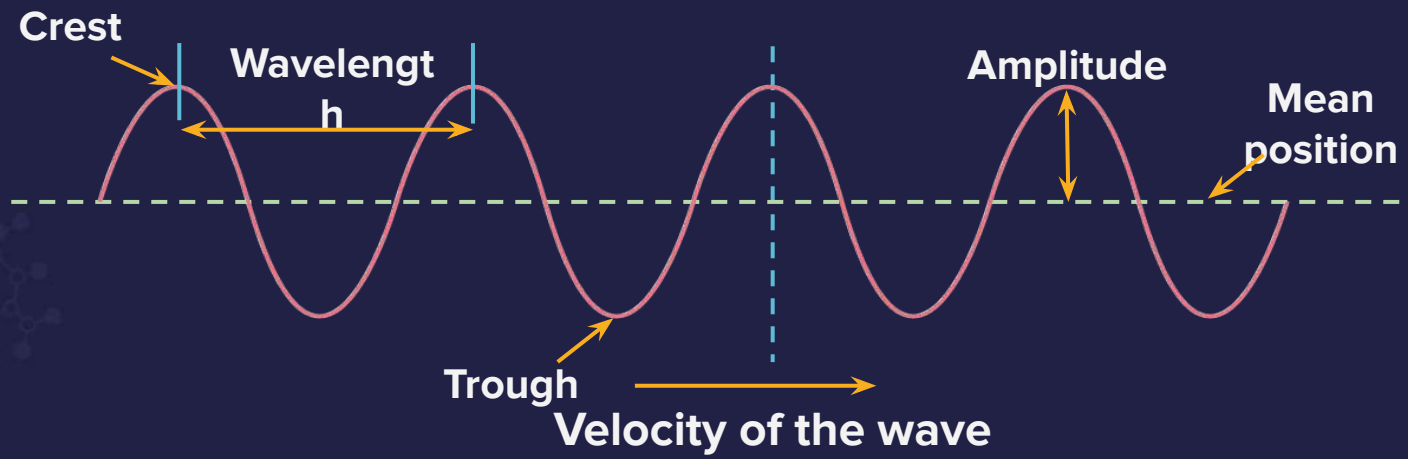
$c = 3 \times 10^8\ ms^{-1}$ (in vaccum)

Propagate at a constant speed i.e. with the speed of light (c)

Characteristics of Electromagnetic waves

- Wavelength
- Time Period
- Frequency
- Wavenumber
- Velocity
- Amplitude

Characteristics of Electromagnetic waves



Frequency: Number of times a wave oscillate from crest to trough per second

Characteristics of Electromagnetic waves

Wavelength (λ)

Distance between two consecutive crests or troughs

SI unit : m

Frequency (ν)

Number of waves passing a given point in one second

SI unit : Hertz (Hz), s^{-1}

Related to time period as:

$$\nu = \frac{1}{T}$$

Characteristics of Electromagnetic waves

Velocity (c or v)

Distance travelled by a wave in one second SI unit : ms^{-1}

Related to frequency (ν) & wavelength (λ) as:

$$c = \nu \lambda$$

Characteristics of Electromagnetic waves

Time Period (T)

Time taken to complete one oscillation

SI unit : s

Wavenumber (ν)

Number of waves per unit length

SI unit : m^{-1}

Amplitude (A)

Height of the crest or the depth of the trough from the mean position

SI unit : m

Characteristics of Electromagnetic waves

Consists of radiations having different wavelength or frequency

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

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

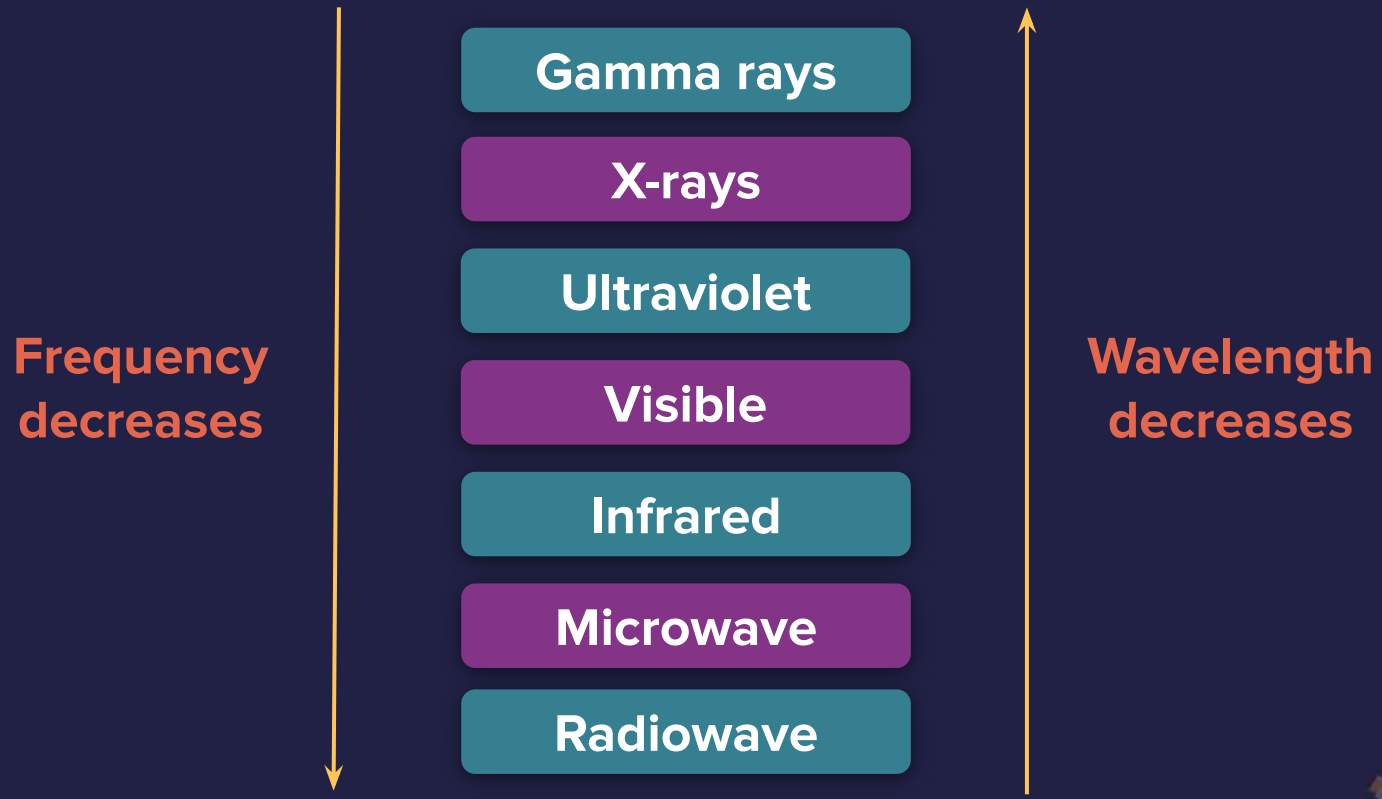
$$\nu = \frac{1}{T}$$

Electromagnetic Spectrum

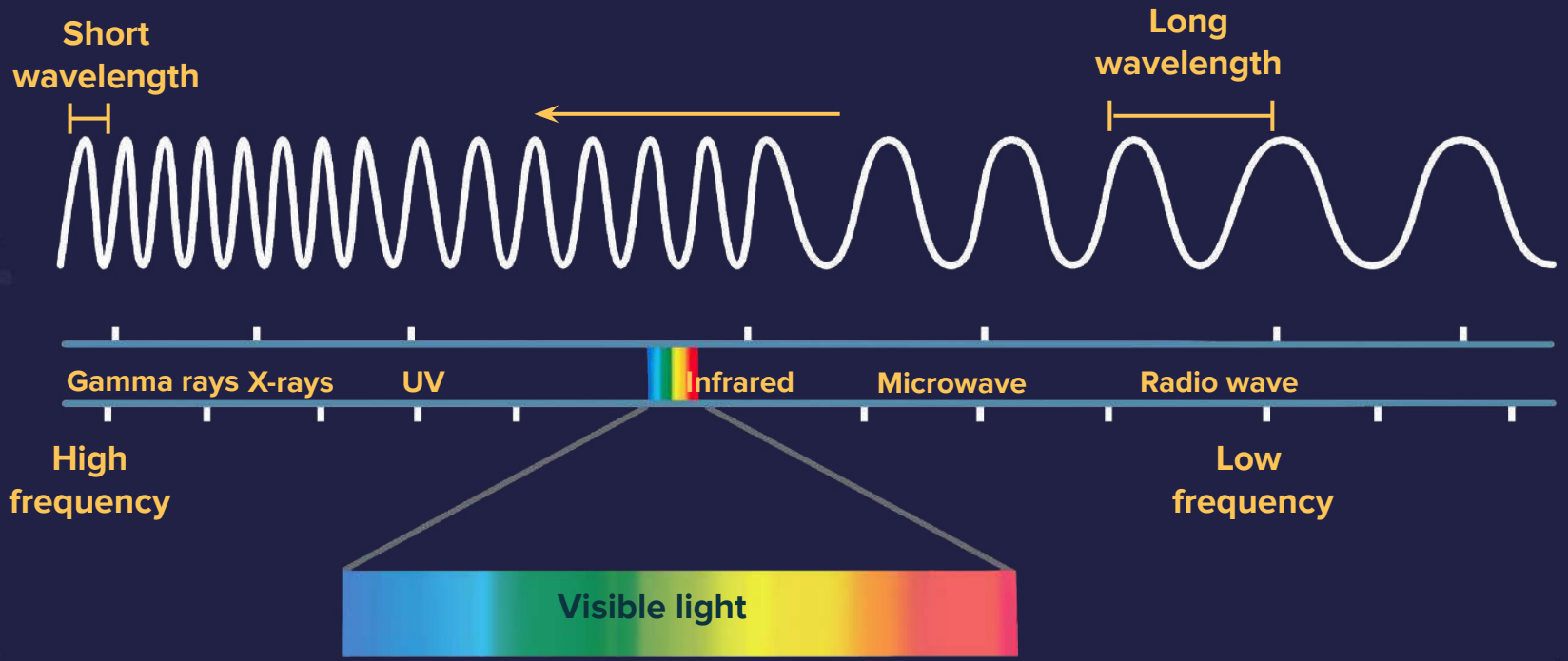
Electromagnetic radiations are arranged in the order of

Decreasing frequency **or** Increasing wavelength

Electromagnetic Spectrum



Electromagnetic Spectrum



EM Radiation: Wave or Particle?

Wave nature of the EM radiation explains

- **Diffraction**
- **Interference**

EM Radiation: Wave or Particle?

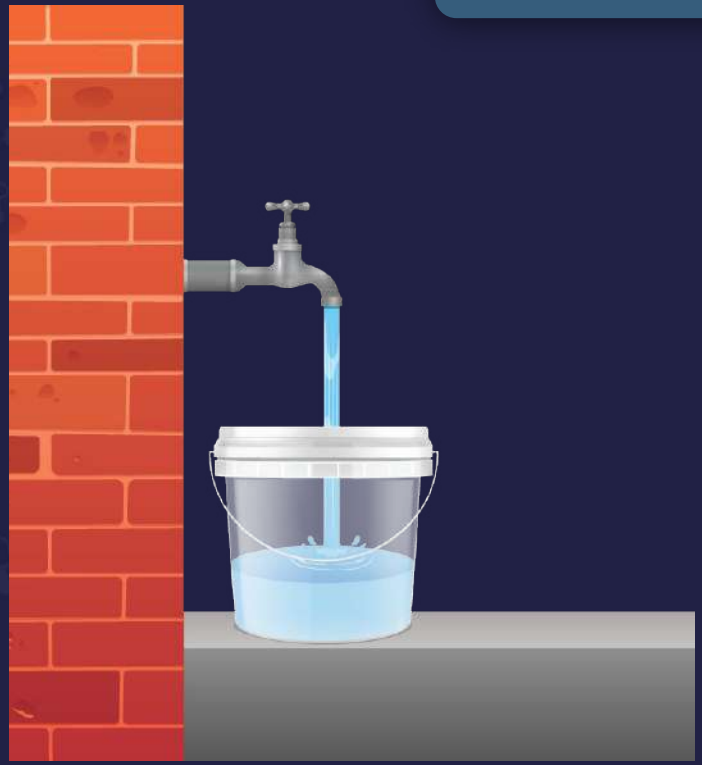
Electromagnetic wave theory could not explain

- Black-body radiation
- Photoelectric effect
- Variation of heat capacity of solids with temperature
- Line spectrum of Hydrogen

Continuous vs Discrete

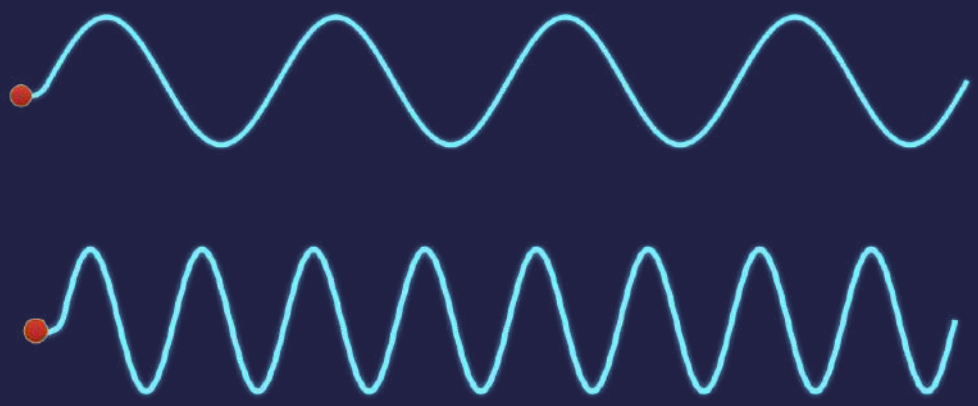
Mass = **N (mass of 1 water molecule)**

Where N ∈ + I



It seems that mass of water (or any other matter) can take any values (suppose we can go till 30 decimal points) and so we can say that mass has continuous range of values. But on microscopic level, we can observe that mass of water is always an integral multiple of 1 molecule of water. i.e., mass is quantized or we can say that quantization is a property of matter.

Back to EM waves



Low temperature
Low frequency
Longer wavelength

High temperature
High frequency
Shorter wavelength

What is a black body?

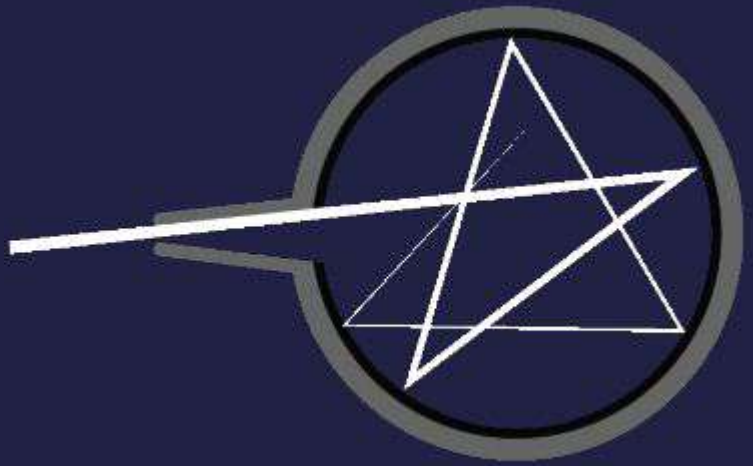
Idealized system

Absorbs & emits all frequencies

Absorbs regardless of the angle of incidence

Why the name, Black Body?

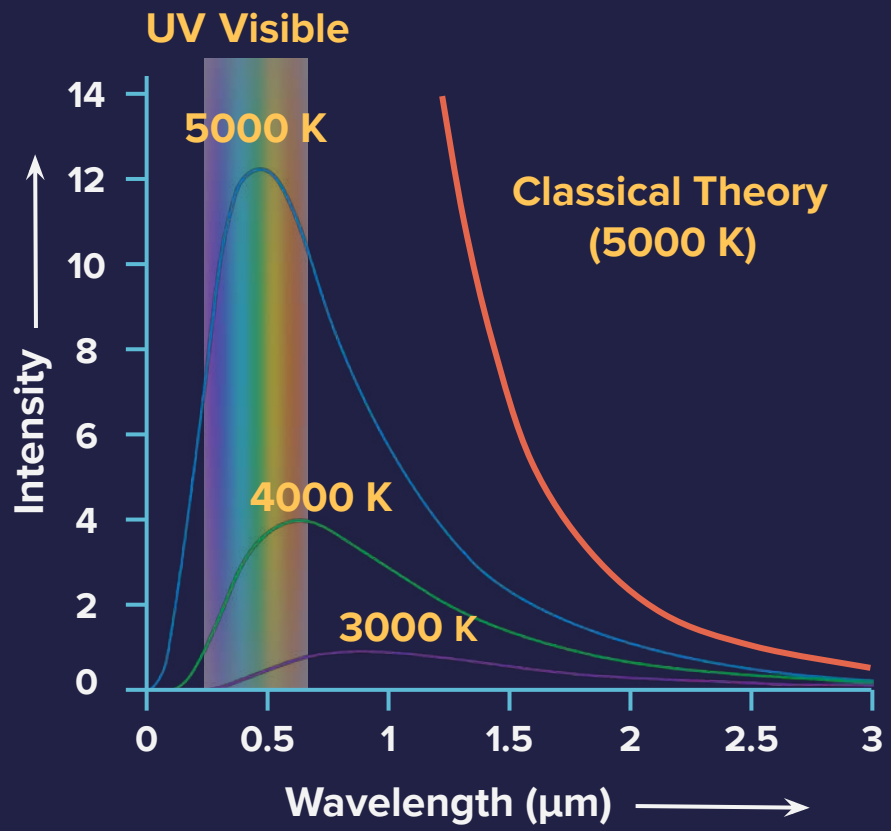
Visually Black body vs **Radiatively Black Body**



A true black body appears black because it is not reflecting any electromagnetic radiation.

However, everything you see to be black can not ber called as blackbody because there could be radiation coming out which is not in the visible range.

Wavelength-Intensity relationship



This graph shows intensity as a function of wavelengths emitted from a black body. It shows how bright it is at what wavelength. It shows quantization nature of energy and hence favours particle nature of light.

Particle Nature of Radiation

Planck's quantum theory explains

- Quantisation of Energy
- Variation of intensity with wavelength

Planck's Quantum theory

The smallest packet or bundle of energy (quantum of radiation) is called a **photon.**

This is the smallest quantity of energy that can be emitted or absorbed in the form of EM radiation.

Quantum theory of Radiation

Energy (E) of a photon is proportional to its frequency (ν)

$$E \propto \nu_{Radiation}$$

$$E = nh\nu$$

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

n = number of photons
= 0, 1, 2, 3, ...

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

One electron volt (eV)

Energy gained by an electron when it is accelerated from rest through a potential difference of 1 V

Important Conversions

$1\ eV = 1.6 \times 10^{-19}\ J$

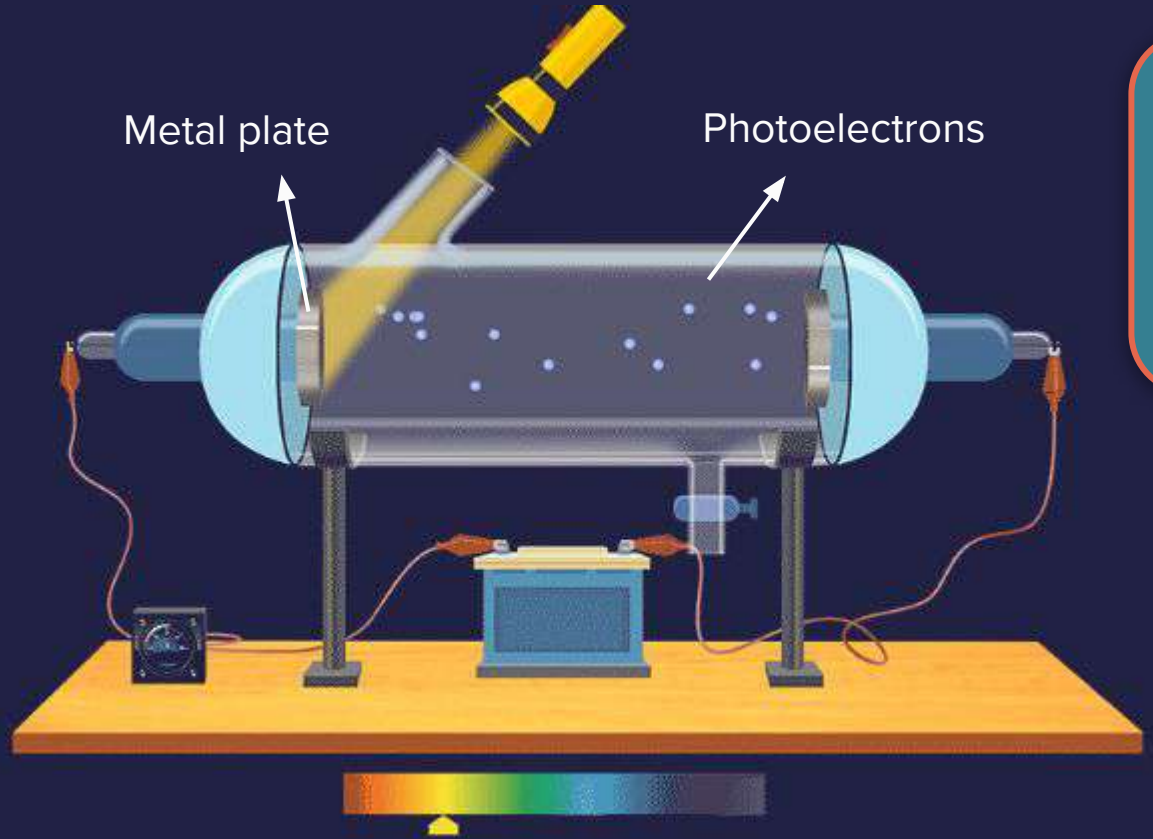
$E\ (eV) = \frac{12{,}400}{\lambda\ (Å)}$

$E\left(\frac{kJ}{mole}\right) = E\left(\frac{eV}{particle}\right) \times 96.48$

Photoelectric Effect

Phenomenon of electrons ejection	When a radiation of sufficient frequency falls on the metal surface
Photoelectrons	Electrons are ejected with the aid of light

Photoelectric Effect



When radiation of sufficient energy falls on the metal plate, there starts emission of electrons called **photoelectrons.**

Observations

Electrons are ejected as soon as the beam of light of sufficient frequency strikes the metal surface

Instant transfer of energy to the electron when a photon of sufficient frequency strikes the metal atom

Threshold frequency (ν_o)

Minimum frequency required to eject a photoelectron from a metal surface

Each metal has a characteristic threshold frequency

Observations

Number of electrons ejected $\propto$ Intensity of light or Brightness of light

Observations

No electron is ejected, regardless of the intensity of light

$\nu_{incident} < \nu_0$

Even at low light intensities, electrons are ejected immediately

$\nu_{incident} > \nu_0$

Particle nature of light

One photon is absorbed by only one electron in a single interaction. Not more than one photon can be absorbed by an electron.

If intense beam of light is used, large number of photons are available and large number of electrons are ejected. This observation shows particle nature of light.

Observations

When $\nu_{incident} > \nu_0$

$K.E._{Ejected\ electron} \propto \nu_{Incident}$

Energy possessed by the photon ↑

Transfer of energy to the electron ↑

K.E. of the ejected electron ↑

Photoelectric Effect

$0 \leq K.E._{\text{Ejected electrons}} \leq K.E._{\text{Max}}$

K.E. is independent of the intensity of radiation

Striking photon's energy $= h\nu$

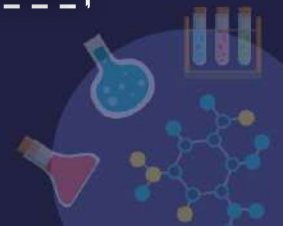
Work function $= \phi$

Work Function (ϕ)

$$\phi = h\nu_0$$

$\phi = W_0$ = Work function

Minimum energy required to eject an electron from the metal surface



Photoelectric Effect

$E_{Photon} - \phi = K.E._{Max}$

From the Law of Energy Conservation

$E_{Incident} = \phi + K.E._{Max}$

$h\nu = h\nu_0 + \frac{1}{2} m_e v_{max}^2$

m_e = mass of the electron

v_{max} = maximum velocity of the electron

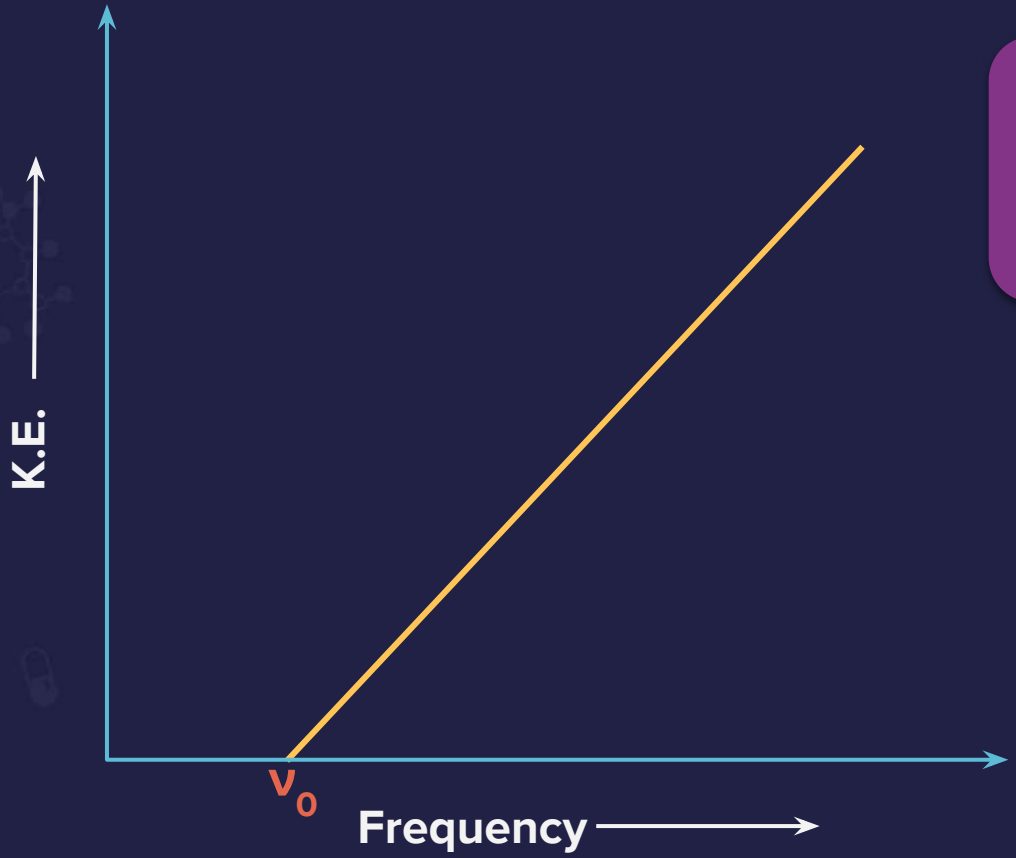
Photoelectric Effect

K.E. of the ejected electron is given as

$$K.E._{Max} = h\nu - h\nu_0$$

$$K.E._{Max} = h\frac{c}{\lambda} - h\frac{c}{\lambda_o}$$

Plotting K.E. vs Frequency



From the plot of kinetic energy vs frequency, it shows linear variation according to the equation:

$$K.E._{Max} = h\nu - h\nu_0$$

Acceleration and Deceleration of Charged Particles

Acceleration:

If a positive charge moves from higher to lower potential (like an electron moves from cathode to anode) or a negative charge moves from lower to higher potential.

Deceleration is just opposite to the acceleration.

Stopping potential(V_s)

Minimum opposing potential required to stop the photoelectron having the maximum K.E.

$$eV_s = K.E._{max}$$

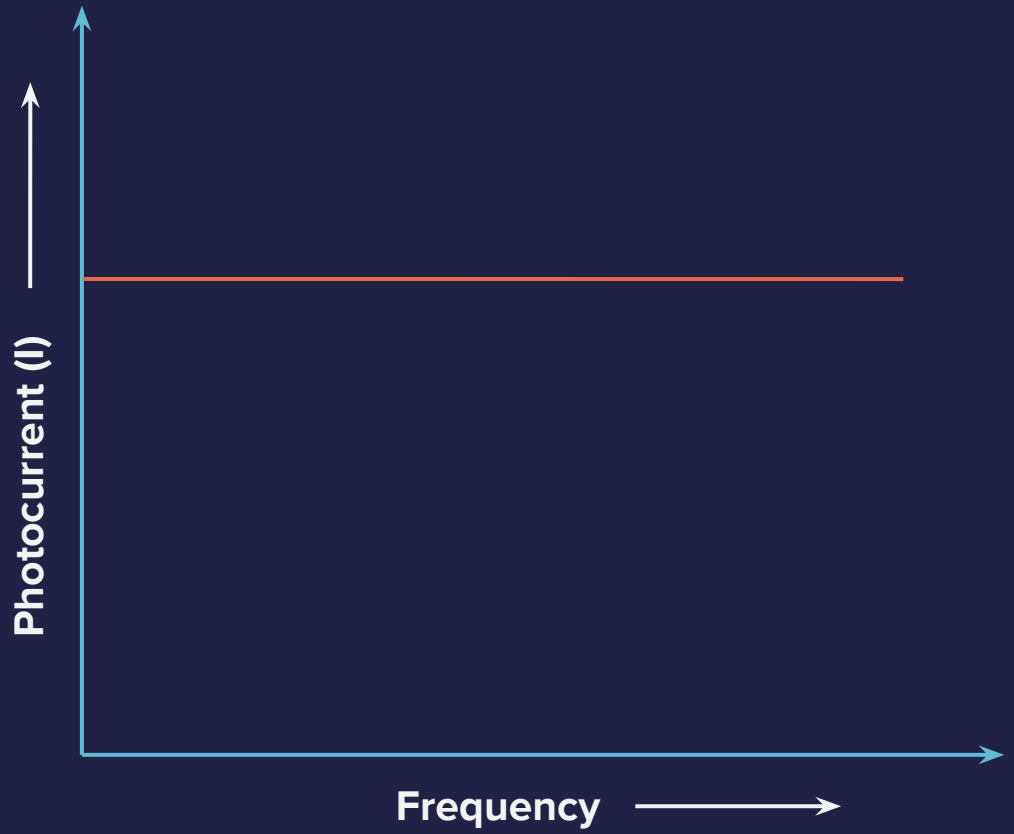
Accelerating potential voltage (V)

Voltage applied to increase the K.E. of an emitted electron

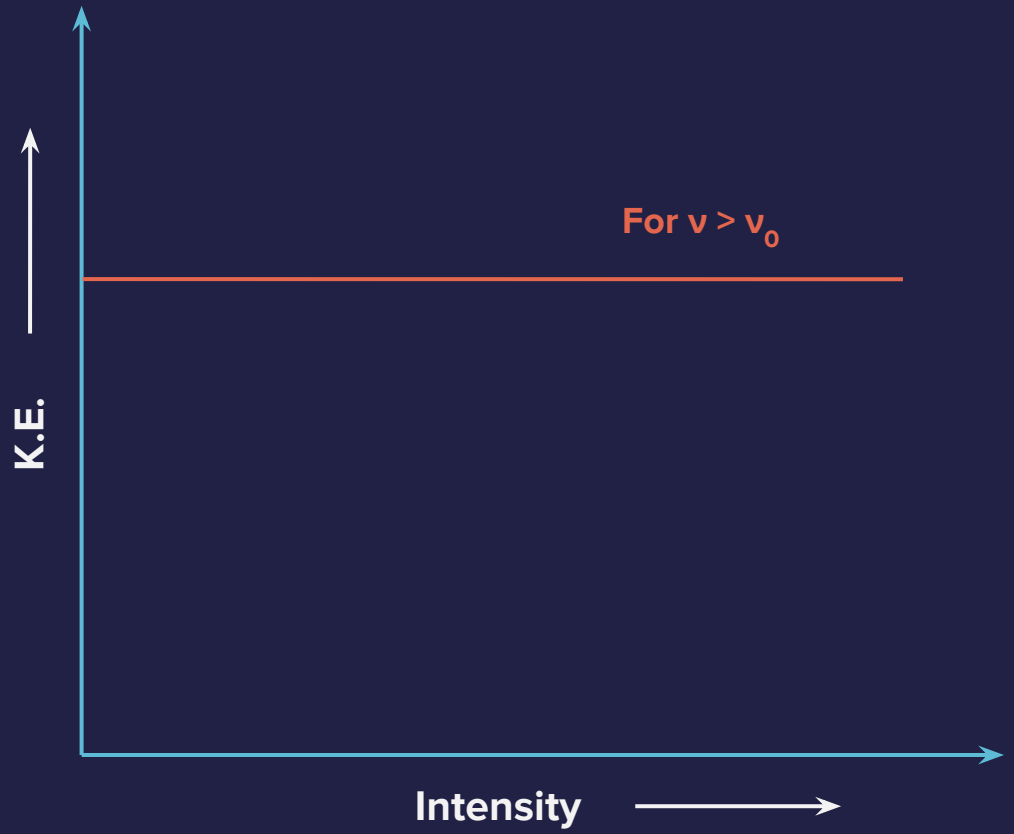
Minimum K.E. ← eV

$K.E._{Max}$ + eV → Maximum K.E.

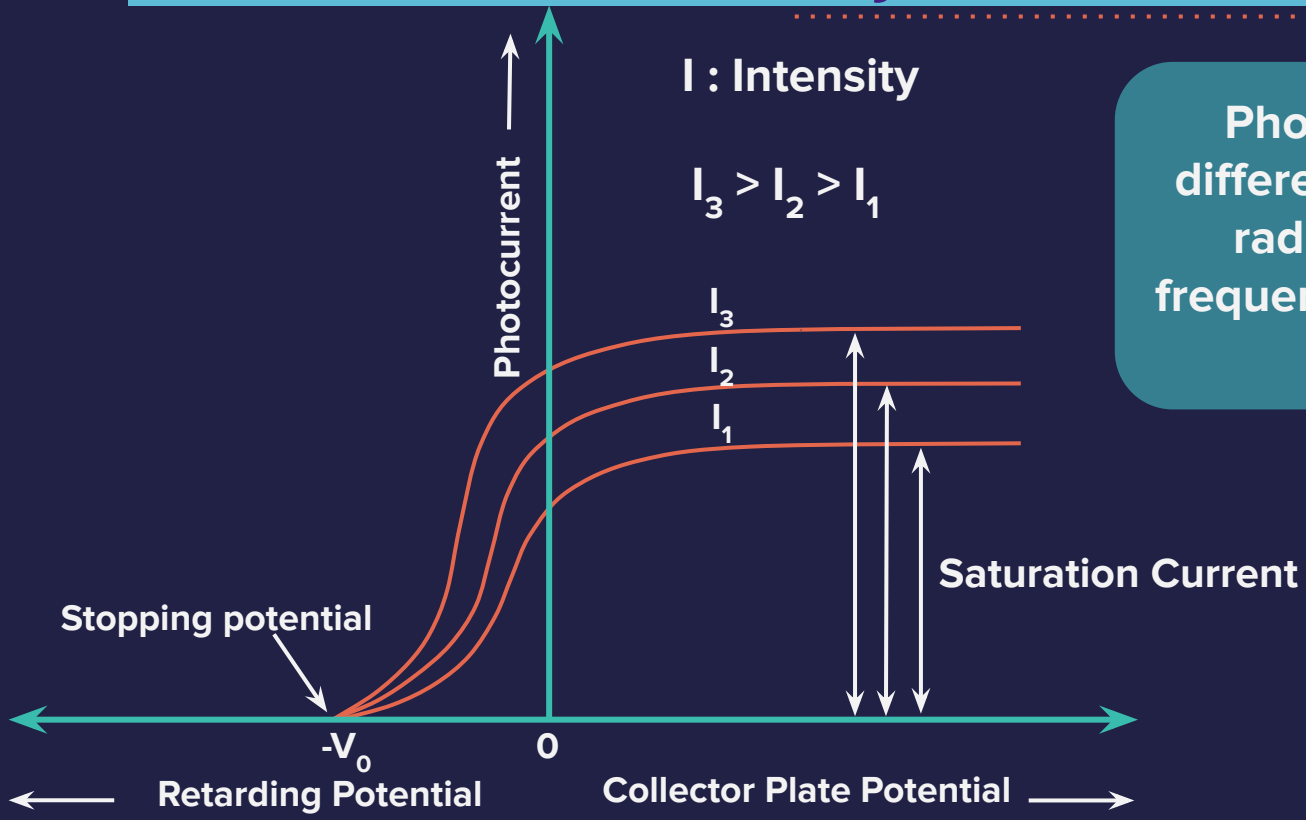
Photocurrent v/s Frequency of the Radiation



Photocurrent v/s Frequency of the Radiation

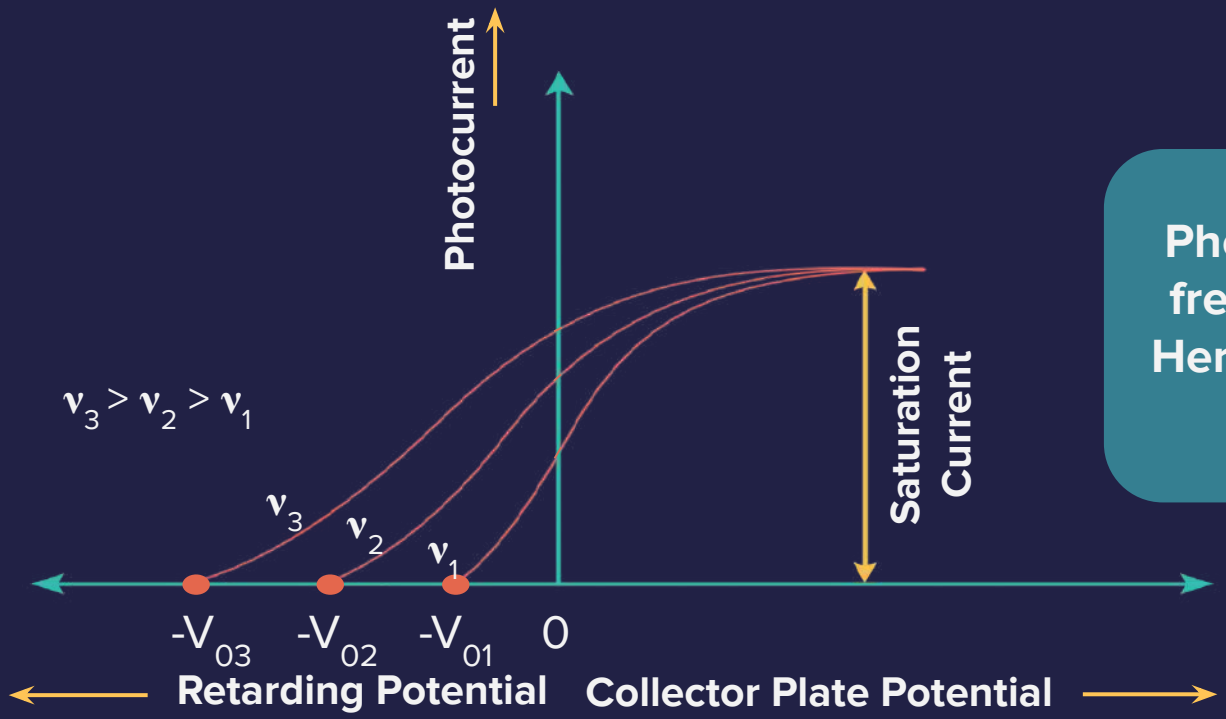


Photocurrent vs Collector Plate Potential at different intensity of radiation



Photocurrent at different intensity of radiation. Here frequency of radiation is same.

Photocurrent vs Collector Plate Potential at different intensity of radiation



Photocurrent at different frequencies of radiation. Here intensity of radiation is same.

Bohr Atomic Model

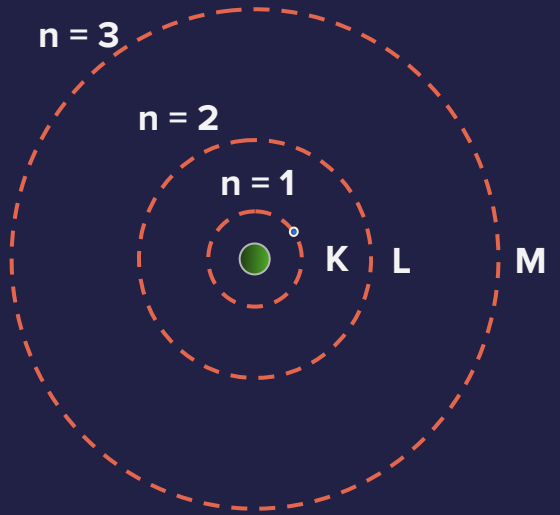
Postulates

Stationary orbits

Concentric circular orbits around the nucleus

These orbits have fixed value of energy

Electrons revolve without radiating energy



Stationary orbits **or** Energy states / levels

Postulates

Quantization of **Angular momentum**

Angular momentum of the electron in these orbits is always an integral multiple of $\frac{h}{2\pi}$

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

n = 1, 2, 3...

- **h** — Planck's constant
- **m** — Mass of electron
- **v** — Velocity of electron
- **r** — Radius of orbit

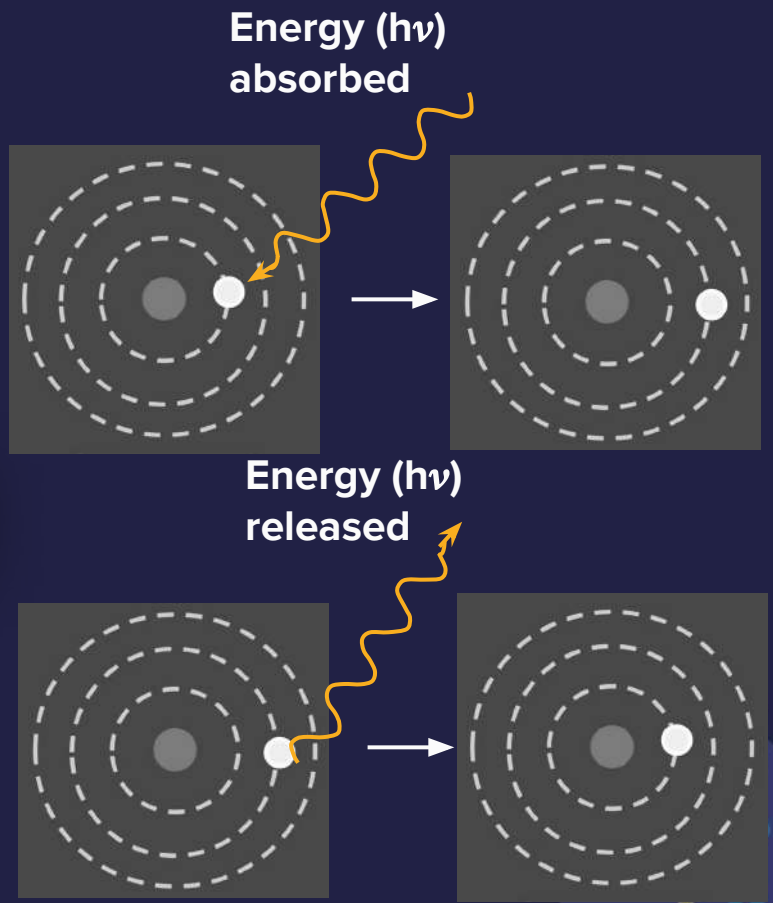
Postulates

Electron can jump from lower to higher orbit by absorbing energy in the form of photon

Energy Absorbed = $E_3 - E_2$

Electrons can jump from higher to lower orbit by releasing energy in the form of photon

Energy Released = $E_2 - E_1$



Postulates

Energy change does takes place in a discrete manner

$$\Delta E = E_{n_2} - E_{n_1}$$

n_1 Initial energy state

n_2 Final energy state

Bohr's Frequency Rule

Frequency (ν) of a **radiation absorbed**
or
emitted when a transition occurs

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

E_1 = Energy of **lower energy state**

E_2 = Energy of **higher energy state**

Bohr's Atomic Theory

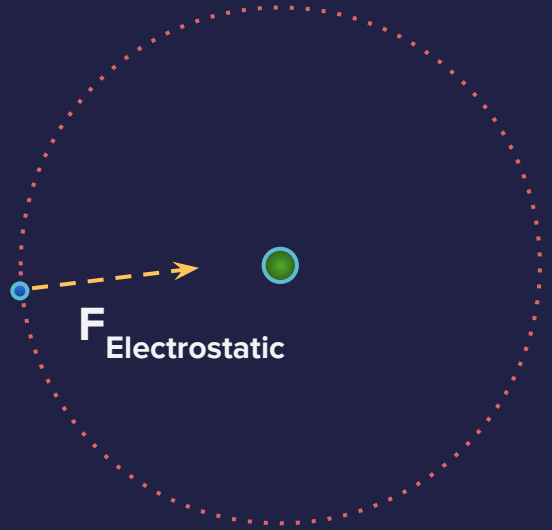
Applicable only for single electron species like H, He^{+}, Li^{2+}, Be^{3+}

Mathematical Analysis

Calculating

- Radius of Bohr orbit
- Velocity of an electron in Bohr orbit
- Time period of an electron in Bohr orbit
- Frequency of an electron in Bohr orbit
- Energy of an electron in Bohr orbit

Postulate



Electron revolves in a circular orbit

Required centripetal force is provided by electrostatic force of attraction

Calculating the radius of Bohr orbit

Equating both the forces,

$$F_{Centripetal} = F_{Electrostatic}$$

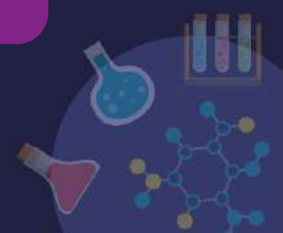
$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

On rearranging,

$$v^2 = \frac{KZe^2}{mr}$$

i



Calculating the radius of Bohr orbit

According to Bohr's Postulates,

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

$$v = \frac{nh}{2\pi rm}$$

$$v^2 = \frac{n^2h^2}{4\pi^2r^2m^2} \dashrightarrow \text{ii}$$

On comparing equation (i) and (ii),

$$\frac{KZe^2}{mr} = \frac{n^2h^2}{4\pi^2r^2m^2}$$

$$r = \frac{n^2h^2}{4\pi^2mKZe^2}$$

Calculating the radius of Bohr orbit

Putting the value of constants,

$$r_n = 0.529 \frac{n^2}{Z} \text{ Å}$$

r_n = Radius of n^{th} Bohr orbit

n = Energy level

Z = Atomic number

$$r_n \propto n^2$$

$$r_n \propto \frac{1}{Z}$$

Calculation of velocity of an electron in Bohr orbit

Angular momentum of the electron revolving in the n^{th} orbit

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

$$v = \frac{nh}{2\pi r m} \quad \text{(i)}$$

$$r = \frac{n^2h^2}{4\pi^2mKZe^2} \quad \text{(ii)}$$

Calculation of velocity of an electron in Bohr orbit

Putting equation (ii) in equation (i),

$$v = \frac{nh}{2\pi m} \times \frac{4\pi^2 mKZe^2}{n^2 h^2}$$

$$v = \frac{2\pi KZe^2}{nh}$$

$$v_n = 2.18 \times 10^6 \frac{Z}{n} ms^{-1}$$

v_n = Velocity of the electron in n^{th} Bohr orbit

Relation between v_n, n and Z

$$v_n \propto Z$$

$$v_n \propto \frac{1}{n}$$

Time period of Revolution (T)

Time period of revolution of an electron in its orbit

$$T = \frac{\text{Circumference}}{\text{Velocity}} = \frac{2\pi r_n}{v_n}$$

$$T = 1.5 \times 10^{-16} \frac{n^3}{Z^2} \text{ s}$$

$$T \propto \frac{n^3}{Z^2}$$

Frequency of Revolution (f)

Frequency of revolution of an electron in its orbit

$$f = \frac{1}{T} = \frac{v_n}{2\pi r_n}$$

Putting the value of constants, r_n & v_n

$$f = 6.6 \times 10^{15} \frac{Z^2}{n^3} \text{ Hz}$$

$$f \propto \frac{Z^2}{n^3}$$

Calculation of Energy of an electron

Total energy (T.E.) of an electron revolving in a particular orbit

$$T.E. = K.E. + P.E.$$

$$K.E. = \frac{1}{2}mv^2$$

$$P.E. = -\frac{KZe^2}{r}$$

K.E.	Kinetic energy
P.E.	Potential energy

$$T.E. = \frac{mv^2}{2} + \left(-\frac{KZe^2}{r}\right)$$

Calculation of Energy of an electron

Centripetal force = Electrostatic force

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

$$K.E. = \frac{mv^2}{2} = \frac{KZe^2}{2r}$$

Calculation of Energy of an electron

$$T.E. = K.E. + P.E.$$

$$T.E. = \frac{KZe^2}{2r} + -\frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

$$T.E. = -K.E. = \frac{1}{2} P.E.$$

Calculation of Energy of an electron

$$T.E. = -\frac{KZe^2}{2r}$$

Substituting the value of 'r' in the equation of T.E.

$$T.E. = -\frac{KZe^2}{2} \times \frac{4\pi^2 Z e^2 m K}{n^2 h^2} = -\frac{2\pi^2 Z^2 e^4 m K^2}{n^2 h^2}$$

$$T.E. = -\frac{2\pi^2 m e^4 K^2}{h^2} \frac{Z^2}{n^2}$$

Calculation of Energy of an electron

Putting the value of constants we get:

$$\text{T.E.} = E_n = -13.6 \left[\frac{Z^2}{n^2}\right] \text{eV/atom}$$

Negative sign of T.E. shows attraction between electrons & nucleus.

Electron in an atom is more stable than a free electron

Energy of an electron

$$E_n \propto -\frac{Z^2}{n^2}$$

$Z \uparrow$ $E_n \downarrow$

$n \uparrow$ $E_n \uparrow$

Energy of an electron

$E_K < E_L < E_M < E_N \dashrightarrow E_\infty = 0$

Distance of electron from the nucleus	↑
Energy	↑

Energy of an electron

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ eV/atom}$$

$$E_n = -2.18 \times 10^{-11} \frac{Z^2}{n^2} \text{ erg/atom}$$

$$E_n = -313.6 \frac{Z^2}{n^2} \text{ kcal/mol}$$

$$E_n = -2.18 \times 10^{-11} \frac{Z^2}{n^2} \text{ erg/atom}$$

$$E_n = -313.6 \frac{Z^2}{n^2} \text{ kcal/mol}$$

Energy of an electron

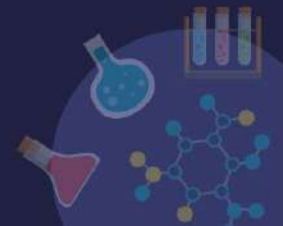
At

$n = \infty$

T.E. = 0

P.E. = 0

K.E. = 0



Energy Difference

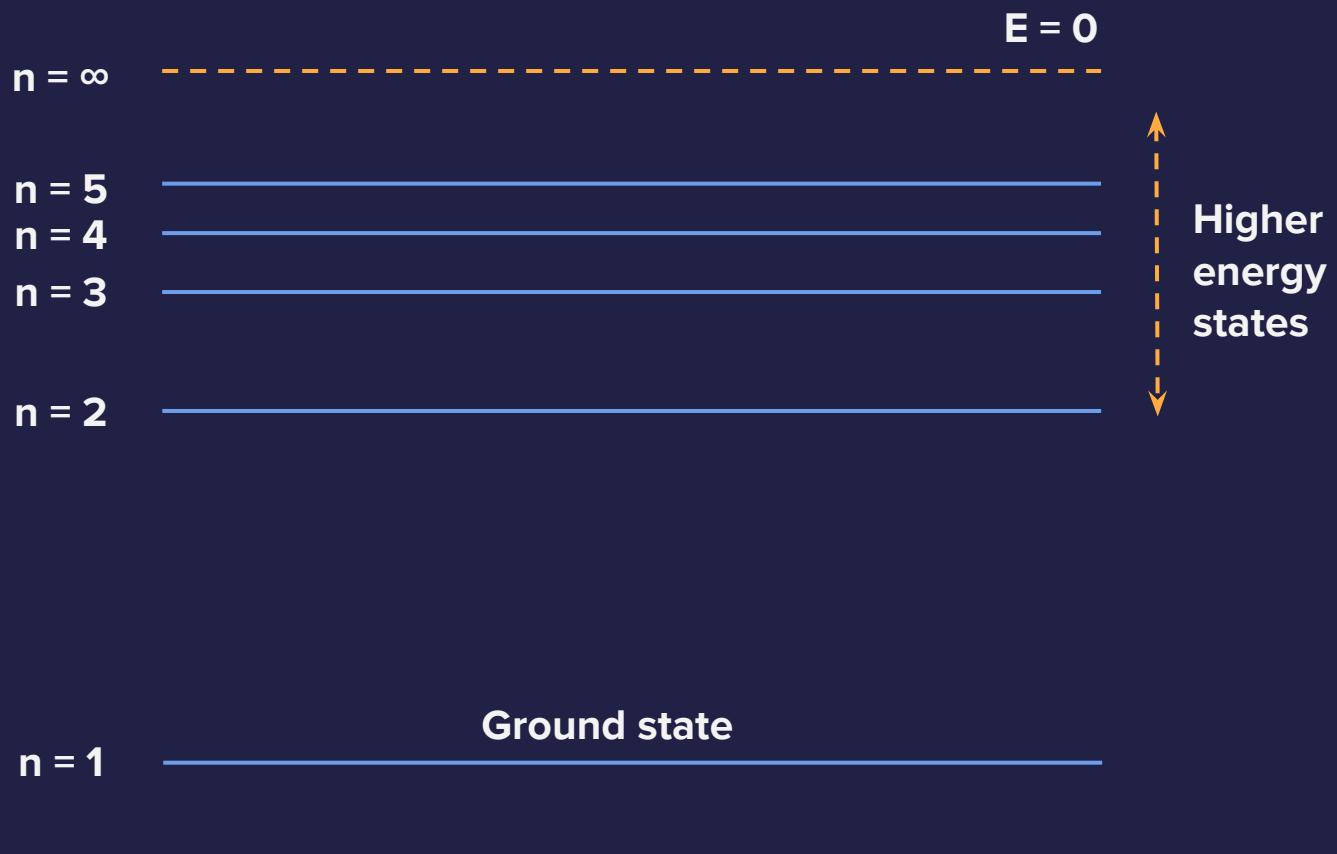
$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E \left(\frac{eV}{atom}\right) = \left(-13.6 \frac{Z^2}{n_2^{\,2}}\right) - \left(-13.6 \frac{Z^2}{n_1^{\,2}}\right)$$

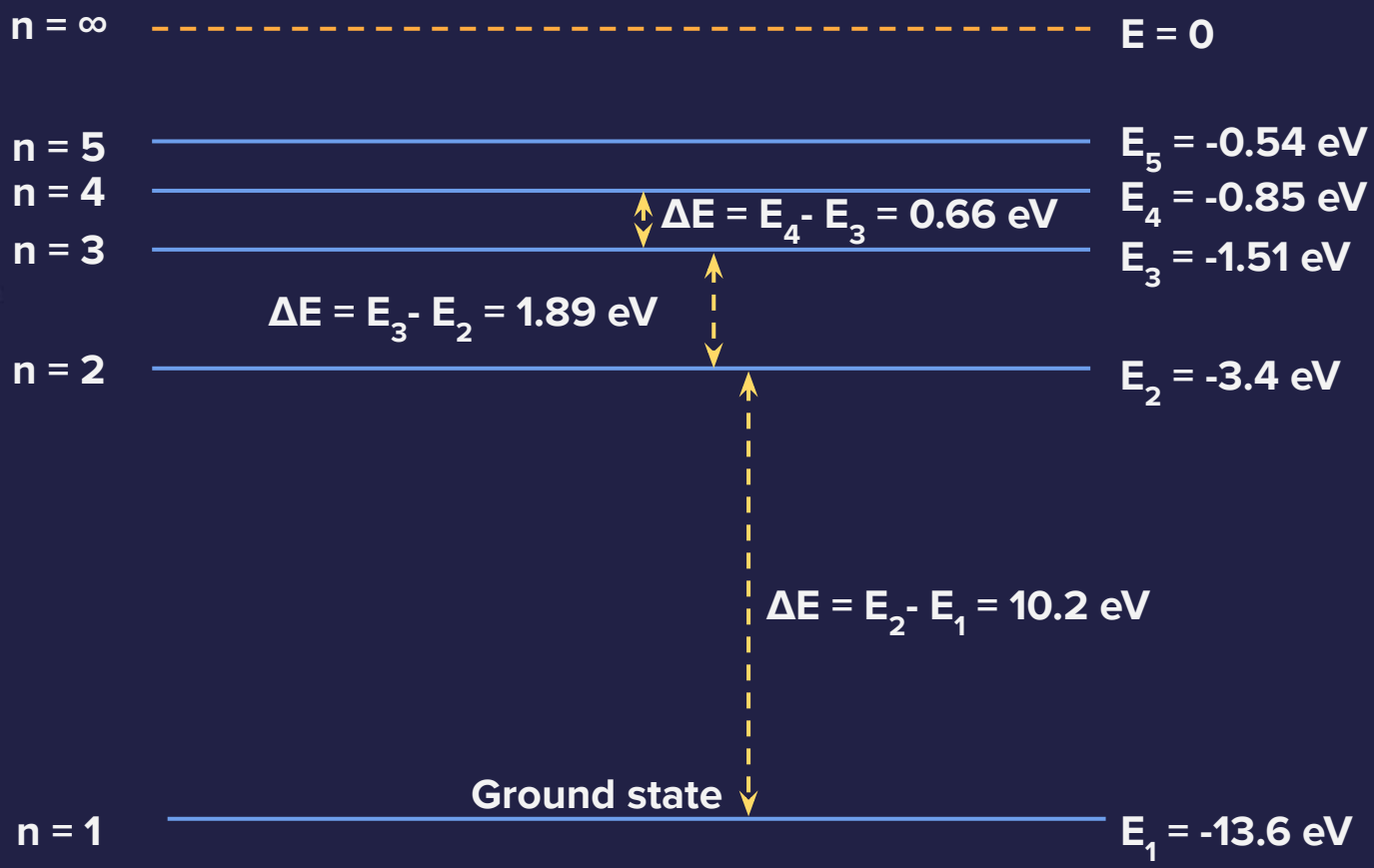
$$\Delta E = 13.6\, Z^2 \left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right) \frac{eV}{atom}$$

$$\Delta E = 2.18 \times 10^{-18}\, Z^2 \left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right) \frac{J}{atom}$$

Energy level diagram



Energy level diagram



Definition For Single Electron Systems

Ground state (G.S.)

Lowest energy state of any atom or ion	n = 1
G.S. energy of H-atom	-13.6 eV
G.S. energy of He^+ ion	-54.4 eV

Excited state

States of atom or ion other than the ground state — $n \neq 1$

$n = 2$	First excited state
$n = 3$	Second excited state
$n = m + 1$	m^{th} excited state

Ionisation energy (I.E.)

Minimum energy required to remove an electron **from $n = 1$ to $n = \infty$**

$$\Delta E = 13.6\, Z^2 \left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}} \right) \frac{eV}{atom}$$

Putting $n_2 = \infty$ & $n_1 = 1$

$$\Delta E = 13.6\, Z^2 \frac{eV}{atom}$$

Ionisation energy (I.E.)

$I.E._{H} = 13.6\ eV$

$I.E._{He^{+}} = 54.4\ eV$

$I.E._{Li^{2+}} = 122.4\ eV$

Ionisation potential (I.P.)

Potential difference through which a free electron must be accelerated from rest

such that its K.E. = I.E.

$I.P. = 13.6\ Z^2\ V$

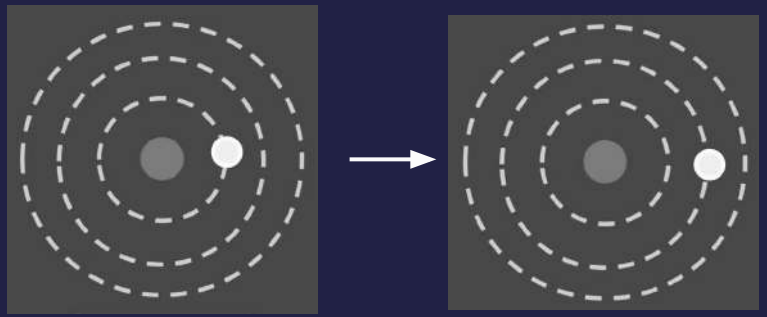
$I.P._H = 13.6\ V$

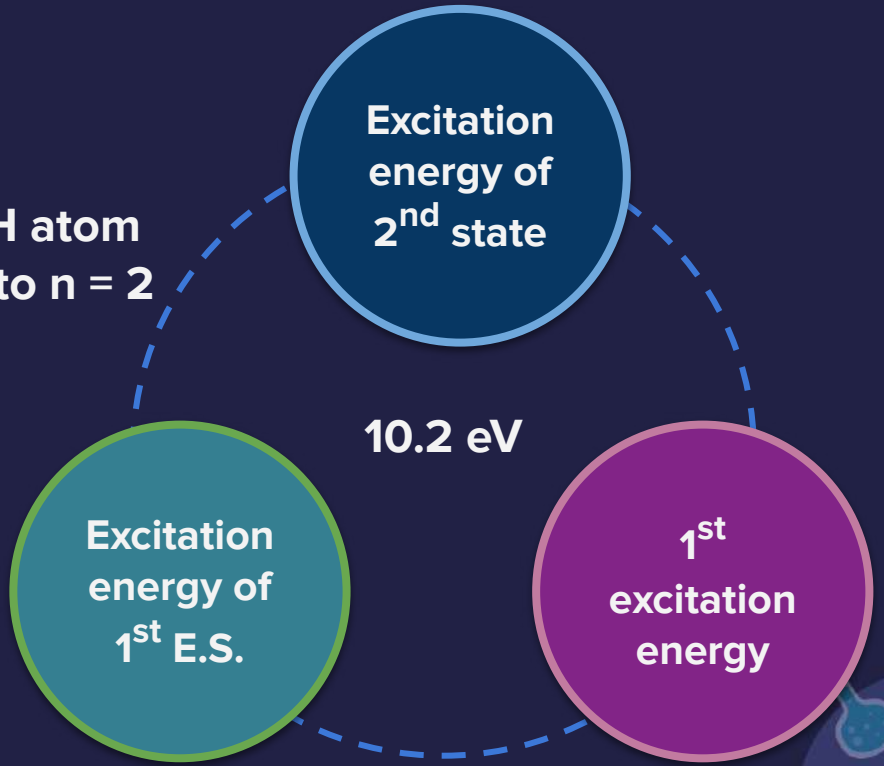
$I.P._{He^+} = 54.4\ V$

Excitation Energy

Energy required to move an electron from n = 1 to any other state

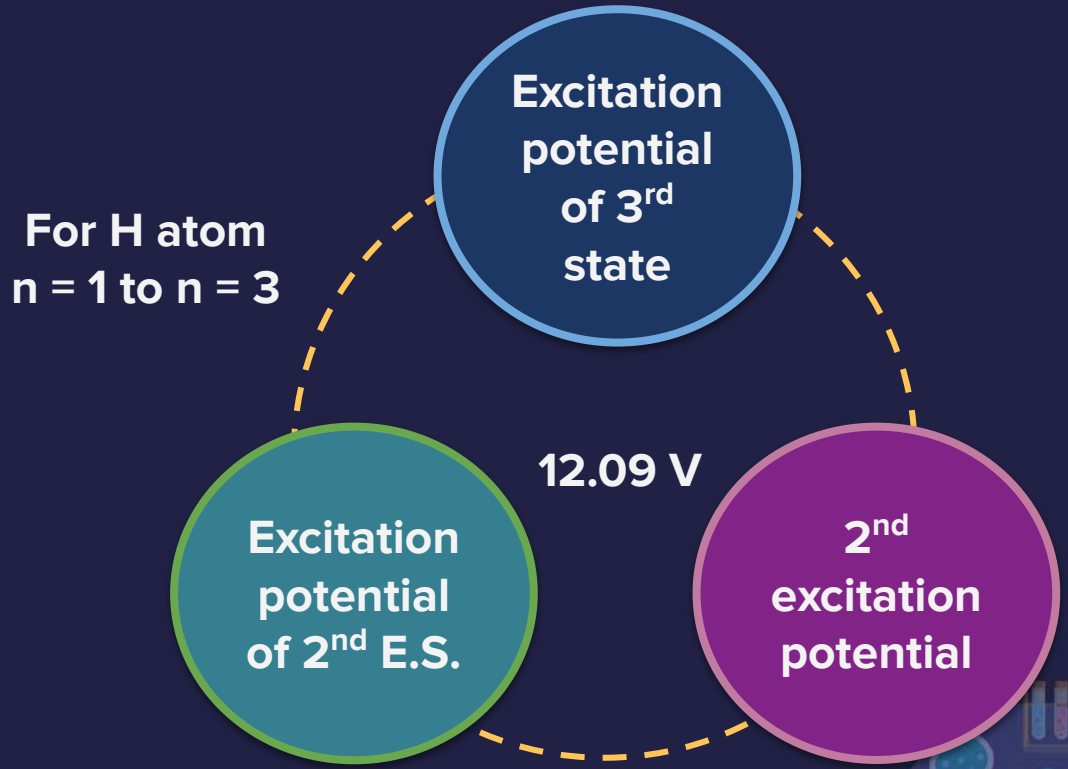
For H atom
n = 1 to n = 2





Excitation potential

Potential difference through which an electron must be accelerated from rest such that its
K.E. = Excitation energy



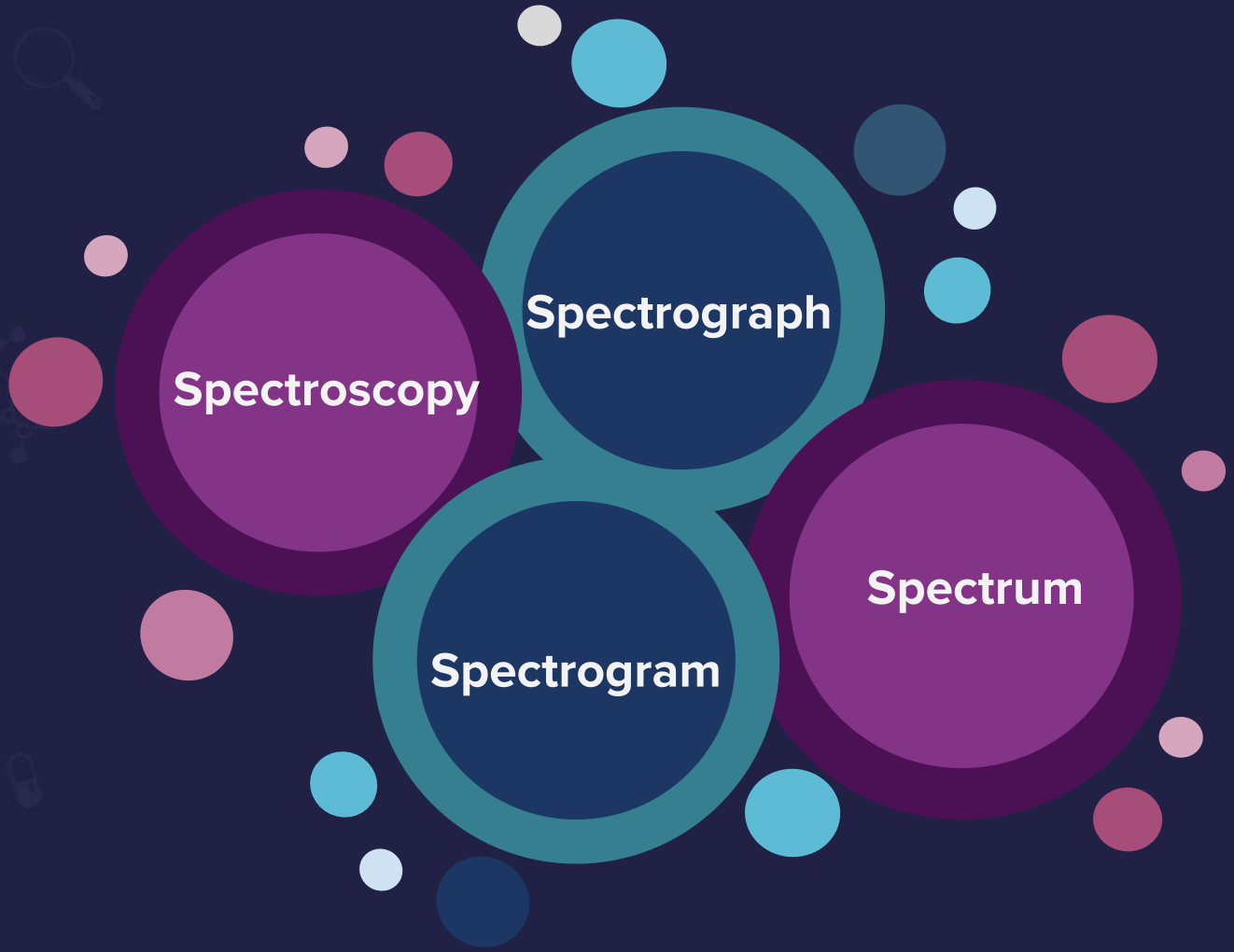
Binding or Separation energy

Energy required to
move an electron from any state to
n = ∞

$B.E._{Ground\ state}$ = $I.E._{Atom\ or\ Ion}$

Summary

Ground State	n = 1
Excited State	n > 1
Ionization Energy	From n = 1 to n = ∞
Binding Energy	From any state to n = ∞
Excitation Energy	From n = 1 to any other state


Spectroscopy
Spectrograph
Spectrogram
Spectrum

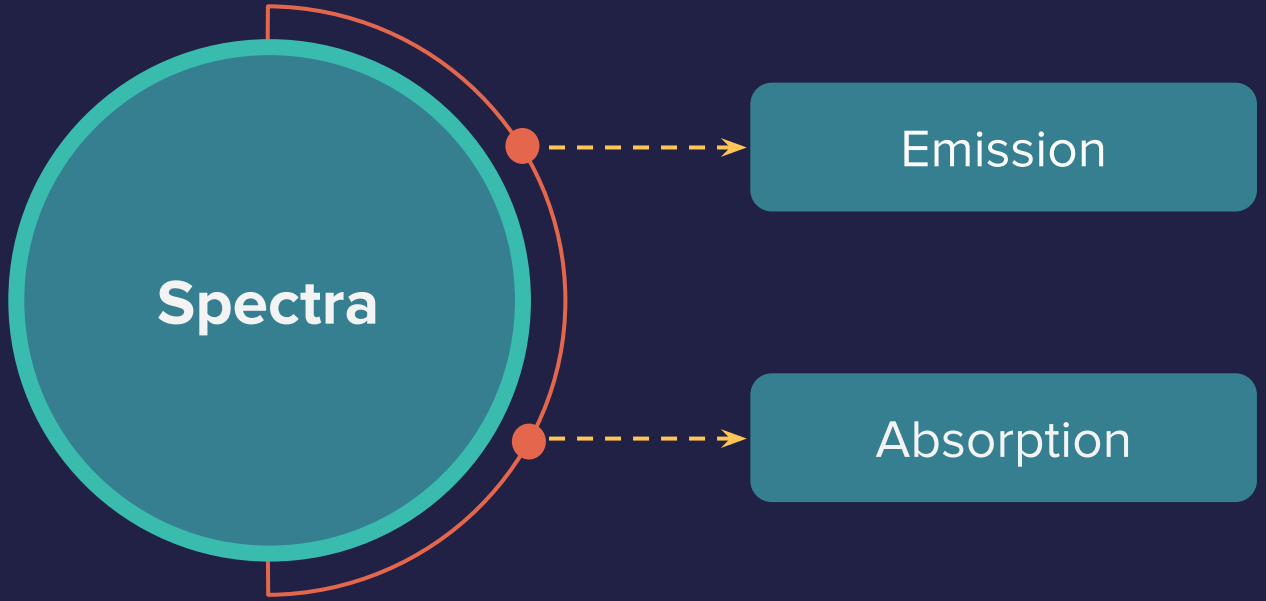
Spectroscopy

Spectroscopy
Branch of science that deals with the study of spectra

Spectrograph/ Spectroscope Ins trument used to separate radiation of different wavelengths

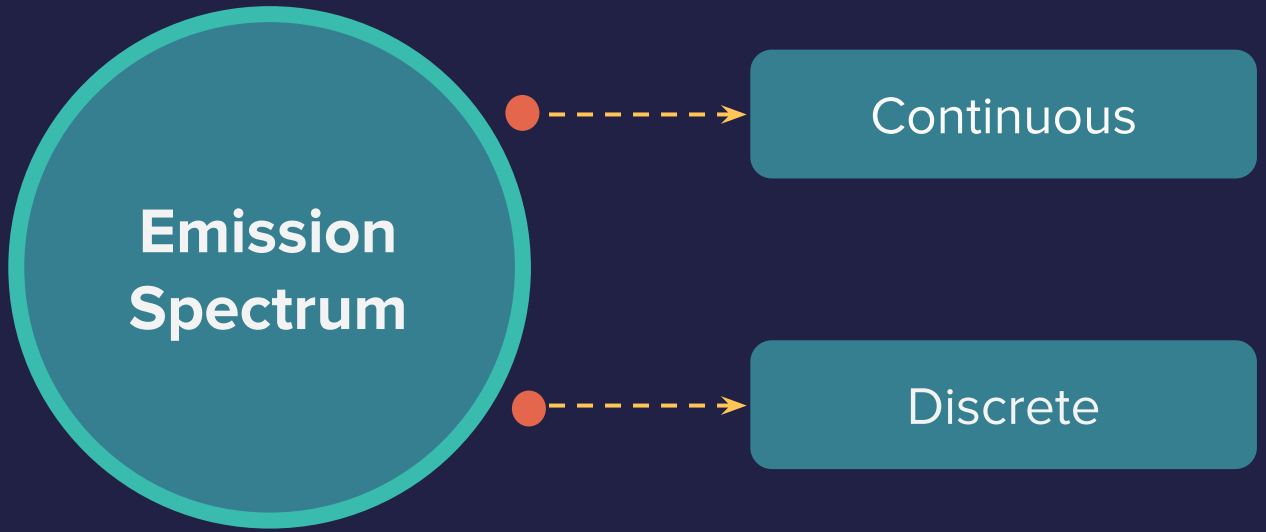
Spectrogram
Spectrum of the given radiation

Classification: Based on Origin



Emission Spectrum

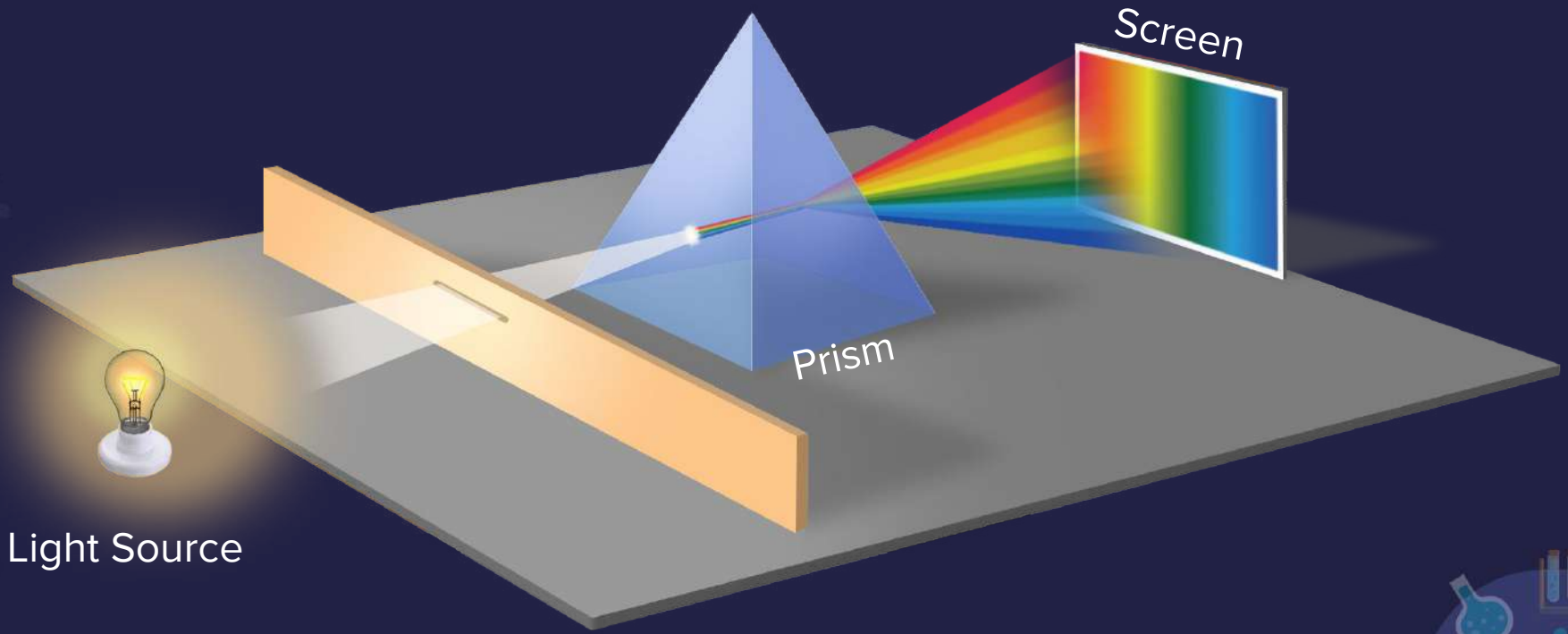
Spectrum of radiation emitted by a substance



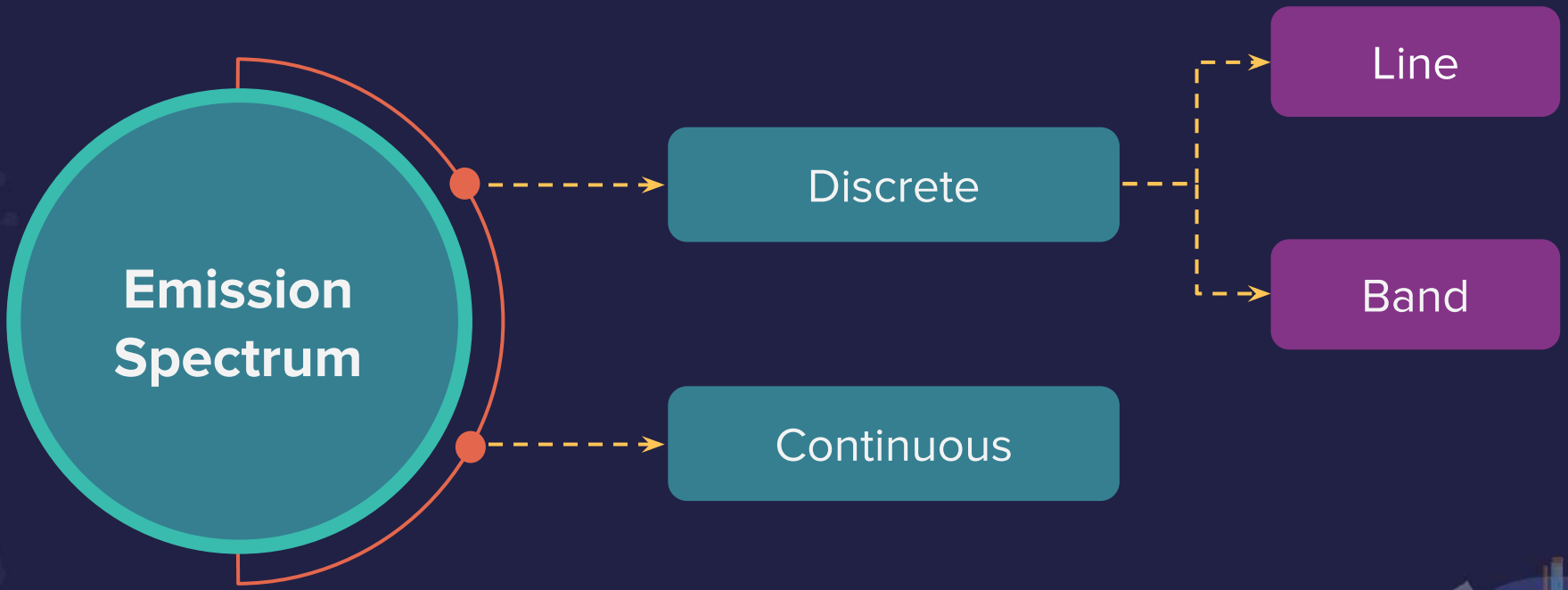
Continuous Spectrum

Continuous distribution of colours (VIBGYOR) such that each colour merges into the next one

Continuous Spectrum



Classification: Based on Nature

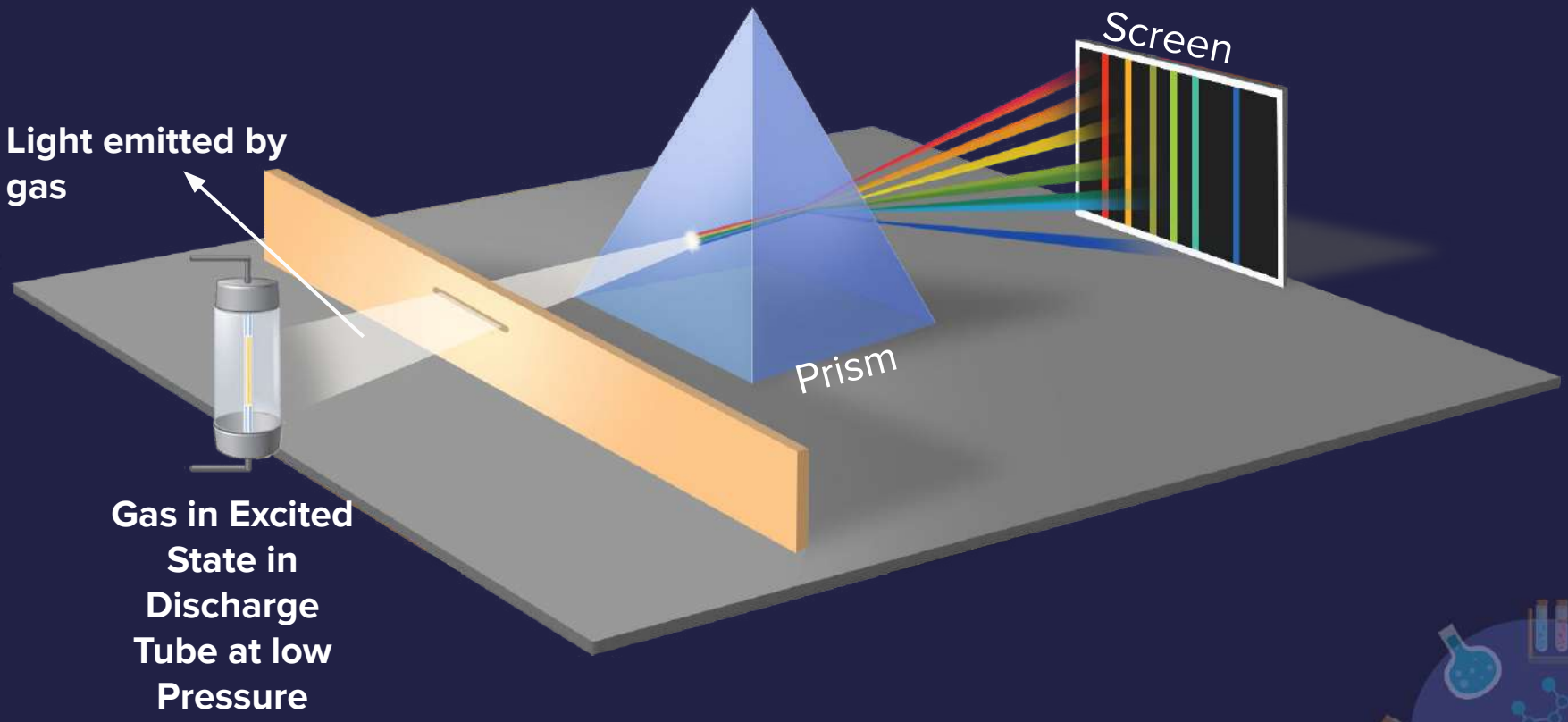


Line Spectrum

Ordered arrangement of lines of a particular wavelength separated by dark space

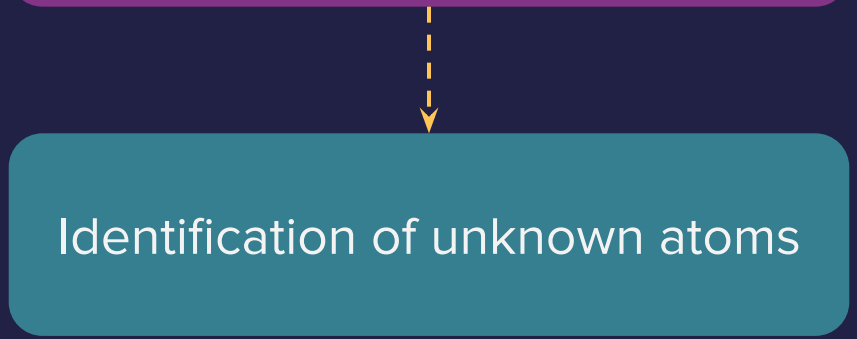
Line spectrum

Emission Spectra



Application of Line Spectrum

Each element has a unique line spectrum

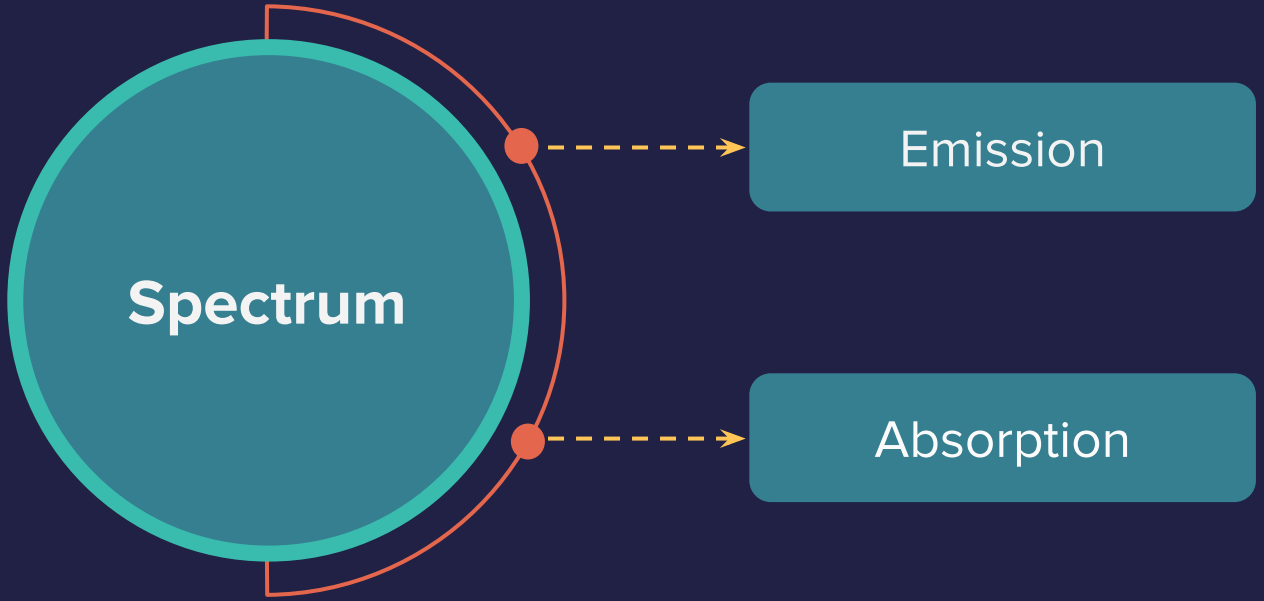


Band Spectrum

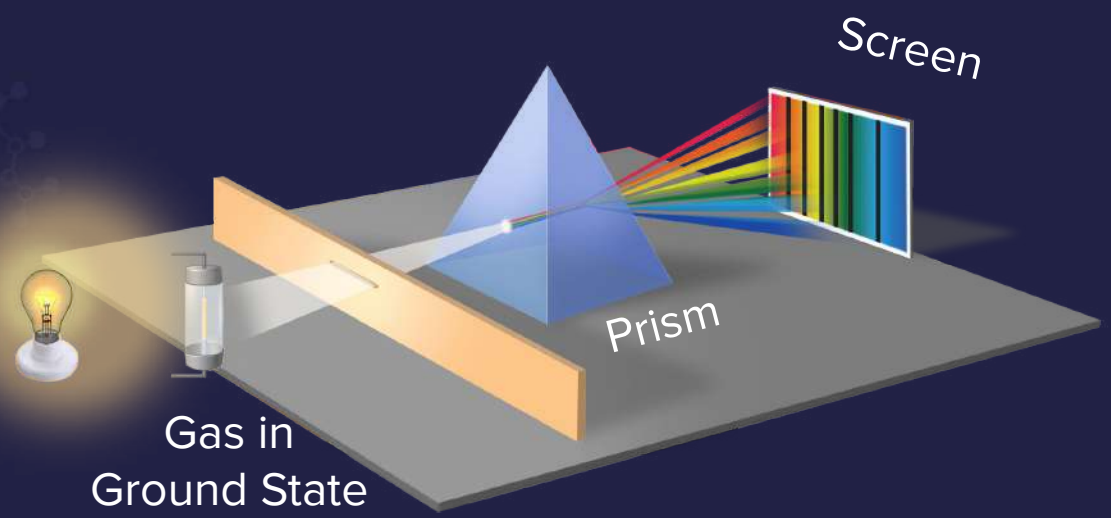
Continuous bands separated by some dark space

Molecular spectrum

Classification : Based on Origin



Absorption Spectrum



The gas in ground state absorbs radiation of particular wavelengths and rediations of remaing wavelength passes through the gas which scatter through a prism and appears as bright lines on the ecreen. The dark lines shows the missing wavelengths which are already absorbed by the gas and no more available to pass through the prism.

Absorption Spectrum

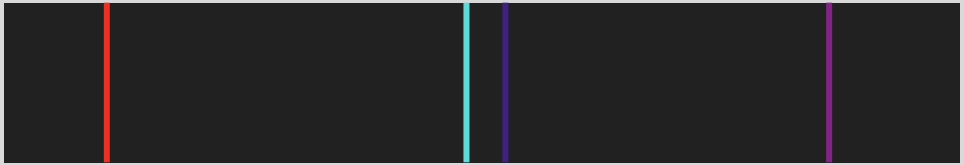
Some dark lines in the continuous spectrum

Represent absorbed radiations

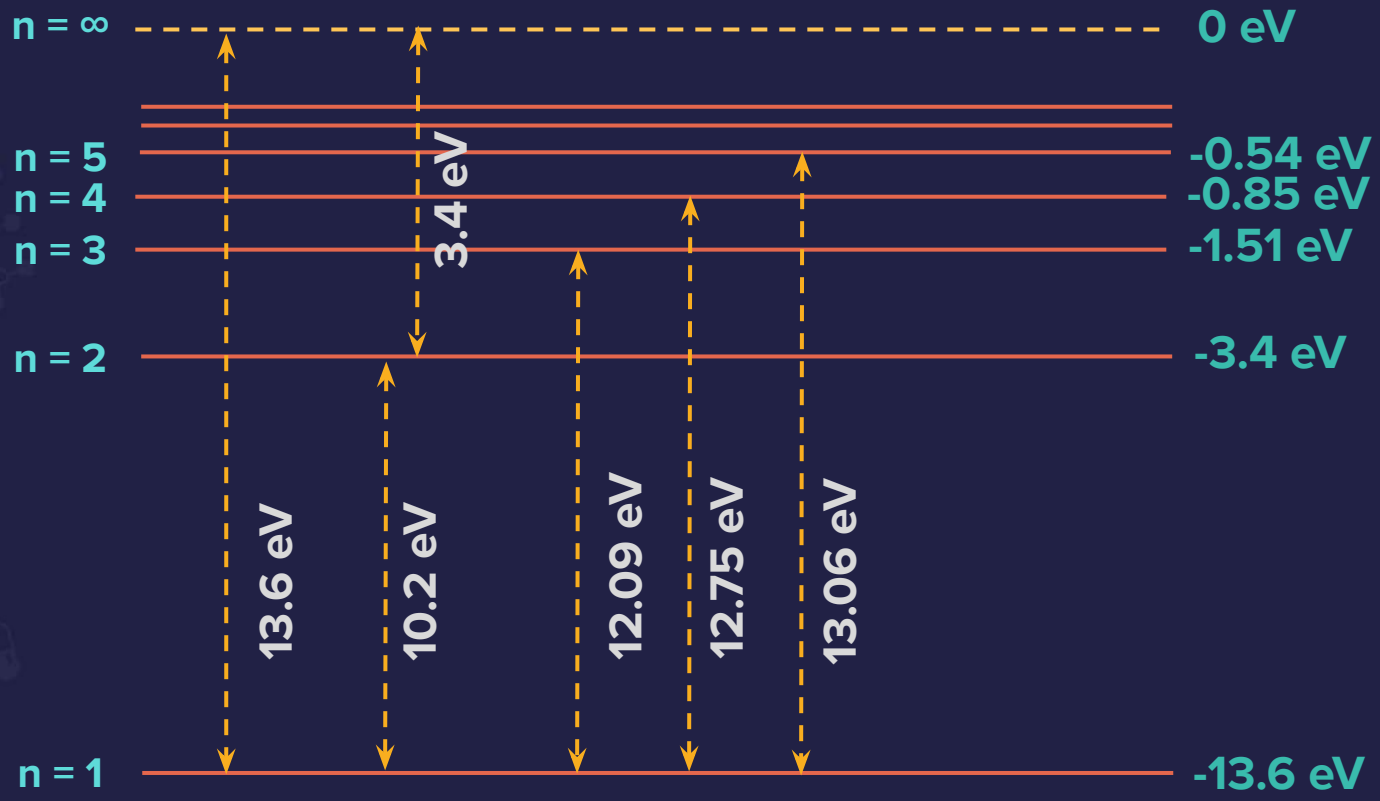
Line Spectrum of Hydrogen

Emission Spectral Lines/
De-Excitation Series

Due to de-excitation of electron
from higher to lower orbit



Energy Level Diagram for H atom



Rydberg's Formula

Electron makes transition from n_2 to n_1

$$\Delta E = \frac{hc}{\lambda} = 2.18 \times 10^{-18} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \frac{J}{atom}$$

$$\frac{1}{\lambda} = \frac{2.18 \times 10^{-18} Z^2}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) m^{-1}$$

Rydberg's Formula

$$\frac{1}{\lambda} = 1.09678 \times 10^{7} \times Z^{2} \left(\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}} \right) m^{-1}$$

$$\frac{1}{\lambda} = 109678 \times Z^{2} \left(\frac{1}{n_1^{2}} - \frac{1}{n_2^{2}} \right) cm^{-1}$$

n_1 1, 2, 3, ...

n_2 $n_1 + 1, n_1 + 2, ...$

R_H Rydberg constant

$$R_H = 1.09678 \times 10^{7}\ m^{-1} \simeq 1.1 \times 10^{7}\ m^{-1}$$

Rydberg's Formula

For any atom

$$\frac{1}{\lambda} = R_H Z^2 \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

n_1 : 1, 2, 3, ...

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

$$\lambda = \frac{912}{Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)} \text{ Å}$$

Rydberg's Formula

For H atom

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

n_1	1, 2, 3, ...
n_2	$n_1 + 1$, $n_1 + 2$, ...

Spectral series of H atom

Lyman

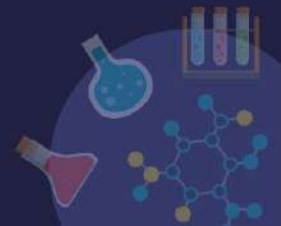
Balmer

Paschen

Brackett

Pfund

Humphrey



Lyman Series

For an electron present in H atom

1^{st} spectral series.
Found in UV region
by Lyman

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{1^2} - \frac{1}{n_2^{\,2}} \right)$$

$n_1 = 1$ (Final state)

$n_2 = 2, 3, 4 \ldots$
(Initial states, $n_2 > 1$)

Lyman Series

1st line of Lyman series (α line)	2 → 1
2nd line of Lyman series (β line)	3 → 1
Last line of Lyman series (Series limit)	∞ → 1

$n_2 = \infty$

$$\text{Wavelength of last line} = \frac{n_1^2}{R_H}$$

$$\lambda_{Lyman} = \frac{1}{R_H}$$

Lyman Series

$$10.2 \text{ eV} \leq (\Delta E)_{\text{Lyman}} \leq 13.6 \text{ eV}$$

$$\frac{12400}{13.6} \text{ Å} \leq \lambda_{\text{Lyman}} \leq \frac{12400}{10.2} \text{ Å}$$

Lyman Series

Longest wavelength = $\lambda_{longest}$ or λ_{max} = $\frac{12400}{\Delta E_{min}}$ Å

Shortest wavelength = $\lambda_{shortest}$ or λ_{min} = $\frac{12400}{\Delta E_{max}}$ Å

Where, E in eV

Lyman Series

1st spectral line	λ_{max}
Last spectral line	λ_{min}

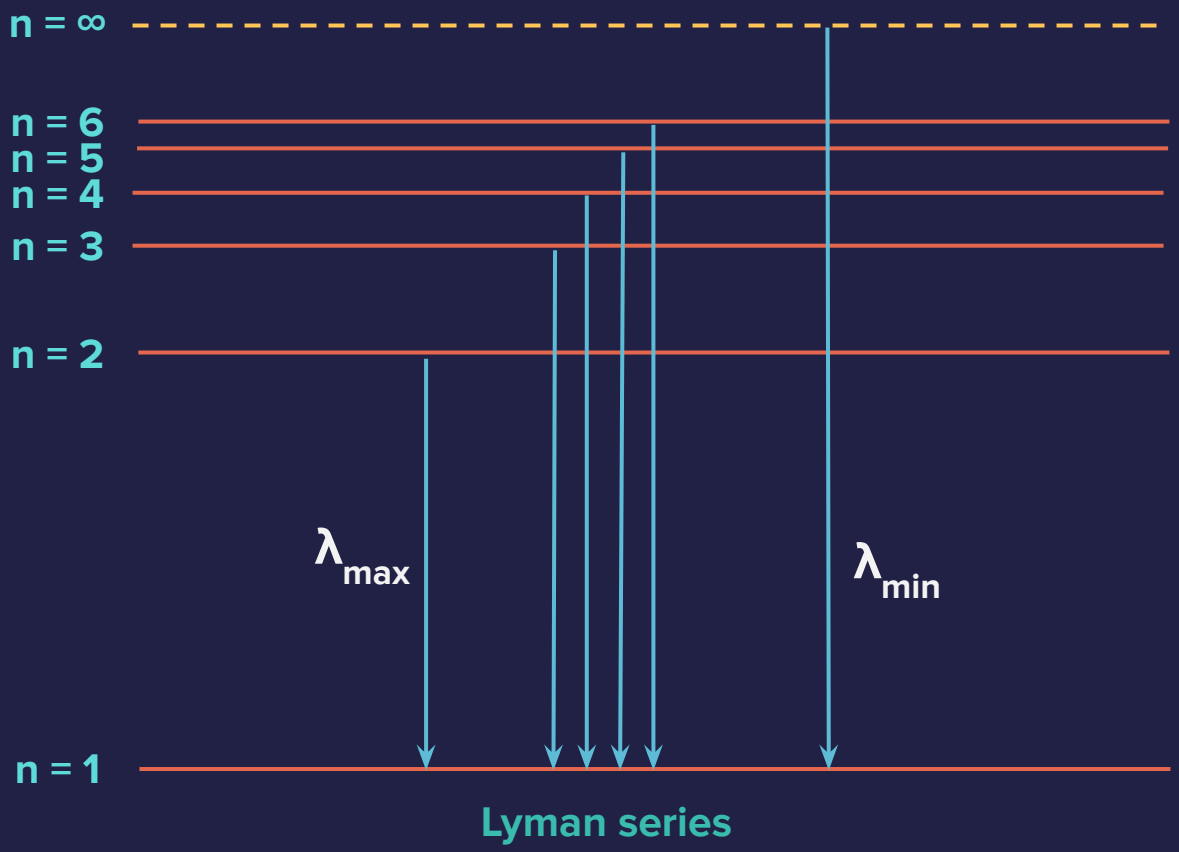
Series limit

Limiting/last line of any spectral series

Since $n_2 = \infty$

$$\bar{\nu}_{\text{last line}} = R_H$$

Lyman Series



Balmer Series

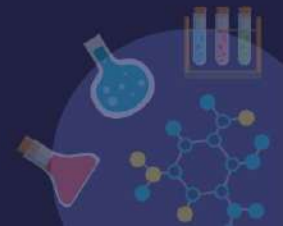
2^{nd} spectral series

Found in visible region by Balmer

For H atom

Only first 4 lines belongs to visible region

Rest belongs to UV region



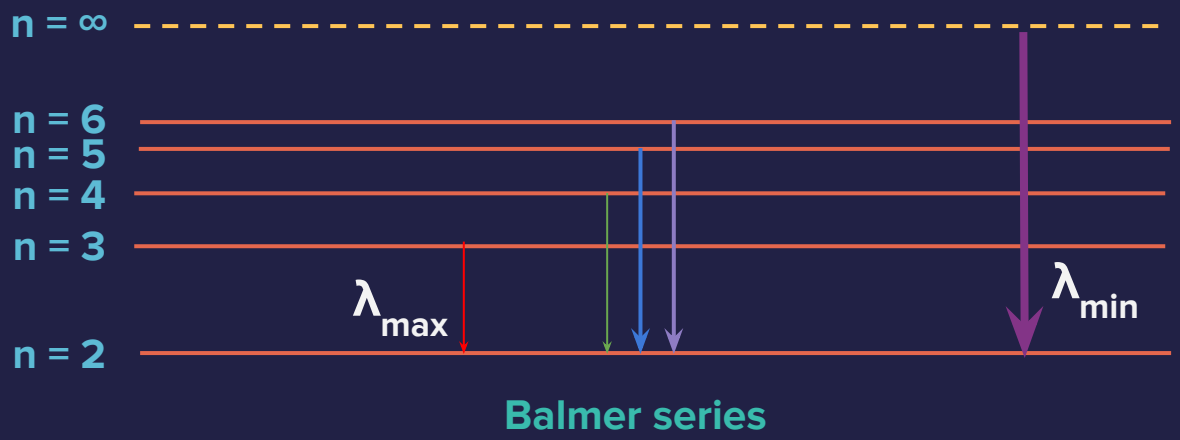
Balmer Series

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$$

$n_1 = 2$ (Final state)

$n_2 = 3, 4, 5 \ldots$
(Initial states, $n_2 > 2$)

Balmer Series



Balmer series

n = 1

Paschen Series

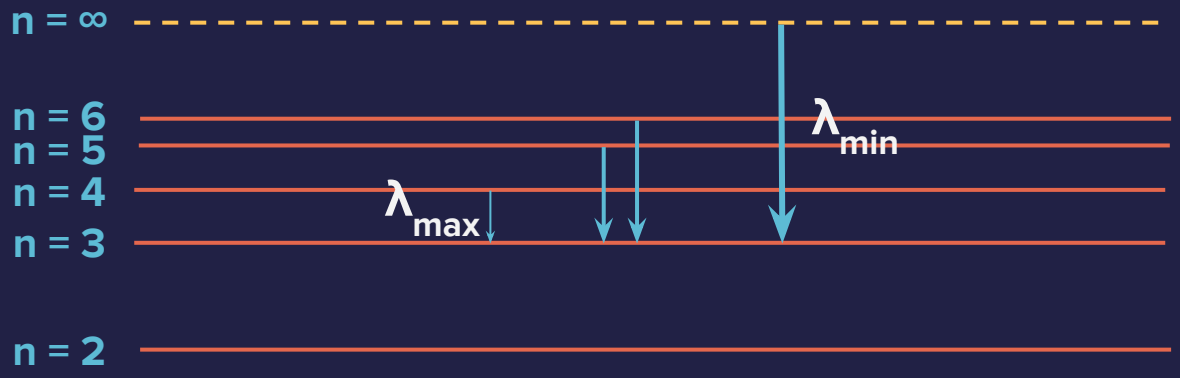
3rd spectral series; Found in IR region by Paschen

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{3^2} - \frac{1}{n_2^2} \right)$$

$n_1 = 3$ (Final state)

$n_2 = 4, 5, 6 \ldots$
(Initial states, $n_2 > 3$)

Paschen Series



Paschen series

Brackett Series

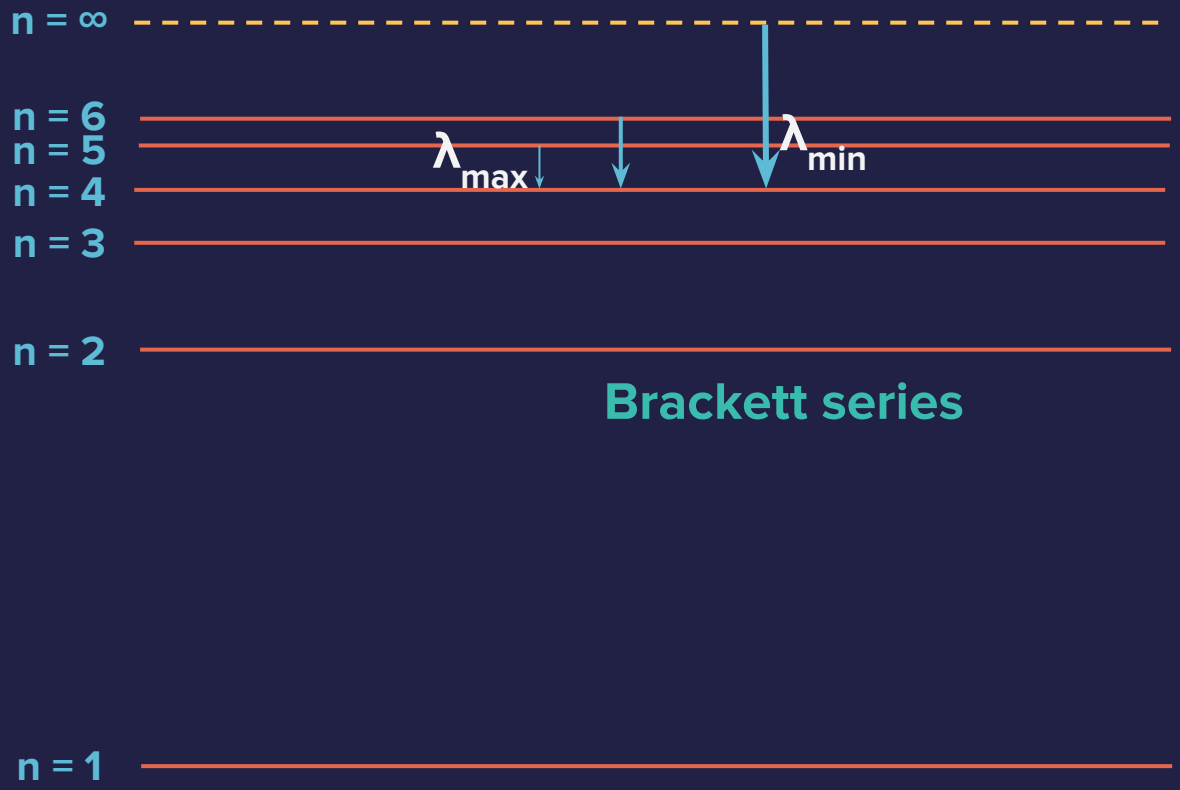
4^{th} spectral series; Found in IR region by Brackett

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{4^2} - \frac{1}{n_2^{\,2}} \right)$$

$n_1 = 4$ (Final state)

$n_2 = 5, 6, 7 \ldots$
(Initial states, $n_2 > 4$)

Brackett Series



Pfund Series

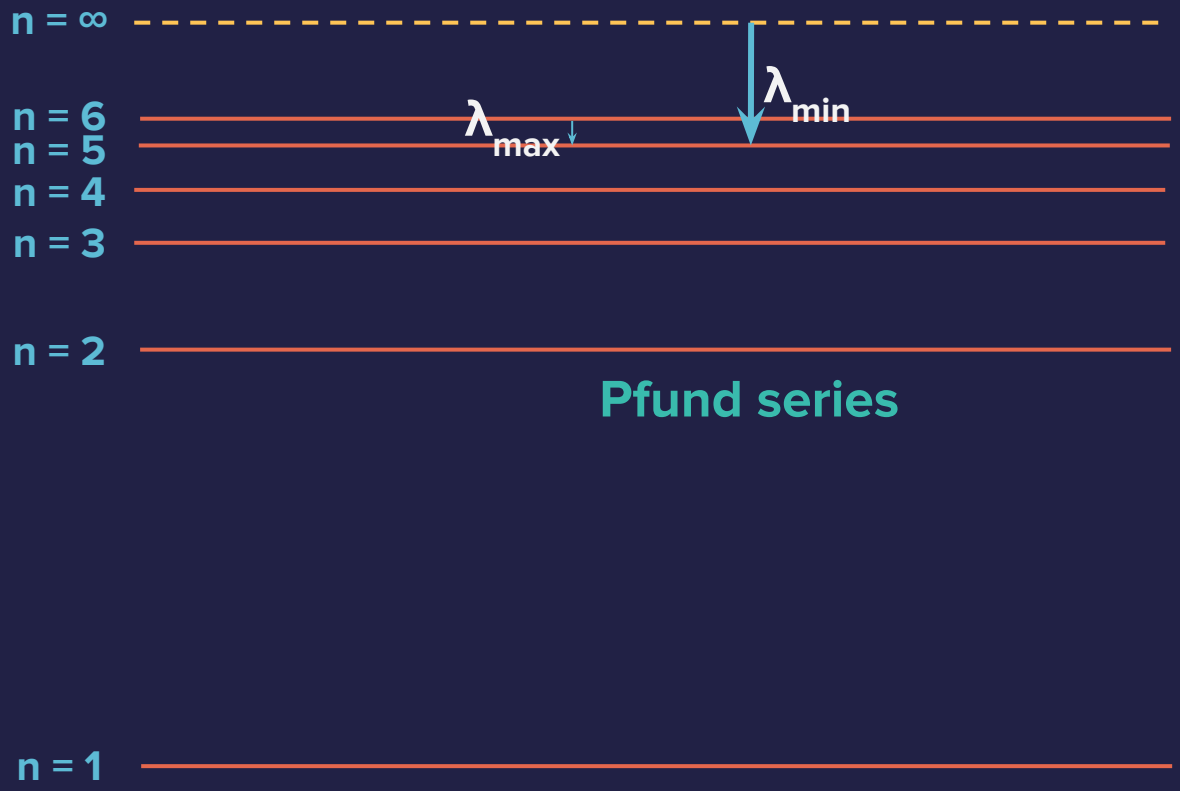
5^{th} spectral series; Found in IR region by Pfund

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{5^2} - \frac{1}{n_2^2} \right)$$

$n_1 = 5$ (Final state)

$n_2 = 6, 7, 8 \ldots$
(Initial states, $n_2 > 5$)

Pfund Series



Humphrey Series

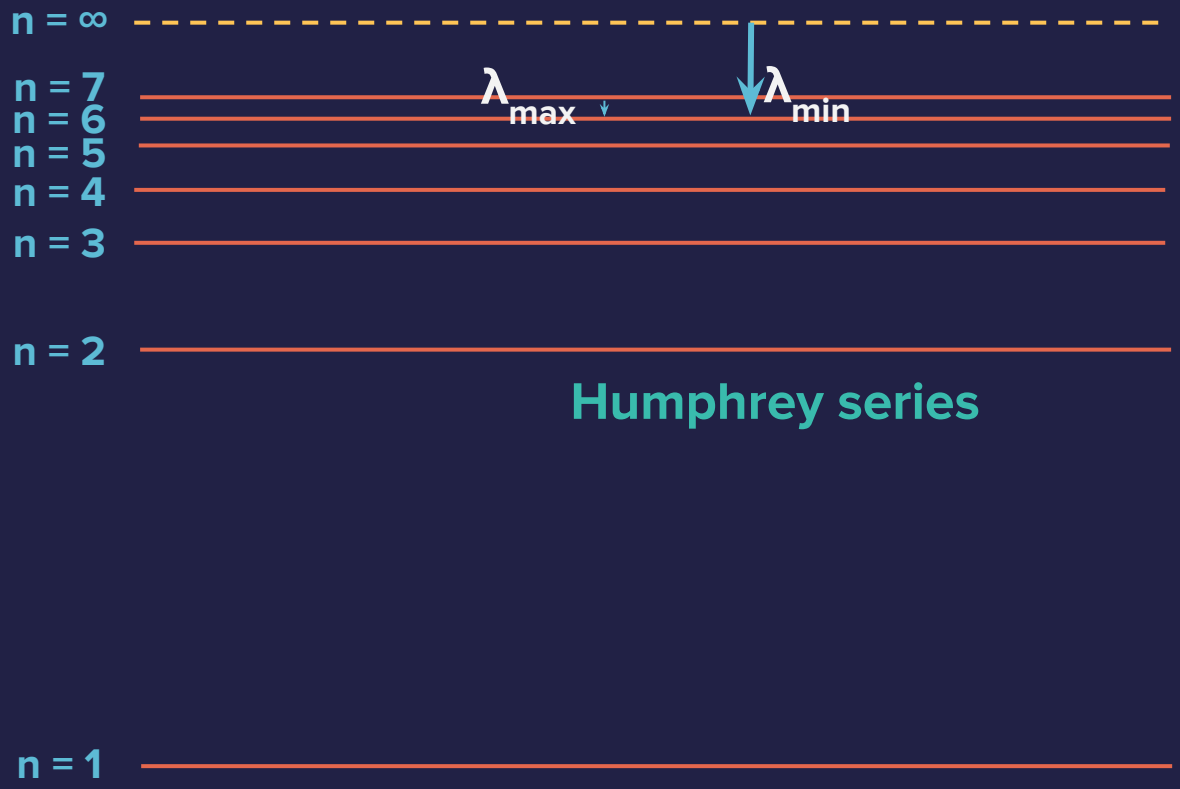
6^{th} spectral series; Found in IR region by Humphrey

$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{6^2} - \frac{1}{n_2^{\,2}} \right)$$

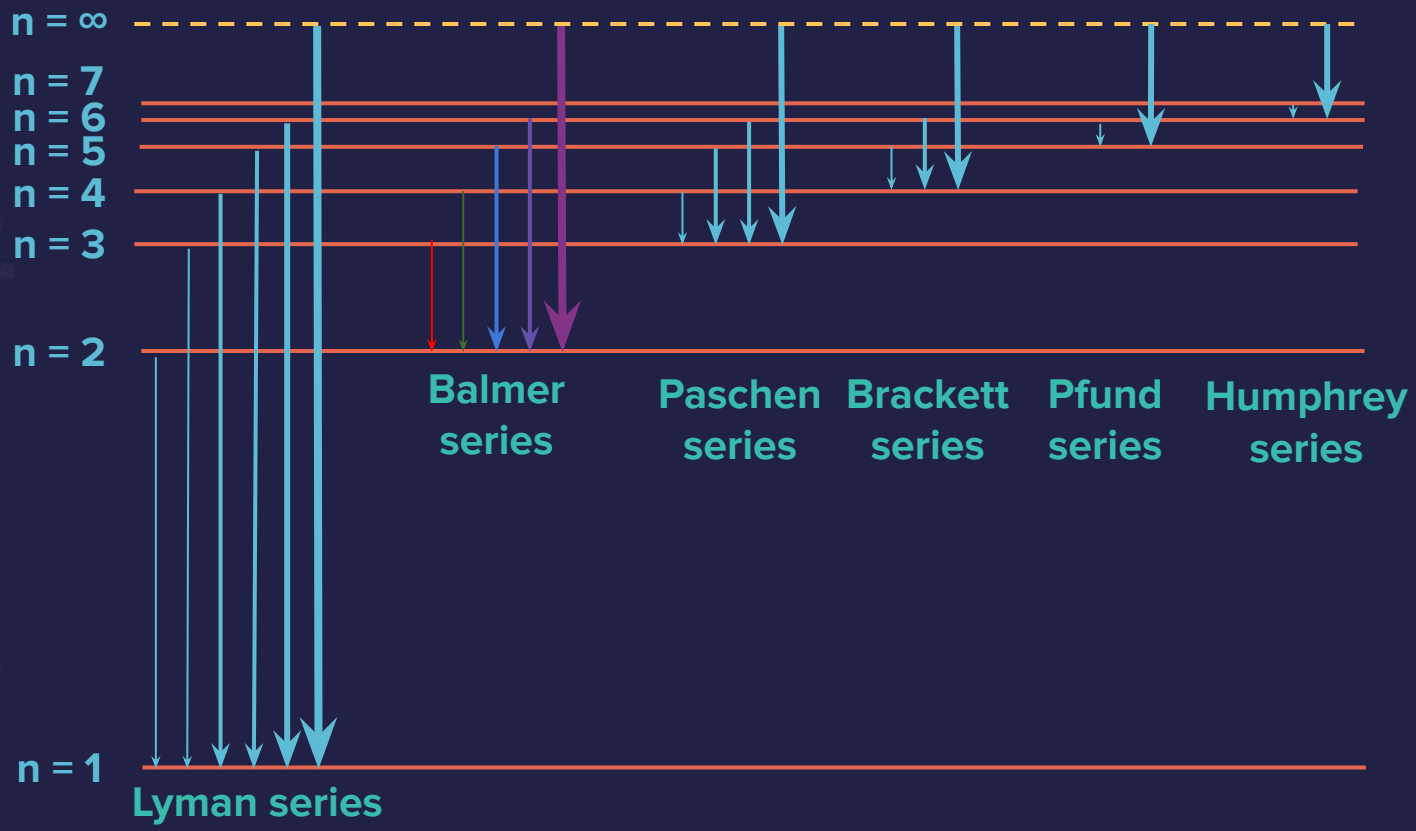
$n_1 = 6$ (Final state)

$n_2 = 7, 8, 9 \ldots$
(Initial states, $n_2 > 6$)

Humphrey Series



Line Spectrum of Hydrogen



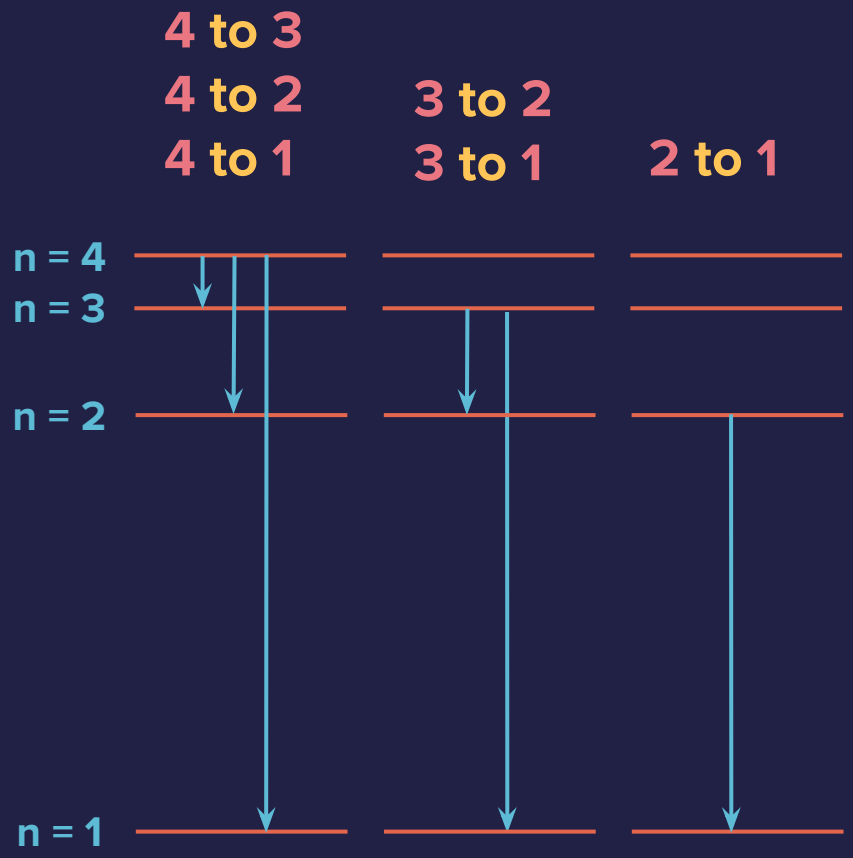
Maximum Number of Spectral Lines

Maximum number of lines

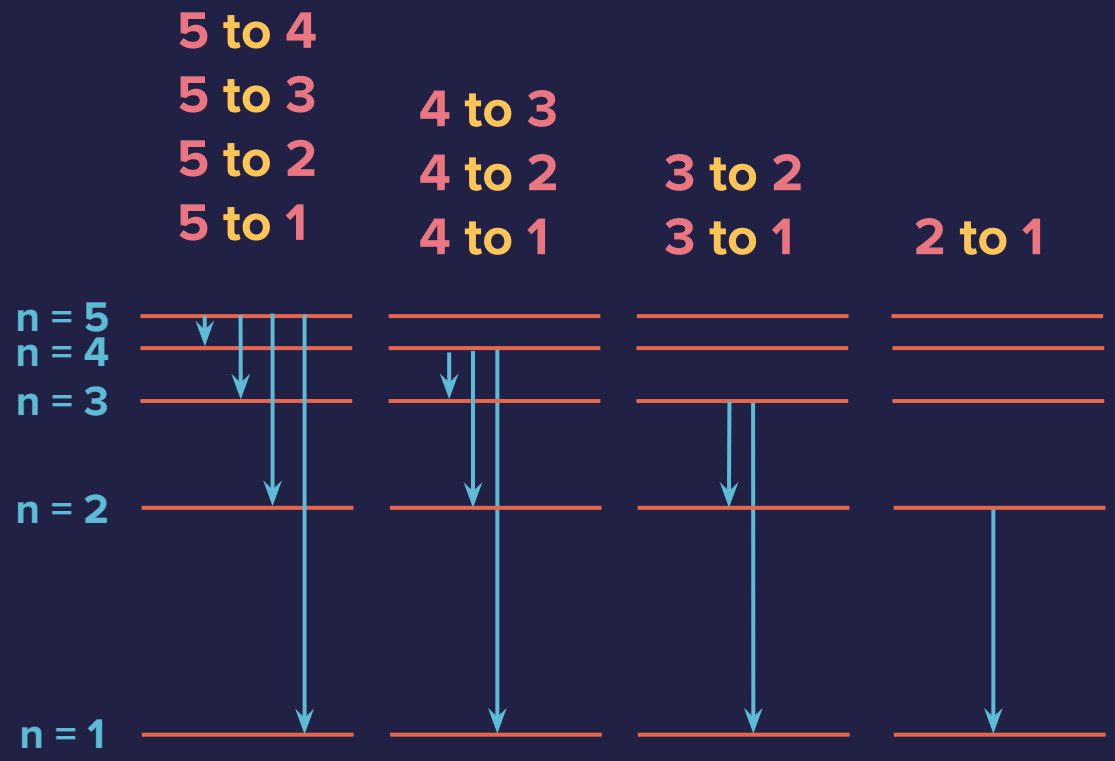
=

Maximum number of different types of photons

Maximum Lines for the transition from 4 to 1



Maximum Lines for the transition from 5 to 1



Maximum Number of Lines

$$\text{Spectral Lines} = \frac{(n_H - n_L + 1)(n_H - n_L)}{2} = \frac{(\Delta n + 1)(\Delta n)}{2}$$

Δn	$n_H - n_L$
n_H	Higher energy level
n_L	Lower energy level

Maximum Number of Lines

For transition upto n = 1 or n = n_{Series}

In Lyman series ($n_{Higher} > 1$)	=	$n_{Higher} - 1$
In Balmer series ($n_{Higher} > 2$)	=	$n_{Higher} - 2$
In Paschen series ($n_{Higher} > 3$)	=	$n_{Higher} - 3$

For a particular series

Spectral lines = $n_{Higher} - n_{Series}$

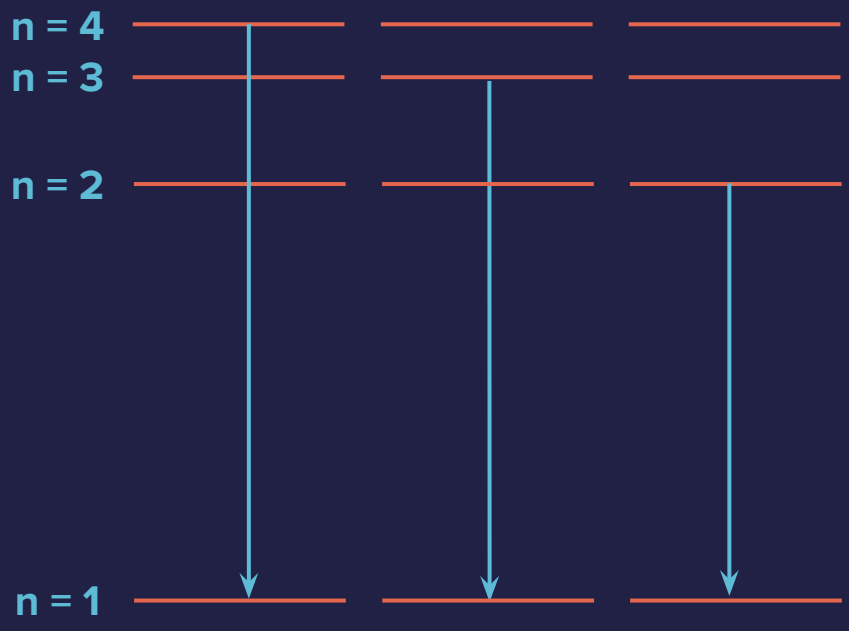
Maximum Number of Lines

In Brackett series ($n_{Higher} > 4$)	=	$n_{Higher} - 4$
In Pfund series ($n_{Higher} > 5$)	=	$n_{Higher} - 5$
In Humphrey series ($n_{Higher} > 6$)	=	$n_{Higher} - 6$

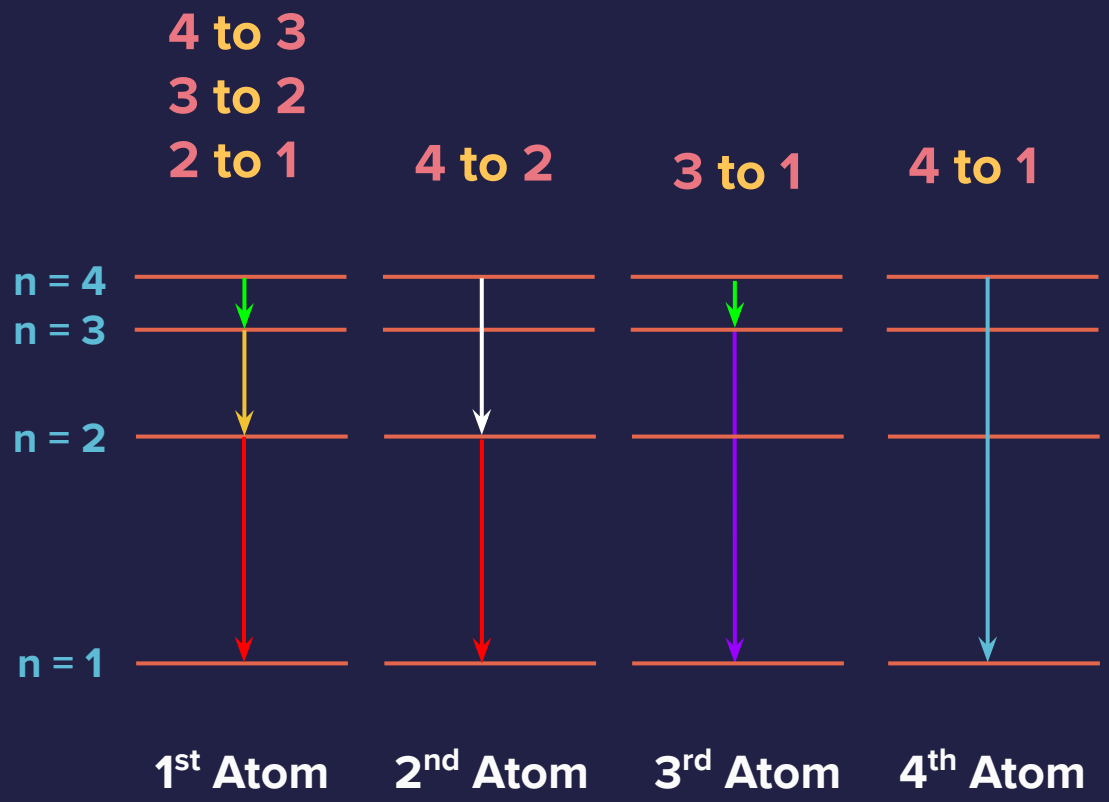
Example

Number of spectral lines in Lyman series from 4^{th} shell

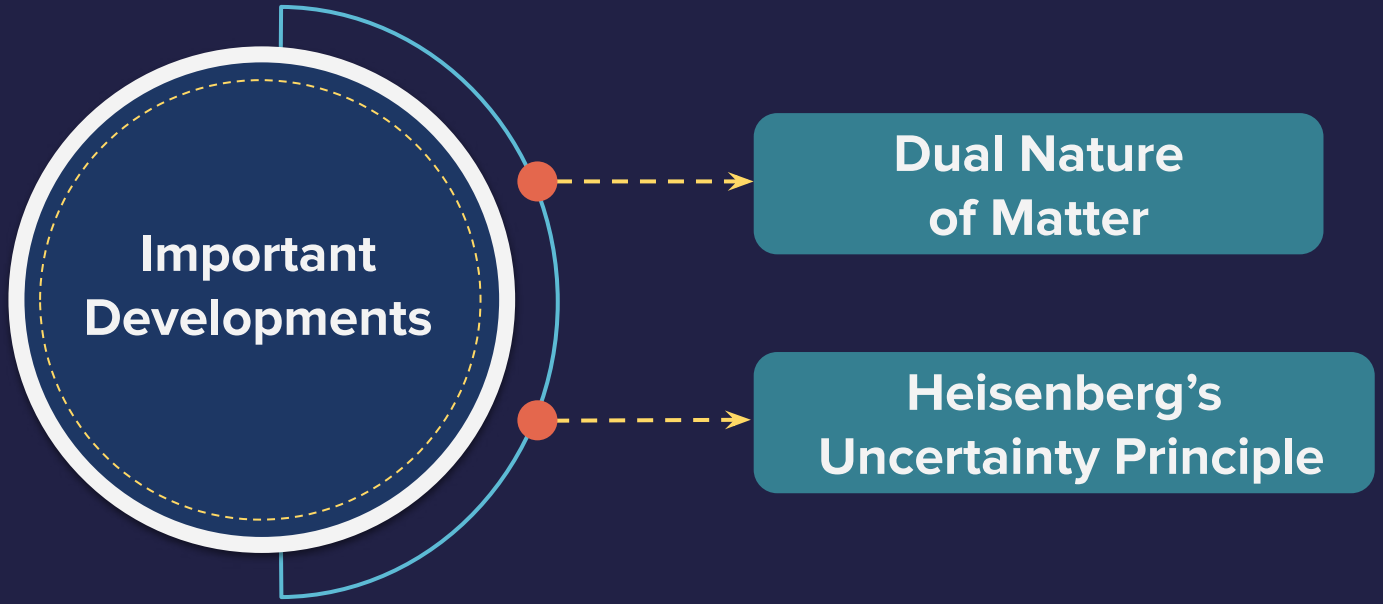
$= n_H - 1 = 4 - 1 = 3$



Example


4 to 3
3 to 2
2 to 1
4 to 2
3 to 1
4 to 1
n = 4
n = 3
n = 2
n = 1
1st Atom
2nd Atom
3rd Atom
4th Atom

Pathway to Quantum Mechanical Model



These developments shows that electron has sufficient wave character and it can not be assumed as a particle only. So, its position or trajectory can not be determined as shown by Bohr model.

Dual Nature of Matter

de Broglie proposed that **particle** has dual nature

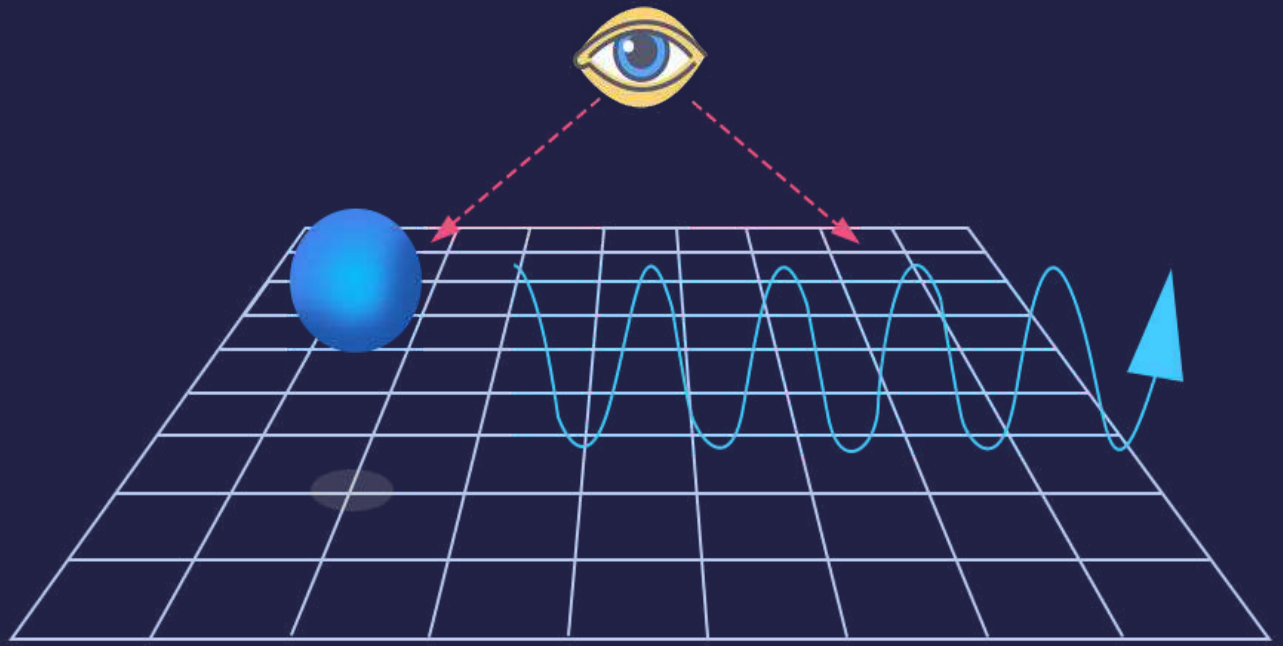
Louis de Broglie

Particle nature

Wave nature

Einstein suggested that **light** has dual nature i.e., particle nature as well as wave nature.

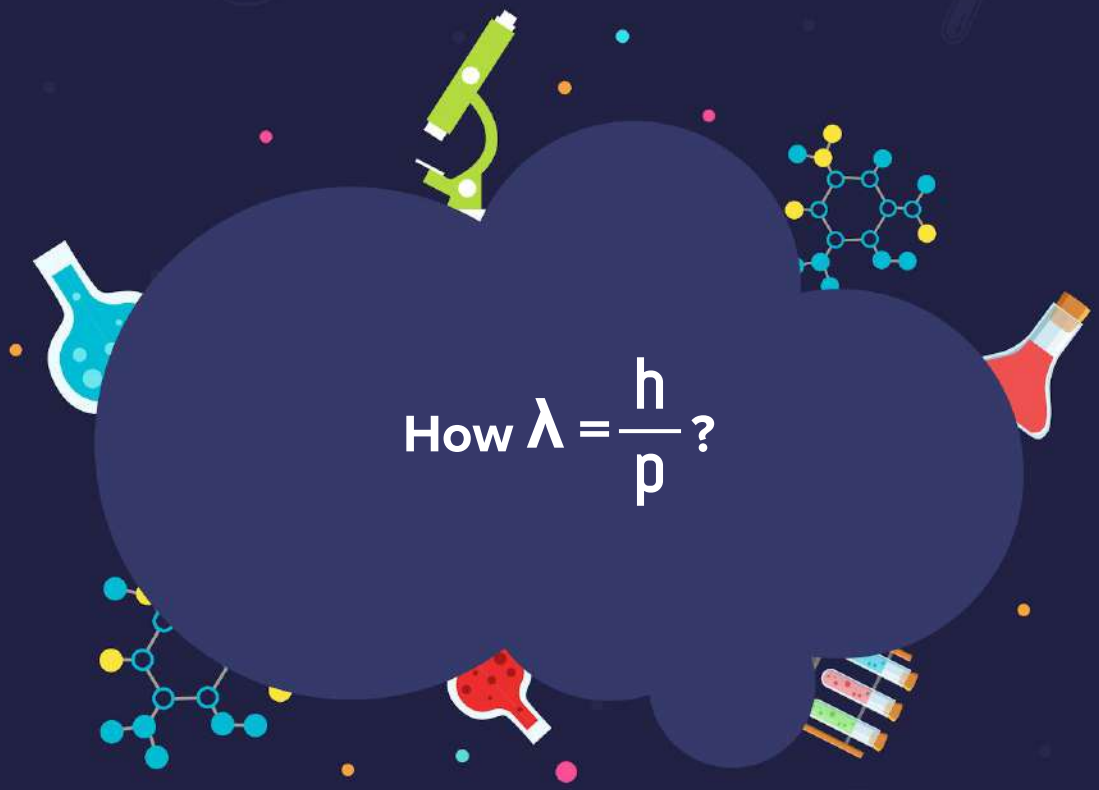
de Broglie Hypothesis



de Broglie Hypothesis

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

Wave associated with **moving particles**


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

de Broglie Hypothesis

Planck's equation

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

Einstein's Mass Energy relationship

$$E = mc^2$$

de Broglie Hypothesis

Equating both

$$\frac{hc}{\lambda} = mc^2$$

For photon

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

By same analogy, de Broglie proposed

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

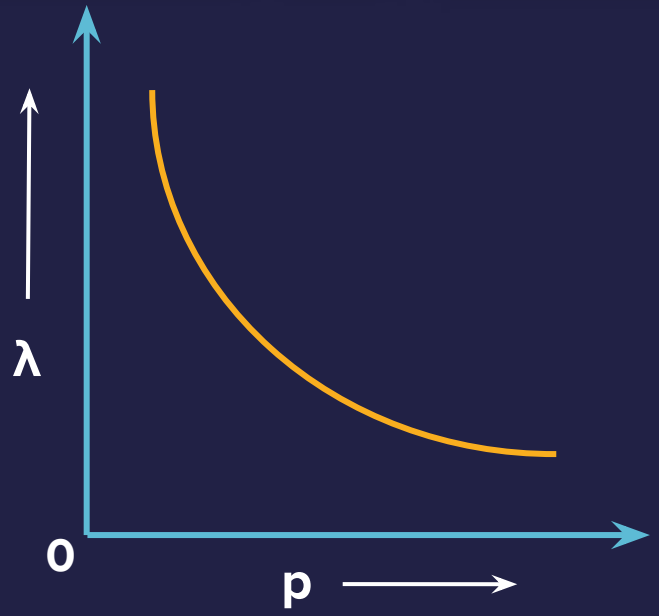
de Broglie Wavelength (λ)

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

- **p** — Momentum of particle
- **v** — Velocity of particle
- **m** — Mass of particle
- **h** — Planck's constant

de Broglie Wavelength (λ)

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



Relativistic Mass

$$m = \frac{m_o}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

- v — Velocity w.r.t. the observer
- c — Velocity of light
- m — Dynamic mass
- m_o — Rest mass

Relativistic Mass

$$m_0 = m \times \sqrt{1 - \left(\frac{v}{c}\right)^2}$$

If $v = c$

$$m_o = 0$$

Rest mass of photon is zero

Davisson and Germer's Experiment

Experimental verification of **de Broglie's prediction**

It was observed that an **electron beam** undergoes **diffraction**

Wavelength of a ball & an electron!

de Broglie wavelength: $\lambda = \frac{h}{mv}$

Cricket ball

$m = 150\ g$

$v = 25\ m\ s^{-1}$

$$\lambda = \frac{6.626 \times 10^{-34}}{(150 \times 10^{-3}) \times 25}$$

$\lambda = 1.767 \times 10^{-34}\ m$

λ is insignificant.

Electron

$m = 9.1 \times 10^{-31}\ kg$

$v = 2 \times 10^{3}\ m\ s^{-1}$

$$\lambda = \frac{6.626 \times 10^{-34}}{(9.1 \times 10^{-31}) \times 2 \times 10^{3}}$$

$\lambda = 0.364 \times 10^{-6}\ m$

$= 364\ nm$

λ is significant.

Matter Waves

Wave nature can't be detected for macroscopic object

because its wavelength is too short due to larger mass.

$$\lambda \propto \frac{1}{m}$$

de Broglie's Equation & Kinetic Energy

$$K.E. = \frac{1}{2}mv^2$$

Multiplying both sides by m & rearranging

$$m^2v^2 = 2\,K.E. \times m$$

$$mv = \sqrt{2\,K.E. \times m}$$

de Broglie's Equation & Kinetic Energy

de Broglie equation

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

Since

$$mv = \sqrt{2 \text{ K.E. x m}}$$

$$\lambda = \frac{h}{\sqrt{2 \text{ K.E.} \times m}}$$

de Broglie's Equation & Kinetic Energy

A charged particle accelerated from rest across a **potential difference of V**

$$|K.E.| = |qV|$$

$$\therefore \quad mv = \sqrt{2m \times K.E.}$$

$$\therefore \quad mv = \sqrt{2m \times qV}$$

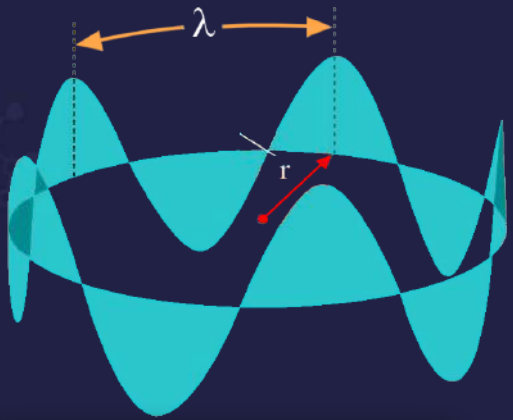
de Broglie's Equation & Kinetic Energy

$$\lambda = \frac{h}{\sqrt{2m \times q\,V}}$$

- λ — Wavelength (m)
- q — Charge on a particle (C)
- m — Mass of charged particle (kg)
- h — Planck's constant (Js)

Electron as a Wave

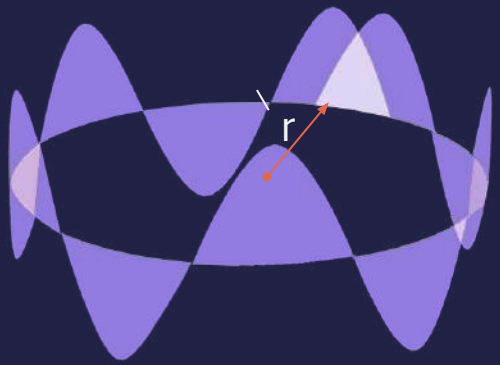
In phase



Electron exist

Circumference,
$2\pi r = n\lambda$

Out of phase



Electron don't exist

Circumference,
$2\pi r \neq n\lambda$

n = Number of waves made in Bohr's orbit

An integral number of complete wavelengths must fit around the circumference of the orbit.

Electron as a Wave

When electrons are in phase,

$$2\pi r = \frac{nh}{mv}$$

Bohr's Postulate verified

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

n = Energy level

Heisenberg's Uncertainty Principle (H.U.P.)

Werner Heisenberg

Exact **position** and **momentum** of a microscopic particle **cannot be determined** simultaneously

Heisenberg's Uncertainty Principle

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

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

- Δx — Uncertainty in position
- Δp — Uncertainty in momentum
- m — Mass of particle
- Δv — Uncertainty in velocity

Principle of Optics

If a light (wavelength ‘λ’) is used to locate the position of a particle, then

Minimum error in the position measurement (Δx) = $\pm \lambda$

Heisenberg's Uncertainty Principle

Since $\Delta x = \lambda$

For accurate position $\Delta x \longrightarrow 0$ $\lambda \longrightarrow 0$

For a photon

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

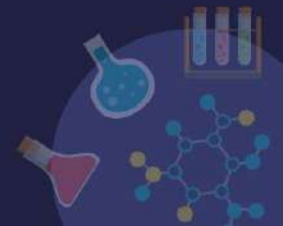
$\lambda \longrightarrow 0$ $E \longrightarrow \infty$

Heisenberg's Uncertainty Principle

High energy photon strikes particle → $\Delta p \uparrow$

Similarly

For accurate momentum → $\Delta x \uparrow$



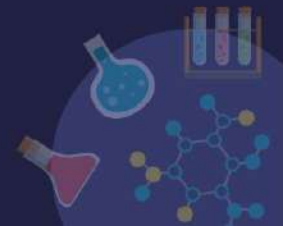
Heisenberg's Uncertainty Principle

For an electron

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

$$\Delta x \cdot \Delta v = \frac{6.626 \times 10^{-34}\ Js}{4 \times 3.14 \times 9.1 \times 10^{-31}\ kg}$$

$$\Delta x \cdot \Delta v \cong 10^{-4}\ m^2 s^{-1}$$



Heisenberg's Uncertainty Principle

If $\Delta x = 10^{-8}$ m then $\Delta v = 10^{4}$ ms^{-1}

Position	High accuracy	Δx is small
Velocity	Uncertain	Δv is large

If $\Delta v = 10^{-8}$ ms^{-1} then $\Delta x = 10^{4}$ m

Velocity	High accuracy	Δv is small
Position	Uncertain	Δx is large

Conclusion:

Heisenberg's uncertainty principle is meaningless for bigger particles.

Energy - Time Variant of H.U.P.

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

Multiplied and divided by Δt

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

$$\frac{\Delta p}{\Delta t} = \text{Rate of change in momentum} = F$$

Energy - Time Variant of H.U.P.

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

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

ΔE Uncertainty in Energy

Δt Uncertainty in Time

Significance of the Uncertainty Principle

1. Not an instrumental error, rather conceptual error
2. Rules out the existence of definite paths of electrons
3. Introduced concept of probability of finding the electrons

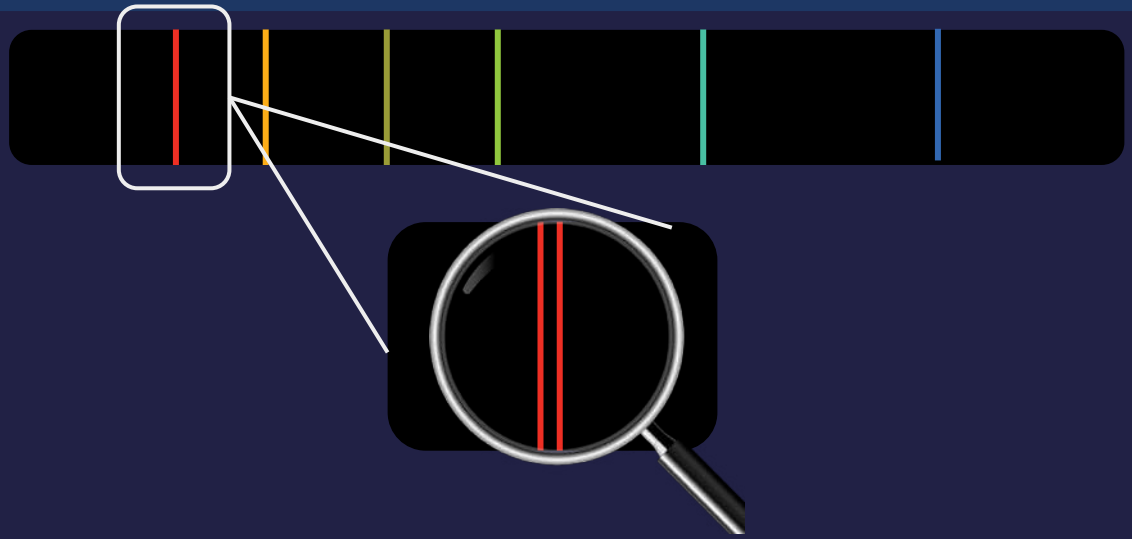
Precise statements of **position**& **momentum** of an electron replaced with probability

Forms the basis of **Quantum Mechanical Model of atom**

Limitations of Bohr Model

1. Could not explain the line spectra of atoms containing more than one electron

2. Could not explain the presence of doublet i.e. two closely spaced lines



Limitations of Bohr Model

3. Unable to explain the splitting of spectral lines in the presence of magnetic field (**Zeeman effect**) and electric field (**Stark effect**).

4. No conclusion was given for the principle of quantisation of angular momentum

5. Unable to explain de Broglie's concept & Heisenberg's Uncertainty Principle

Quantum Mechanical Model

Schrodinger Wave Equation (SWE)

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

- x, y, z = Cartesian coordinates
- Ψ = Amplitude of the electron wave or Wave function
- h = Planck's constant
- V = Potential energy of the electron
- E = Total energy of the electron

Wavefunction

SWE is solved to get values of Ψ and their corresponding **energies**

Ψ

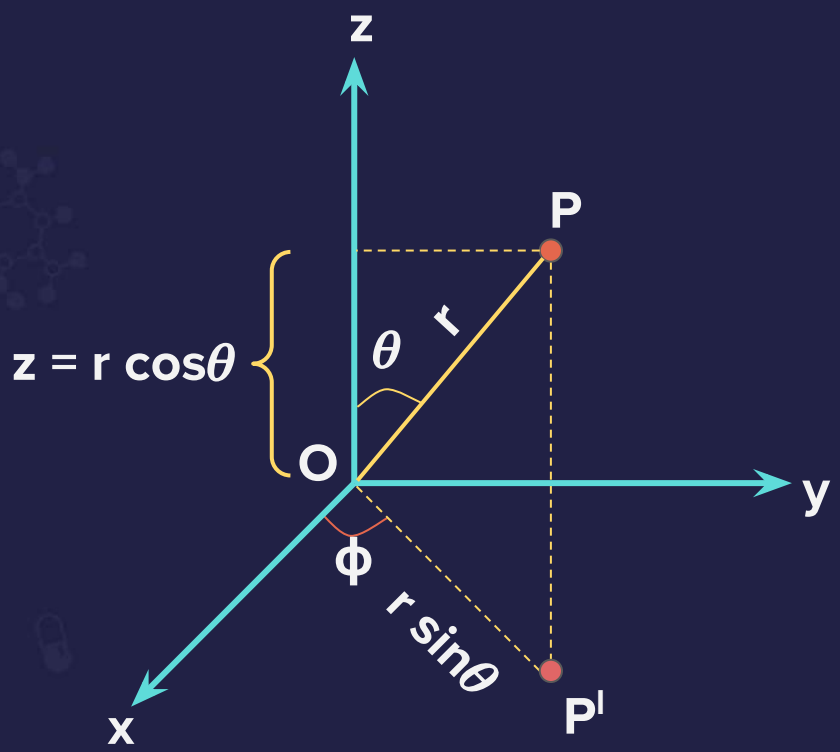
A function that contains all the **dynamical information** about a system

SWE can be solved for H like species more easily in

Spherical polar coordinates

(r , θ , ϕ)

Spherical Coordinate System



x	=	r sinθ cosϕ
y	=	r sinθ sinϕ
z	=	r cosθ

Wavefunction

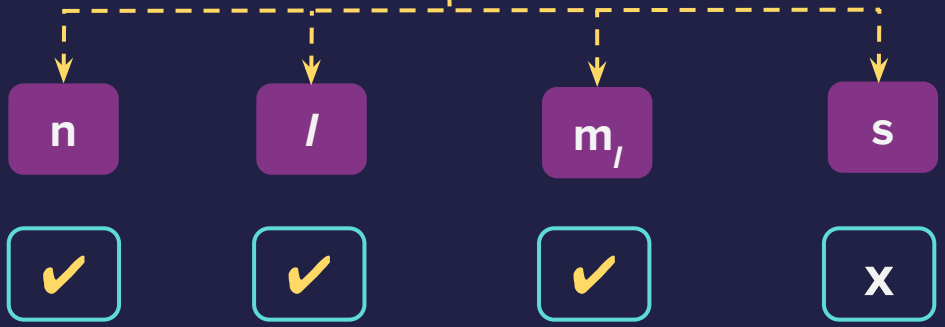
When SWE is solved for **H like species**, the obtained values of Ψ could be factorized into one containing only 'r' and the other containing (θ, ϕ).

Wave function		Radial part of wave function		Angular part of wave function
$\Psi(r, \theta, \phi)$	=	$\Psi(r)$	×	$\Psi(\theta, \phi)$
		n, *l*		*l*, m_l

Schrodinger Wave Equation

Ψ corresponds to **atomic orbital**

Characterized by a **set of quantum numbers**



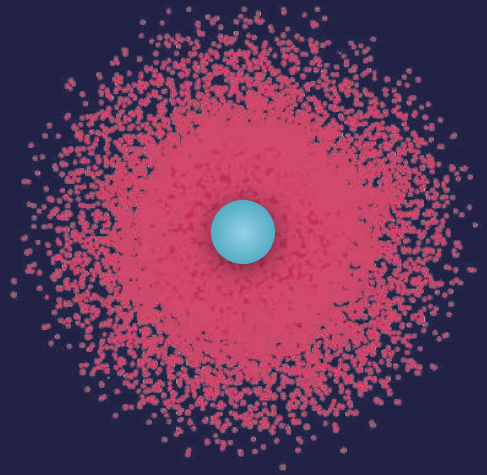
First three quantum numbers (n, l, m) were derived from Schrodinger equation. The spin quantum number added later.

What is an Orbital?

Orbital

3D region around the nucleus

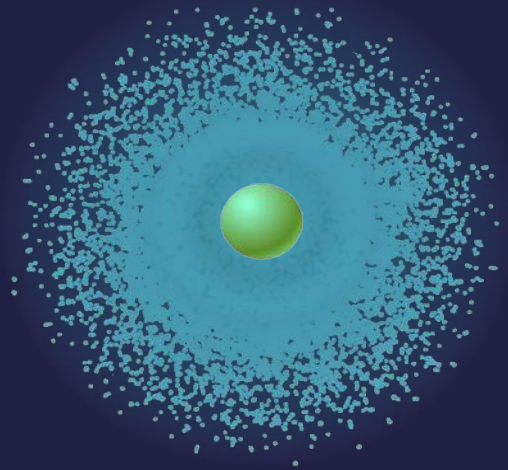
Probability of finding an electron is maximum



What is an Orbital?

Defines the probability of finding an electron

Does not define a definite path of electrons



Quantum Numbers

Set of **four numbers** required to **define an electron** in an atom completely

1. Principal Quantum Number (n)
2. Azimuthal Quantum number (*l*)
3. Magnetic Quantum Number (m_l)
4. Spin Quantum Number (s)

Principal Quantum Number (n)

Proposed by
Niels Bohr

1. Designates the **shell** to which the electron belongs
2. Signifies energy level for **single electron species**
3. Accounts for the **main lines** in the atomic spectrum

Principal Quantum Number (n)

Describes the **size** of electron wave & the **total energy** of the electron

n = 1, 2, 3...

Represented as K, L, M, N,...

Angular momentum in any shell = $\frac{nh}{2\pi}$

Azimuthal Quantum Number (*l*)

Proposed by Sommerfeld

1. Designates the **subshell** to which the electron belongs
2. Energy of the orbital in **multielectron species** (both n&l)
3. Accounts for the **fine lines** in atomic spectrum

Azimuthal Quantum Number (*l*)

Describes the **3-D shape** of the **orbital** or the electron cloud

Also known as

Subsidiary Quantum Number

Orbital Angular momentum Quantum Number

For a given value of Principal Quantum Number (n)

l	=	**0 to (n - 1)**

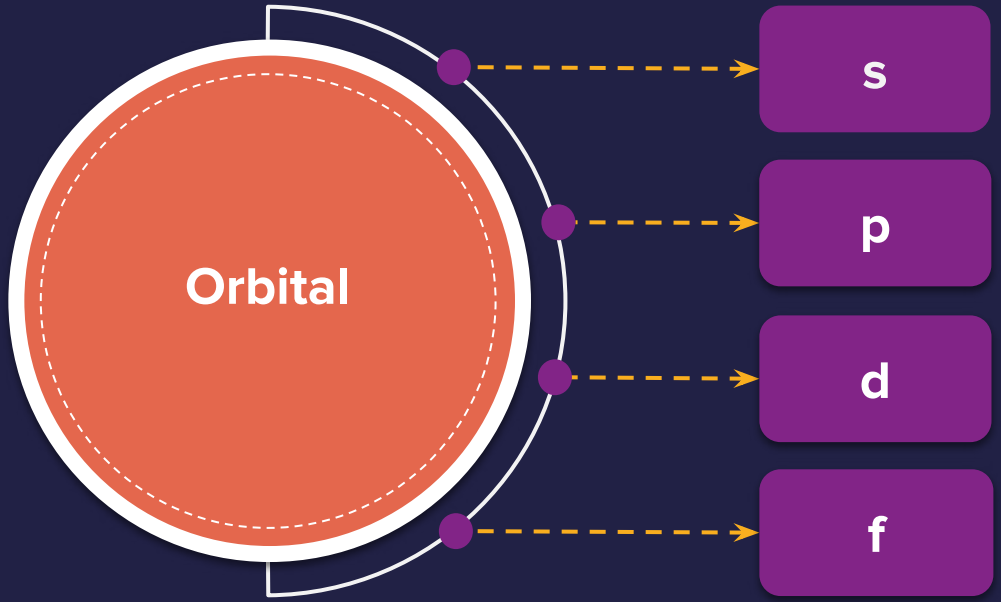
Boundary Surface Diagram

Encloses the 3D region where probability of finding electrons is maximum

Example

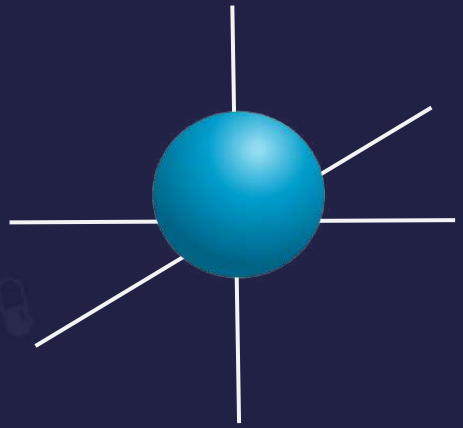
Shape : **Spherical**

Classification of Orbitals

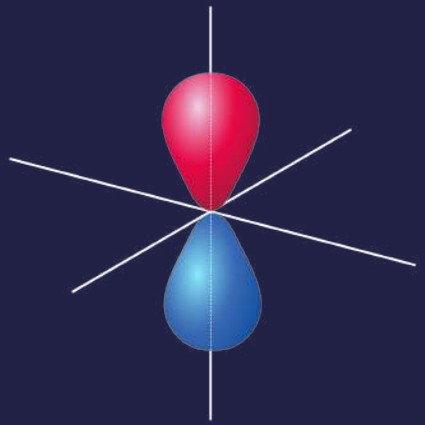


Shape of Orbitals

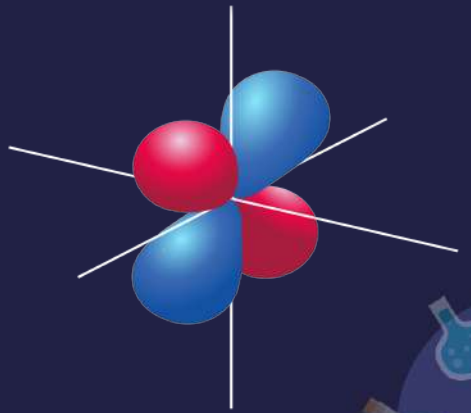
s - orbital
Shape : **Spherical**



p - orbital
Shape : **Dumb bell**

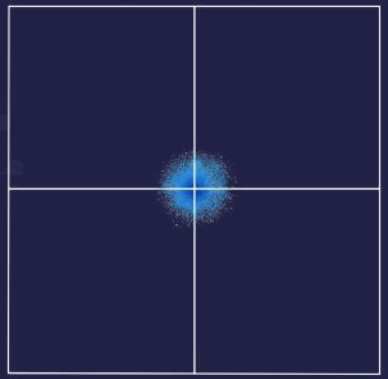


Shape : **Double dumb bell**

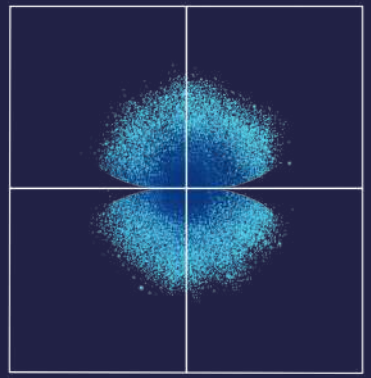


Probability Density Plots

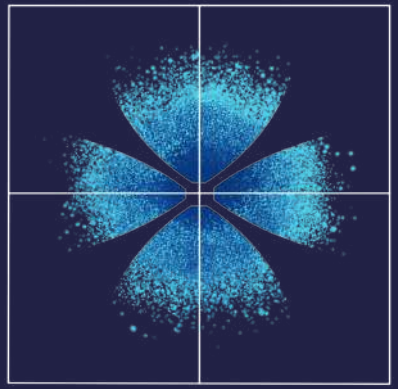
s orbital



p orbital



d orbital



Shapes of Orbitals

Orbital	Shape
s	Spherical
p	Dumb bell
d	Double dumb bell
f	Leaf like / Complicated

Subshell

Collection of **similar shaped orbitals** of same **n**.

Subshell

l	Subshell	Description
0	s	Sharp
1	p	Principal
2	d	Diffused
3	f	Fundamental
4	g	Generalised

Subshell Representations

Number of subshells in the n^{th} shell

n	*l*	Subshell notation
1	0	1s
2	0, 1	2s, 2p
3	0, 1, 2	3s, 3p, 3d
4	0, 1, 2, 3	4s, 4p, 4d, 4f

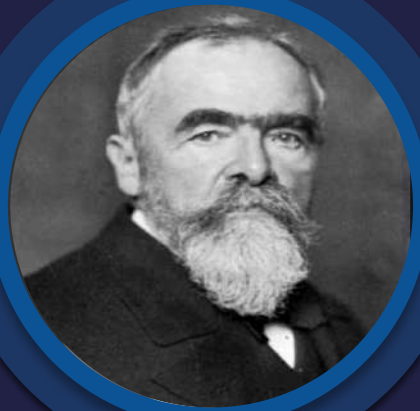
Azimuthal Quantum Number (*l*)

Orbital angular momentum (L) = $\sqrt{l(l+1)}\ \hbar$

$\hbar = \frac{h}{2\pi}$

Subshell	Orbital angular momentum
s	0
p	$\sqrt{2}\ \hbar$
d	$\sqrt{6}\ \hbar$

Magnetic Quantum Number (m_l)



Proposed by Linde

1. Designates the **orbital** to which the electron belongs
2. Describes the **orientation** of orbitals
3. Accounts for the **splitting of lines** of atomic spectrum in **magnetic field**

Magnetic Quantum Number (m_l)

Can have values from **- *l* to + *l*** including **zero**

Each value corresponds to an **orbital**

For d subshel, *l* = 2

m_l = -2, -1, 0, 1, 2

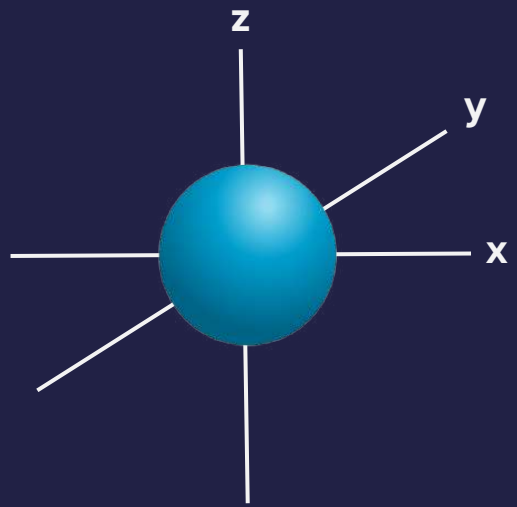
Magnetic Quantum Number (m_l)

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

Subshell	Number of orbitals
s	1
p	3 (p_x, p_y, p_z)
d	5 (d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2})
f	7

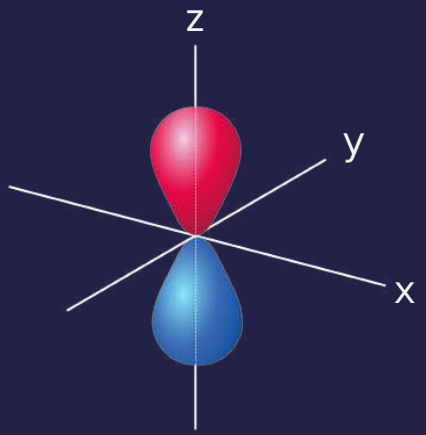
s - orbital

Shape : **Spherical**
Non-directional in nature

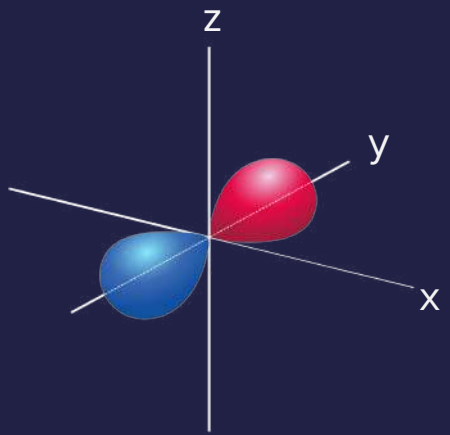


p - orbital

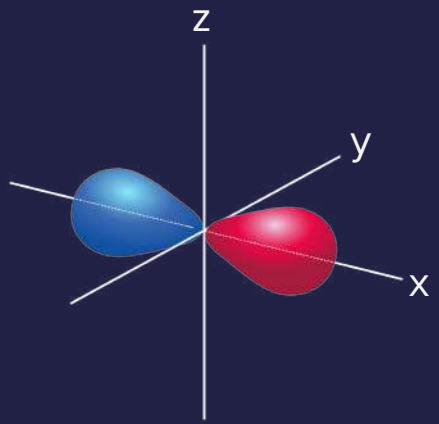
Shape : **Dumb bell**
Directional in nature



p_z

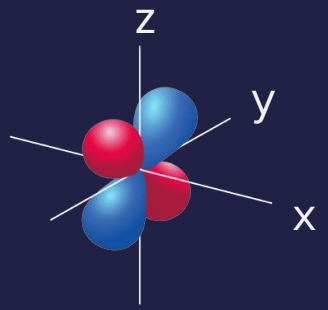


p_y

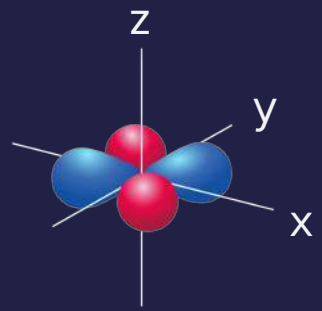


p_x

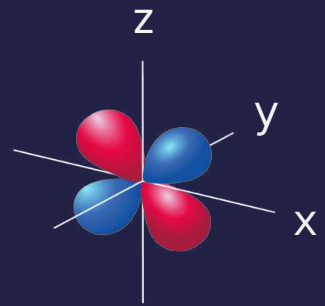
d - orbital



d_{yz}



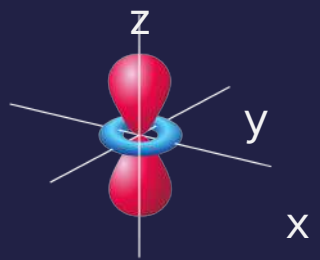
d_{xy}



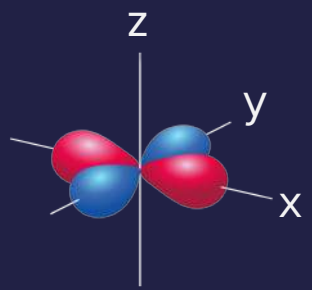
d_{xz}

Non axial d-orbitals

Shape : **Dumb bell**
Directional in nature



d_{z^2}



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

Axial d-orbitals

Remember!

An **orbitals** can accommodate maximum of **2 electrons**.

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

Subshell	s	p	d	f
l	0	1	2	3
Number of electrons	2	6	10	14

Spin Quantum Number (s or m_s)

Presence of **two closely spaced lines** in **atomic spectrum**

↓

Spin of an **electron**

Proposed by George Uhlenbeck (left) and Samuel Goudsmit (Right)

$$s = +\frac{1}{2}$$

$$s = -\frac{1}{2}$$

Spin Quantum Number (s)

Spin magnetic moment (μ)	=	$\sqrt{n(n+2)}$ B.M.

n = number of unpaired electron

Spin Quantum Number (s)

Spin angular momentum	=	$\frac{h}{2\pi}\sqrt{s(s+1)}$
Maximum Spin of an atom (S)	=	$\frac{1}{2}n$
Spin multiplicity	=	$2\|S\| + 1$

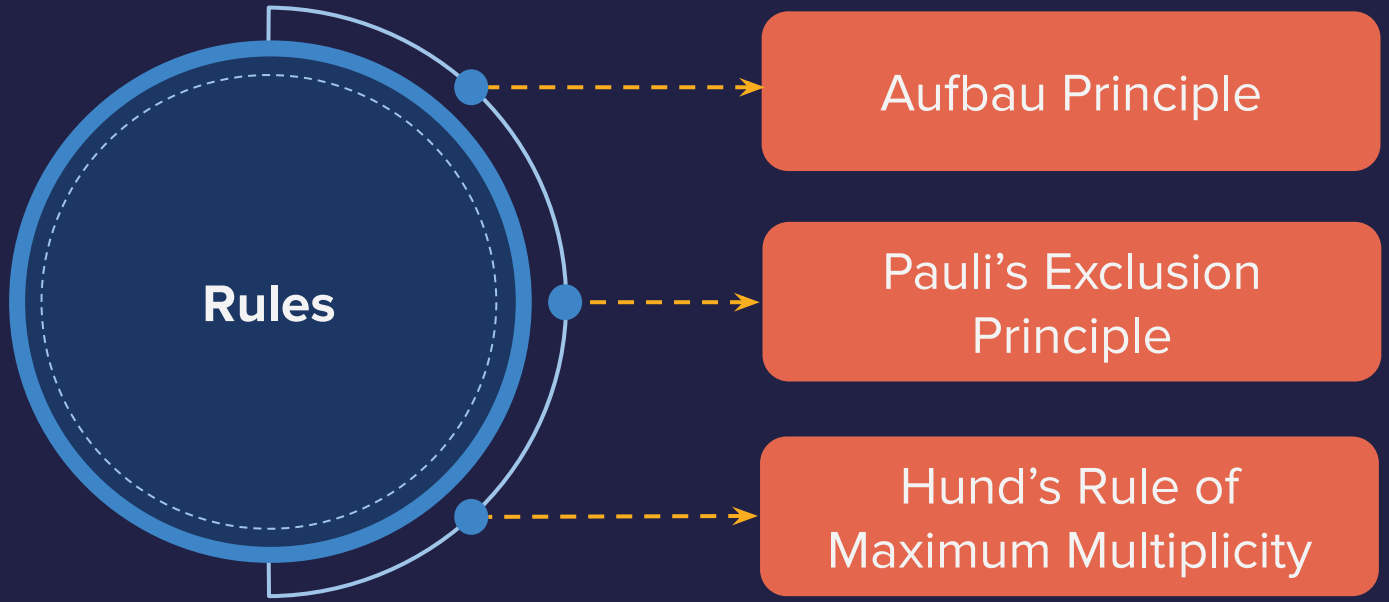
Orbit and Orbital

Orbit	Orbital
Well defined circular path around the nucleus where electrons revolve	**3D region** around the nucleus where electrons are most likely to be found
Maximum number of electrons in n^{th} orbit is $\mathbf{2n^2}$	**Cannot accommodate** more than **two electrons**

Orbit and Orbital

Orbit	Orbital
Not in accordance with Heisenberg's Uncertainty Principle	**In accordance** with Heisenberg's Uncertainty Principle
Designated as **K, L, M, N, ...**	Designated as **s, p, d, f, ...**

Rules for Filling Electrons in Orbitals



Aufbau Principle

Electrons are filled in various orbitals in order of their increasing energies

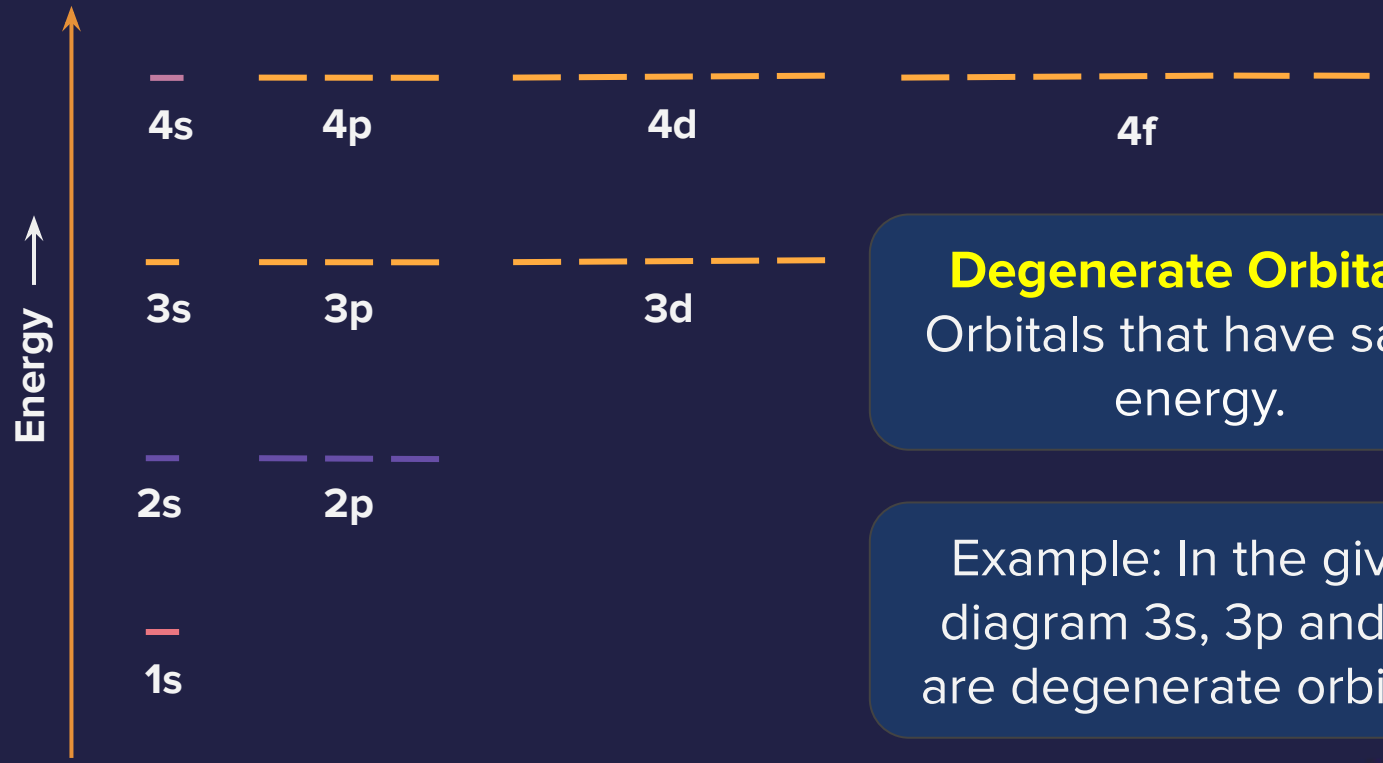
Energies of Subshells of H-like Species

Energy of **single electron species** depends only on the **Principal Quantum Number**

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

Order of Energy

Energies of Subshells of H-like Species



Degenerate Orbitals: Orbitals that have same energy.

Example: In the given diagram 3s, 3p and 3d are degenerate orbitals.

Energy of Subshells of Multi-electron Species

Different subshells have different energy which depends on:

- **Principal Quantum Number**
- **Azimuthal Quantum Number**

(n + l) rule or Bohr-Bury's Rule

Lower value of **(n + l)**

Lower will be **energy of subshell**

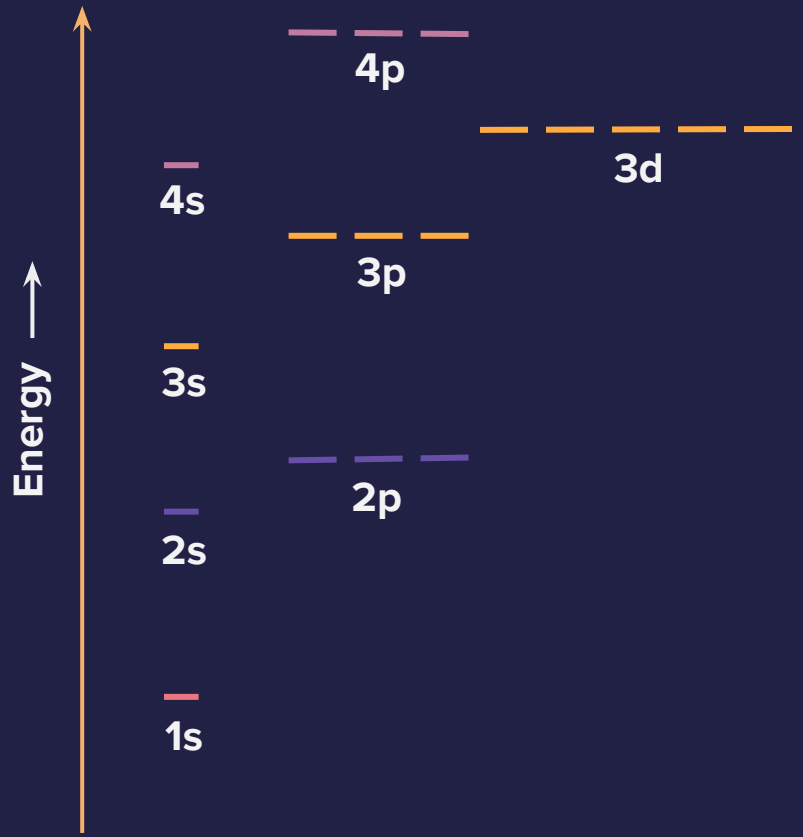
Two subshells with **same (n + l)** value

Subshell with **lower 'n'** value has **lower energy**

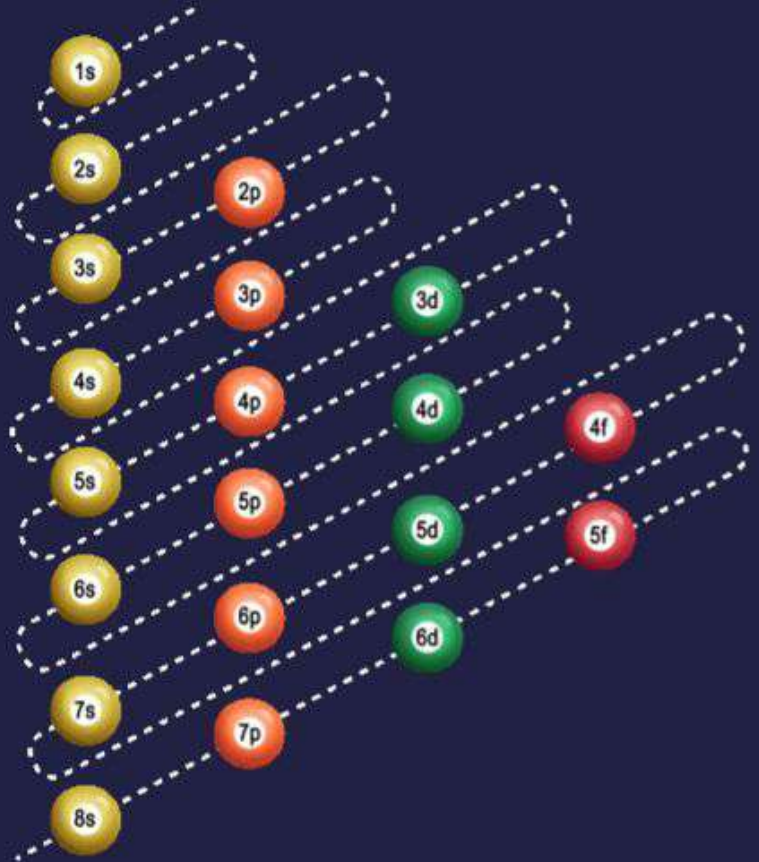
Comparison of orbital energy

1s	<	2s
2s	<	2p
5p	>	4d
2p	<	3p
3d	<	4p

Energies of Subshells of Multi electron Species



Energies of Subshells of Multi electron Species

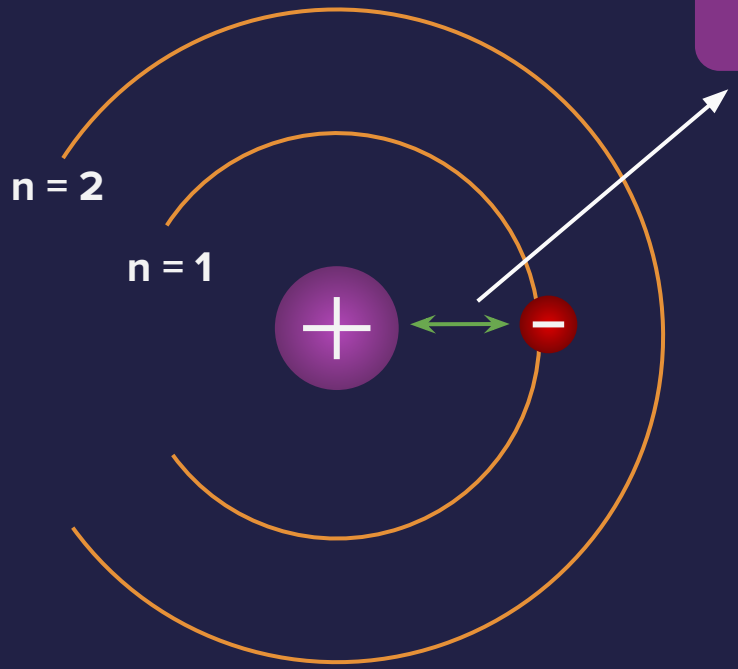


H-like v/s Multi-electron species

H-like species	Multi-electron species
Energy of a subshell depends on **'n' only**.	Energy of a subshell depends on **(n + l)**.
Only **attractive forces** are present between the **nucleus** and the **electron**.	Electrons experience **attractive forces** towards the **nucleus** as well as **repulsive forces** from other **electrons**.

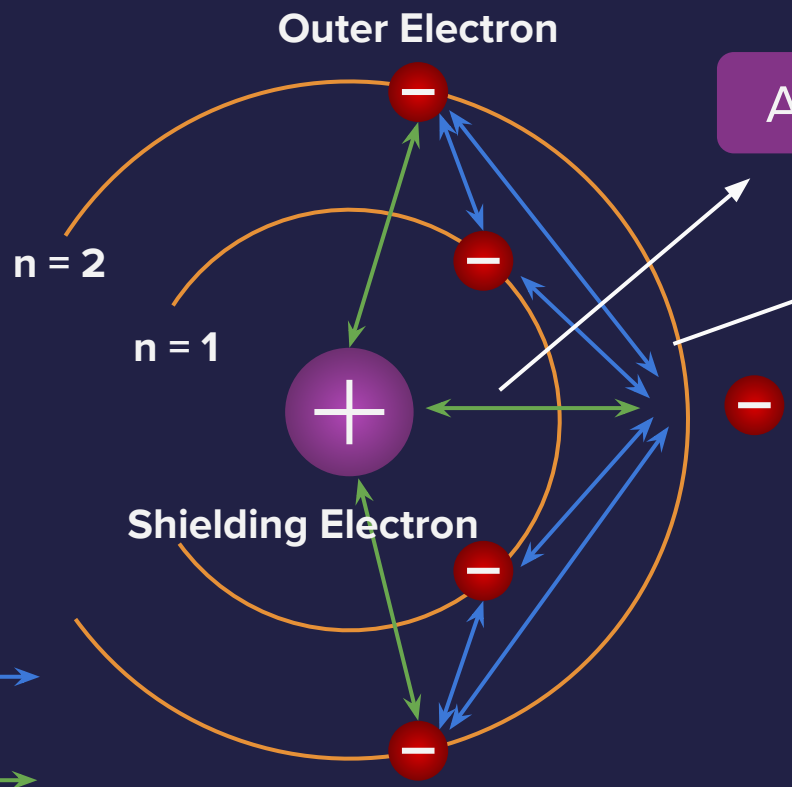
One-electron species

There is only attractive force here



Attraction ⟷

Multiple-electron species



Attractive Force

Repulsive Force

Repulsion ⟷

Attraction ⟷

Pauli's Exclusion Principle

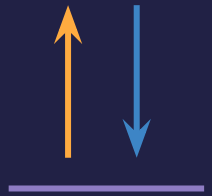
Wolfgang Pauli

No two electrons in an atom can have **the same set of all four quantum numbers**

Pauli's Exclusion Principle

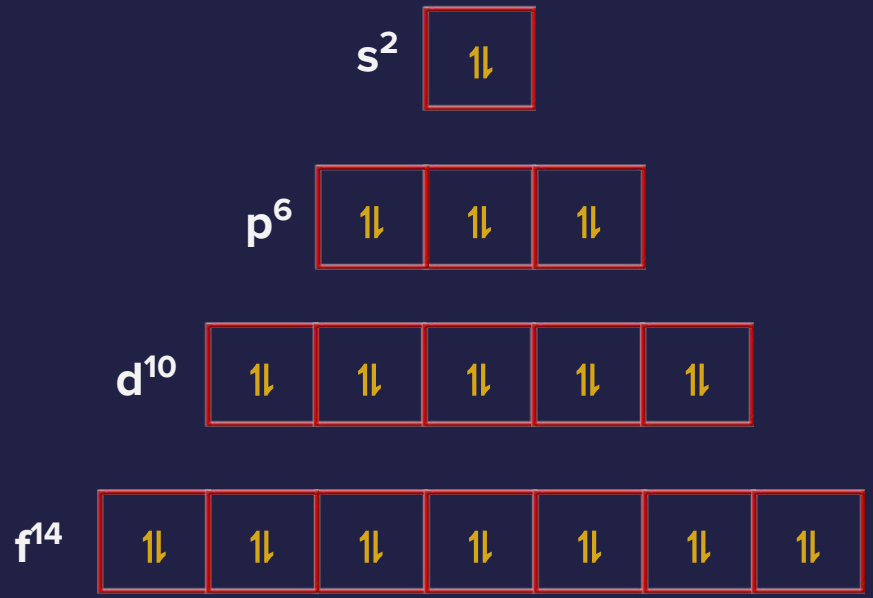
Restrict the **filling** of number of **electrons** in an **orbital**

Wrong



Right

Subshell electron capacity



Hund's Rule of Maximum Multiplicity

Friedrich Hund

Hund's Rule of Maximum Multiplicity

No **electron pairing** takes place in the orbitals in a subshell

Until each orbital is occupied by **1 electron** with **parallel spin**

Hund's rule is an **empirical rule**

Determines the **lowest energy arrangement** of electrons

Why Maximum multiplicity?

Maximum spin of an atom (S) = $\frac{1}{2} \times n$

Spin Multiplicity (S.M.) = $2S + 1$

Spin Multiplicity (S.M.) ↑ ----→ **Stability** ↑

Electrons with **parallel spins**

↓

Repel each other

↓

Have a **tendency to stay apart**

↓

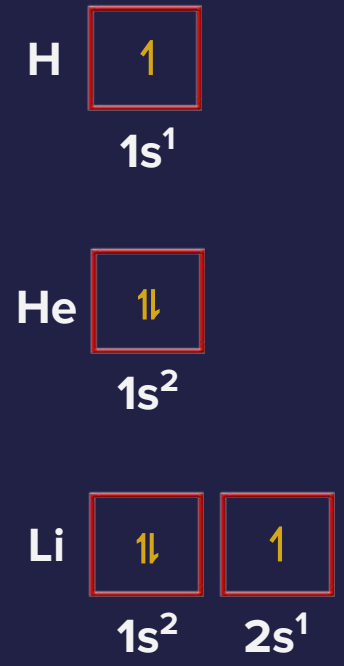
Atom **shrink** slightly

↓

Electron-nucleus interaction is **improved**

Electronic Configuration

Distribution of electrons in orbitals of an atom

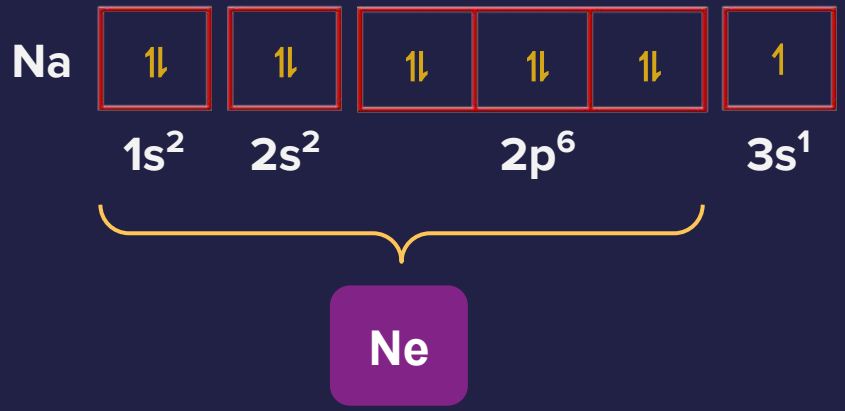


Electronic Configuration of Various Elements

Electronic Configuration of Various Elements

Simplified Electronic Configuration

Configuration of Sodium:



Simplified configuration:

Electronic Configuration

a) $_{21}Sc \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$

$\rightarrow [Ar]\ 4s^2\ 3d^1$

$\rightarrow [Ar]\ 3d^1\ 4s^2$

45
21 Sc
Scandium

$3d^1$ $4s^2$

Number of unpaired electrons	1
Total spin	$+\frac{1}{2}$ or $-\frac{1}{2}$

Electronic Configuration

b) $_{26}Fe \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

$\rightarrow [Ar]\ 4s^2\ 3d^6$

$\rightarrow [Ar]\ 3d^6\ 4s^2$

$3d^6$ $4s^2$

Number of unpaired electrons	4
Total spin	$+\frac{4}{2}$ or $-\frac{4}{2}$

Exceptions

$_{24}Cr$ $[Ar]\ 4s^2\ 3d^4$ — Not Correct

$_{24}Cr$ $[Ar]\ 4s^1\ 3d^5$ — Correct

d^5 is more stable than d^4 configuration

Exceptions

$_{29}Cu$ [Ar] $4s^2\ 3d^9$ — Not Correct

$_{29}Cu$ [Ar] $4s^1\ 3d^{10}$ — Correct

d^{10} is more stable than d^9 configuration

Half-filled & Fully Filled Orbitals

Exactly **half filled** & **fully filled** orbitals make the configuration more stable

p^3, p^6, d^5, d^{10}, f^7 & f^{14} configurations are stable

Stability of **half filled** & **fully filled** orbitals

- Symmetry
- Exchange Energy

Symmetry

Symmetrical distribution of electrons

Symmetry leads to stability

Electrons in the **same subshell** → Equal energy → Different spatial distribution

Consequently, their **shielding** of one another is **relatively small**

Electrons are more **strongly attracted** by the nucleus

Have **less energy and more stability**

Exchange Energy

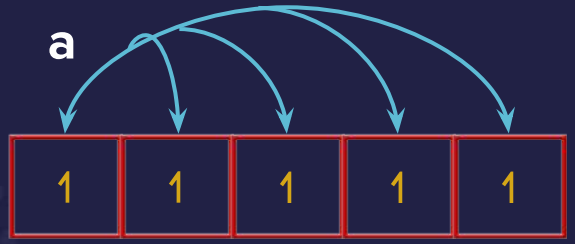
Energy released when **two or more electrons** with the **same spin** in the **degenerate** orbitals

Tends to **exchange** their **positions**

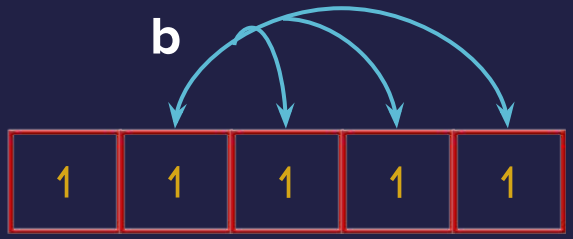
Number of exchanges that can take place is **maximum**

When subshell is either **half filled or fully filled**.

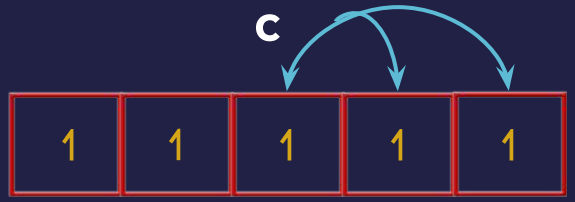
Exchange Energy



4 exchange by electron ‘a’



3 exchange by electron ‘b’



2 exchange by electron ‘c’

1 exchange by electron ‘d’

Electronic Configuration of Ions

Electronic Configuration of Cations

Formed by **removing outermost electron** from a **neutral atom**

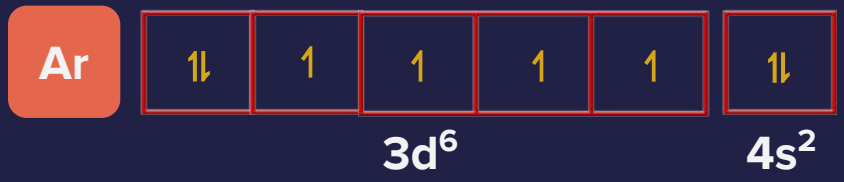
Electronic Configuration of Cations

In **d-block** metals

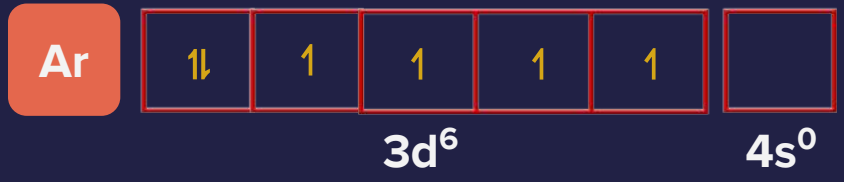
electrons are **first removed** from **ns** orbital, then from the penultimate **(n-1)d** orbital

Examples

Fe: [Ar] $3d^6\ 4s^2$ or

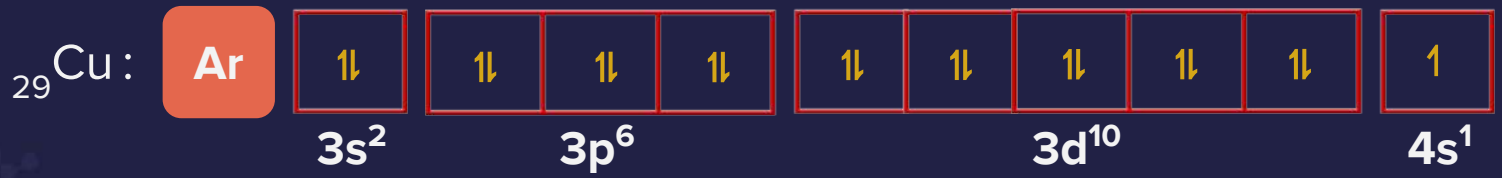


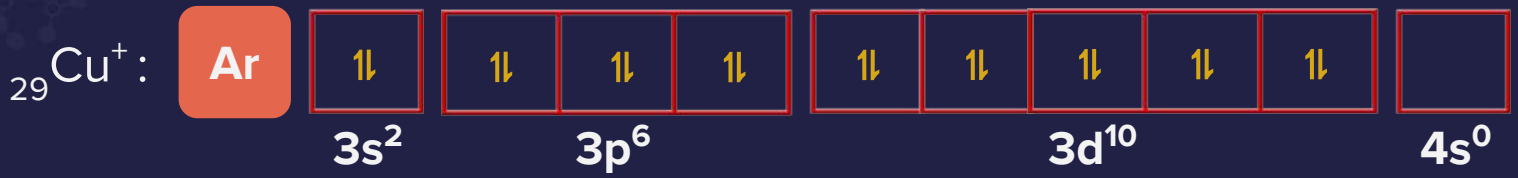
Fe^{2+}: [Ar] $3d^6\ 4s^0$ or



Fe^{3+}: [Ar] $3d^5\ 4s^0$ or

Examples





18 electrons

Pseudo inert gas configuration

Electronic Configuration of Anions

Formed by **adding electrons to a neutral atom** according to the 3 rules **(Pauli's, Aufbau & Hund's rule)**

Schrodinger Wave Equation (SWE)

Based on the **dual nature of matter**

Describes the behavior of **electron** around the nucleus

Schrodinger Wave Equation

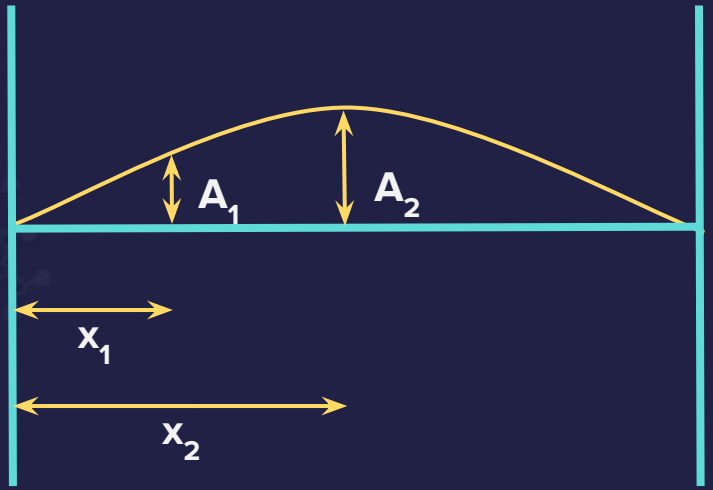
$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

- x, y, z = Cartesian coordinates

  Ψ = Amplitude of the electron wave or Wave function

- h = Planck's constant
- V = Potential energy of the electron
- E = Total energy of the electron

Wavefunction



Ψ corresponds to the allowed solutions of SWE

Ψ contains all the information related to the **motion of an electron** in an atom

Amplitude of a standing wave is a function of x

Similarly, Ψ is a **function of coordinates**

Wavefunction

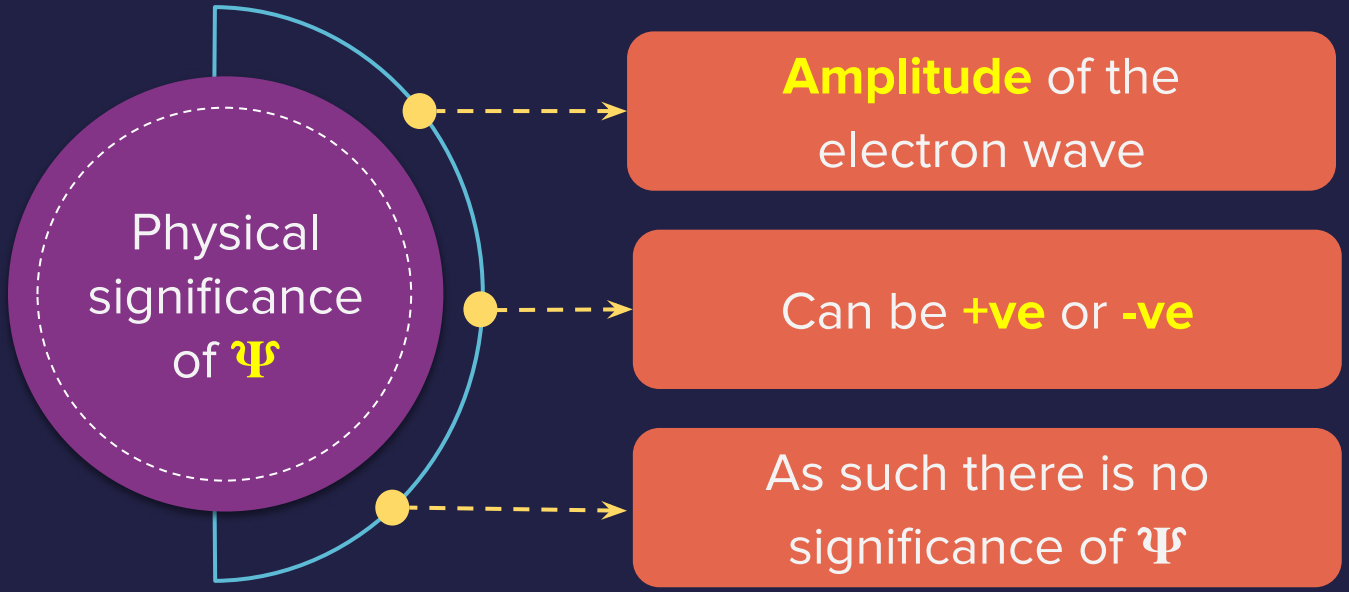
Wave function | Radial part of wave function | Angular part of wave function

$$\Psi(r, \theta, \phi) = \Psi(r) \times \Psi(\theta, \phi)$$

$\Psi(r)$: n, l

$\Psi(\theta, \phi)$: l, m_l

Physical Significance of Ψ



Physical significance of Ψ^2

Maxwell's wave theory

Intensity of wave $\propto$ Square of amplitude

Max Born suggested that

Ψ^2 ----➤ Probability of finding an electron per unit volume or **probability density**

Probability density

$$\Psi(r,\theta,\phi) = \Psi(r) \times \Psi(\theta,\phi)$$

$$\Psi^2(r,\theta,\phi) = \Psi^2(r) \times \Psi^2(\theta,\phi)$$

Probability density

Radial probability density

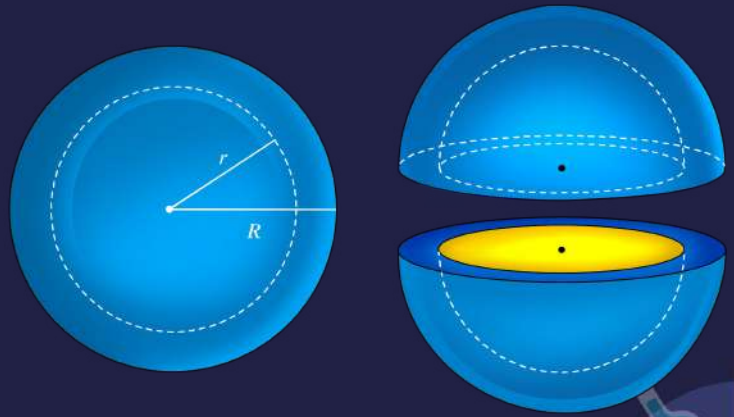
Angular probability density

Radial Distribution Function

Radial probability of finding an **electron** in a shell of thickness ‘dr’ at a radial distance ‘r’ = $\Psi_R^2 \times dV$

This probability which is independent of direction is called radial probability and is equal to $[4\pi r^2 dr R^2]$.

It gives the probability of finding the electron at a distance r from the nucleus regardless of direction.



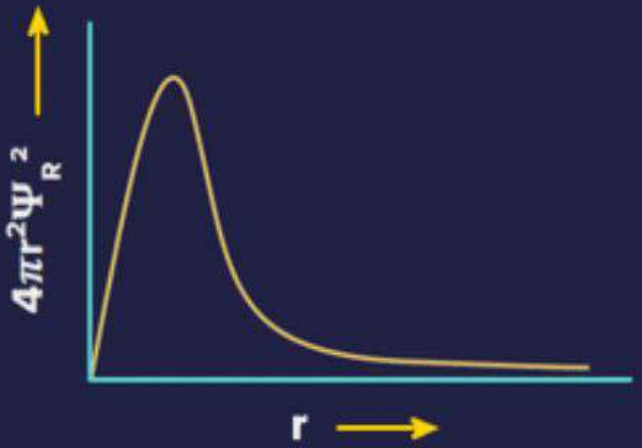
Radial Distribution Function

$$dV = \frac{4}{3}\pi (r + dr)^3 - \frac{4}{3}\pi r^3 = 4\pi r^2 \cdot dr$$

Radial probability density on a layer × Volume of that layer = $\Psi_R^2 \cdot 4\pi r^2 \cdot dr$

Radial distribution function = $\Psi_R^2 \cdot 4\pi r^2$

Radial Distribution Function



Summary

Radial wave function	Ψ_R
Radial probability density	Ψ_R^2
Radial probability distribution	$4\pi r^2 \Psi_R^2$

Nodes

Region where the **probability density** is **zero** i.e. where the **probability of finding** an **electron** is **zero**

$$\Psi^2 . dV = 0$$

$\therefore$ dV can't be zero

$$\Rightarrow \Psi^2 = 0$$

Nodes

Node

$\therefore$ $\Psi(r,\theta,\phi) = \Psi(r) \times \Psi(\theta,\phi) = 0$

$\Rightarrow$ $\Psi(r) = 0$ or $\Psi(\theta,\phi) = 0$

Radial Node

Spherical region around nucleus

Ψ_R or Ψ_R^2 is zero

Number of **radial nodes** in an **orbital** = **n - l - 1**

Angular Node

Plane or a surface passing through the **nucleus**

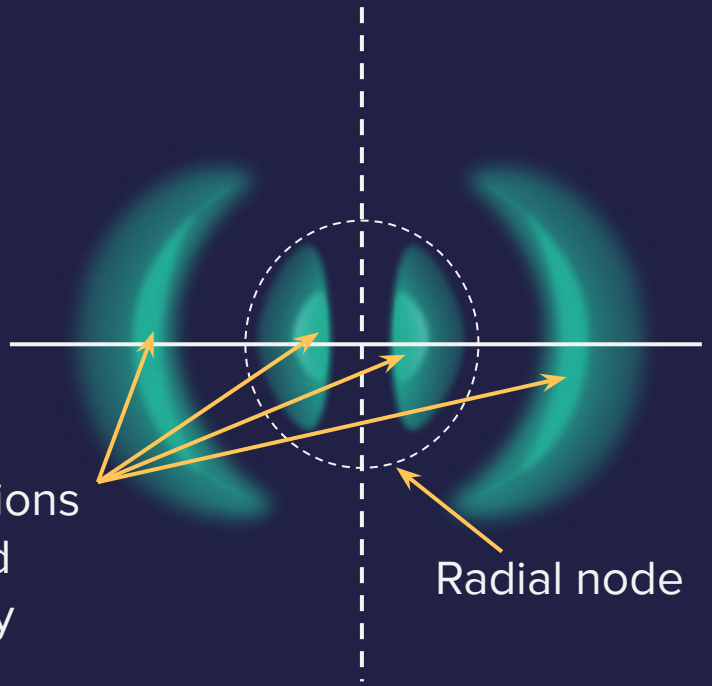
$\Psi_{\theta, \Phi}$ or $\Psi^2_{\theta, \Phi}$ is zero

Number of **angular nodes** in an **orbital** = ***l***

Nodes

Total number of nodes	=	Radial nodes (n - *l* - 1)	+	Angular nodes (*l*)	=	n - 1

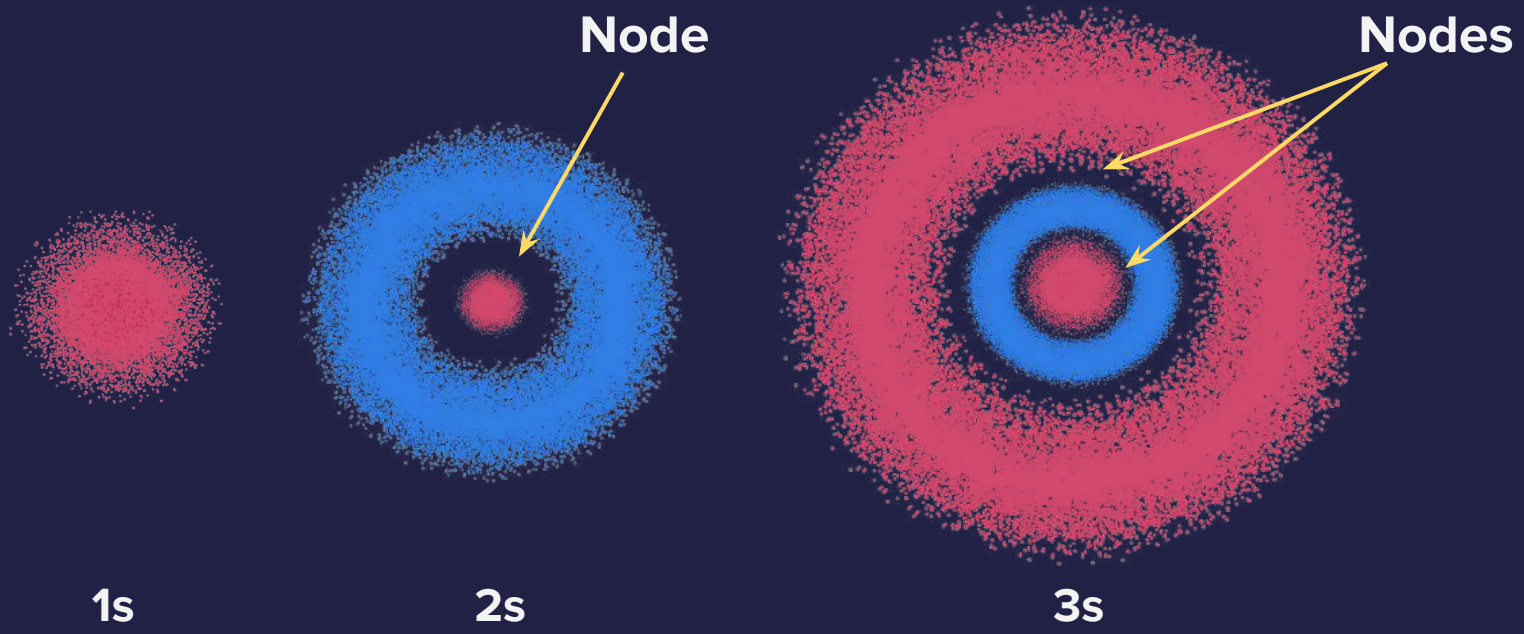
What are these radial and angular nodes?



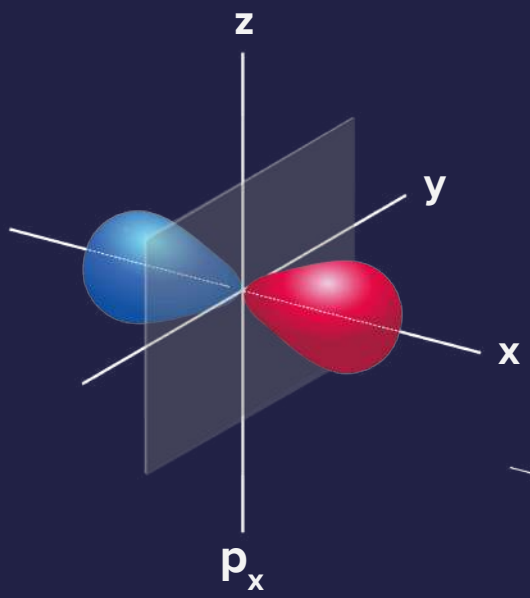
Radial Node vs Angular Node

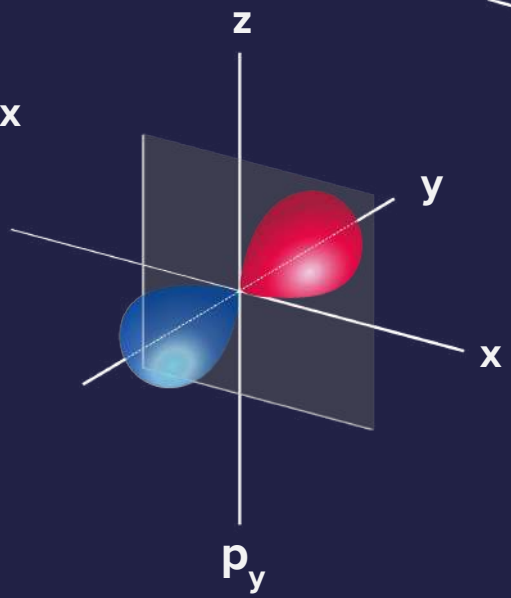
Radial node	Angular node
Spherical regions where the probability of finding an electron is **zero**.	**Flat planes** or **cones** where the probability of finding an electron is **zero**.
Have **fixed radii**.	Have **fixed angles**.
Number of radial nodes is given by (**n - *l* - 1)**	Number of angular nodes is given by (***l***)

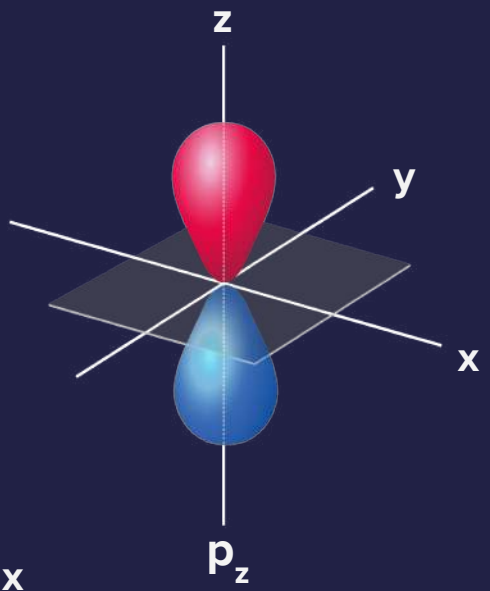
Nodes of ‘s’ orbitals



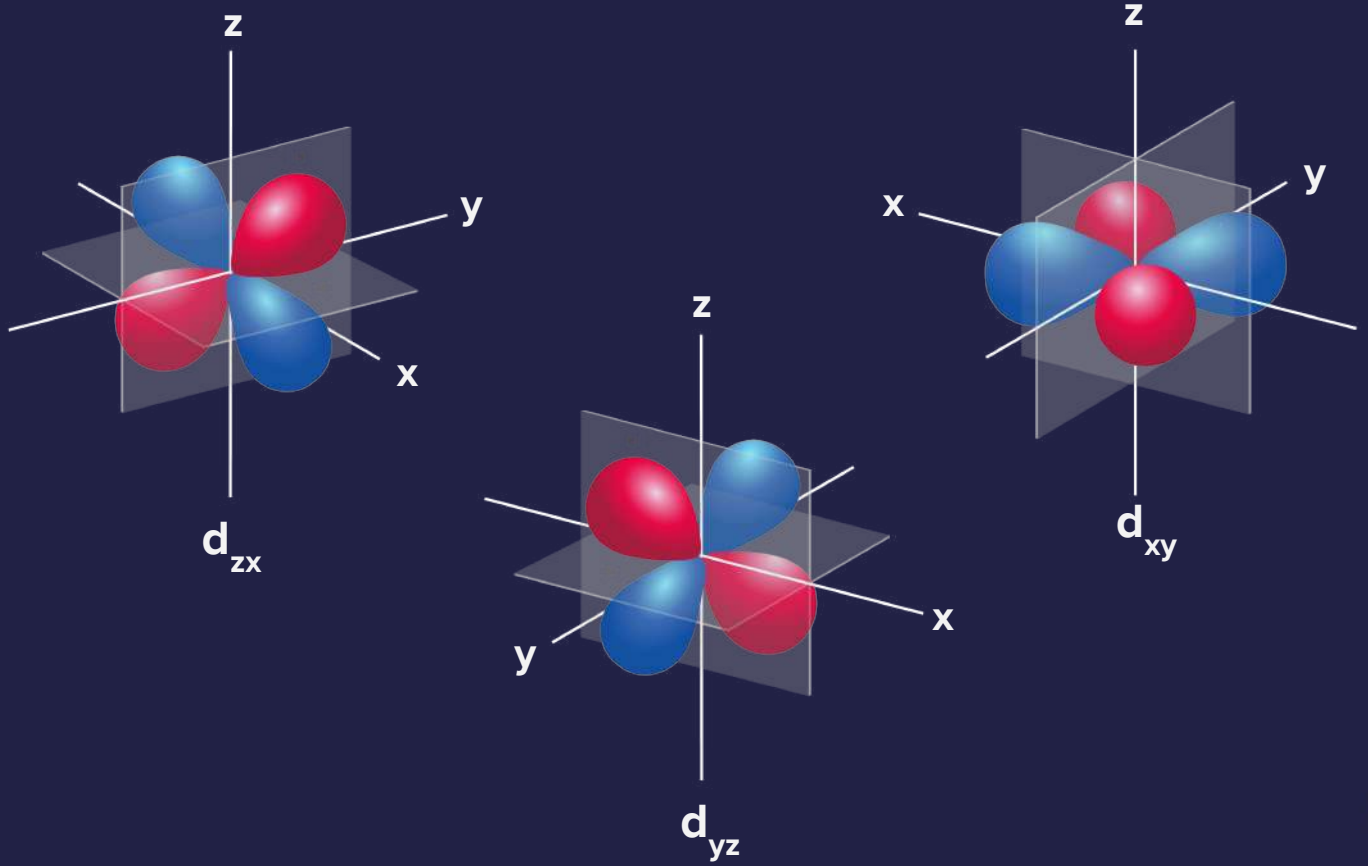
Angular Nodes of ‘p’ orbitals



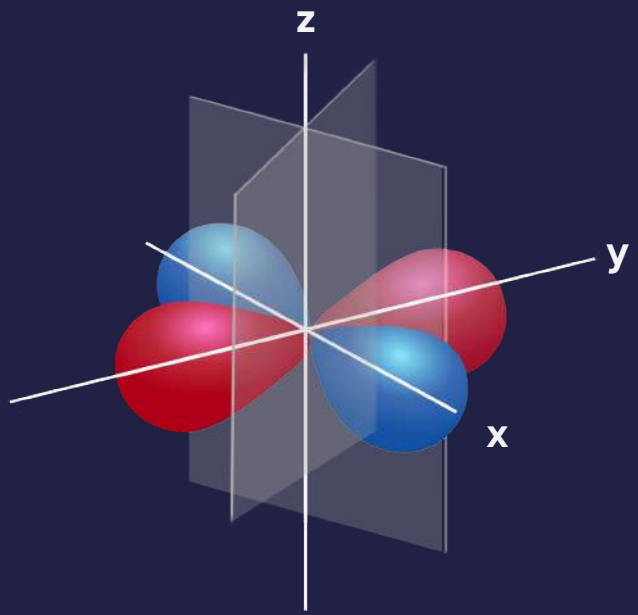




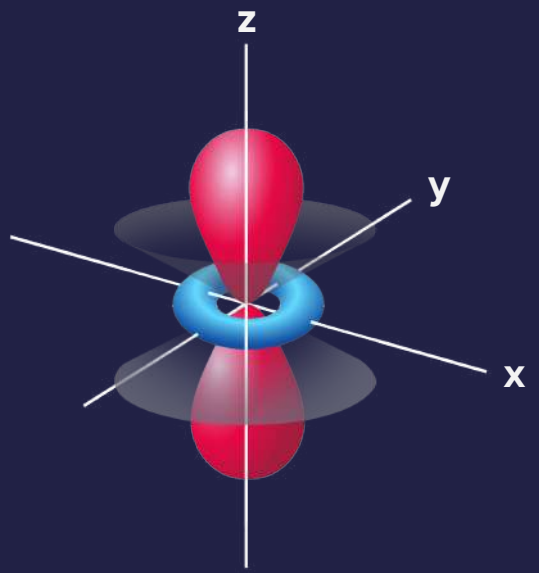
Angular Nodes of ‘d’ orbitals



Angular Nodes of ‘d’ orbitals



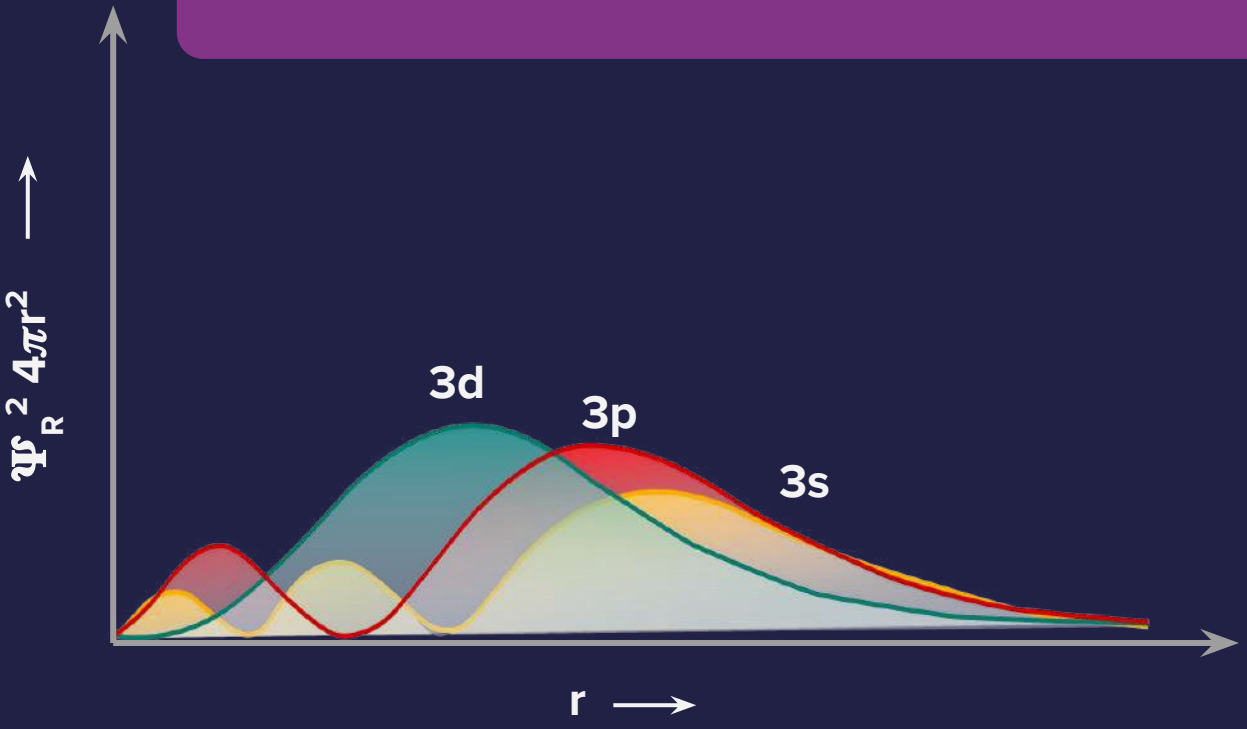
$d_{x^2 - y^2}$



d_{z^2}

Comparison of Penetration Power

Measure of orbital's **closeness** to the nucleus



Comparison of Penetration Power

Additional maximas in **3s curve**

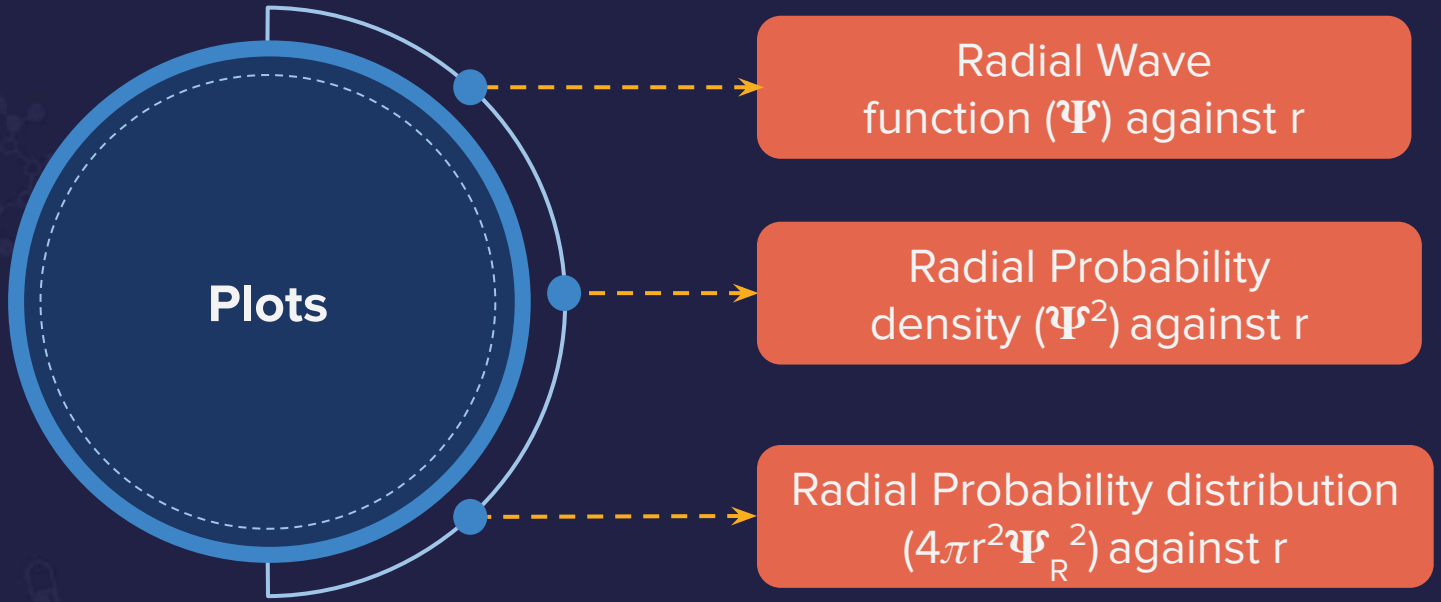
↓

Electron in **3s** spends **maximum time near the nucleus** compared to **3p and 3d.**

↓

Penetration power : 3s > 3p > 3d

Probability Curves

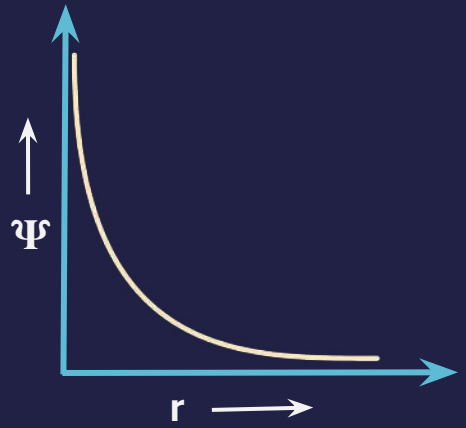


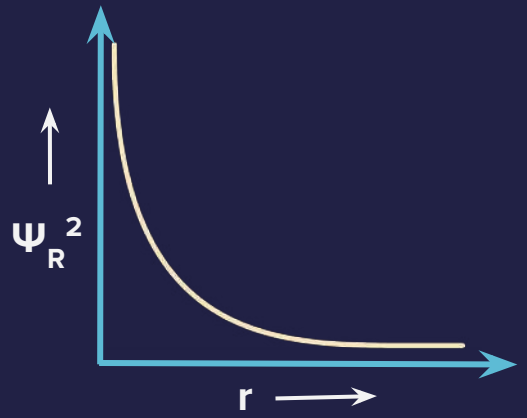
s-orbital

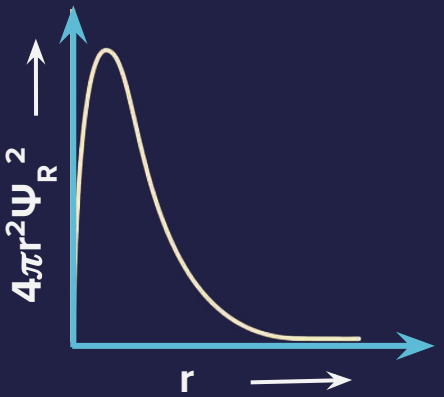
Density of electron cloud is **spherical**

Probability density is **maximum** at the **nucleus** and **decreases** at **large distance**

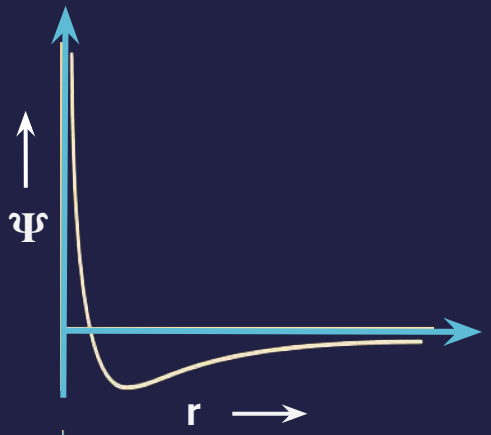
Radial Probability of 1s

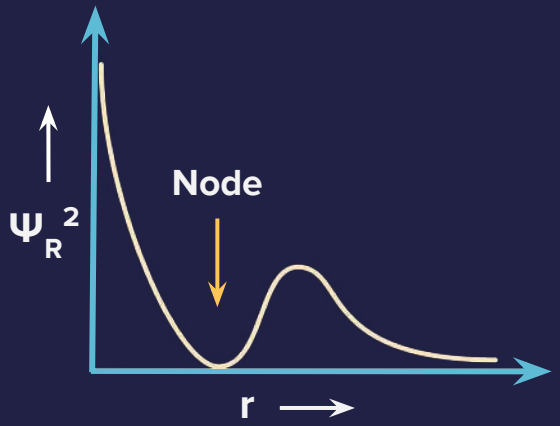


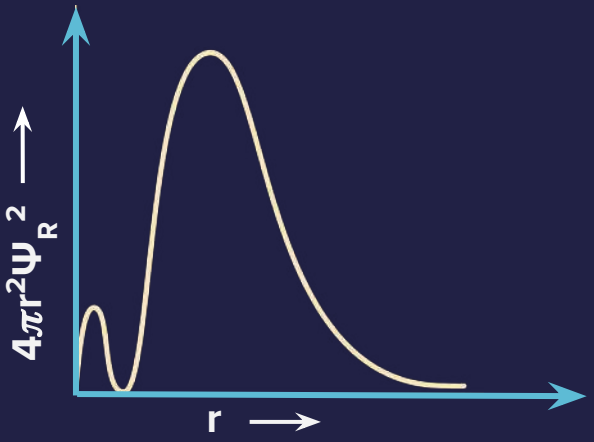




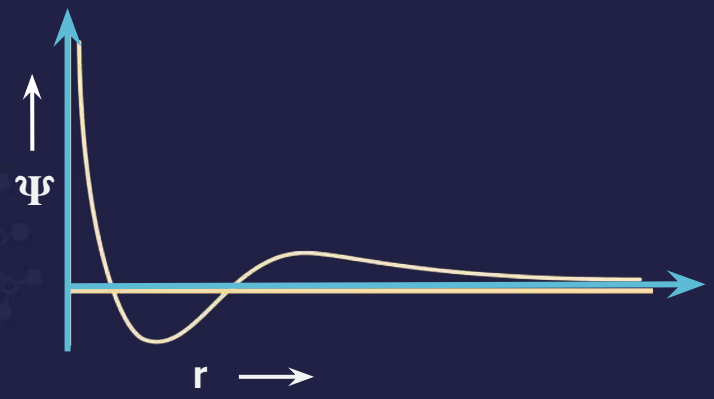
Radial Probability of 2s

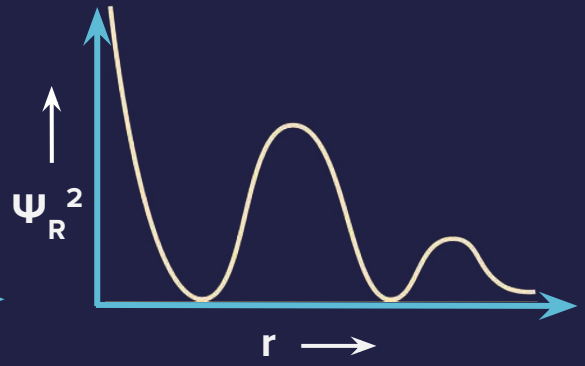


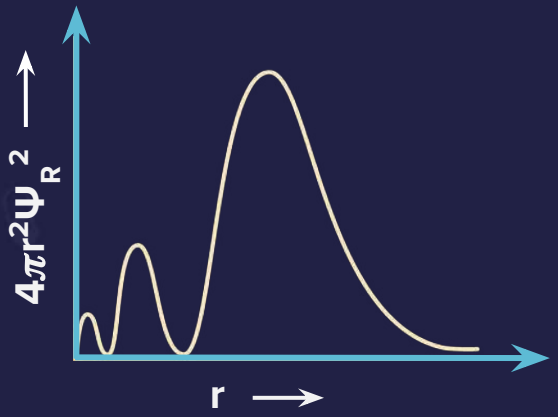




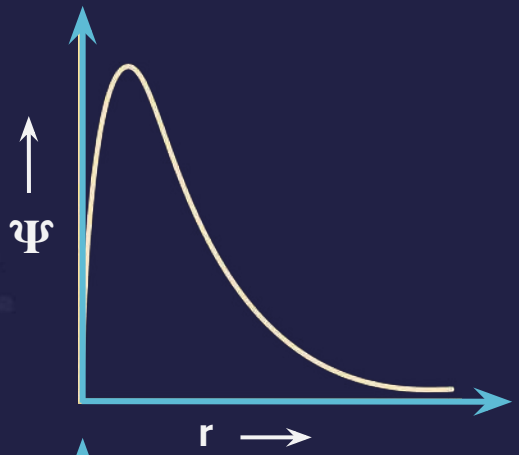
Radial Probability of 3s

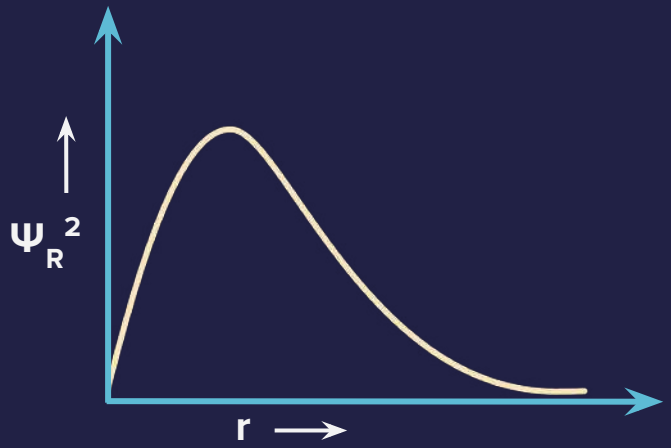


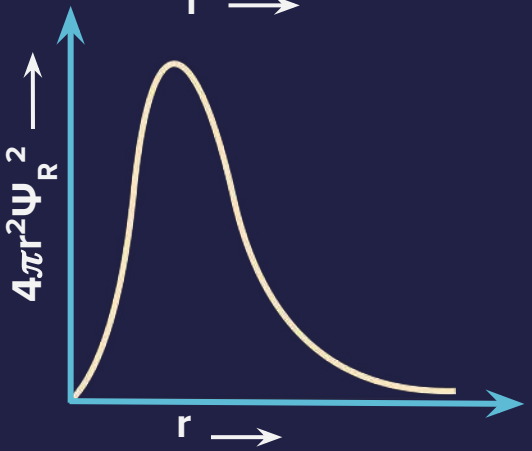




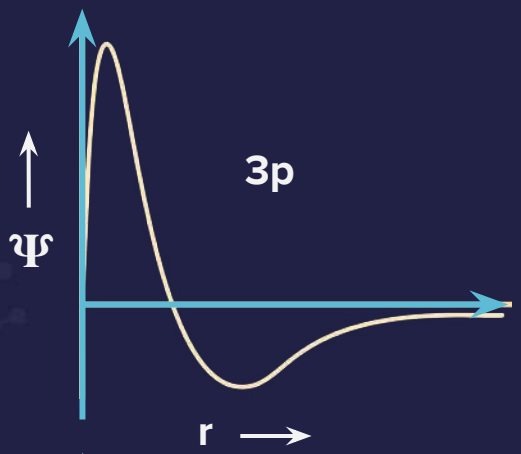
Radial Probability of 2p

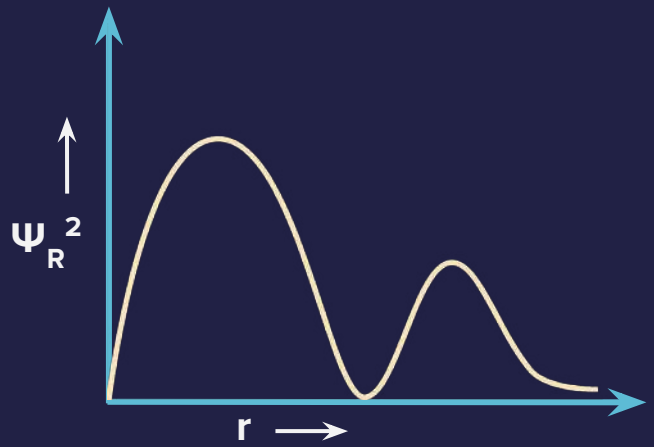


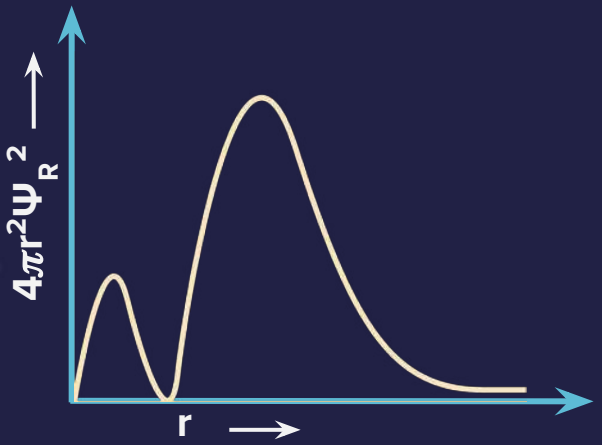


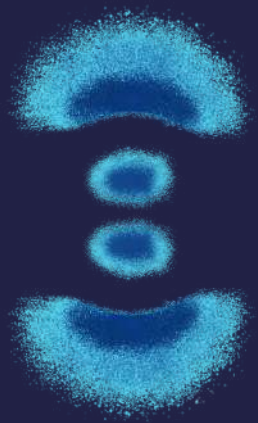


Radial Probability of 3p

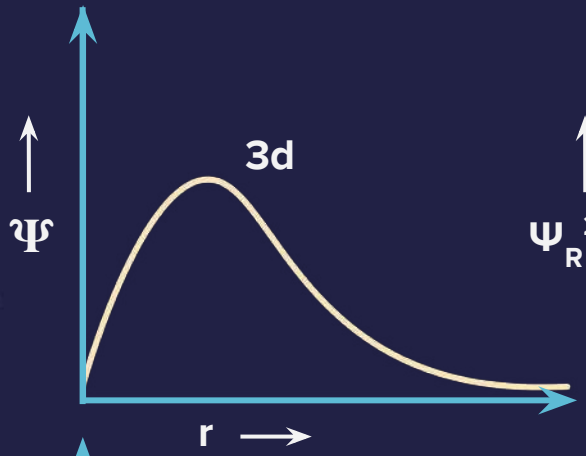


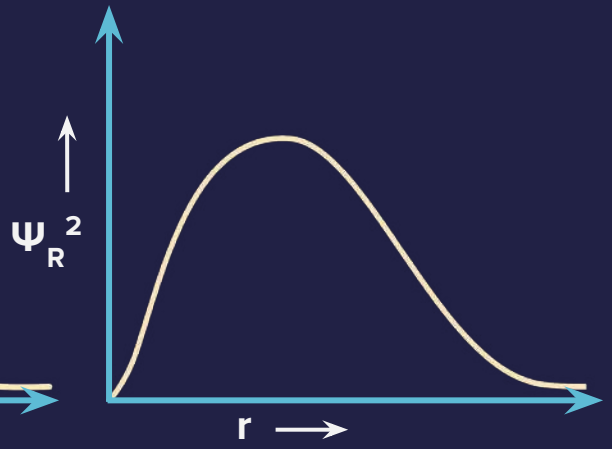


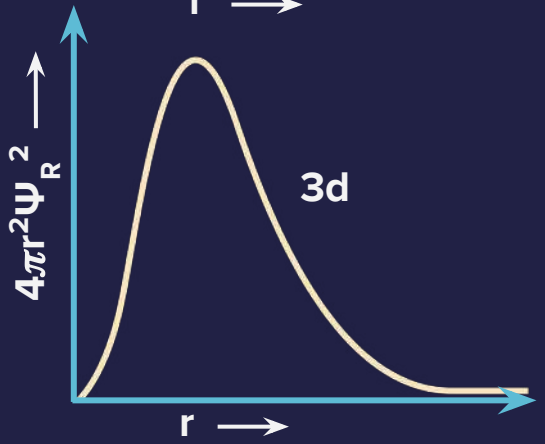


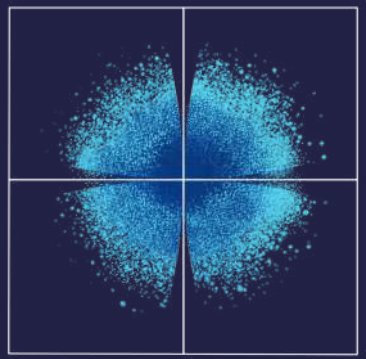


Radial Probability of 3d

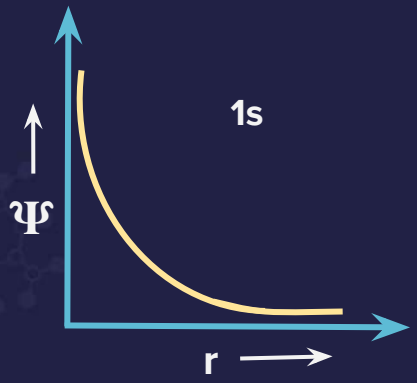


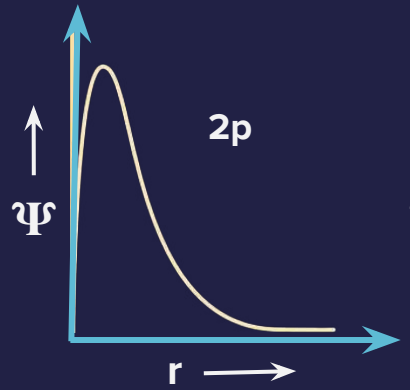


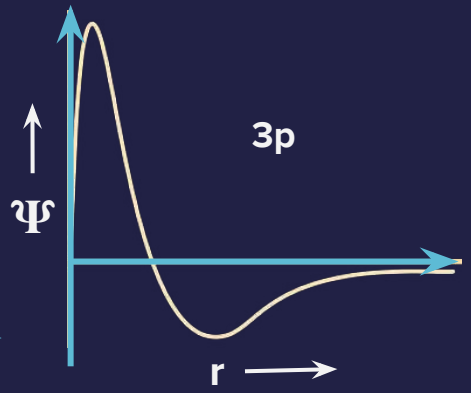


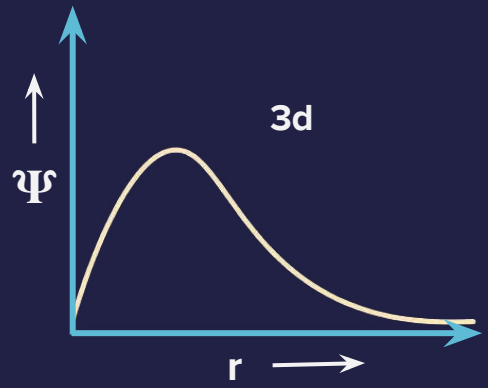


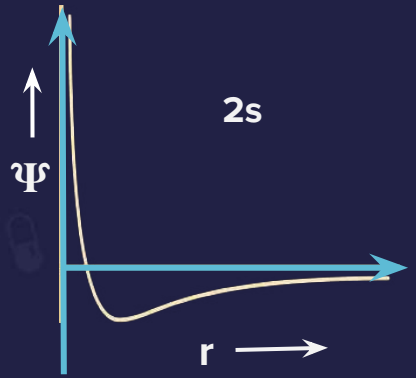
Analysis: Ψ Plots

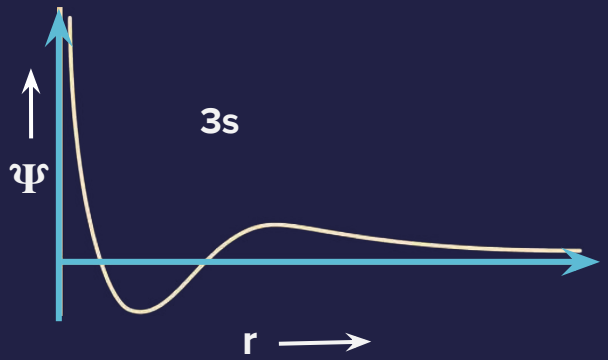




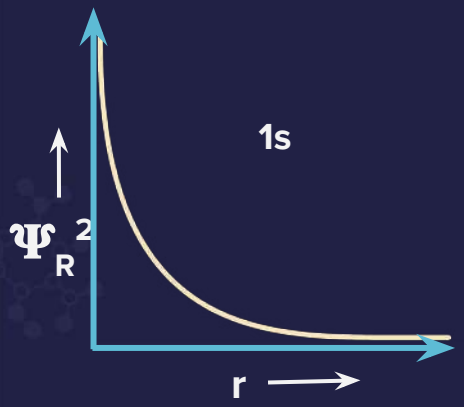


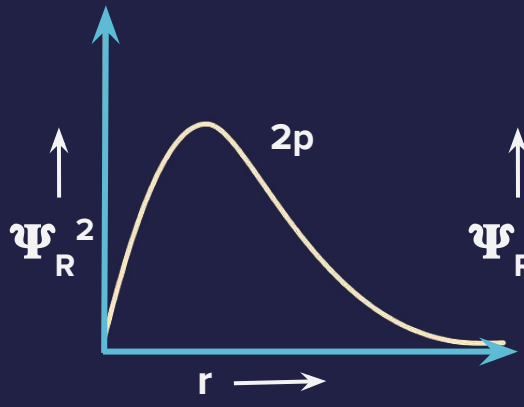


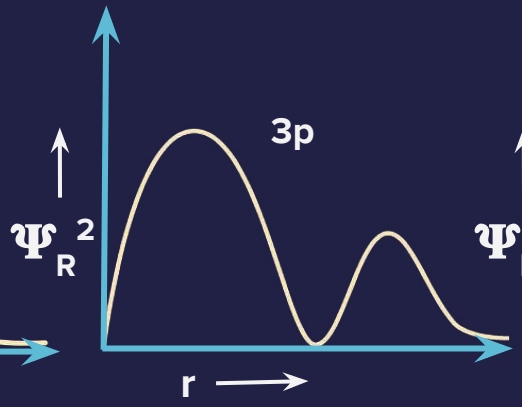


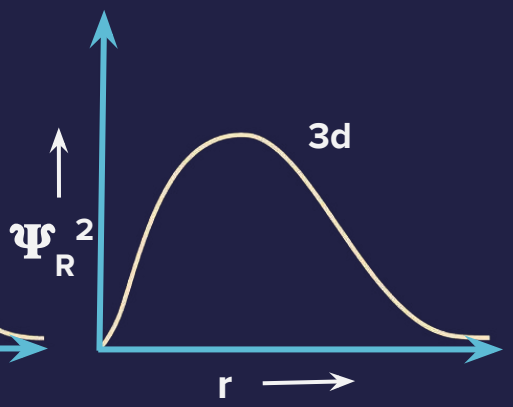


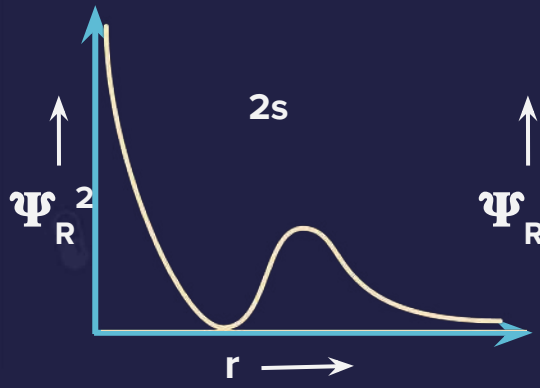
Analysis: Ψ^2 Plots

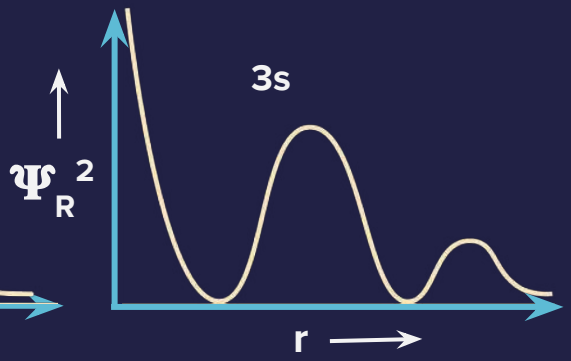




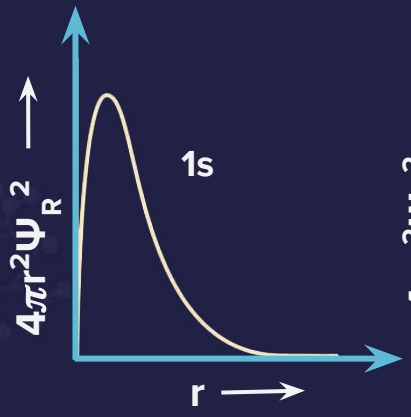


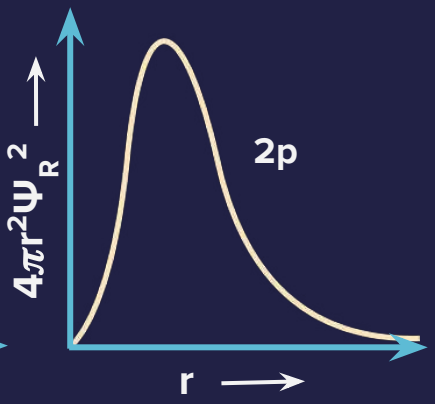


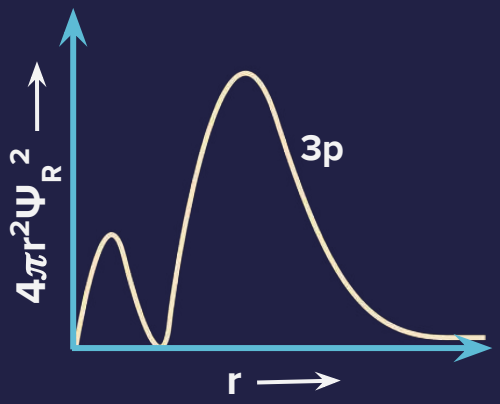


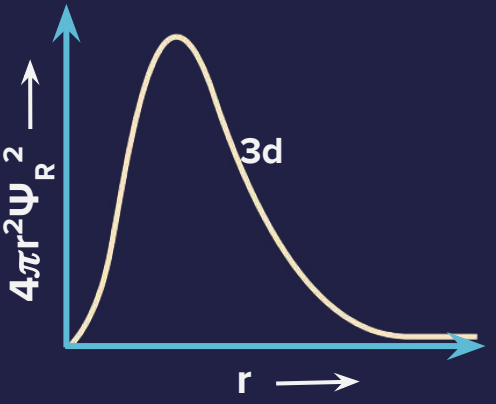


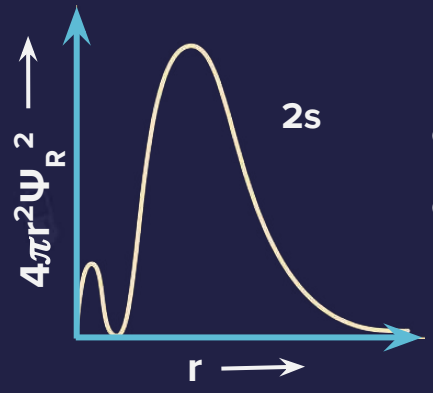
Analysis: $\Psi^2.4\pi r^2$ Plots

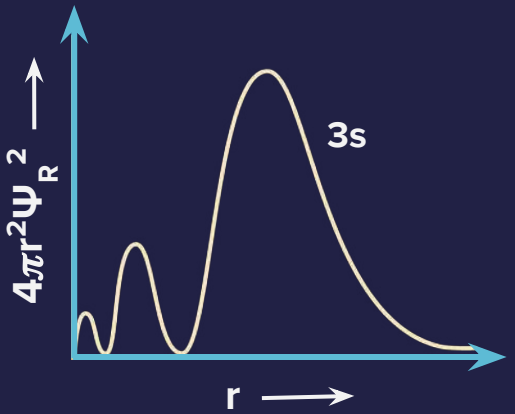


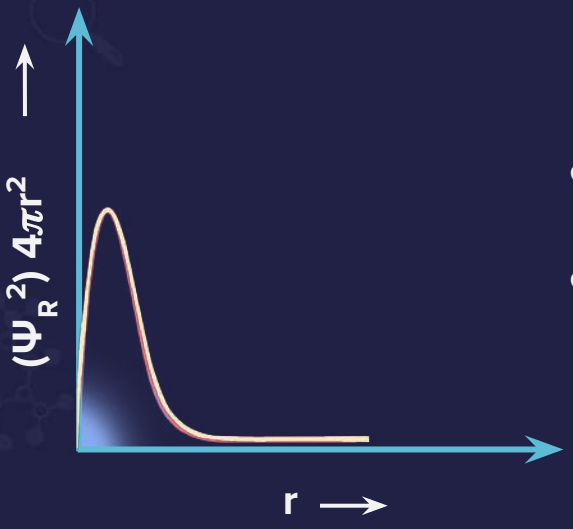


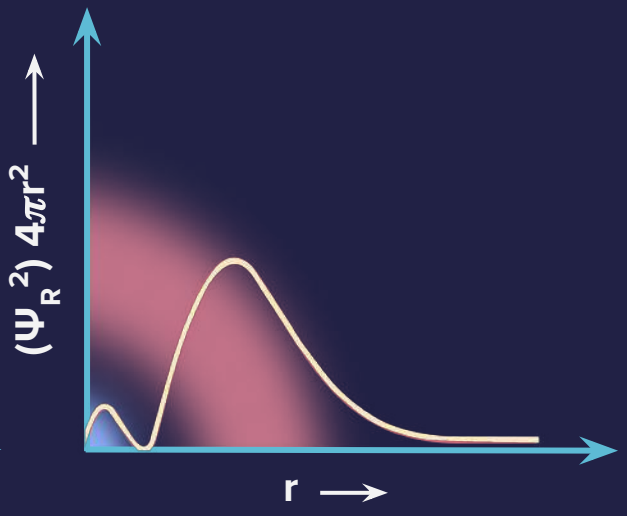


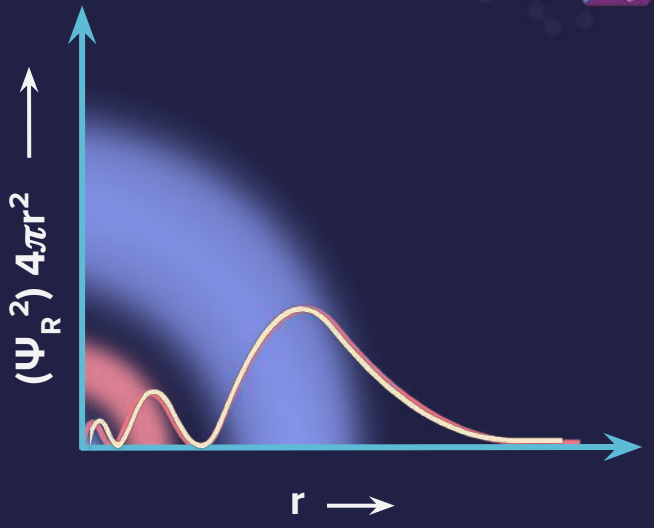


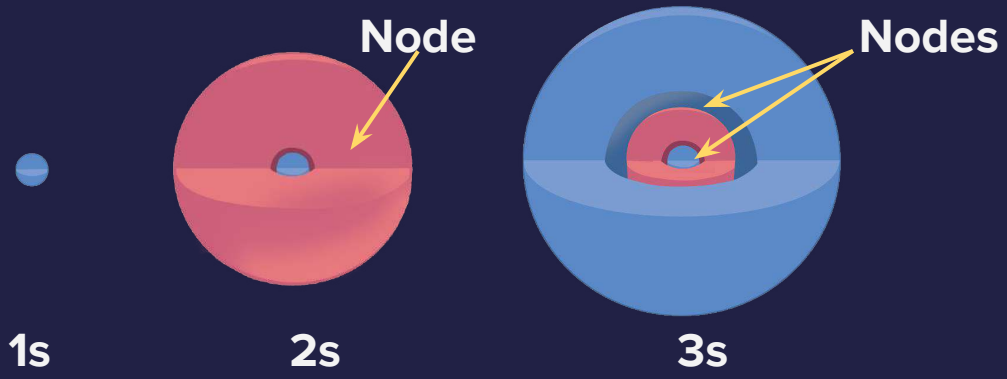


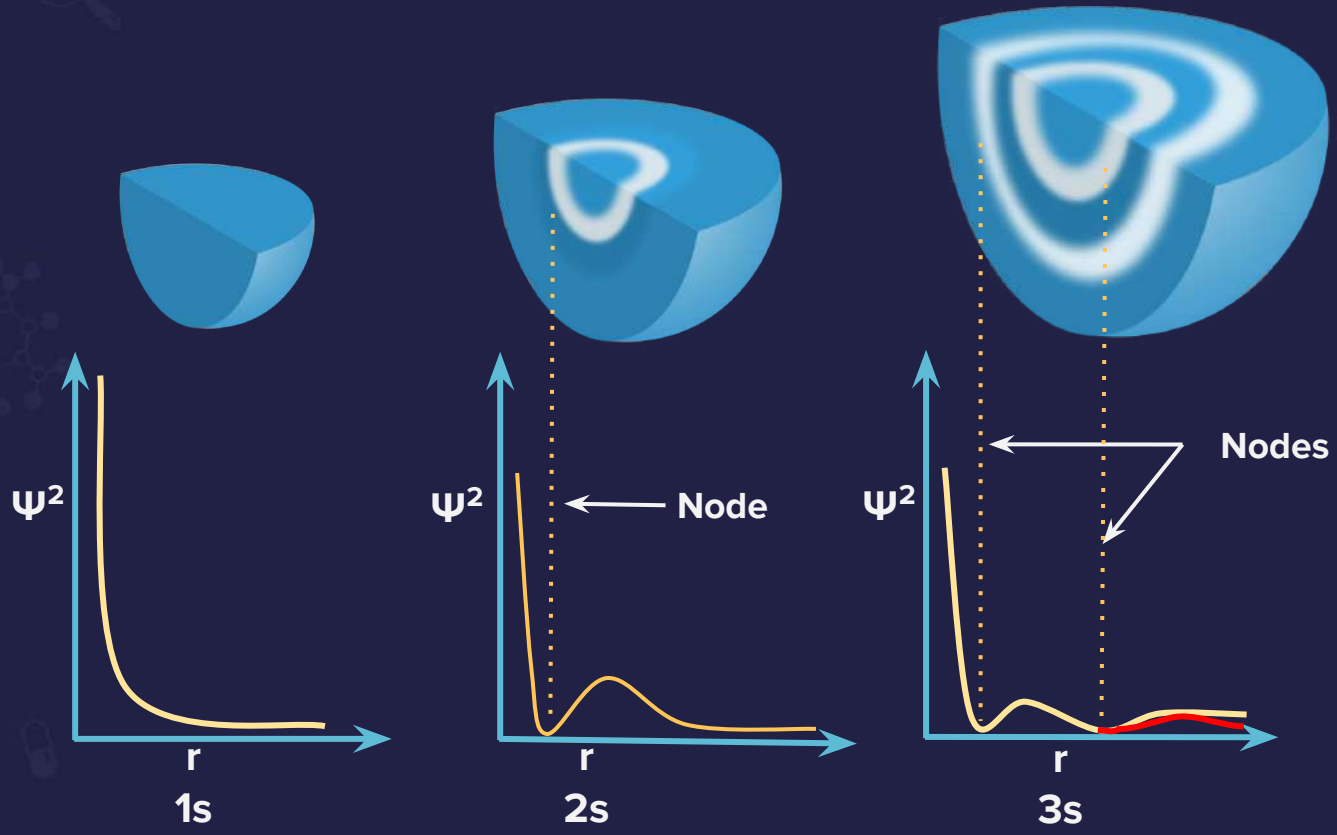



$(\Psi_R^2)\ 4\pi r^2$
r


$(\Psi_R^2)\ 4\pi r^2$
r


$(\Psi_R^2)\ 4\pi r^2$
r


Node
Nodes
1s
2s
3s


ψ²
r
1s
ψ²
Node
r
2s
ψ²
Nodes
r
3s

Radial Wavefunction of Hydrogenic Atoms

$$R_{n/}(r) = \left(\frac{2Z}{na_0}\right)^{3/2} \left(\frac{(n - / - 1)!}{2n\,[(n + /)!]^3}\right)^{1/2} e^{-Zr/na_0} \left(\frac{2Zr}{na_0}\right)^{/} L^{2/ + 1}_{n - / - 1}\left(\frac{2Zr}{na_0}\right)$$

Laguerre Polynomial

$$L_{n-l-1}^{2l+1}(\varrho) = \sum_{i=0}^{n-l-1} \frac{(-1)^i [\,(n+l)!\,]^2 \varrho^i}{i!\,(n-l-1-i)!\,(2l+1+i)!}$$

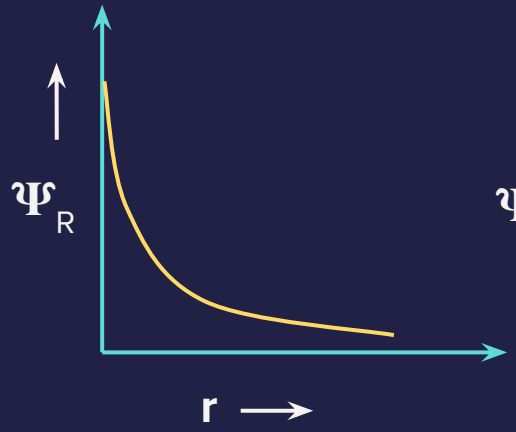
where $\varrho = 2kr$ and $k_n = \frac{Z}{a_0 n}$

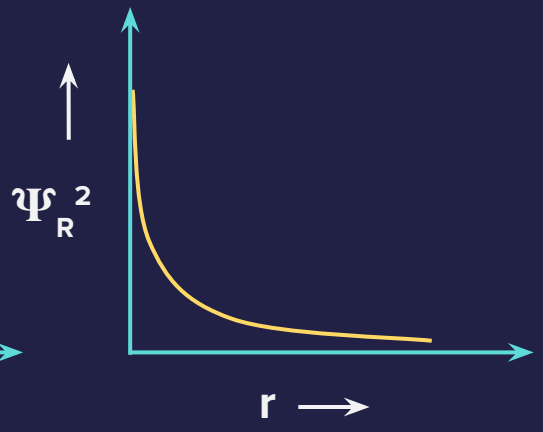
1s orbital

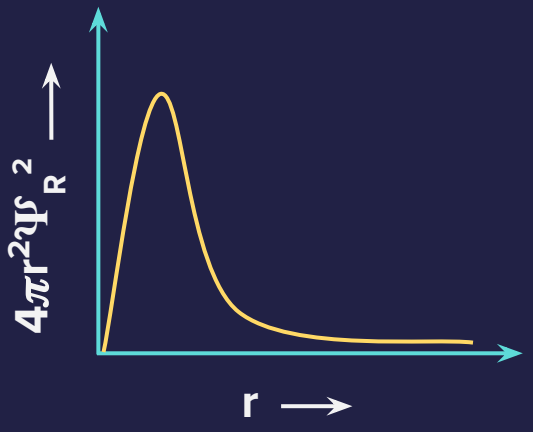
$$R(1s) = K_1 \sigma e^{-\sigma/2} \quad \text{where,} \quad \sigma = \frac{2Zr}{n a_0}$$

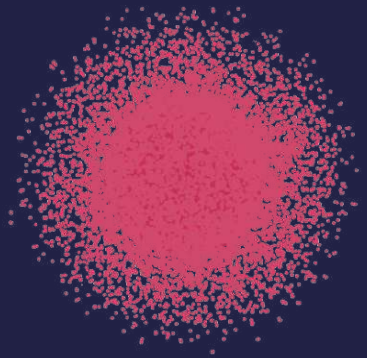
$$\text{Number of radial nodes} = n - l - 1 = 1 - 0 - 1 = 0$$

Radial Probability of 1s







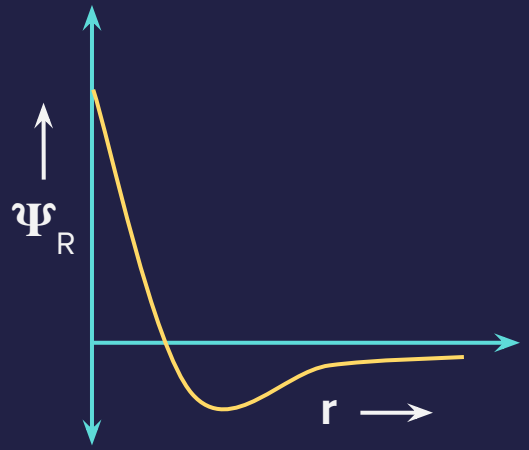


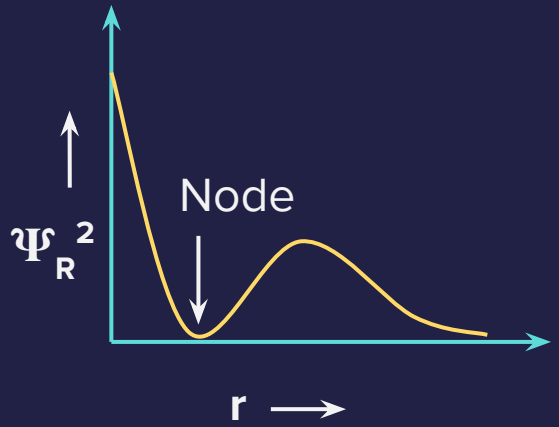
2s orbital

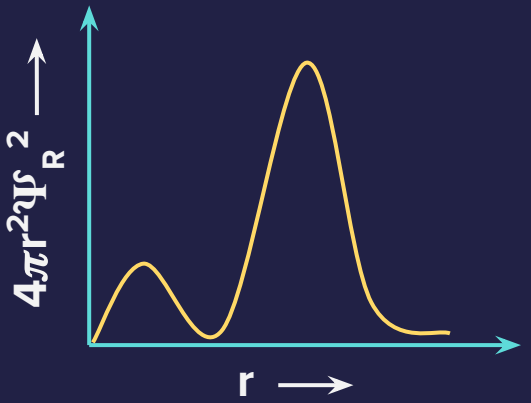
$$R(2s) = K_2(2 - \sigma)\, e^{-\sigma/2}$$

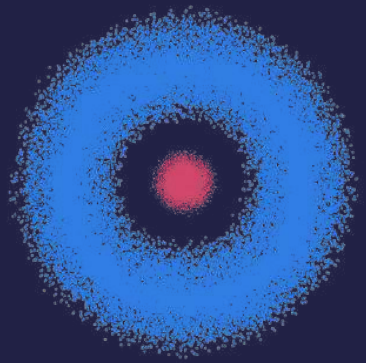
$$\text{Number of radial nodes} = n - l - 1 = 2 - 0 - 1 = 1$$

Radial Probability of 2s



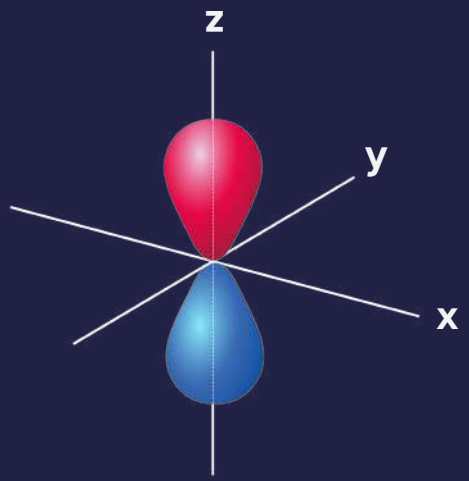






p-orbitals

p-orbitals consist of **lobes**



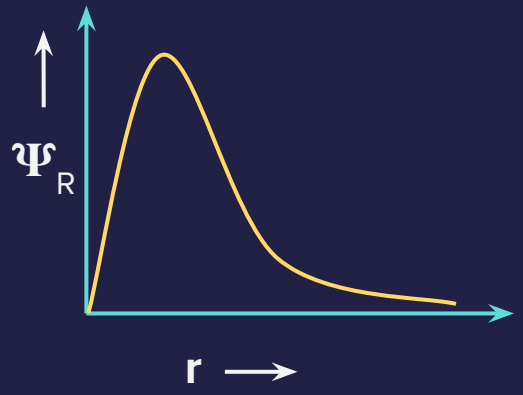
Dumb bell Shaped

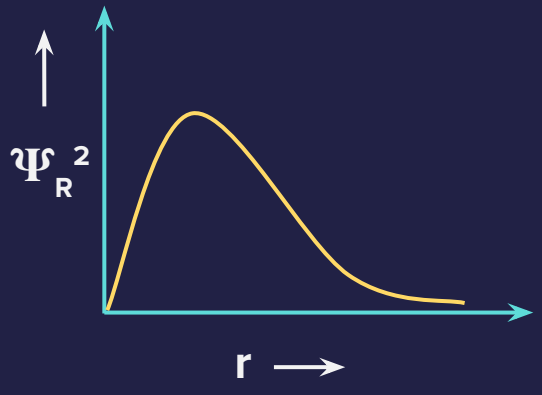
2p orbital

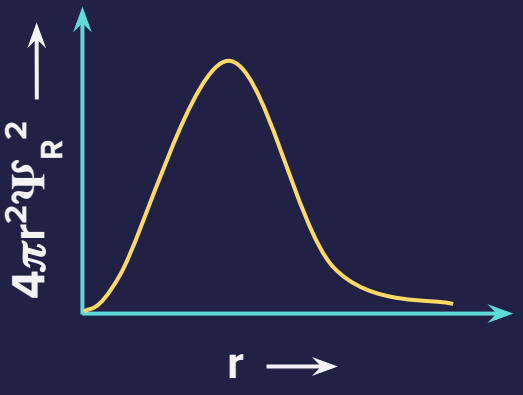
$$R(2p) = K_3 \sigma e^{-\sigma/2}$$

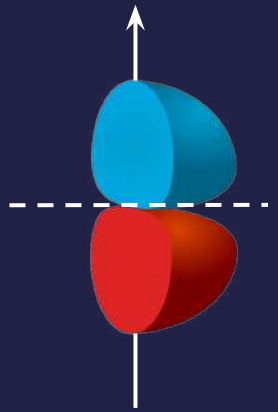
$$\text{Number of radial nodes} = n - l - 1 = 2 - 1 - 1 = 0$$

Radial Probability of 2p







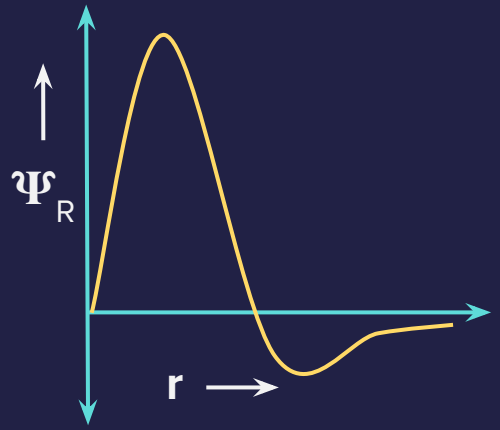


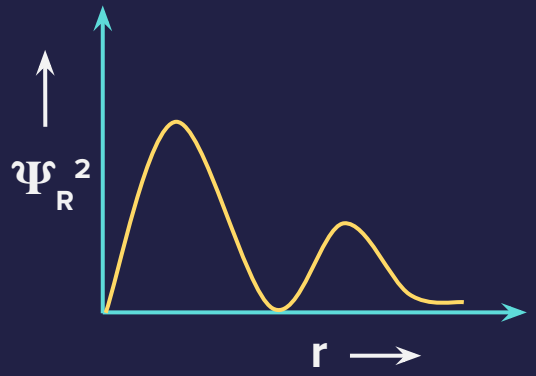
3p orbital

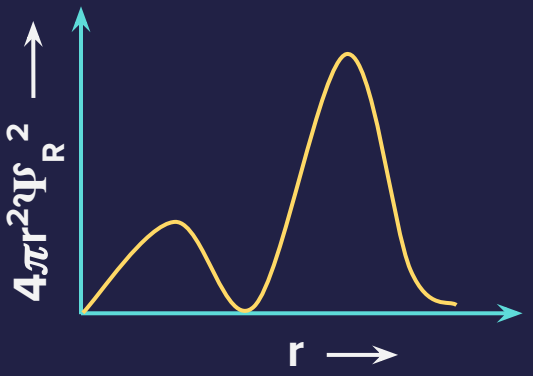
$$R(3p) = K_4(4 - \sigma)\,\sigma\, e^{-\sigma/2}$$

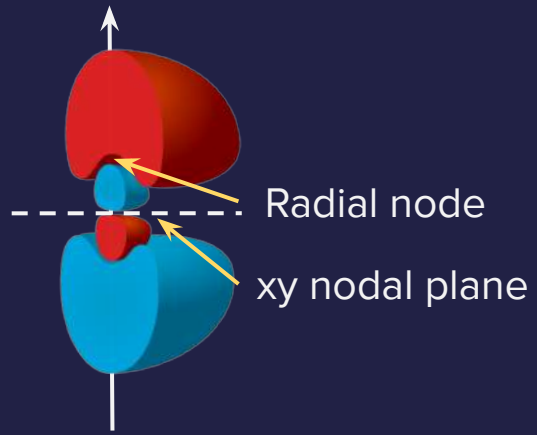
Number of radial nodes $= n - l - 1 = 3 - 1 - 1 = 1$

Radial Probability of 3p

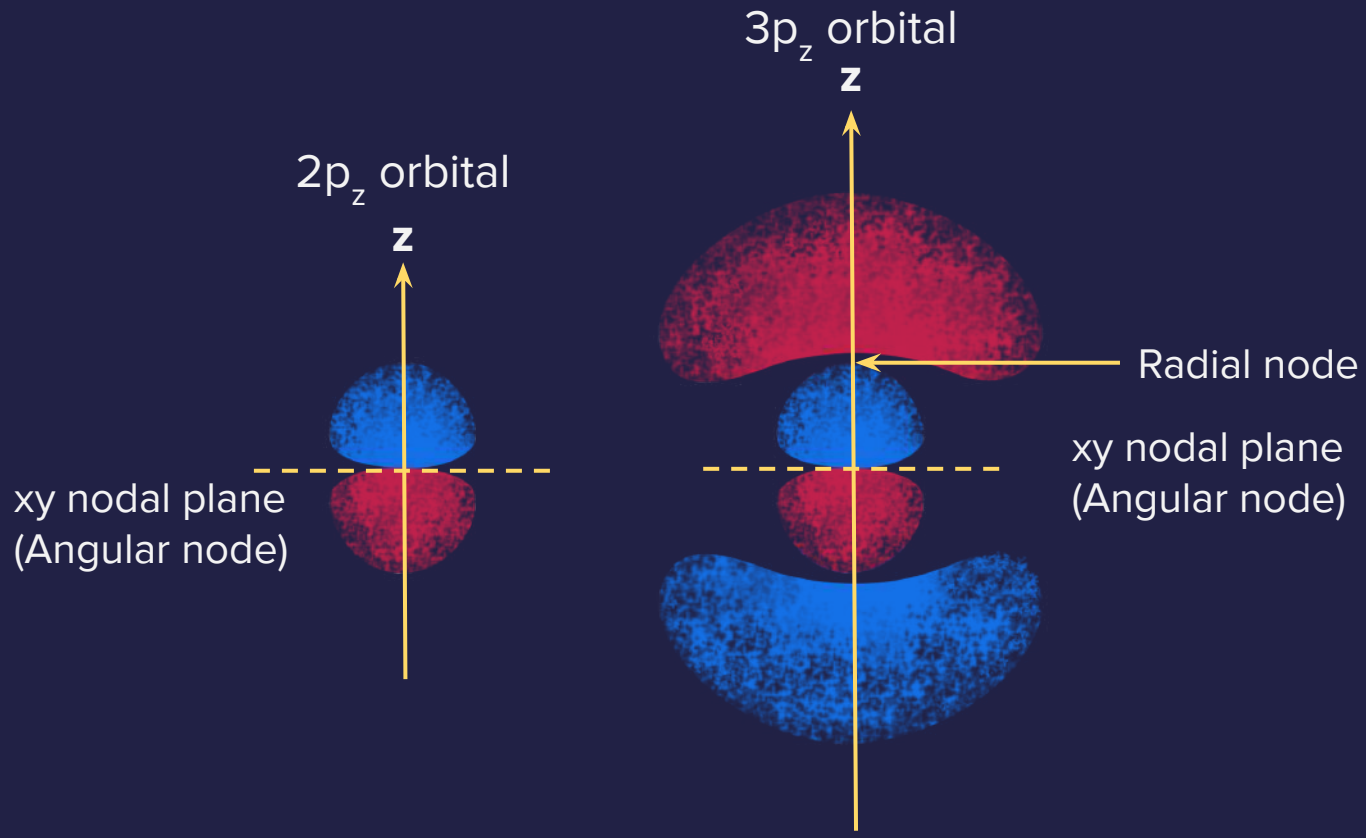




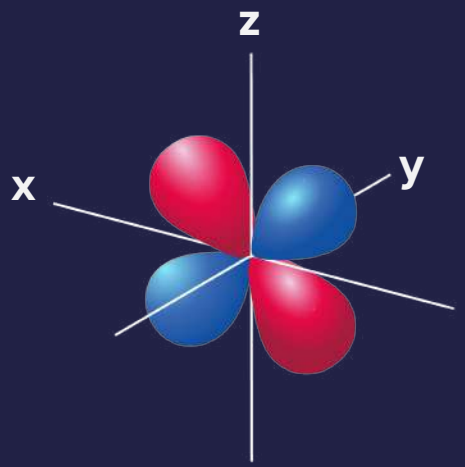




Nodes in p-orbital



Nodes in d-orbitals



Double Dumb bell Shaped

3d orbital

$$R(3d) = K_5 \sigma^2 e^{-\sigma/2}$$

$$\text{Number of radial nodes} = n - l - 1 = 3 - 2 - 1 = 0$$