Atomic Structure

J. J. Thompson Model ⇒ Watermelon Model or Plum pudding model

Mo. Rutherford Model →

→ Most of the α-ray passed undeviated ⇒ empty spaces
→ Few α-ray passed ^ deviated by certain angle
→ very few α-ray deviated by 180 ← central part dense
└ Most of the mass is concentrated at centre



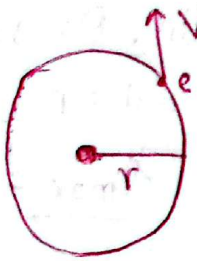
• The classical theory, proposed circular path of an electron → spiral.
• contribution of to the discovery of Nucleus goes to Rutherford

Limitations:
→ Electron radiates energy and ~~finally~~ decreases the radius and finally collapse into nucleus.
→ Can't explain the spectral line.

Bohr's Model:

→ Electrostatic force between electron and nucleus

$$\frac{e.Ze}{4\pi\varepsilon_0 r^2} = \frac{mv^2}{r}$$



→ Angular momentum $(L) = \frac{nh}{2\pi}$

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

Ze ⇒ charge of nucleus

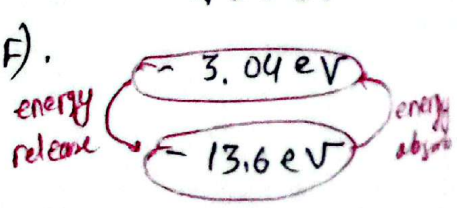
$$\frac{q_1 q_2}{4\pi\varepsilon_0 r^2}$$

[Plank's constant का dimension is same as angular momentum.]

→ When electron jump from higher to lower orbit.
└ energy is released (hf).

lower to higher orbit → energy is absorbed.

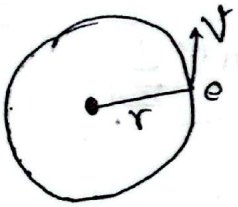
$$E_2 - E_1 = hf$$



Success: stability of atom.
→ spectral line of mono-electronic system. Like (H-like atom) eg. Na^{10+}, He^{+}, C^{5+}
→ Radius, velocity & energy of electron in the orbit.

⇒
Failure: Spectral line of multielectron system → can't explain.
→ Stark effect (electric field splitting) and Zeeman effect (magnetic field splitting).
→ can't explain 3-D model of atom. (Shape of ~~module~~ molecule)
→ De-broglie wavelength can't be explained. (Dual nature)

Radius of electron in n^{th} orbit:



$$\frac{e \cdot Ze}{4\pi\varepsilon_0 r_n^2} = \frac{mv^2}{r_n}$$

$$\frac{Ze^2}{4\pi\varepsilon_0 m v^2} = r_n$$

$\left[\because mvr_n = \frac{nh}{2\pi}\right]$

$$v = \frac{nh}{2\pi m r_n}$$

Electrons are held in atom due to Columb force.

$$r_n = \frac{Ze^2}{4\pi\varepsilon_0 \frac{n^2h^2}{4\pi^2 m^2 r_n^2}}$$

$$r_n = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2 Z}$$

for, H-atom, $Z = 1$,

$$r_n = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2}$$

For 1st orbit, $n = 1$,

$$r_1 = \frac{\varepsilon_0 h^2}{\pi m e^2}$$

$$r_1 = 0.53\ A^\circ$$

$\varepsilon_0 = 8.85 \times 10^{-12}\ F/m$

So, for n^{th} orbit,

~~$r_n = 0.53\ A^\circ$~~

$$r_n = \frac{0.53\ n^2}{Z}$$ - Imp

For constant Z,

$$r_n \propto n^2$$

$$r_1 : r_2 : \dots = 1^2 : 2^2 : 3^2 : \dots n^2 = 1 : 4 : 9 : \dots : n^2$$

Q. If radius of 3rd orbit of H-atom is x. What is the radius of 5th orbit?

→

$$\frac{r_3}{r_5} = \frac{3^2}{5^2}$$

$$\frac{x}{r_5} = \frac{9}{25}$$

$$\boxed{r_5 = \frac{25}{9}x}$$

* For constant (n)

$$r_n = \frac{0.53\,n^2}{Z}$$

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

H → Z = 1 → (n = 3) → $r \propto \frac{1}{Z}$

He^+ → Z = 2 → (n = 3) → $r' \propto \frac{1}{Z'}$

$\because r \propto \frac{1}{Z}$

$$\frac{r_H}{r_{He}} = \frac{Z_{He}}{Z_H} = \frac{2}{1}$$

$\therefore r_H : r_{He} = 2:1$

$\therefore \boxed{r_H > r_{He}}$ when, n → equal

Q. What is the radius of third orbit of C^{5+}?

→ $r_3 = \frac{0.53 \times 3^2}{6}$ A° (n = 3)

$= \frac{0.53 \times 9\,3}{62} \approx 0.75$ A°

Velocity of electron in nth orbit

$$V_n = \frac{Ze^2}{2\varepsilon_0 nh}$$

For H-atom, Z = 1

$$V_n = \frac{e^2}{2\varepsilon nh}$$

For 1st orbit, n = 1,

$$V_1 = \frac{e^2}{2\varepsilon_0 h} = \frac{c}{137}\ m/s = 2.16 \times 10^6\ m/s$$

In General

$$v_n = \frac{c \cdot z}{137\, n}$$

for constant Z – different obit but same atom

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

$$v_1 : v_2 : v_3 \ldots = 1 : \frac{1}{2} : \frac{1}{3} : \ldots \frac{1}{n}$$

$$v_1 : v_2 : v_3 = 1 : \frac{1}{2} : \frac{1}{3}$$

If, $v_1 = x$, $v_2 = \frac{x}{2}$, $v_3 = \frac{x}{3}$

$$v_1 : v_2 : v_3 = 6 : 3 : 2$$

Q. IF $v_3 = x$, $v_5 = ?$

$$\therefore v_5 = \frac{3}{5}x$$

$$\therefore \frac{v_5}{v_3} = \frac{3}{5}$$

$$v_5 = \frac{3}{5} v_3$$

for constant n → different atom but same obit

$$v_n \propto Z$$

$$v_1 : v_2 : v_3 : \ldots = 1 : 2 : 3 \ldots$$

H → $Z = 1$, $(n=3)$, $v_3 \propto 1$

He^+ → $Z' = 2$, $(n=3)$, $v_3' \propto 2$

So, $v_3' > v_3$

$$\left(\frac{v_3}{v_3'} = \frac{Z}{Z'}\right)$$

$$v_3' = 2 v_3$$

Q. C^{5+}, $n = 3$

$v = ?$

$$v_3 = \frac{c}{137} \frac{6^2}{3} = \frac{2c}{137} \text{ m/s}.$$

$$v_3 = \frac{2c}{137} \text{ m/s}$$

$$= 2 \times 2.16 \times 10^6$$

$$= 4.32 \times 10^6 \text{ m/s}.$$

Q. Na^{10+}, $n = 5$

$$v_5 = \frac{c}{137} \frac{11}{5}$$

$$v_5 = 2.16 \times 10^6 \times 2.2$$

$$= 4.752 \times 10^6 \text{ m/s}.$$

Energy of electron in n^{th} orbit

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

$$K.E = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{ze^2}{2\varepsilon_0 nh}\right)^2$$

$$\boxed{K.E = \frac{Z^2me^4}{8\varepsilon_0^2 n^2h^2}}$$

$$\boxed{P.E = \frac{-e.ze}{4\pi\varepsilon_0 r_n} = \frac{-Z^2me^4}{4\varepsilon_0^2 n^2h^2}}$$

$$\therefore \boxed{T.E = \frac{-Z^2me^4}{8\varepsilon_0^2 n^2h^2} = -K.E}$$

$$\because \underset{(-x)}{T.E} = \underset{(x)}{-K.E} \quad \underset{(-2x)}{P.E}$$

So. ~~$T.E = 2P.E = -K.E$~~

$$\boxed{K.E = -TE}$$

$$\boxed{P.E = 2T.E}$$

$$T.E = \frac{-me^4z^2}{8\varepsilon_0^2 n^2h^2}$$

For H-atom, $Z = 1$

$$E_n = \frac{-me^4}{8\varepsilon_0^2 n^2h^2}$$

if $n = 1$,

$$E_1 = \frac{-me^4}{8\varepsilon_0^2 h^2} = -13.6 \text{ eV}$$

$$\therefore \boxed{E_n = \frac{-13.6 \text{ eV}}{n^2}}$$

In General

$$\boxed{E_n = -13.6\frac{Z^2}{n^2}}$$

For H-atom, $Z = 1$.

$$E_1 = -13.6 \text{ eV}$$

$$E_2 = \frac{-13.6}{4} \text{ eV} = -3.45 \text{ eV}$$ ~~-3.54 eV~~

$$E_3 = \frac{-13.6}{9} \text{ eV} = -1.54 \text{ eV}$$

$E_\infty = 0$ (Max. at infinity)

$\frac{E_3}{E_5} = ?$ $\left[E \propto \frac{1}{n^2}\right]$ → actually: $E_5 > E_3$

$\frac{E_3}{E_5} = \frac{25}{9}$ ↳ incorrect.

$9E_3 = 25E_5$

So, $\frac{E_3}{E_5} = \frac{9}{25}$

$\frac{E_3}{E_4} = \frac{9}{16}$

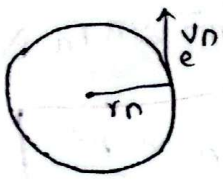
Conclusion

- ✓ T.E $\propto n^2$
- ✓ P.E $\propto n^2$
- ✓ K.E $\propto \frac{1}{n^2}$

$\frac{T.E_2}{T.E_3} = \frac{P.E_2}{P.E_3} = \frac{4}{9}$

but $\frac{K.E_2}{K.E_1} = \frac{1}{4}$

On moving towards the outer orbit → T.E ↑, P.E ↑, K.E ↓



Time period of electron in nth orbit

$T_n = \frac{2\pi r_n}{v_n} \propto \frac{r_n}{v_n}$

$\left[r_n \propto \frac{n^2}{Z}, \quad v_n \propto \frac{Z}{n}\right]$

$T_n \propto \frac{r_n}{v_n} \propto \frac{n^2/Z}{Z/n} \propto \frac{n^3}{Z^2}$

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

For an atom:- (Z → constant)

$T_n \propto n^3$

$T_n^2 \propto (n^3)^2$ $[\because r_n \propto n^2]$

$T_n^2 \propto (n^2)^3$

$T_n^2 \propto r_n^3$

Q. Electron revolves in the circular orbit of radius R and 4R respectively. What is ratio of time period?

$T_n^2 \propto r_n^3$

$T_n \propto r_n^{3/2}$

$\frac{T_R}{T_{4R}} = \left(\frac{R}{4R}\right)^{3/2} = \frac{1}{8}$

$\therefore \boxed{T_R : T_{4R} = 1:8}$

Frequency (f_n)

$$\boxed{f_n = \frac{1}{T_n} \propto \frac{Z^2}{n^3}}$$

Angular velocity (ω)

$$\boxed{\omega_n = 2\pi f_n \propto f_n \propto \frac{Z^2}{n^3}}$$

(2π = const.)

Circumference

$C_n = 2\pi r_n \propto r_n \propto \frac{n^2}{Z}$

$$\boxed{C_n \propto \frac{n^2}{Z}}$$

Area

$A_n = \pi r_n^2 \propto r_n^2 \propto \left(\frac{n^2}{Z}\right)^2$

$$\therefore \boxed{A_n \propto \frac{n^4}{Z^2}}$$

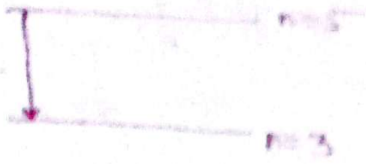
Q. For an atom, area of 3rd orbit & 4th orbit will be:-

Z = const.

$\frac{A_3}{A_4} = \left(\frac{3}{4}\right)^4$

$$\boxed{\frac{A_3}{A_4} = \frac{81}{256}}$$

When electron jumps from $n=2$ to $n=3$



→ Angular momentum (L) → decreases $\left[L = \frac{nh}{2\pi}\right]$

→ Velocity (v) → increase

$v_n = \frac{c}{137}\frac{Z}{n}$

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

→ Linear momentum (p) → increases

$p = mvr$

→ frequency (F) → increases

$F \propto \frac{1}{T}$

→ Kinetic energy ($K.E$) → increases

innershell → $K.E$ ↑

$\left(K.E \propto \frac{1}{n^2}\right)$

→ Total energy ($T.E$) → decreases

→ circumference (C) → decreases

$C \propto r_n$ (r_5 - more than r_3)

→ Area (A) → decreases

→ Time period (T) → decreases

$T_n^2 \propto r_n^3$

→ Angular velocity (ω) → $2\pi F$ → increases

→ Potential energy ($P.E$) → decreases

* When electron jumps from $n=2$ to $n=5$:- reverse of all above

Transition of electron → electron higher energy level to lower energy level → loss

→ electron lower energy level to lower energy level → gain energy

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

$\left(E_n = \frac{-me^4Z^2}{8\varepsilon_0^2 n^2 h^2}\right)$

$\Delta E = \frac{-me^4Z^2}{8\varepsilon_0 n_2^2 h^2} + \frac{me^4Z^2}{8\varepsilon_0 n_1^2 h^2}$

$hF = \frac{me^4Z^2}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$\frac{hc}{\lambda} = \frac{me^4Z^2}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$\frac{1}{\lambda} = \frac{me^4Z^2}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

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

R → Rydberg constant → different for different

↳ 1.1×10^7 m^{-1}

For Hexatom, $Z = 1$

$$\boxed{\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$ (n_2 बाट n_1 मा आउने)

थाहा बाट आउने

* Lyman series

$n_1 = 1$ मा, $n_2 = 2, 3, 4, \ldots \infty$ बाट

For 1st member,

$n_1 = 1$, $n_2 = 2$

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

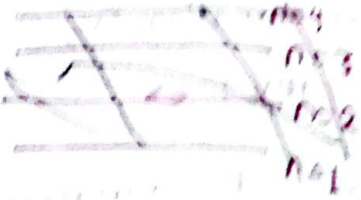
$$\frac{1}{\lambda} = R\left(\frac{3}{4}\right)$$

For 2nd member,

$n_1 = 1$; $n_2 = 3$

Series Limit

$n_1 = 1$ & n_2



→ Lies in UV-region.

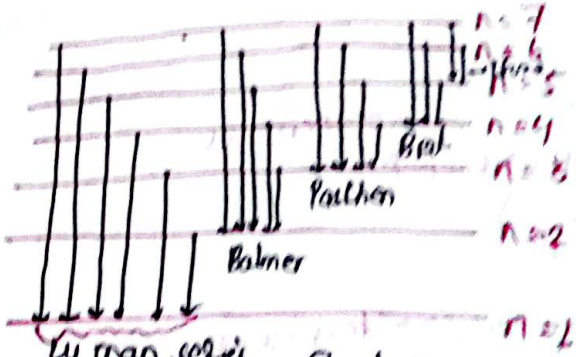
for 1st member, → $n_1 = 1$ मा $n_2 = 2$ बाट

↳ Longest wavelength

↳ Freq. or energy minimum.

$$\frac{1}{\lambda_1} = R\left(\frac{3}{4}\right)$$

$$\boxed{\lambda_1 = \frac{4}{3R}}$$ → Longest



$n=2$ to $n=1$ कम $\xi = hF = \frac{hc}{\lambda}$ बाट

For 2nd member → $n = 1$ मा $n = 3$ बाट ~~$n = 4, 5, \ldots \infty$ बाट~~

* Balmer series

$n_1 = 2$ मा, $n_2 = 3, 4, \ldots \infty$ बाट

→ lies in visible region.

For 1st member, $n_1 = 2$ & $n_2 = 3$

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

$$\frac{1}{\lambda} = R\left(\frac{9-4}{36}\right) = \frac{5}{36}R$$

$$\boxed{\lambda = \frac{36}{5R}}$$

Series limit:- $n_1 = 2$ & $n_2 = \infty$

$$\frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{\infty}\right)$$

$$\boxed{\lambda = \frac{4}{R}}$$

* Paschen series :-
→ lies near infrared.
$n_1 = 3$ मा, $n_2 = 4, 5, 6 \ldots$ ∞ बाट

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{4^2}\right) = R\left(\frac{7}{144}\right)$$

$$\lambda = \frac{144}{7R}$$

* Bracket series:
- lies infrared
- $n_1 = 4$ मा $n_2 = 5, 6, 7 \ldots \infty$ बाट

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{5^2}\right) = R\left(\frac{9}{400}\right)$$

$$\lambda = \frac{400}{9R}$$

* P-fund series
- lies for infrared
→ $n_1 = 5$ मा $n_2 = 6, 7 \ldots \infty$ बाट

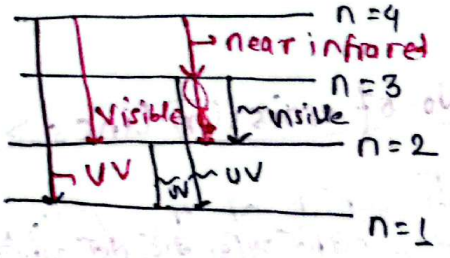
$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{6^2}\right) = \frac{11R}{900}$$

$$\lambda = \frac{900}{11R}$$

• ~~No of emission and~~
• सबै series मध्ये lyman मा आउनेको highest Frequency (lowest wavelength) र P-fund मा आउनेको lowest Frequency (highest wavelength).

• सबैभन्दा बढी Freq → series limit of lyman

No. of emission (माथिबाट तल) and absorbtion Line (तलबाट माथि)



emission Line : $n_2 = 4$ to $n_1 = 1$

$\left(\text{No.} = \frac{n(n-1)}{2}\right) \rightarrow$ ($n_1 = 1$ मै आउनु पर्यो)

e.g. $n_2 = 25$ to $n_1 = 1$

for $n = 4$

$$= \frac{4(4-1)}{2} = 6.$$

or,

$$\text{No.} = \frac{\Delta n(\Delta n + 1)}{2}$$ → सबैलाई गिन्दा

$\Delta n = 4 - 1 = 3.$ $n_1 = 1$, $n_2 = 4$.

$$= \frac{3(3+1)}{2}$$

$= 6.$

e.g. $n_2 = 25$, $n_1 = 3$

$\Delta n = 22.$

$$= \frac{22(22+1)}{2}$$

$= 11 \times 23$

$= 253$ lines.

or, $N_o = \Sigma \Delta n$ $\quad \Delta n = 4-1 = 3$

$= \Sigma 3$

$= 3 + 2 + 1$

UV — Lyman. Vis — Bal. IR — Paschen.

Q. How many emission ~~transitions~~ lines are possible when ~~electron jumps from~~ transition takes place from 5th excited state to 2nd excited state?

→ $N_o = \Sigma \Delta n$ $\quad \boxed{\Delta n = 6-3 = 3}$

$= \Sigma 3$

$= 3 + 2 + 1 = 6$ (Pash, Brack, Pfund)

~~Lyman Bal Pascen~~

1st ex. state, $n=2$

2nd " $n=3$

5th ex. st $= n=6$.

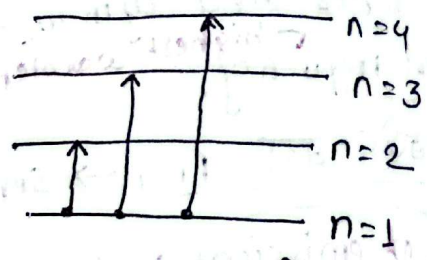
ground state $= n=1$

No. of absorbtion line

(तल देखि माथि)

No. of absorbtion line $n=4$, $= 3$

So, $\boxed{N_o = n-1}$



5th excisted state मा गयो from gr

$n=6$ $\quad N_o = n-1 = 6-1 = 5$

* $\boxed{\text{No. of emission lines} > \text{No. of absorbtion lines}}$

Q. In which of the following transition, the energy released will be maximum

जति माथि बाट तल आउछ त्यति

(1) (a) $5 \to 1$ (b) $4 \to 1$ (c) $3 \to 1$ (d) $2 \to 1$

(2) (a) $5 \to 4$ - Bracket (IR) (b) $4 \to 3$ - Paschen (IR) (c) $3 \to 2$ - Balmer visible (d) $2 \to 1$ - Lyman (UV) ∟ max^m energy

(3) (a) $16 \to 4$ - Bracket (b) $9 \to 3$ - Paschen (c) $5 \to 2$ - Balm (d) $2 \to 1$ - Lyman ∟ max energy

(4) (a) $12 \to 2$ ∟ Balm ∟ max (b) $9 \to 3$ ∟ Paschen (c) $7 \to 4$ ∟ Bracket (d) $10 \to 2$ ∟ Balmer ∟ less than (a)

Q. In which of the following transition, the energy absorbtion is maximum?

(1) (a) 6 → 1 ✗
(b) 5 → 2 ✗
(c) 4 → 3 ✗
(d) 1 → 4

no absorbt

(2) (a) 1 → 2 → 10.2 eV (max.)
(b) 2 → 3 → 2 eV
(c) 3 → 4 → 0.75 eV
(d) 4 → 5 → 0.7 eV

(3) (a) 1 → 2
(b) 1 → 3
(c) 1 → 4
(d) 1 → 5

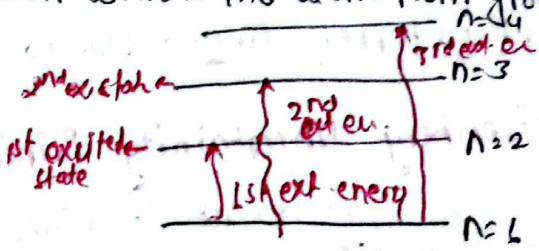
सबै ground

(4) (a) 1 → 2 → 1 बाट जाने ले max. absorbtion गर्छ।
(b) 2 → 9
(c) 3 → 6
(d) 4 → 5

→ Emission मा Higher बाट 1 मा आउनेले धेरै energy release गर्छ।

→ Absorbtion मा 1 बाट जानेले धेरै energy absorb गर्छ।

Excitation energy :- process of raising of an electron within the atom from ground state (lower) to higher state.

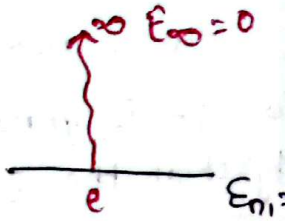


1st excitation energy $= E_{n_2} - E_{n_1}$
$= -3.54 - (-13.6)$
$= 10.2\ eV$

2nd excitation energy $= E_{n_3} - E_{n_1}$
$= -1.51 - (-13.6)$
$= 12.1\ eV$

1st excitation potential = 10.2 V
2nd excitation potential = 12.1 V

Ionisation energy: Removal of electron completely from an atom.



ionisation energy $= E_\infty - E_{n_1}$
$= 0 - (-13.6\ eV)$
$= 13.6\ eV$

Ionization potential = 13.6 eV

Spectrum

Line
- atomic state
- in vapour or gaseous state
- eg. H, O_2
- characteristise of elements
- two different element can't give identical line spectra.

Band
- molecular state
- In vap. or gaseos state.
- eg gas NaCl.
- characteristics of compound.
- two different compound can't give identical spectra.

Continuous spectrum : consists of all the wavelength
→ Incandescent solid and liquids — atoms & molecule
→ (4500 Å° - 7500 Å°) → continuous
→ When black body is heated → continuous spectrum
→ α-particle and γ-ray → line spectra
- β-particle → continuous spectra
→ Electric bulb, black body → continuous spectra
→ also called white spectra

Note: Sun's spectrum → continuous spectrum with few absorbtion line
↓ (Fraunhoffer's spectra)

- Fraunhoffer's line → Due to absorbtion of sun's radiation by sun's atmosphere

Heisenberg Uncertainity Principle

Classical concept: exact location can be determined.
but in quantum mechanics, it can't be localized.
↳



Δx is well defined
λ is ill defined



Δx is ill defined.
λ is well defined.

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

- p is also ill defined.

→ So, it is impossible to know both exact position and exact momentum of an object at the same time.

- If x-component of momentum of particle is measured with uncertainity Δp_x, then the uncertainity in position x is given by:

$$\Delta x \geq \frac{h}{2\pi \cdot \Delta p_x}$$

$$\boxed{\Delta x \cdot \Delta p_x \geq \frac{h}{2\pi}}$$

In General:

$$\boxed{\Delta x \cdot \Delta p \geq \frac{h}{2\pi}}$$

When $\Delta x \rightarrow 0$
then $\Delta p_x \rightarrow \infty$

for y-component: $\Delta y \cdot \Delta p_y \geq \frac{h}{2\pi}$

for z-comp.: $\Delta z \cdot \Delta p_z \geq \frac{h}{2\pi}$

abishek singh