Spectroscopy

- measures the interaction of the molecules with em radiation

Cosmic ray X-rays UV Visible Infrared Heat
γ rays

→ Energy ↓
→ frequency ↓
→ wavelength ↑

γ / X-ray → Transition of inner electrons

UV or Visible → Transition of outer most valence e⁻
- UV spectroscopy
- Atomic absorption spectroscopy

Infra-red → Molecular vibration → Infra-red

Microwave → Molecular Rotation

Radio waves

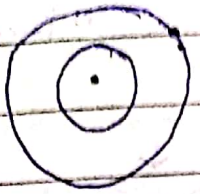
Selection rule:

dipole selection rule ←
① $\Delta l = \pm 1$; $\Delta L = \pm 1$
② $\Delta j = 0, \pm 1, \pm 2$; $\Delta J = 0, \pm 1, \pm 2$

Models of atoms:

Bohr Model:

Hydrogen & hydrogen like atoms: H, He^+, Li^{++}.



$$\frac{Ze^2}{r_n^2} = \frac{mv^2}{r_n}$$

$mvr = n\frac{h}{2\pi}$

$$r_n = \frac{h^2}{4\pi^2 me^2}\frac{n^2}{Z}$$

$$\text{or } \boxed{r_n = r_1\frac{n^2}{Z}}$$

n: principal quantum number.

$r_n \propto n^2$

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

$$v_n = \frac{2\pi e^2}{h}\frac{Z}{n} = v_1\frac{Z}{n}$$

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

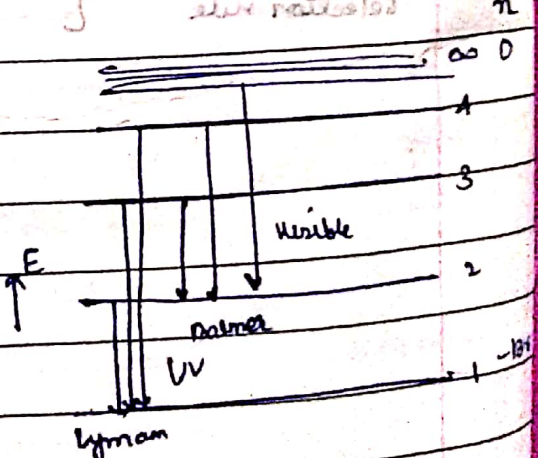
$$K_n = K.E = \frac{1}{2}mv_n^2 = \frac{2\pi^2 me^4}{h^2}\frac{Z^2}{n^2}$$

Potential energy, $U_n = -\frac{4\pi^2 me^4}{h^2}\frac{Z^2}{n^2}$

Total energy, $E_n = K_n + U_n$

$$= -\frac{2\pi^2 me^4}{h^2}\frac{Z^2}{n^2} = -E_1\frac{Z^2}{n^2} \qquad n = 1, 2, 3\ldots$$

for hydrogen atom, $E_1 = -13.6\,eV$



quantum of energy

$$h\nu = E_f - E_i$$

for hydrogen,

$$h\nu = E_f - E_i$$

$$= -\frac{E_1}{n_f^2} + \frac{E_1}{n_i^2}$$

$$\text{or } \frac{hc}{\lambda} = \frac{-E_1}{n_f^2} + E_1/n_i^2$$

$$\text{or } \frac{1}{\lambda} = -\frac{E_1}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\bar{\upsilon} = -\frac{E_1}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$= -R_\infty\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

R_∞ → Rydberg constant

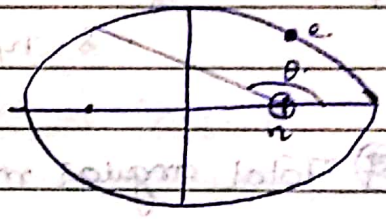
Principal quant. Selection Rule = $\pm 1, \pm 2, \ldots$

Balmer Series: $n=3 \rightarrow n=2$
- → more than one line (Stark & Zeeman splitting)
- → Red color (our eyes more sensitive to red)

Extension of Bohr's Model was given by Sommerfeld.

Bohr-Sommerfeld Model:-

- The atomic orbitals are not circular but elliptical.



$\int P_r dr = n_r h$ → Radial part

$\int P_\theta d\theta = n_\theta h$ → Azimuthal part

$n_{er} = n_\theta$

$n = n_r + n_\theta$

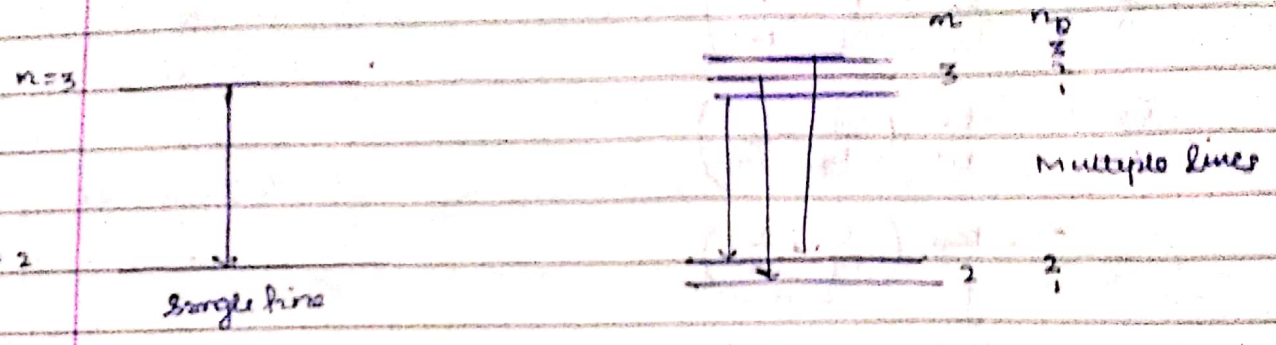
Degenerate State = more than one state in one level having same energy.

Total energy: $E_n = -E_1 \frac{Z^2}{n^2}$, $m = \frac{m_0}{\sqrt{1-(v/c)^2}}$

$$E_n = -\frac{E_1 Z^2}{n^2}\left[1 + \frac{Z^2\alpha^2}{n^2}\left(\frac{n}{n_\theta} - \frac{3}{4}\right)\right]$$ = Correction in energy considering correction in mass.

α: fine structure constant

$= \frac{1}{137}$

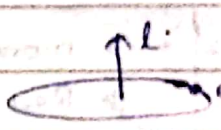


Selection rule: $\Delta n_0 = \pm 1, \pm 2, \ldots$ but applicable only to $n_0 =$

Vector Model:

① Principal quantum number $n = 1, 2, 3 \ldots$

$k \leq l \leq m$



l orbital angular momentum

② $l^* = \sqrt{l(l+1)}\,\hbar$

$l = 0, 1, 2, 3 \ldots$

l	
0	s
1	p
2	d
3	f

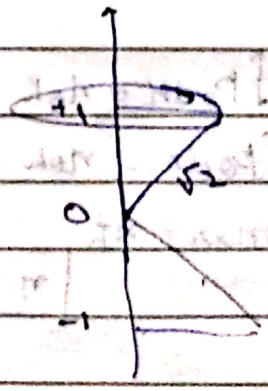
Degeneracy $= 2l+1$.

$l = 0, 1, 2 \ldots n-1$

③ Spin angular momentum

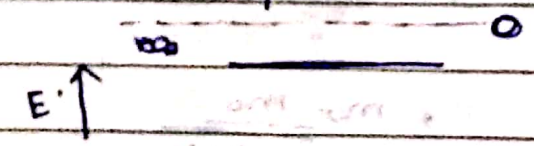
$s = \hbar/2$

④ Total angular momentum: j (J)



for d state: $+2, +1, 0, -1, -2$

Term: The quantum number designation of states. Each term



definitive energy.

Term energy $= -\frac{W}{hc}$