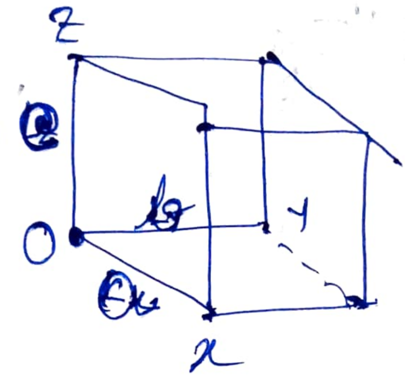
$\boxed{\text{Lec 10}}$

Energy for the particle in a 3-D box



$V(\vec{r}) = 0$

~~when $0 \le x \le L_x$~~

when $\begin{cases} 0 < x < a \\ 0 < y < b \\ 0 < z < c \end{cases}$ $\psi(x, y, z) \neq 0$

$V(\vec{r}) = \infty$ elsewhere $\psi = 0$

$$\psi_{n_x, n_y, n_z}(x, y, z) = \left(\sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}\right)\left(\sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}\right) \times \left(\sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}\right)$$

$$E_{n_x, n_y, n_z} = \frac{n_x^2 \pi^2 \hbar^2}{2ma^2} + \frac{n_y^2 \pi^2 \hbar^2}{2mb^2} + \frac{n_z^2 \pi^2 \hbar^2}{2mc^2}$$

$$= \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

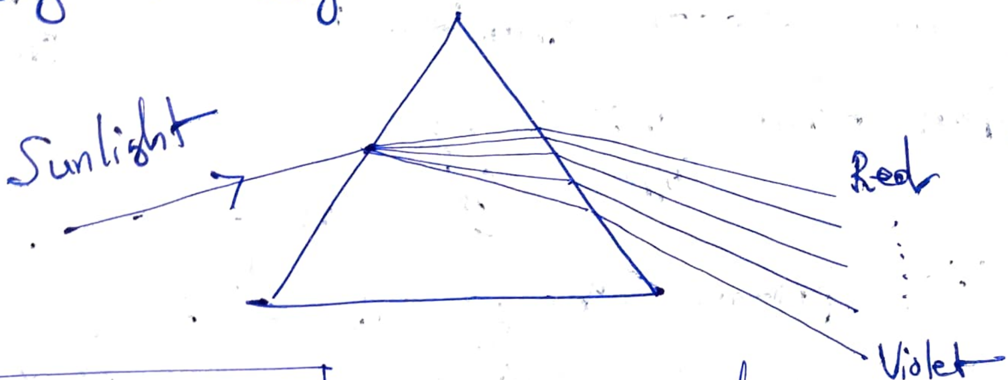
Spectroscopy

Spectroscopy → Atomic, Molecular

light ⟷ Matter (interaction)

(~~[illegible]~~)

Spectrum → Presence of different frequency or wavelenght in a light



$$\boxed{\hbar\omega = \frac{hc}{\lambda} = h\nu}$$

(Different colour represent different λ or ω)

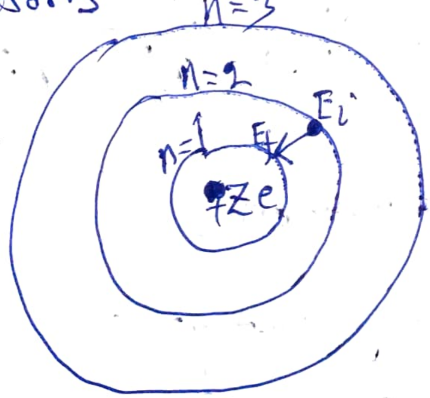
Light - Matter Interaction

↓

atoms/molecules.

Simplest ~~ex~~ example. H atom or H-like atoms

Bohr model (semi classical)



Emitted light

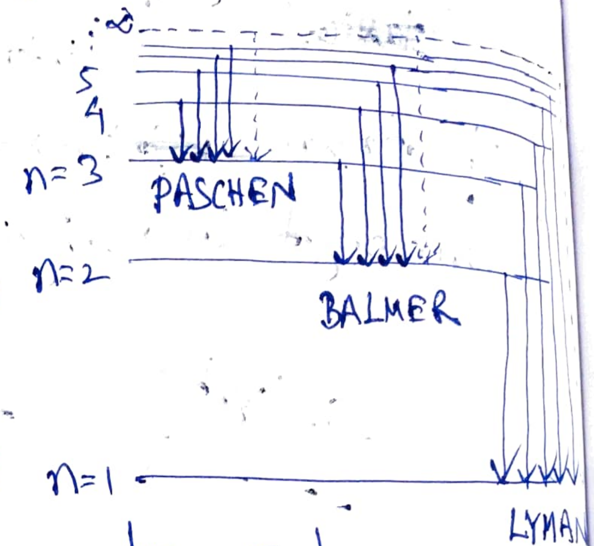
$h\nu = \Delta E$

$= |E_f - E_i|$

The energy levels of H-like atoms

$$E_n = -\frac{mZ^2e^4}{8\epsilon_0^2h^2}\frac{1}{n^2} \quad \text{(Electronic energy levels)}$$

$\cancel{= Z^2 R_\infty (}$



If an electron transition happen from n_i (upper) to n_f (lower)

emitted photon energy $= \Delta E = |E_i - E_f|$

$$= h\nu = \left(-\frac{mZ^2e^4}{8\epsilon_0^2h^2}\frac{1}{n_i^2}\right) - \left(-\frac{mZ^2e^4}{8\epsilon_0^2h^2}\frac{1}{n_f^2}\right)$$

$$= \frac{mZ^2e^4}{8\epsilon_0^2h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = \frac{hc}{\lambda}$$

$$\Rightarrow \frac{1}{\lambda} = Z^2 \underbrace{\frac{me^4}{8\epsilon_0^2ch^3}}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

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

Z = atomic number

R_∞ = Rydberg constant

$= 1.09737 \times 10^7 \ m^{-1}$

Quantum Mechanics & atomic states

One-electron atomic state is defined by quantum numbers $n\ l\ m_l\ m_s$ or $n\ l\ j\ m_j$

n = principal quantum number

l = orbital angular momentum quantum number

$$\boxed{\begin{array}{l} \Delta n = \text{anything} \\ \Delta l = \pm 1 \text{ only} \\ \text{For transitions} \\ 1s \to np \quad ns \leftarrow 2p \to nd \end{array}}$$

$n = 1, 2, 3, \ldots$

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

m_l = magnetic quantum number

$\{-l, -l+1, -l+2, \ldots (l-2), (l-1), +l\}$

m_s = spin magnetic quantum number

$(+\frac{1}{2}, -\frac{1}{2})$

$j = l + s$ total angular momentum by coupling the orbital angular momentum & spin angular momentum.

Fine structure in H-atom energy levels

(Relativistic effect of spin-orbit coupling)

$$E_{nj} = -\frac{13.6\ eV}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]$$

α = finestructure constant $\approx \frac{1}{137}$ (dimensionless)

Δn = anything, $\Delta l = \pm 1$ only $\Delta j = 0, \pm 1$

Types of ~~Ato~~ Atomic Spectroscopy

1. Emission spectroscopy (AES)
2. absorption spectroscopy (AAS)
3. fluorescence spectroscopy (AFS)
4. Mass spectroscopy (MS)

Another : X-ray fluorescence (XRF)

$\underbrace{\text{AAS , AES, AFS}}$

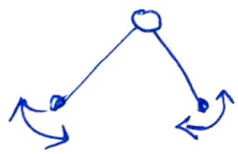
Interactions between UV-visible light and the valence electrons of free gaseous atoms.

XRF } high energy photon or charged particles collide with inner-shell electrons of atom, initiating transitions with eventual emission of X-ray photons.

XAS – X-ray absorption spectroscopy

Moleculer spectra

In case of molecules, (1) the vibration



Gives rise to

→ vibrational energy which is also quantized (Quantum Mechanics)

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

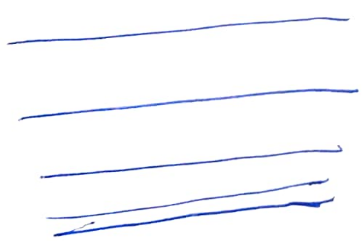
$\lambda \sim$ Infra-red

order of

~~$100 \mu m < \lambda < 1 \mu m$~~

1 um < lambda < 100 um

(2) the rotation gives rise to rotational energy which is also quantized (Quantum Mechanics)



The separations are of the order corresponding to microwave

$\sim 100 \mu m < \lambda < \sim 1$ cm