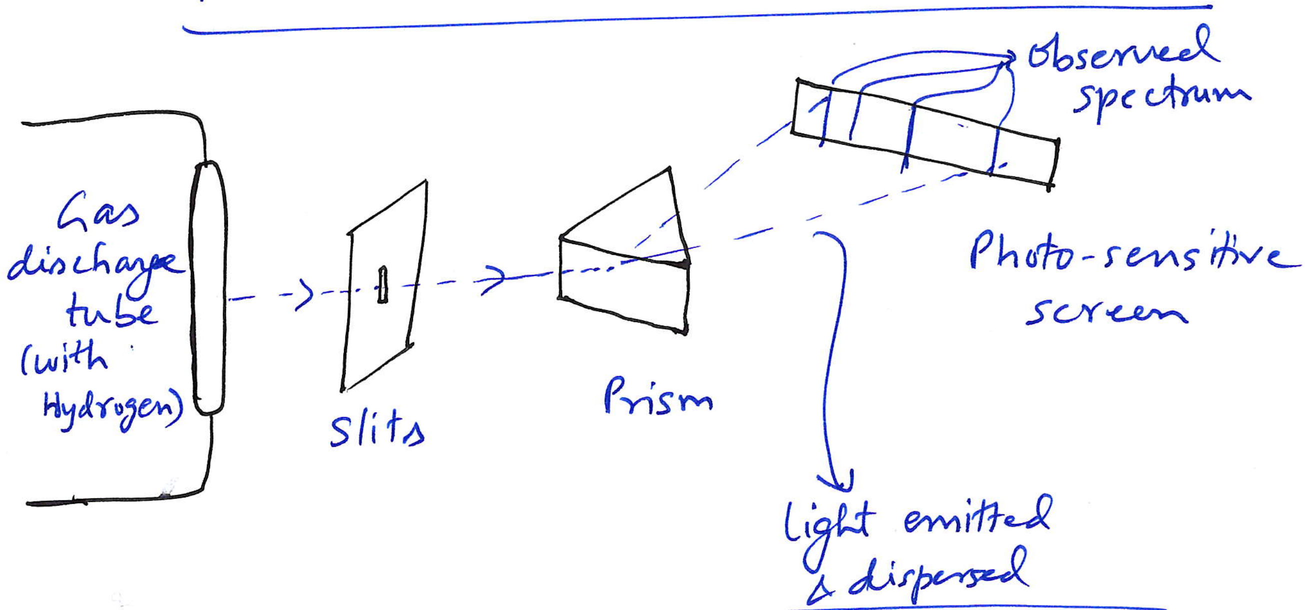
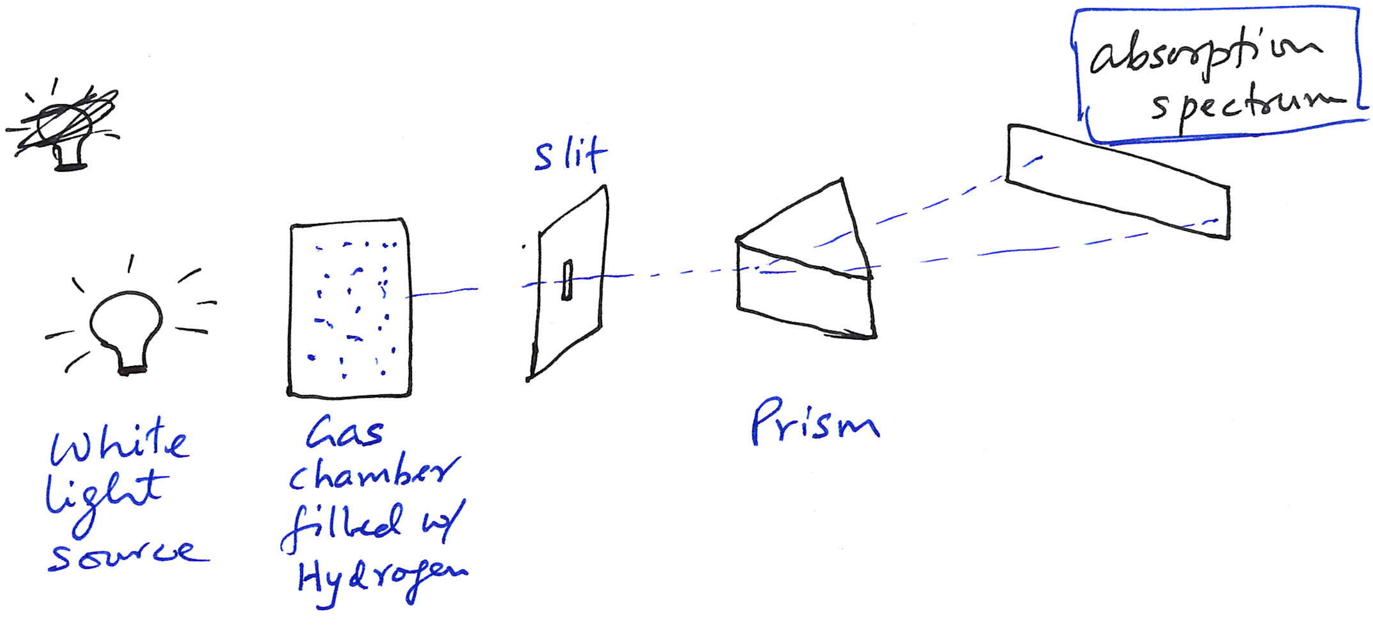
UNIT-2

1-e^- atoms: Interaction with EM fields.



The Emission spectrum of H-atom

Now, let's consider a second setup:



→ What can we infer from the emission and absorption spectrum of H-atom?

Inferences:

- → Emission of light by H-atom
- → Absorption of light by H-atom.
- ⇒ Interaction of H-atom with light!!

This leads to the question:

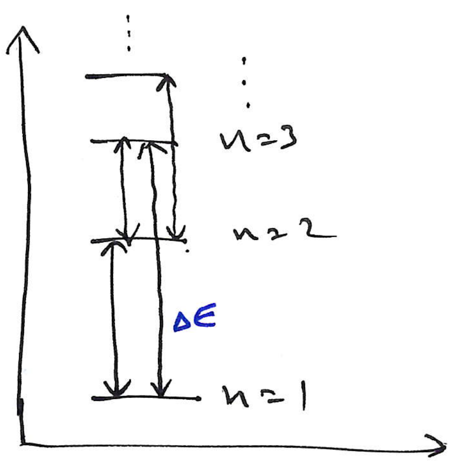
(*) How does the H-atom interact with light?

(*) Why is this interaction so selective?

→ In this chapter, our goal is to understand, or rather, answer these questions (at least partially!).

Empirical evidence:

→ Given our knowledge of the ~~ener.~~ quantized energy levels of $\bar{e}$'s orbiting the nucleus of a Hydrogenic atom, it turns out that the particular "lines" of radiation observed in the power spectra correspond exactly to the energy differences ~~between~~ of various transitions of $\bar{e}$ between energy levels!!



[Q] What is the physics of electronic transitions?

Inferences (extended):

→ It seems: When a photon (light) comes into contact with H-atom (interaction), it ~~is~~ actually interacts with the ~~photon!~~ e^-!!

→ Depending on the energy level of e^- and the energy of light (photon), the e^- can transition to a higher level by absorbing the light or to a lower energy level by emitting a new light.

~~As we will witness later,~~

→ To correctly describe this interaction, light must be treated as a quantum particle viz-a-viz "photon".

↓

And, photons are created and destroyed during these interactions!!

↓

Requires Quantum electrodynamics

↓

outside the scope of this course!

What do we do then?

→ Use an approximate formulation so as to describe this interaction with reasonable accuracy, using quantum mechanics.

⊛ Interaction of charged particles with electromagnetic field:

→ First step: Hamiltonian of a particle of mass m and spinless charge q in the presence of light.

→ The approximation: ← $\boxed{\text{"semi-classical approach"}}$

Instead of $\underbrace{\text{photons}}_{\to \text{ quantum}}$, we treat light as $\underbrace{\text{EM waves}}_{\text{classical!}}$.

→ Consider, the ~~force~~ EoM of charge in EM field:

$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$$

And, recalling the Lagrange's eq.

H-W Derive the Lagrangian and Hamiltonian.

$$\boxed{H = \frac{1}{2m}(\vec{p} - q\vec{A})^2 + q\phi}$$

where, $\vec{p}$ → momentum of charge

$\vec{A}$ → vector potential

ϕ → scalar "

∴ The Hamiltonian of an e^- in EM field:

$$H = \frac{1}{2m}(\vec{p} + e\vec{A})^2 - e\phi$$

$$= \frac{\vec{p}^{\,2}}{2m} + \frac{e^2}{2m}\vec{A}^2 + \frac{e}{2m}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) - e\phi$$

→ TDSE :

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + i\hbar\frac{e}{2m}(\vec{A}\cdot\vec{\nabla} + \vec{\nabla}\cdot\vec{A}) + \frac{e^2}{2m}\vec{A}^2 + q\phi\right]\psi(\vec{r},t)$$

Note:

→ The potentials $(\phi, \vec{A})$ can undergo transformation such that H is unchanged:

$$\left.\begin{aligned} \vec{A}(\vec{r},t) &\longrightarrow \vec{A}(\vec{r},t) + \vec{\nabla}\chi(\vec{r},t) \\ \phi(\vec{r},t) &\longrightarrow \phi(\vec{r},t) + \frac{\partial}{\partial t}\chi(\vec{r},t) \end{aligned}\right\}$$

$\boxed{\text{Gauge transformation}}$

Also, if $\psi(\vec{r},t) \longrightarrow \psi(\vec{r},t)\, e^{+ie\chi(\vec{r},t)/\hbar}$

then, TDSE remains unchanged under the gauge transformation.

$\boxed{\text{Gauge symmetry}}$

→ Gauge transformations ⟷ symmetry is an internal symmetry

⇒ All observables (measurable quantities) must be $\boxed{\text{gauge-invariant}}$

(e.g. probability density, expectation value)

→ This means, we can choose ~~a p.~~ to perform calculations employing a particular gauge for our convenience, without affecting the physics!!

→ Let us choose "Coulumb gauge":

$$\boxed{\phi = 0}, \quad \boxed{\vec{\nabla}\cdot\vec{A} = 0}$$

[convenient choice in the absence of sources]

⇒ TDSE: [~~$\psi(\vec{r},t)$~~ $\psi = \psi(\vec{r},t)$ assumed]

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = \left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 - i\hbar\frac{e}{\cancel{2}m}\vec{A}\cdot\vec{\nabla} + \frac{e^2}{2m}\vec{A}^2\right]\psi}$$

where,

$$\vec{\nabla}\cdot(A\psi) = \vec{A}\cdot\vec{\nabla}\psi \quad [\text{How?}] \longrightarrow \text{H/W}$$

→ How to incorporate this Hamiltonian in the TDSE for a H-atom that we solved already?

(*) Assuming that $m_{nucleus} \to \infty$

$\Downarrow$

interaction of nucleus with EM field can be ignored.

Therefore,

$$H(t) = \underbrace{-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}}_{H_0} \underbrace{- i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla} + \frac{e^2}{2m}\vec{A}^2}_{H_{int}}$$

$$\Rightarrow \quad i\hbar\frac{\partial\psi}{\partial t} = [H_0 + H_{int}]\psi$$

$\boxed{Q}$ When can we treat H_{int} as small (or perturbative) in comparison to H_0?

→ In the weak field limit, where

$$|\vec{A}^2| << |\vec{A}|$$

$$\Rightarrow \quad H_{int} \simeq \underbrace{-i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla} \equiv H'(t)}_{\text{perturbation.}}$$

$\boxed{Q}$ Is the weak-field limit consistent with the semi-classical approximation?

→ Read about the high photon density reqd. for semi-classical approx.

[Sec. (4.1) p184-186, Bransden]

$$\Rightarrow c_b^{(1)}(t) = -\frac{e}{2m}\int_0^\infty d\omega\, A_0(\omega)\Big[e^{i\delta_\omega}\langle\psi_b|e^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\psi_a\rangle \times \int_0^t dt'\exp[i(\omega_{ba}-\omega)t'] \quad \text{I}$$

$$+ e^{-i\delta_\omega}\langle\psi_b|e^{-i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\psi_a\rangle\int_0^t dt'\exp[i(\omega_{ba}+\omega)t']\Big] \quad \text{II}$$

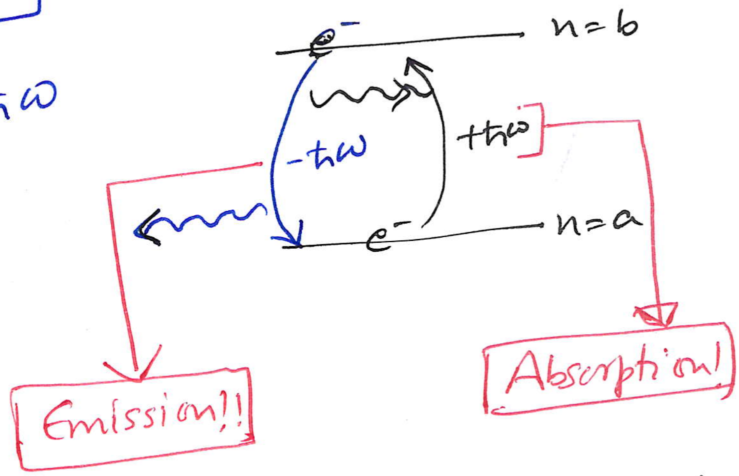
A typical radiation pulse lasts for a duration $\boxed{\Delta t \sim 10^{-15}\,s \ll \omega_{ba}^{-1} \sim \frac{\hbar}{\Delta E}}$

$$\Rightarrow \int_0^t dt'\exp[it'(\omega_{ba}\pm\omega)] \approx 0 \quad [\text{oscillatory fn}]$$

$\Rightarrow$ For a non-zero ~~soln.~~ integral,

$$\boxed{\omega_{ba} = \pm\omega}$$

$$\Rightarrow E_b - E_a = \pm\hbar\omega$$



Example of discrete transition
(bound state $\rightarrow$ bound state)

Q. Example of bound-fee state transition?

Case - I : Absorption $[\omega_{ba} = \omega]$

$$c_b^{(1)}(t) = -\frac{e}{2m}\int_0^\infty d\omega\, A_0(\omega)\, e^{i\delta_\omega} \underbrace{\langle \psi_b | e^{i\vec{k}\cdot\vec{r}}\, \hat{\varepsilon}\cdot\vec{\nabla} | \psi_a \rangle}_{M_{ba}} \underbrace{\int_0^t dt'\, e^{i(\omega_{ba}-\omega)t'}}_{\left.\frac{e^{i(\omega_{ba}-\omega)t'}}{i(\omega_{ba}-\omega)}\right|_0^t}$$

$$\Rightarrow \cancel{|c_b^{(1)}(t)|^2 = \left(\frac{e}{2m}\right)^2 \left| \int_0^\infty d\omega \int_0^\infty d\omega'\, A_0(\omega) A_0(\omega') e^{i\delta_\omega} e^{i\delta_{\omega'}} M_{ba} \left[\frac{e^{i\bar{\omega}t} - 1}{i(\bar{\omega})}\right] \right|^2}$$

$\boxed{\text{H/w : Derive the following:}}$

$$\Rightarrow |c_b^{(1)}(t)|^2 = \frac{1}{2}\left(\frac{e}{m}\right)^2 \int_0^\infty A_0^2(\omega)\, |M_{ba}(\omega)|^2\, F(t, \omega-\omega_{ba})\, d\omega$$

where,

$$F(t, \omega - \omega_{ba}) \equiv F(t, \bar{\omega}) \qquad [\because \bar{\omega} \equiv \omega - \omega_{ba}]$$

$$= \frac{1-\cos(\bar{\omega}t)}{\bar{\omega}^2}$$

$$= \left| \frac{e^{i\bar{\omega}t} - 1}{i\bar{\omega}} \right|^2$$

From the properties of $F(t,\omega)$, we can set $\omega = \omega_{ba}$ (i.e $\bar{\omega} = 0$) in $\underbrace{A_0^2(\omega) \text{ \& } |M_{ba}(\omega)|^2}_{\text{assumed to be slowly varying.}}$

$$\Rightarrow \quad |c_b^{(1)}(t)|^2 \simeq \frac{\pi}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba})|M_{ba}(\omega_{ba})|^2 t$$

Therefore, the rate of transition for absorption from $a \to b$:

$$W_{ba} = \frac{d}{dt}|c_b^{(1)}(t)|^2 = \frac{\pi}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba})\,|M_{ba}(\omega_{ba})|^2$$

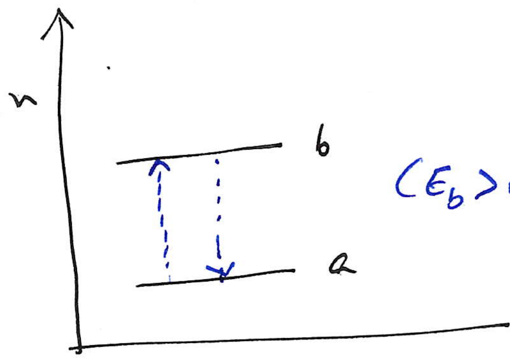
In terms of intensity,

$$I(\omega) = \frac{1}{2}\epsilon_0 c\,\omega^2 A_0^2(\omega)$$

$$\Rightarrow \quad \boxed{W_{ba} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}\,|M_{ba}(\omega_{ba})|^2}$$

The Einstein Coefficients

→ Consider an atom with non-degenerate energy levels, interacting with a weak field with energy density "$\rho(\omega_{ba})$."



$(E_b > E_a)$

→ Let there be "N_a" such atoms with energy level E_a. ← Different from "1" atom system we've been studying so far!!

Then, the # of atoms making a transition from a to b by absorbing radiation is [applying the decay rate equation from statistical mech., treating ~~this transition~~ atomic transitions as random statistical decay process.]:

$$\dot{N}_{ba} \propto N_a \rho(\omega_{ba})$$

$$\Rightarrow \boxed{\dot{N}_{ba} = B_{ba} N_a \rho(\omega_{ba})}$$

→ B_{ba} ← Einstein coefficient for absorption.

~~The Einst~~

[Q] What is B_{ba}?

From prior calculations of W_{ba}, we know that:

$\rightarrow W_{ba}$ is the transition rate per atom

i.e $$W_{ba} \longleftrightarrow \frac{\dot{N}_{ba}}{N_a}$$

$$\Rightarrow \quad W_{ba} = B_{ba}\, \rho(\omega_{ba})$$

$$\Rightarrow \quad B_{ba} = \frac{W_{ba}}{\rho(\omega_{ba})}$$

$$\Rightarrow \quad \boxed{B_{ba} = \frac{4\pi^2}{3\hbar^2}\left(\frac{1}{4\pi\epsilon_0}\right)|\vec{D}_{ba}|^2}$$

Illy, the no. of atoms making transition from $b \rightarrow a$:

$$\cancel{\dot{N}_{ba}} \quad \dot{N}_{ab} = \underbrace{A_{ab} N_b}_{\text{Spontaneous emission}} + \underbrace{B_{ab} N_b\, \rho(\omega_{ba})}_{\text{stimulated emission}}$$

$N_b \rightarrow$ # of atoms at energy level E_b.

$A_{ab} \rightarrow$ Coeff. for spontaneous emission.

$B_{ab} \rightarrow$ Coeff. for stimulated emission

From prior calculations:

$$A_{ab} = W^s_{ab} = \frac{\dot{N}_{ab}}{N_b}$$

& $$B_{ab} = \frac{W_{ab}}{\rho} \quad \cancel{B_{ba}}$$

At equilibrium, we have:

$$\dot{N}_{ab} = \dot{N}_{ba}$$

$$\Rightarrow A_{ab} N_b + B_{ab} N_b \rho(\omega_{ba}) = B_{ba} N_a \rho(\omega_{ba})$$

$$\Rightarrow \frac{N_a}{N_b} = \frac{A_{ab} + B_{ab}\rho(\omega_{ba})}{B_{ba}\rho(\omega_{ba})}$$

Moreover, the no. distribution at ~~eq~~ temp. T in equilibrium is : [Maxwell-Boltzmann dist.]

$$N(E) = N_0 \exp(-E/k_B T)$$

$$\Rightarrow \frac{N_a}{N_b} = \exp\left[-(E_a - E_b)/k_B T\right] = \exp(\hbar\omega_{ba}/k_B T)$$

$$\Rightarrow \boxed{\rho(\omega_{ba}) = \frac{A_{ab}}{B_{ba}\exp[\hbar\omega_{ba}/k_B T] - B_{ab}}} \quad \text{———} \; (*)$$

→ At equilibrium b/w atoms and radiation, the energy density is given by the Planck distribution ::

$$\rho(\omega_{ba}) = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \frac{1}{\exp[\hbar\omega_{ba}/k_B T] - 1} \quad \text{———} \; (**)$$

From ✱ & ✱✱:

$$\frac{\frac{\hbar\omega_{ba}^3}{\pi^2 c^3}}{\exp[\hbar\omega_{ba}/k_B T]-1} = \frac{A_{ab}}{B_{ba}\exp[\hbar\omega_{ba}/k_B T]-B_{ab}}$$

$$= \frac{A_{ab}/B_{ab}}{\frac{B_{ba}}{B_{ab}}\exp[\hbar\omega_{ba}/k_B T]-1}$$

$$\Rightarrow \boxed{\frac{A_{ab}}{B_{ab}} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3}}$$

$$\& \quad \boxed{\frac{B_{ba}}{B_{ab}} = 1} \Rightarrow \boxed{B_{ab} = B_{ba}}$$

→ Confirms our calculations for the ~~sig.~~ single atom - system!!

→ Now recall: Nature is selective!!

$$W_{ba} : \begin{cases} = 0, & \hat{\varepsilon}\cdot\vec{D} \sim \hat{\varepsilon}\cdot\vec{r}_{ba} = 0 \\ \neq 0, & \text{''} \neq 0 \end{cases}$$

[Q8] How to identify the allowed and forbidden transitions?