PH 585
AMO

Lecture #3

①

Absorption and emission

Absorption $\Rightarrow$ $C_b^{(1)}(t) = -\frac{e}{2m}\int_0^\infty d\omega\, A_0(\omega)\, e^{i\delta_\omega}$

↑ if EM is not monochromatic

$$\underbrace{\langle \Psi_b | e^{i\vec{k}\cdot\vec{r}}\, \hat{\vec{\varepsilon}}\cdot\vec{p} | \Psi_a \rangle}_{= M_{ba}} \underbrace{\int_0^t dt'\, e^{i(\omega_{ba}-\omega)t'}}_{= \frac{\cancel{2}}{\cancel{2}} e^{i\frac{\omega_{ba}-\omega}{2}t}\, t\, \mathrm{sinc}\frac{\omega_{ba}-\omega}{2}t}$$

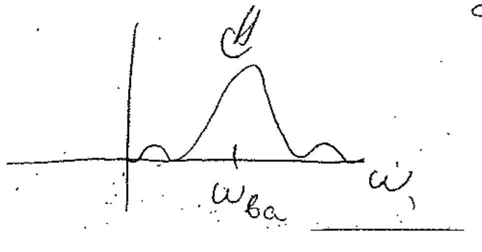
The probability to find the system in some state $b \neq a$ as a result of light absorption $\Rightarrow$

↑ initial state

$$|C_b^{(1)}(t)|^2 = \frac{1}{4}\left(\frac{e}{m}\right)^2 \int_0^\infty A_0^2(\omega)\, |M_{ba}|^2\, t^2\, \underbrace{\mathrm{sinc}^2 \frac{\omega_{ba}-\omega}{2}t}\, d\omega \approx$$

↑ incoherent radiation

$\int f(x)dx \int f^*(x')dx' \Rightarrow \int |f(x)|^2 dx$
(cross-terms vanish)



$$\approx \frac{1}{4}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba})\,|M_{ba}|^2\, t^{2} \cdot \frac{2}{\cancel{t}} \underbrace{\int_{-\infty}^{\infty} \frac{\sin^2 \frac{\omega-\omega_{ba}}{2}t}{\left(\frac{\omega_{ba}-\omega}{2}t\right)^2}\, d\left(\frac{\omega}{2}t\right)}_{= \frac{\pi}{2}\cdot 2 = \pi} =$$

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

Transition rate for absorption:

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

Intensity per frequency $I(\omega) = \underset{\substack{\uparrow \\ \text{energy density}}}{\rho(\omega)}\, c = \frac{1}{2}\varepsilon_0 c \mathcal{E}_0^2(\omega) =$

$$= \frac{1}{2}\varepsilon_0 c\, \omega^2 A_0^2(\omega)$$

$$\boxed{=}\ \frac{\pi}{\varepsilon_0 c}\left(\frac{e}{m}\right)^2 \frac{I(\omega_{ba})}{\omega_{ba}^2}\,|M_{ba}|^2$$

Rate of absorption of energy $\Rightarrow \underset{J}{\hbar\omega_{ba}} \cdot \underset{\frac{1}{s}}{W_{ba}}$

Absorption cross-section $\sigma_{ba} = \frac{\pi}{\varepsilon_0 c}\left(\frac{e}{m}\right)^2 \frac{\hbar}{\omega_{ba}}\,|M_{ba}|^2$

$\sigma_{ba} = \frac{W_{ba}\hbar\omega_{ba}}{I}$ ↗ rate of abs of energy per atom per $I(\omega)$

$\sim \frac{J}{s\,m^2}$

$I = I_0 e^{-n\sigma l}$

(3)

Emission $\Rightarrow$ Very similar to absorption $\Rightarrow$

$$\bar{W}_{ab} = \frac{\pi}{\varepsilon_0 c}\left(\frac{e}{m}\right)^2 \frac{I(\omega_{ba})}{\omega_{ba}^2} |\bar{M}_{ab}|^2 = \frac{\pi}{\varepsilon_0}\left(\frac{e}{m}\right)^2 \frac{\hbar N(\omega_{ba})}{V\omega_{ba}} |\bar{M}_{ab}$$

$I(\omega_{ba}) = \frac{\hbar\omega_{ba} N(\omega_{ba}) c}{V}$ ← # photons ← volume

Photon flux

↑ transition rate $b \to a$

↑ higher energy state

$$\bar{M}_{ab} = \langle \psi_a | e^{-i\vec{k}\cdot\vec{r}} \hat{\vec{\varepsilon}}\cdot\vec{\nabla} | \psi_b \rangle =$$

$$= \int \psi_a^*(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}\, \hat{\vec{\varepsilon}}\cdot\vec{\nabla}\psi_b(\vec{r})\, d\vec{r} = -M_{ba}^*$$

↑ Show!

So, $\bar{W}_{ab} = W_{ba}$

$\bar{\sigma}_{ab} = \sigma_{ba}$

↑ consistent with the principle of detailed balance: in enclosure containing atoms and radiation in equilibrium, transition probability from b to a is the same as from a to b for any states a & b

Note: 1) $\bar{W}_{ab} \sim I(\omega_{ba}) \Rightarrow$ stimulated emission

(if $I = 0 \Rightarrow \bar{W}_{ab} = 0$)

2) Although $W_{ba} = \bar{W}_{ab}$, stimulated emission is less intense, since population of b is $e^{-\hbar\omega_{ba}/kT}$ · population of

According to W_{ab}, we need EM wave to bring atom from the excited state to the groun state ⇒ wrong! ⇒ classical description of EM wave is not good enough for <u>spontaneous</u> emission

⇙

Need to replace $\vec{A}$ (and $\vec{\mathcal{E}}$ & $\vec{B}$) with operators ⇒

e.g. $\vec{A}_{\lambda,\vec{k}} = \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\, a_{\lambda,\vec{k}}$

$$H = \sum_{\underset{\underset{\text{wave number}}{\uparrow}}{\vec{k}}} \sum_{\underset{\underset{\text{polarization}}{\nwarrow}}{\lambda}} \hbar\omega_k \left(a^+_{\lambda,\vec{k}} a_{\lambda,\vec{k}} + \frac{1}{2}\right) \leftarrow \text{similar to harmonic oscillator}$$

$$\text{Eigenstates of } H \Rightarrow \underbrace{|n_{\lambda_1,\vec{k}_1}, n_{\lambda_2,\vec{k}_2}, \dots\rangle}_{\nwarrow \text{ EM field with } n_{\lambda_1,\vec{k}_1} \text{ photons in the mode } (\lambda_1,\vec{k}_1) \text{ etc}}$$

$$\underset{\underset{\text{energy}}{\uparrow}}{E} = \hbar \sum_{\vec{k}} \sum_{\lambda} \omega_k \left(n_{\lambda,\vec{k}} + \frac{1}{2}\right)$$

⇓ see <u>QM notes</u>

$$\overline{W}_{ab} = \frac{\pi}{\varepsilon_0}\left(\frac{e}{m}\right)^2 \frac{\hbar\,(\overset{\text{stimulated}}{N(\omega_{ba})} \overset{\text{spontaneous}}{+1})}{V\omega_{ba}} \overset{|M_{ba}|^2 \,=}{|\overline{M}_{ab}|^2}$$

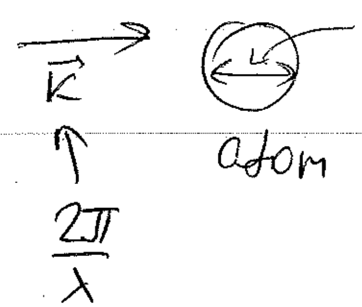
The dipole approximation

Once the frequency $\underset{\substack{\uparrow \\ \text{EM wave}}}{\omega}$ matches $\underset{\substack{\uparrow \\ \text{atomic transition}}}{\omega_{ba}} \Rightarrow$

the strength of absorption or emission is determined by $|M_{ba}|^2$, or selection rules. If M_{ba} is 0 $\Downarrow$ transition is strictly forbidden

$$M_{ba} = \langle \Psi_b | e^{i\vec{k}\cdot\vec{r}}\, \hat{\vec{\varepsilon}} \cdot \vec{\nabla} | \Psi_a \rangle$$

$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} + \frac{1}{2!}(i\vec{k}\cdot\vec{r})^2 + \dots$$



$\sim 2a_0 \sim 1\,\text{Å}$

$$\Rightarrow \vec{k}\cdot\vec{r} \sim \frac{2\pi}{\underset{\substack{\uparrow \\ \sim 500\,nm \\ (\text{visible})}}{\lambda}} \cdot \overbrace{2a_0}^{0.1\,nm} \sim 10^{-3} \ll 1$$

Then, $e^{i\vec{k}\cdot\vec{r}} \approx 1$ ← $\overset{\text{electric}}{\text{dipole}}$ approximation

(neglects spatial variation of the radiation field, i.e. retardation effects, across the atom)

Note: if $\lambda \downarrow \Rightarrow$ dipole approx. is not sufficient (e.g. can't use with X-ray)

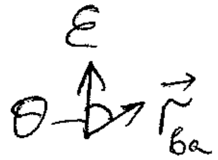
So, $$M^{D}_{ba} = \hat{\vec{\varepsilon}} \cdot \langle \psi_b | \vec{\nabla} | \psi_a \rangle \underset{\uparrow \atop \vec{p} = -i\hbar\vec{\nabla}}{=} \frac{i}{\hbar} \hat{\vec{\varepsilon}} \underbrace{\langle \psi_b | \vec{p} | \psi}_{\vec{p}_{ba}}$$

$$\underset{\uparrow \atop \text{show!}}{=} \frac{i}{\hbar} \cdot \hat{\vec{\varepsilon}} \cdot i m \omega_{ba} \underbrace{\langle \psi_b | \vec{r} | \psi_a \rangle}_{\vec{r}_{ba}} = - \frac{m\omega_{ba}}{\hbar} \hat{\vec{\varepsilon}} \cdot \vec{r}_{ba}$$

Then, $$W^{D}_{ba} = \frac{\pi e^2}{\varepsilon_0 c \hbar^2} I(\omega_{ba}) | \hat{\vec{\varepsilon}} \cdot \vec{r}_{ba} |^2$$

Electric dipole moment operator ⇒ $\vec{D} = -e\vec{r}$ ⇒

$$M^{D}_{ba} = \frac{m\omega_{ba}}{\hbar e} \hat{\vec{\varepsilon}} \cdot \underbrace{\vec{D}_{ba}}_{\langle \psi_b | \vec{D} | \psi_a \rangle}$$



$$W^{D}_{ba} = \frac{\pi}{\varepsilon_0 c \hbar^2} I(\omega_{ba}) | \hat{\vec{\varepsilon}} \cdot \vec{D}_{ba} |^2 \overset{\downarrow}{=} \frac{\pi e^2}{\varepsilon_0 c \hbar^2} I(\omega_{ba}) |\vec{r}_{ba}|^2 \cos^2\theta$$

If $\vec{D}_{ba} = 0$ ⇒ the transition is forbidden in the electric dipole approximation

If unpolarized light ⇒ θ is not defined (random) ⇒

$$\frac{1}{4\pi} \int \cos^2\theta \, d\Omega = \frac{1}{3} \Rightarrow W^{D}_{ba} = \frac{1}{3\varepsilon_0 c \hbar^2} I(\omega_{ba}) |\vec{D}_{ba}|^2$$