$$\dot{C}_a = \frac{1}{i\hbar} V_{ab}\, e^{-i\omega_0 t}\, C_b \qquad\qquad \omega_0 = \omega_b - \omega_a = \frac{E_b - E_a}{\hbar}$$

$$\dot{C}_b = \frac{1}{i\hbar} V_{ba}\, e^{+i\omega_0 t}\, C_a$$

For light $\lambda \gg$ atom & $\vec{E}$ in direction $\hat{n}$ $\quad V = eE_0\, \vec{r}\cdot\hat{n}\, \cos(\omega t)$

$$V_{ba} = \underbrace{e E_0 \langle \psi_b | \vec{r}\cdot\hat{n} | \psi_a \rangle}_{\text{does not depend on } t \,\to\, \tilde{V}_{ba}} \left(\frac{e^{i\omega t} + e^{-i\omega t}}{2} \right)$$

This is important term as $e^{i(\omega_0-\omega)t}$ has low freq — doesn't oscillate to zero.

Approx: use
$$\begin{cases} V_{ba} = \dfrac{\tilde{V}_{ba}}{2}\, e^{-i\omega t} \\[2ex] V_{ab} = \dfrac{\tilde{V}_{ab}}{2}\, e^{+i\omega t} \end{cases}$$
& solve diff eq exactly

$$\left.\begin{aligned} \dot{C}_a &= \frac{1}{i\hbar} \frac{\tilde{V}_{ab}}{2}\, e^{-i(\omega_0-\omega)t}\, C_b \\ \dot{C}_b &= \frac{1}{i\hbar} \frac{\tilde{V}_{ba}}{2}\, e^{+i(\omega_0-\omega)t}\, C_a \end{aligned}\right\}$$

go to dimensionless time $x = (\omega_0-\omega)t$

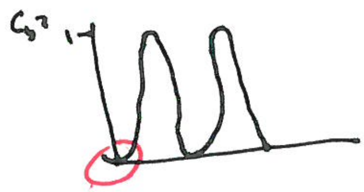
let $h = \dfrac{\tilde{V}_{ab}}{2\hbar(\omega_0-\omega)} \in \mathbb{R}$

unitless

$$\left.\begin{aligned} \frac{d}{dx} C_a &= -i\, h\, e^{-ix}\, C_b \\ \frac{d}{dx} C_b &= -i\, h\, e^{+ix}\, C_a \end{aligned}\right\}$$
exactly as in homework → Mathematica

$$C_b^2 = \underbrace{\frac{4h^2}{1+4h^2}}_{\substack{\text{amplitude of oscillation} \\ \text{small for small } h \\ \text{as } h\to\infty \text{ amplitude}\to 1}} \sin^2\left[\underbrace{\frac{\sqrt{1+4h^2}}{2}\, *}_{\substack{\text{for small } h \text{ oscillate} \\ \text{at } \frac{(\omega_0-\omega)}{2} \text{ for larger} \\ h \,\to\, (\omega_0-\omega)h}} \right]$$

small h



large h

in all cases for small t $C_b^2 \propto t^2$

Remark: for light on atom $h \sim \frac{E \text{ of light}}{E \text{ of nucleus}}$

E of H-atom @ Bohr radius $\sim 5 \times 10^{11}$ V/m, so generally h is quite small

missing from yesterdays handout

Remark 2: $|c_b|^2 = \frac{|\tilde{V}_{ba}|^2}{4\hbar^2} \underbrace{\frac{\sin^2[\Delta t]}{\Delta^2}}$ $\quad \Delta = \frac{\omega_0 - \omega}{2}$

For human scale times & $\Delta >$ GHz this is essentially a δ function [ie concentrated to essentially $\Delta = 0$. This has a height $\propto t^2$ & a width $\propto \frac{1}{t}$ so expect total integral $\propto t$

$$\int_{-\infty}^{\infty} \underbrace{\frac{\sin^2[\Delta t]}{\Delta^2}} d\Delta = |t| \pi$$

sometimes define function

$\text{sinc}(x) = \frac{\sin(x)}{x}$, so this is $[\text{sinc}(\Delta t)\, t]^2$

$$\delta\left(\frac{\omega_0 - \omega}{2}\right) = 2\,\delta(\omega_0 - \omega)$$

so $|c_b|^2 \approx \frac{|V_{ba}|^2}{4\hbar^2} \pi |t| \overbrace{\delta(\Delta)}$

$$\text{Rate} = \frac{2\pi}{\hbar^2} \left|\frac{V_{ba}}{2}\right|^2 \delta(\omega_0 - \omega) \leftarrow$$ Fermi's Golden Rule

unit check: $\hbar = E \cdot T$

$V_{ba} = E$

$\delta(\omega_0 - \omega) = T$ ← yes δ function has units!

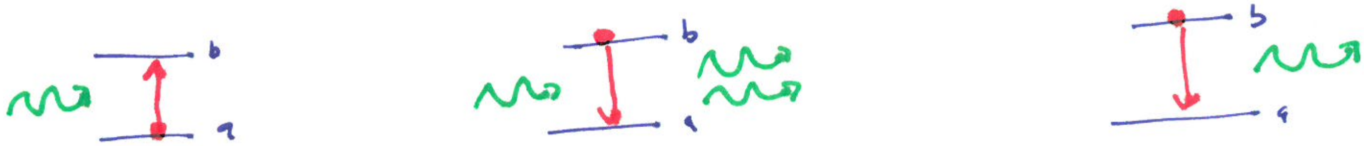
$\frac{E^2}{(E \cdot T)^2} T = \frac{1}{T}$ ← correct for a rate

Remark 3: Stimulated Emission ... if $E_b < E_a$ then $\omega_0 < 0$ & $\omega + \omega_0$ is small ... works exactly the same except

$$\Delta = \frac{\omega + \omega_0}{2} = \frac{\omega - |\omega_0|}{2}$$

($\frac{\sin^2 \Delta t}{\Delta^2}$ is even in Δ so sign Δ does not matter)

Conclude: Rate of Stimulated emission = Rate absorption.



Absorption — electron gains energy

Stimulated Emission — electron releases energy

Spontaneous Emission — electron releases energy

Remark 4: Typically the δ-function in Fermi's Golden Rule resolves itself because the initial state or final state is not exactly <u>one</u> state ... a sum of states is involved. In the cases of Absorption or Stimulated Emission the initial light is not exactly monochromatic [it might have a very narrow range of frequencies but not narrow compared to that δ-function]. In the case of photoelectric effect (where photon absorption results in emission of electron) the resulting free electron has a range of possible outgoing momenta ... might be going this way or that at slightly different speeds

$\frac{\text{Energy}}{\text{volume}}$ in light $= \frac{\varepsilon_0}{2} E_0^2$ (this formula includes magnetic & electric energy... they are in fact equal... E_0 is peak E not rms)

$u = \rho(\omega)\,d\omega$

$$V_{ba} = E_0 \underbrace{e \langle \psi_b | \vec{r} | \psi_a \rangle}_{\text{electric dipole}} \cdot \hat{n}$$ ← direction of E field

$$= E_0 \; \vec{p} \cdot \hat{n}$$

$$\text{Rate} = \frac{2\pi}{\hbar^2} \left| \frac{V_{ba}}{2} \right|^2 \delta(\omega_0 - \omega)$$

$$= \frac{E_0^2 \pi}{2\hbar^2} |\vec{p}\cdot\hat{n}|^2 \, \delta(\omega_0 - \omega)$$

$$= \frac{1}{\varepsilon_0} u \frac{\pi}{\hbar^2} |\vec{p}\cdot\hat{n}|^2 \delta(\omega_0 - \omega)$$

$\rho(\omega)\,d\omega$

add up over all freq: $\frac{\pi}{\varepsilon_0 \hbar^2} \rho(\omega_0) |\vec{p}\cdot\hat{n}|^2$

$\vec{p}$ is in some fixed direction — we adjust our coordinate system so z is in that direction

$\hat{n}$ is mix of all directions equally — average

$$\langle (\vec{p}\cdot\hat{n})^2 \rangle = p^2 \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \cos^2\theta \sin\theta \, d\theta\, d\phi$$

$$= p^2 \frac{1}{2} \int_{-1}^{1} c^2\, dc = \frac{1}{3} p^2$$

$$\Rightarrow \text{Rate} = \underbrace{\frac{\pi}{3\varepsilon_0 \hbar^2}}_{\text{"B" coef}} p^2 \rho(\omega_0)$$

In this version of QM spontaneous emission rate is zero (we need to quantize the EM field - light; photons - in order to directly calculate it)

Two methods to come up with correct formula:

① Bohr's Correspondence principle: QM must match classical physics for large n ... in 341 showed power in light radiated $= \frac{2}{3} \frac{\delta^2 a^2}{4\pi\varepsilon_0 c^3}$

unit check: $\frac{\delta^2}{4\pi\varepsilon_0} = E \cdot L$, $a = L/T^2$, $c = L/T$ $\Bigg\}$ $\frac{E \cdot L \, (L/T^2)^2}{(L/T)^3} = \frac{E}{T}$ ✓

② Einstein's clever, general argument based on Thermodynamic equilibrium. In 370 you learned about Planck's blackbody formula: $\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/kT} - 1}$

& Boltzmann factor: $\frac{N_a}{N_b} = e^{-\Delta E/kT}$

$$0 = \frac{dN_b}{dt} = \underbrace{-N_b A}_{\text{spontaneous emission rate}} \underbrace{- N_b B_{ba} \rho(\omega_0)}_{\text{stimulated emission rate}} + \underbrace{N_a B_{ab} \rho(\omega_0)}_{\text{Absorption rate}}$$

$$N_b A = (N_a B_{ab} - N_b B_{ba}) \rho(\omega_0)$$

$$\frac{A}{\left(\frac{N_a}{N_b} B_{ab} - B_{ba}\right)} = \rho(\omega_0) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/kT} - 1}$$

$$\frac{A / B_{ba}}{\left(\underbrace{\frac{N_a}{N_b}}_{\text{Boltzm}} \underbrace{\frac{B_{ab}}{B_{ba}}}_{1} - 1\right)}$$

$A / B_{ba} = \frac{\hbar}{\pi^2 c^3} \omega^3$ & $B_{ba} = \frac{\pi}{3\varepsilon_0 \hbar^2} p^2$

$\hookrightarrow A = \frac{\omega^3 p^2}{3\pi\varepsilon_0 \hbar c^3}$

units: $E \cdot L^3$