Einstein coefficients

To properly account for both stimulated and spontaneous processes, we need to consider a non-monochromatic radiation

Energy density of e-m field

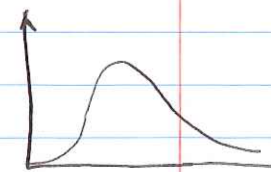
$\cancel{\mathcal{E}(\omega) = \frac{\varepsilon_0}{2}}$

monochromatic field $\qquad \rho(\omega) = \frac{\varepsilon_0}{2} E_0^2 \, \delta(\omega + \omega_{rad})$

non-monochromatic:

thermal light (Black body radiation)

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$



laser light $\qquad \rho(\omega) = \frac{\varepsilon_0}{2} E_0^2 \frac{\gamma^2}{\gamma^2 + (\omega - \omega_{rad})^2}$

where $1/\gamma$ is a coherence time, or c/γ – coherence length

For a monochromatic radiation the stimulated transition probability – monochromatic case

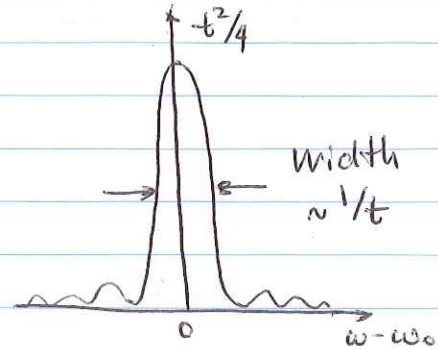
$$P_b(t)\Big|_{\omega} = \left(\frac{p_{ab}\,\mathcal{E}_0}{\hbar}\right)^2 \frac{\sin^2 \frac{\omega-\omega_0}{2} t}{(\omega-\omega_0)^2} = \frac{2}{\varepsilon_0}\left(\frac{p_{ab}}{\hbar}\right)^2 \underbrace{\left[\frac{\varepsilon_0 \mathcal{E}_0^2}{2}\right]}_{\rho(\omega)} \frac{\sin^2 \frac{\omega-\omega_0}{2} t}{(\omega-\omega_0)^2}$$

For the non-monochromatic light all spectral components contribute to the transition, so we need to sum them up

$$P_b(t) = \int_0^\infty P_b(t)\Big|_{\omega} d\omega = \frac{2 p_{ab}^2}{\varepsilon_0 \hbar^2} \int_0^\infty \rho(\omega') \frac{\sin^2 \frac{\omega'-\omega_0}{2} t}{(\omega'-\omega_0)^2} d\omega'$$

Let's look at the $\dfrac{\sin^2\left(\frac{\omega-\omega_0}{2}t\right)}{(\omega-\omega_0)^2}$ function

It peaks at $\omega = \omega_0$ $\qquad \lim\limits_{\omega\to\omega_0} \dfrac{\sin^2\frac{(\omega-\omega_0)t}{2}}{(\omega-\omega_0)^2} = \dfrac{t^2}{4}$



As time progresses, this function approaches $\frac{\pi}{2}\,\delta(\omega-\omega_0)$

So after a while, only the narrow range of frequencies around ω_0 will give non-zero contribution into the integral. Assuming that $g(\omega)$ does not chang dramatically around these frequencies, we can replace $g(\omega)$ with $g(\omega_0)$

$$P_b(t) = \frac{2p_{ab}^2}{\varepsilon_0\hbar^2}\, g(\omega_0) \int_0^\infty \frac{\sin^2\frac{\omega'-\omega}{2}t}{(\omega'-\omega_0)^2}\, d\omega' =$$

$$= \frac{2p_{ab}^2}{\varepsilon_0\hbar^2}\, g(\omega_0)\cdot\frac{t}{2}\int_{\substack{-\omega_0 t\\ \to -\infty}}^{\infty} \frac{\sin^2 x}{x^2}\,dx = \frac{\pi p_{ab}^2}{\varepsilon_0\hbar^2}\, g(\omega_0)\, t \qquad \left[\int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}\,dx = \pi/2\right.$$

So $P_b(t)$ grows linearly with time, thus the <u>transition rate</u> dP_b/dt is constant

$$B_{ab} = \frac{dP_b}{dt} = \frac{\pi p_{ab}^2}{\varepsilon_0\hbar^2}\, g(\omega_0)'$$

We also need to average over the polarization direction: $p_{ab} = \langle\psi_a|\vec{r}\cdot\vec{e}_0|\psi_b\rangle$

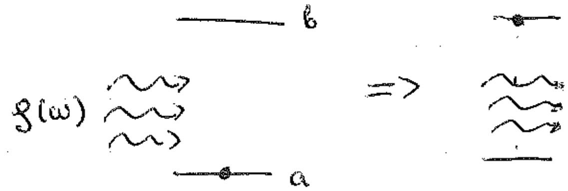
$$\langle p_{ab}^2\rangle_{\vec{e}} = \frac{1}{3}\left(\langle\psi_a|r|\psi_b\rangle\right)^2 = \frac{p^2}{3}$$

$$B_{ab} = \frac{\pi p^2}{3\varepsilon_0\hbar^2}\, g(\omega_0)$$

We can go over same calculations, replacing $a\leftrightarrow b$, and we'll obtain $B_{ba} = \dfrac{\pi p^2}{3\varepsilon_0\hbar^2}\, g(\omega_0) = B_{ab}$

Einstein coefficients

Stimulated absorption rate



Transition rate $\frac{dP_{ab}}{dt}$

$R_{a\to b} = B_{ab}\,\rho(\omega_0)$

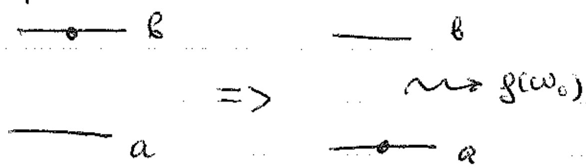
Stimulated emission rate

<u>Same</u> transition rate

$R_{b\to a} = B_{ba}\,\rho(\omega_{ab})$

$(B_{ba} = B_{ab})$

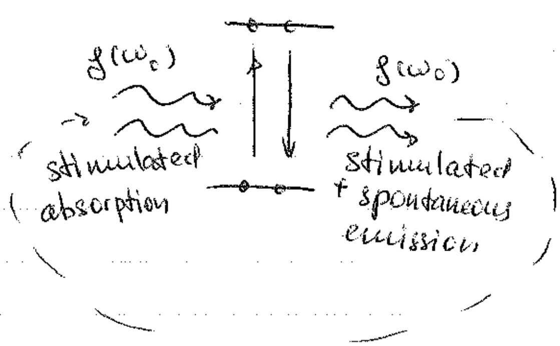
Spontaneous ~~rate~~ emission rate



Constant rate

$R_{sp} = A$

Consider equilibrium situation



N_a atoms in state a

N_b atoms in state b

$$\frac{dN_b}{dt} = \underbrace{-AN_b}_{\text{spont. emission}} - \underbrace{B_{ba}\,\rho(\omega_0)N_b}_{\text{stimulated emission}} + \underbrace{B_{ab}\,\rho(\omega_0)N_a}_{\text{stimulated absorption}}$$

Equilibrium: $dN_b/dt = 0$

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

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

Boltzmann distribution

$$\frac{N_b}{N_a} = \frac{e^{-E_b/kT}}{e^{-E_a/kT}} = e^{(E_a-E_b)/kT} =$$

$$= e^{-\hbar\omega_0/kT}$$

Thus, the electromagnetic spectrum in thermal distribution is

$$\rho(\omega_0) = \frac{A}{B_{ab}\,(e^{\hbar\omega_0/kT} - 1)}$$

Compare to the black body radiation spectrum

$$\rho_{BB}(\omega) = \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3}{e^{\hbar\omega/kT} - 1}$$

$$\frac{A}{B_{ab}} = \frac{\hbar\omega_0^3}{\pi^2 c^3}$$

Since $B_{ab} = \frac{\pi}{3\varepsilon_0\hbar^2}\wp^2$, $A = \frac{\omega_0^3\,\wp^2}{3\pi\varepsilon_0\hbar c^3}$

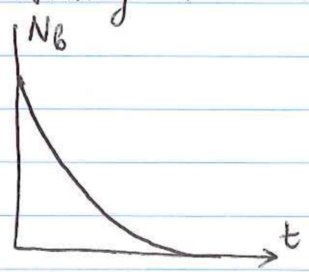
Note that $A \propto \wp^2$, so the stronger is the transition, the stronger is the spontaneous emission rate!

This rate also defines the lifetime of the excited energy levels.
If at time $t=0$ all the atoms are in the excited state,

$$\frac{dN_b}{dt} = -A\cdot N_b$$

$$\frac{dN_b}{N_b} = -A\,dt \quad \Rightarrow \quad N_b(t) = N_b(0)\,e^{-A\cdot t}$$

Defining the lifetime τ as the time interval after which $N_b(\tau) = \frac{1}{e}N_b(0)$



$$\tau = \frac{1}{A}$$

Stronger transition — shorter lifetime