

Rate of Absorption and Stimulated Emission

The rate of absorption induced by the field is

$$w_{k\ell}(\omega) = \frac{\pi}{2\hbar^2} |E_0(\omega)|^2 |\langle k | \hat{\epsilon} \cdot \vec{\mu} | \ell \rangle|^2 \delta(\omega_{k\ell} - \omega)$$

The rate is clearly dependent on the strength of the field. The variable that you can most easily measure is the intensity I (energy flux through a unit area), which is the time-averaged value of the Poynting vector, S

$$S = \frac{c}{4\pi} (\vec{E} \times \vec{B})$$

$$I = \langle S \rangle = \frac{c}{4\pi} \langle \vec{E}^2 \rangle = \frac{c}{8\pi} E_0^2$$

Another representation of the amplitude of the field is the energy density

$$U = \frac{I}{c} = \frac{1}{8\pi} E_0^2 \quad (\text{for a monochromatic field})$$

Using this we can write

$$w_{k\ell} = \frac{4\pi^2}{\hbar^2} U(\omega) |\langle k | \hat{\epsilon} \cdot \vec{\mu} | \ell \rangle|^2 \delta(\omega_{k\ell} - \omega)$$

or for an isotropic field where $|\vec{E}_0 \cdot \hat{x}| = |\vec{E}_0 \cdot \hat{y}| = |\vec{E}_0 \cdot \hat{z}| = \frac{1}{3} |\vec{E}_0|^2$

$$w_{k\ell} = \frac{4\pi^2}{3\hbar^2} U(\omega) |\vec{\mu}_{k\ell}|^2 \delta(\omega_{k\ell} - \omega)$$

or more commonly

$$w_{k\ell} = B_{k\ell} U(\omega_{k\ell})$$

$$B_{k\ell} = \frac{4\pi^2}{3\hbar^2} |\mu_{k\ell}|^2 \quad \text{Einstein B coefficient}$$

(this is sometimes written as $B_{k\ell} = (2\pi/3\hbar^2) |\mu_{k\ell}|^2$ when the energy density is in v).

U can also be written in a quantum form, by writing it in terms of the number of photons N

$$N\hbar\omega = \frac{E_0^2}{8\pi} \quad U = N \frac{\hbar\omega^3}{\pi^2 c^3}$$

B is independent of the properties of the field. It can be related to the absorption cross-section, σ_A .

$$\begin{aligned} \sigma_A &= \frac{\text{total energy absorbed / unit time}}{\text{total incident intensity (energy / unit time / area)}} \\ &= \frac{\hbar\omega \cdot w_{k\ell}}{I} = \frac{\hbar\omega \cdot B_{k\ell} U(\omega_{k\ell})}{c U(\omega_{k\ell})} \\ \sigma_A &= \frac{\hbar\omega}{c} B_{k\ell} \end{aligned}$$

More generally you may have a frequency dependent absorption coefficient

$\sigma_A(\omega) \propto B_{k\ell}(\omega) = B_{k\ell} g(\omega)$ where $g(\omega)$ is a lineshape function.

The golden rule rate for absorption also gives the same rate for stimulated emission. We find for two levels $|m\rangle$ and $|n\rangle$:

$$w_{nm} = w_{mn}$$

$$B_{nm} U(\omega_{nm}) = B_{mn} U(\omega_{mn}) \quad \text{since } U(\omega_{nm}) = U(\omega_{mn})$$

$$B_{nm} = B_{mn}$$

The absorption probability per unit time equals the stimulated emission probability per unit time.

Also, the cross-section for absorption is equal to an equivalent cross-section for stimulated emission, $(\sigma_A)_{nm} = (\sigma_{SE})_{mn}$.

Now let's calculate the change in the intensity of incident light, due to absorption/stimulated emission passing through sample (length L).

$$dI = -N_n \sigma_A I dx + N_m \sigma_{SE} I dx$$

$$\begin{array}{l} |m\rangle \text{---} \\ |n\rangle \text{---} \end{array}$$

$$\frac{dI}{I} = -(N_n - N_m) \sigma_a dx$$

$N_n; N_m$ populations

$\Delta N = N_n - N_m$: pop. difference

$$\frac{I}{I_0} = e^{-\Delta N \sigma_a L}$$

for high freq. $\Delta N \approx N_n \equiv N$

$$\approx e^{-N \sigma_a L}$$

N : cm^{-3} σ_n : cm^2 L : cm

or
$$\frac{I}{I_0} = 10^{-C \epsilon L}$$

C : mol/L ϵ : ℓ /molecule

$$\epsilon = 2303 N_n \sigma_A$$

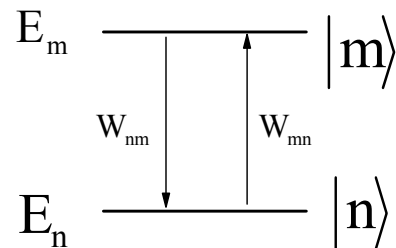
SPONTANEOUS EMISSION

What doesn't come naturally out of semi-classical treatments is spontaneous emission—transitions when the field isn't present.

To treat it properly requires a quantum mechanical treatment of the field, where energy is conserved, such that annihilation of a quantum leads to creation of a photon with the same energy. We need to treat the particles and photons both as quantized objects.

You can deduce the rates for spontaneous emission from **statistical arguments** (Einstein).

For a sample with a large number of molecules, we will consider transitions between two states $|m\rangle$ and $|n\rangle$ with $E_m > E_n$.



The Boltzmann distribution gives us the number of molecules in each state.

$$N_m / N_n = e^{-\hbar\omega_{mn}/kT}$$

For the system to be at equilibrium, the time-averaged transitions up W_{mn} must equal those down W_{nm} . In the presence of a field, we would want to write for an ensemble

$$N_m B_{nm} U(\omega_{mn}) \stackrel{?}{=} N_n B_{mn} U(\omega_{mn})$$

but clearly this can't hold for finite temperature, where $N_m < N_n$, so there must be another type of emission independent of the field.

So we write

$$W_{nm} = W_{mn}$$

$$N_m (A_{nm} + B_{nm} U(\omega_{mn})) = N_n B_{mn} U(\omega_{mn})$$

If we substitute the Boltzmann equation into this and use $B_{mn} = B_{nm}$, we can solve for A_{nm} :

$$A_{nm} = B_{nm} U(\omega_{mn}) \left(e^{\hbar\omega_{mn}/kT} - 1 \right)$$

For the energy density we will use Planck's blackbody radiation distribution:

$$U(\omega) = \underbrace{\frac{\hbar\omega^3}{\pi^2 c^3}}_{U_\omega} \underbrace{\frac{1}{e^{\hbar\omega_{mn}/kT} - 1}}_{\langle N_\omega \rangle}$$

U_ω is the energy density per photon of frequency ω .

$\langle N_\omega \rangle$ is the mean number of photons at a frequency ω .

$$\therefore A_{nm} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{nm} \quad \text{Einstein A coefficient}$$

The total rate of emission from the excited state is

$$\begin{aligned} w_{nm} &= B_{nm} U(\omega_{nm}) + A_{nm} && \text{using } U(\omega_{nm}) = N \frac{\hbar\omega^3}{\pi^2 c^3} \\ &= \frac{\hbar\omega^3}{\pi^2 c^3} B_{nm} (N+1) \end{aligned}$$

Notice, even when the field vanishes ($N \rightarrow 0$), we still have emission.

Remember, for the semiclassical treatment, the total rate of stimulated emission was

$$w_{nm} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{nm} (N)$$

If we use the statistical analysis to calculate rates of absorption we have

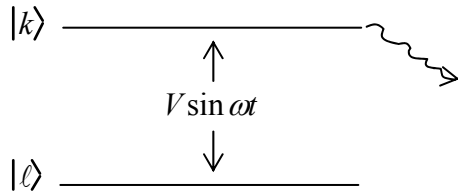
$$w_{mn} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{mn} N$$

The A coefficient gives the rate of emission in the absence of a field, and thus is the inverse of the radiative lifetime:

$$\tau_{\text{rad}} = \frac{1}{A}$$

Relaxation Leads to Line-broadening

What happens to the probability of absorption if an excited state decays exponentially?



$|k\rangle$ relaxes exponentially
... for instance by coupling to continuum

$$P_k \propto \exp[-\Gamma t]$$

First-order result:

$$b_k = \frac{-i}{\hbar} \int_{t_0}^t d\tau \langle k|V|\tau\rangle$$

$$\text{or } i\hbar \frac{\partial}{\partial t} b_k = e^{i\omega_{kl}t} V_{kl}(t)$$

If we add relaxation to description of b_k :

$$i\hbar \frac{\partial}{\partial t} b_k = e^{i\omega_{kl}t} V_{kl}(t) - \frac{\Gamma}{2} b_k$$

(We write this in analogy to coupling to continuum $|n\rangle$ where $\Gamma = \bar{w}_{nk}$.)

Now we have

$$\begin{aligned} \frac{\partial}{\partial t} b_k &= \frac{-i}{\hbar} e^{i\omega_{kl}t} \sin \omega t V_{kl} - \frac{\Gamma}{2} b_k(t) \\ &= \frac{E_0 \omega_{kl}}{2i\hbar \omega} \left[e^{i(\omega_{kl} + \omega)t} - e^{i(\omega_{kl} - \omega)t} \right] \bar{\mu}_{kl} - \frac{\Gamma}{2} b_k(t) \end{aligned}$$

The solution to the differential equation

$$\dot{y} + ay = b e^{iat} \quad \text{is}$$

$$y(t) = A e^{-at} + \frac{b e^{i\alpha t}}{a + i\alpha}$$

$$b_k(t) = A e^{-\Gamma t/2} + \frac{E_0 \omega_{kl} \bar{\mu}_{kl}}{2i\hbar\omega} \left[\frac{e^{i(\omega_{kl} + \omega)t}}{\Gamma/2 + i(\omega_{kl} + \omega)} - \frac{e^{i(\omega_{kl} - \omega)t}}{\Gamma/2 + i(\omega_{kl} - \omega)} \right]$$

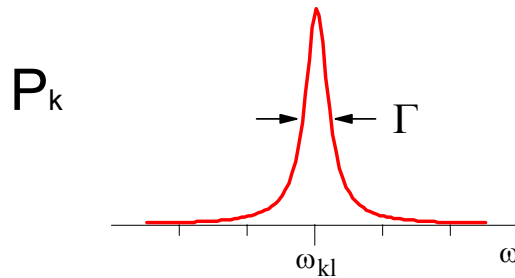
Let's look at absorption only—long time limit:

$$b_k(t) = \frac{E_0 \omega_{kl} \bar{\mu}_{kl}}{2\hbar\omega} \left[\frac{e^{i(\omega_{kl} - \omega)t}}{\omega_{kl} - \omega - i\Gamma/2} \right]$$

The probability of transition:

$$P_k = |b_k|^2 = \frac{E_0^2 |\mu_{kl}|^2}{4\hbar^2} \frac{1}{(\omega_{kl} - \omega)^2 + \Gamma^2/4}$$

Lorentzian lineshape:



The linewidth is related to the system rather than how we introduced the perturbation.

Linewidth related to relaxation dynamics.