Supplement to Rate of Absorption and Stimulated Emission

Here are a couple of more detailed derivations:

Let's look a little more carefully at the rate of absorption $w_{k\ell}$ induced by an isotropic, broadband light source

$$w_{k\ell} = \int w_{k\ell}(\omega)\rho_E(\omega)d\omega$$

where, for a monochromatic light source

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

For a broadband isotropic light source $\rho(\omega)d\omega$ represents a number density of electromagnetic modes in a frequency range $d\omega$—this is the number of standing electromagnetic waves in a unit volume.

For one frequency we wrote:

$$A = A_0\,\hat{\epsilon}\, e^{i(\bar{k}\cdot\bar{r} - \omega t)} + c.c.$$

but more generally:

$$\mathrm{A} = \sum_{\bar{k},j} \mathrm{A}_{0_{\bar{k}}}\,\hat{\epsilon}_j\, \mathrm{e}^{\mathrm{i}(\bar{k}\cdot\bar{r} - \omega t)} + \mathrm{c.c.}$$

where the sum is over the $\bar{k}$ modes and j is the polarization component.

By summing over wave vectors for a box of fixed volume, the number density of modes in a frequency range $d\omega$ radiated into a solid angle $d\Omega$ is

$$\mathrm{dN} = \frac{1}{(2\pi)^3}\frac{\omega^2}{c^3}\,\mathrm{d}\omega\,\mathrm{d}\Omega$$

and we get ρ_E by integrating over all Ω

$$\rho_E(\omega)\,\mathrm{d}\omega = \frac{1}{(2\pi)^3}\frac{\omega^2}{c^3}\,\mathrm{d}\omega \underbrace{\int \mathrm{d}\Omega}_{4\pi} = \frac{\omega^2}{2\pi^2 c^3}\,\mathrm{d}\omega$$

↖ number density at ω

We can now write the total transition rate between two discrete levels summed over all frequencies, direction, polarizations

$$w_{k\ell} = \int d\omega \, \frac{\pi}{2\hbar^2} \left|E_0(\omega)\right|^2 \delta(\omega_{k\ell} - \omega) \frac{1}{(2\pi)^3} \frac{\omega^2}{c^3} \underbrace{\sum_j \int d\Omega \left|\langle k | \hat{\epsilon}_j \cdot \bar{\mu} | \ell \rangle\right|^2}_{\frac{8\pi}{3}|\bar{\mu}_{k\ell}|^2}$$

$$= \frac{\left|E_0(\omega_{k\ell})\right|^2 \omega^2}{6\pi \hbar^2 c^3} \left|\bar{\mu}_{k\ell}\right|^2$$

We can write an energy density which is the number density in a range $d\omega$ × # of polarization components × energy density per mode.

$$U(\omega_{k\ell}) = \frac{\omega^2}{2\pi^2 c^3} \cdot 2 \cdot \frac{E_0^2}{8\pi}$$ ← rate of energy flow/c

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

$$B_{k\ell} = \frac{4\pi^2}{3\hbar^2} \left|\mu_{k\ell}\right|^2$$ is the Einstein B coefficient for the rate of absorption

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

$$N\hbar\omega = \frac{E_0^2}{8\pi} \qquad U(\omega_{k\ell}) = N \frac{\hbar \omega^3}{\pi^2 c^3}$$

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

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

$$B_{nm} \, U(\omega_{nm}) = B_{nm} \, U(\omega_{nm}) \qquad since \; U(\omega_{nm}) = U(\omega_{mn})$$

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

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

Version 2:

Let's calculate the rate of transitions induced by an isotropic broadband source—we'll do it a bit differently this time. The units are cgs.

The power transported through a surface is given by the Poynting vector and depends on k.

$$S = \frac{c}{4\pi}\overline{E}\times\overline{B} = \frac{c\,\omega^2 A_0^2}{8\pi}\hat{k} = \frac{\omega^2 E_0^2}{2\pi}$$

and the energy density for this single mode wave is the time average of S/c.

The vector potential for a single mode is

$$A = A_0\,\hat{\in} e^{i(\bar{k}\cdot\bar{r}-\omega t)} + c.c.$$

with $\omega = ck$. More generally any wave can be expressed as a sum over Fourier components of the wave vector:

$$A = \sum_{\bar{k},j} A_{\bar{k}_j}\,\hat{\in}_j \frac{e^{i(\bar{k}\cdot\bar{r}-\omega t)}}{\sqrt{V}} + c.c.$$

The factor of $\sqrt{V}$ normalizes for the energy density of the wave—which depends on k.

The interaction Hamiltonian for a single particle is:

$$V(t) = \frac{-q}{m}A\cdot\bar{\rho}$$

or for a collection of particles

$$V(t) = -\sum_i \frac{q_i}{m_i}\overline{A}\cdot\bar{p}_i$$

Now, the momentum depends on the position of particles, and we can express p in terms of an integral over the distribution of particles:

$$p = \int d^3r\,p(r) \qquad\qquad p(r) = \sum_i p_i\,\delta(r - r_i)$$

So if we assume that all particles have the same mass and charge—say electrons:

$$V(t)=\frac{-q}{m}\int d^3r\,\bar{A}(\bar{r},t)\cdot\bar{p}(r)$$

The rate of transitions induced by a single mode is:

$$\left(w_{k\ell}\right)_{\bar{k},j}=\frac{2\pi}{V\hbar^2}\delta\left(\omega_{k\ell}-\omega\right)\frac{q^2}{m^2}\left|A_{\bar{k},j}\right|^2\left|\left\langle k\left|\hat{\epsilon}_j\cdot\bar{p}\left(r\right)\right|\ell\right\rangle\right|^2$$

And the total transition rate for an isotropic broadband source is:

$$w_{k\ell}=\sum_{\bar{k},j}\left(w_{k\ell}\right)_{\bar{k},j}$$

We can replace the sum over modes for a fixed volume with an integral over k :

$$\frac{1}{V}\sum_k\ \Rightarrow\int\frac{d^3k}{(2\pi)^3}\rightarrow\int\frac{dk\,k^2\,d\Omega}{(2\pi)^3}\rightarrow\int\frac{d\omega\,\omega^2\,d\Omega}{(2\pi\,C)^3}$$

So for the rate we have: $d\Omega=\sin\theta\,d\theta\,d\o$

$$w_{k\ell}=\int d\omega\,\frac{2\pi}{\hbar^2}\frac{\omega^2}{\left(2\pi c\right)^3}\,\delta\left(\omega_{k\ell}-\omega\right)\frac{q^2}{m^2}\int d\Omega\sum_j\left|\left\langle k\left|\hat{\epsilon}\cdot\bar{p}\left(r\right)\right|\ell\right\rangle\right|^2\left|A_{\bar{k},j}\right|^2$$

(can be written as $\bar{k}$)

The matrix element can be evaluated in a manner similar to before:

$$\frac{q}{m}\left\langle k\left|\hat{\epsilon}_j\cdot p\left(r\right)\right|\ell\right\rangle=\frac{-q}{m}\sum_i\left\langle k\left|\hat{\epsilon}\cdot\bar{p}_i\delta\left(\bar{r}\cdot\bar{r}_i\right)\right|\ell\right\rangle$$

$$=\frac{-i}{\hbar}q\sum_i q\,\hat{\epsilon}\cdot\left\langle k\left|\left[\bar{r}_i,H_0\right]\delta\left(\bar{r}-\bar{r}_i\right)\right|\ell\right\rangle$$

$$=-i\omega_{k\ell}\sum_i q\,\hat{\epsilon}\cdot\left\langle k\left|\bar{r}_i\right|\ell\right\rangle$$

$$=-i\omega_{k\ell}\left\langle k\left|\hat{\epsilon}\cdot\bar{\mu}\right|\ell\right\rangle \qquad \text{where } \bar{\mu}=\sum_i q_i\,r_i$$

For the field

$$\sum_{k_{ij}}\left|A_{\bar{k}_j}\right|^2=\sum_{k_{ij}}\left|\frac{E_{\bar{k}_{ij}}}{2_i\,\omega}\right|^2=\frac{E_0^2}{4\omega^2}$$

$$W_{k\ell} = \int d\omega \frac{2\pi}{4\hbar^2} \frac{\omega^2}{(2\pi c)^3} \delta(\omega_{k\ell} - \omega) \frac{\omega_{k\ell}^2}{\omega^2} E_0^2 \underbrace{\int d\Omega \sum_j \left| \langle k | \hat{\epsilon}_j \cdot \overline{\mu} | \ell \rangle \right|^2}_{\substack{8\pi/3|\mu_{k\ell}|^2 \\ \textit{for isotropic}}}$$

$$= \frac{\omega^2}{6\pi\hbar^2 c^3} |E_0|^2 |\mu_{k\ell}|$$

For a broadband source, the energy density of the light

$$U = \frac{I}{c} = \frac{\omega^2 E_0^2}{8\pi^3 c^3}$$

$$W_{k\ell} = B_{k\ell} U(\omega_{k\ell}) \qquad\qquad B_{k\ell} = \frac{4\pi^2}{3\hbar^2} |\mu_{k\ell}|^2$$

We can also write the incident energy density in terms of the quantum energy per photon. For N photons in a single mode:

$$N\hbar\omega = B_{k\ell} N \frac{\hbar\omega^3}{\pi^2 c^3}$$

where $B_{k\ell}$ has molecular quantities and no dependence or field. Note $B_{k\ell} = B_{\ell k}$—ratio of S.E. = absorption.

The ratio of absorption can be related to the absorption cross-section, δ_A

$$\sigma_A = \frac{P}{I} = \frac{\text{total energy absorbed/unit time}}{\text{total intensity (energy/unit time/area)}}$$

$$P = \hbar\omega \cdot W_{k\ell} = \hbar\omega B_{k\ell} U(\omega_{k\ell})$$

$$I = cU(\omega_{k\ell})$$

$$\sigma_a = \frac{\hbar\omega}{c} B_{k\ell}$$

or more generally, when you have a frequency-dependent absorption coefficient described by a lineshape function $g(\omega)$

$$\sigma_a(\omega) = \frac{\hbar\omega}{c} B_{k\ell}\, g(\omega) \qquad\qquad \text{units of cm}^2$$