4.4 Rate of Absorption and Stimulated Emission

The rate of absorption induced by the field is

$$w_{k\ell}(\omega) = \frac{\pi}{2\hbar^2}\left|E_0(\omega)\right|^2 \left|\langle k|\hat{\epsilon}\cdot\overline{\propto}|\ell\rangle\right|^2 \delta(\omega_{k\ell}-\omega) \tag{4.56}$$

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*

$$\mathrm{S} = \frac{\mathrm{c}}{4\pi}\left(\overline{\mathrm{E}}\times\overline{\mathrm{B}}\right) \tag{4.57}$$

$$\mathrm{I} = \langle \mathrm{S}\rangle = \frac{\mathrm{c}}{4\pi}\left\langle \overline{\mathrm{E}}^2\right\rangle = \frac{\mathrm{c}}{8\pi}\mathrm{E}_0^2 \tag{4.58}$$

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

$$\mathrm{U} = \frac{\mathrm{I}}{\mathrm{c}} = \frac{1}{8\pi}\mathrm{E}_0^2 \qquad \text{(for a monochromatic field)} \tag{4.59}$$

Using this we can write

$$\mathrm{w}_{k\ell} = \frac{4\pi^2}{\hbar^2}\mathrm{U}(\omega)\left|\langle \mathrm{k}|\hat{\epsilon}\cdot\overline{\propto}|\ell\rangle\right|^2 \delta(\omega_{k\ell}-\omega) \tag{4.60}$$

or for an <u>isotropic field</u> where $\left|\overline{\mathrm{E}}_0\cdot\hat{\mathrm{x}}\right| = \left|\overline{\mathrm{E}}_0\cdot\hat{\mathrm{y}}\right| = \left|\overline{\mathrm{E}}_0\cdot\hat{\mathrm{z}}\right| = \frac{1}{3}\left|\mathrm{E}_0\right|^2$

$$\mathrm{w}_{k\ell} = \frac{4\pi^2}{3\hbar^2}\mathrm{U}(\omega)\left|\overline{\propto}_{k\ell}\right|^2 \delta(\omega_{k\ell}-\omega) \tag{4.61}$$

or more commonly

$$\mathrm{w}_{k\ell} = \mathrm{B}_{k\ell}\,\mathrm{U}(\omega_{k\ell}) \tag{4.62}$$

$$\mathrm{B}_{k\ell} = \frac{4\pi^2}{3\hbar^2}\left|\propto_{k\ell}\right|^2 \qquad \text{Einstein B coefficient} \tag{4.63}$$

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

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

$$N\hbar\omega = \frac{E_0^2}{8\pi} \qquad U = N\frac{\hbar\omega^3}{\pi^2 c^3} \tag{4.64}$$

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

$$\sigma_A = \frac{\text{total energy absorbed / unit time}}{\text{total incident intensity}\left(\text{energy / unit time / area}\right)}$$
$$= \frac{\hbar\omega \cdot w_{k\ell}}{I} = \frac{\hbar\omega \cdot B_{k\ell}\, U\left(\omega_{k\ell}\right)}{c\, U\left(\omega_{k\ell}\right)} \tag{4.65}$$

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

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(ω) 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 $|n\rangle$:

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

$$B_{nm} U\left(\omega_{nm}\right) = B_{nm} U\left(\omega_{nm}\right) \qquad \text{since } U\left(\omega_{nm}\right) = U\left(\omega_{mn}\right) \tag{4.66}$$

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

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, $\left(\sigma_A\right)_{nm} = \left(\sigma_{SE}\right)_{mn}$.

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

$$\frac{dI}{I} = -N_n \sigma_A \, dx + N_m \sigma_{SE} \, dx \qquad (4.67) \qquad \text{——————} \; |m\rangle$$

$$\frac{dI}{I} = -(N_n - N_m)\sigma_a \, dx \qquad (4.68) \qquad \text{——————} \; |n\rangle$$

N_n, N_m These are population of the upper and lower states, but expressed as a population densities. If N is the molecule density,

$$N_n = N\left(\frac{e^{-\beta E_n}}{Z}\right) \qquad (4.69)$$

$\Delta N = N_n - N_m$ is the thermal population difference between states.

Integrating over a pathlength L:

$$\frac{I}{I_0} = e^{-\Delta N \sigma_a L} \qquad \textit{for high freq.} \;\; \Delta N \approx N \qquad (4.70)$$

$$\approx e^{-N\sigma_a L} \qquad N : cm^{-3} \quad \sigma_n : cm^2 \quad L : cm$$

or written as Beer's Law:

$$A = -log\frac{I}{I_0} = C \in L \qquad C : \text{mol / liter} \quad \in : \text{liter / mol cm} \qquad (4.71)$$

$$\in = 2303 \, N \, \sigma_A$$

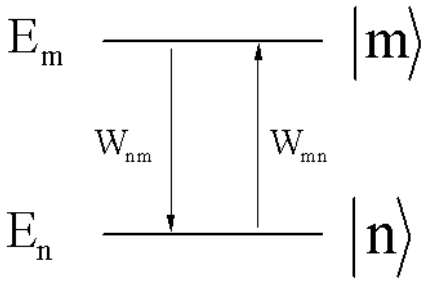
4.5 SPONTANEOUS EMISSION

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 $|\mathrm{m}\rangle$ and $|\mathrm{n}\rangle$ with $E_m > E_n$.



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

$$N_m / N_n = e^{-\hbar\omega_{mn}/kT} \tag{4.72}$$

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

$$N_m B_{nm} U(\omega_{mn}) \stackrel{?}{=} N_n B_{mn} U(\omega_{mn}) \tag{4.73}$$

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

$$\begin{gathered} \mathrm{W_{nm}} = \mathrm{W_{mn}} \\ \mathrm{N_m}\left(\mathrm{A_{nm}} + \mathrm{B_{nm}}\,\mathrm{U}(\omega_{mn})\right) = \mathrm{N_n}\,\mathrm{B_{mn}}\,\mathrm{U}(\omega_{mn}) \end{gathered} \tag{4.74}$$

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

$$A_{nm} = B_{nm}\, U\left(\omega_{mn}\right)\left(e^{\hbar\omega_{mn}/kT} - 1\right) \tag{4.75}$$

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

$$\mathrm{U}(\omega) = \underbrace{\frac{\hbar\omega^3}{\pi^2 c^3}}_{\mathrm{U}_\omega} \underbrace{\frac{1}{e^{\hbar\omega_{mn}/\mathrm{kT}} - 1}}_{\langle \mathrm{N}_\omega \rangle} \tag{4.76}$$

U_ω is the energy density per photon of frequency ω.
$\langle \mathrm{N}_\omega \rangle$ is the mean number of photons at a frequency ω.

$$\therefore \quad \mathrm{A_{nm}} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B_{nm}} \qquad \text{Einstein A coefficient} \tag{4.77}$$

The total rate of emission from the excited state is

$$\mathrm{w_{nm}} = \mathrm{B_{nm}}\,\mathrm{U}(\omega_{nm}) + \mathrm{A_{nm}} \qquad \text{using } \mathrm{U}(\omega_{nm}) = \mathrm{N}\frac{\hbar\omega^3}{\pi^2 \mathrm{C}^3} \tag{4.78}$$

$$= \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B_{nm}}(\mathrm{N}+1) \tag{4.79}$$

Notice, even when the field vanishes $(N \to 0)$, we still have emission.
Remember, for the semiclassical treatment, the total rate of stimulated emission was

$$\mathrm{w_{nm}} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B_{nm}}(\mathrm{N}) \tag{4.80}$$

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

$$\mathrm{w_{mn}} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B_{mn}}\mathrm{N} \tag{4.81}$$

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

$$\tau_{\mathrm{rad}} = \frac{1}{\mathrm{A}} \tag{4.82}$$