SPONTANEOUS EMISSION: EINSTEIN'S ARGUMENT

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 9.8.

We've seen that external radiation can stimulate the emission and absorption of photons by the electron in an atom. However, even without any external radiation, an electron in an excited state will spontaneously decay to a lower state. Although a proper theory of spontaenous emission requires quantum electrodynamics, in 1917 Einstein devised a simple argument that gave a formula for the spontaneous decay rate without using quantum electrodynamics (which didn't exist then).

The idea is based on a counting argument. Suppose we have a collection of atoms in thermal equilibrium, which means that the populations of the various energy states are all constant. Restricting ourselves to a 2-state system, let N_a be the number of atoms in the lower state and N_b the number in the excited state. Then $\frac{dN_b}{dt}=0$ (because of thermal equilibrium), but the rate of change of N_b must be due to stimulated absorption, stimulated emission and spontaneous emission. The sum of these three rates must therefore be zero. The rates of stimulated absorption and emission are each proportional to $\rho(\omega_0)$, the density of stimulating radiation at frequency $\omega_0=(E_b-E_a)/\hbar$, so let B_{ab} and B_{ba} be the constants of proportionality for these two rates (from our earlier analysis, we know that $B_{ab}=B_{ba}$, but we'll keep them separate for now), and let A be the rate of spontaneous emission. Then

$$N_aB_{ab}\rho(\omega_0)-N_bB_{ba}\rho(\omega_0)-N_bA=0 \tag{0.1}$$

One of the results from statistical mechanics is that, in thermal equilibrium, the number of particles with energy E_i is proportional to the Boltzmann factor e^{-E_i/k_BT}, where k_B is the Boltzmann constant and T is the absolute temperature. Therefore

$$\frac{N_a}{N_b} = \frac{e^{-E_a/k_BT}}{e^{-E_b/k_BT}} \tag{0.2}$$

$$= e^{(E_b-E_a)/k_BT} \tag{0.3}$$

$$= e^{\hbar\omega_0/k_BT} \tag{0.4}$$

Dividing 0.1 through by N_b we get

$$\rho\left(\omega_0\right)=\frac{A}{e^{\hbar\omega_0/k_BT}B_{ab}-B_{ba}} \tag{0.5}$$

However, we know from our study of bosons that the density of radiation is given by Planck's formula:

$$\rho\left(\omega_0\right)=\frac{1}{\left(e^{\hbar\omega_0/k_BT}-1\right)}\frac{\hbar\omega_0^3}{\pi^2c^3} \tag{0.6}$$

Comparing these two formulas, we see that the condition $B_{ab}=B_{ba}$ is required if they are to be equal, and also that the rate A of spontaneous emission must be proportional to B_{ab}:

$$A=\frac{\hbar\omega_0^3}{\pi^2c^3}B_{ab} \tag{0.7}$$

For the lower frequency case, where we can approximate the electric field over the extent of the atom by a constant, we can follow a similar derivation to the one we did earlier (this derivation is done by Griffiths in his section 9.3) to find that, for radiation incident along the z direction we get for the stimulated absorption/emission rate:

$$R_{a\to b}=\frac{\pi\left|\mathfrak{p}\right|^2}{\epsilon_0\hbar^2}\rho\left(\omega_0\right) \tag{0.8}$$

where

$$\mathfrak{p}\equiv q\left\langle a\left|z\right|b\right\rangle \tag{0.9}$$

Griffiths also shows that if we average the radiation over all incident directions and all polarization directions we introduce a factor of $\frac{1}{3}$ into the rate, so we get

$$R_{a\to b}=\frac{\pi\left|\boldsymbol{\mathfrak{p}}\right|^2}{3\epsilon_0\hbar^2}\rho\left(\omega_0\right) \tag{0.10}$$

where

$$\boldsymbol{\mathfrak{p}}\equiv q\left\langle a\left|\mathbf{r}\right|b\right\rangle \tag{0.11}$$

The coefficient $B_{ab}=B_{ba}$ is therefore

$$B_{ab} = \frac{\pi |\mathfrak{p}|^2}{3\varepsilon_0 \hbar^2} \tag{0.12}$$

for general incoherent radiation (all directions and polarizations). The spontaneous emission rate is then

$$A = \frac{\omega_0^3 |\mathfrak{p}|^2}{3\varepsilon_0 \pi \hbar c^3} \tag{0.13}$$

The ratio of spontaneous to stimulated emission is therefore

$$\frac{A}{R_{b\to a}} = \frac{\omega_0^3 \hbar}{\pi^2 c^3 \rho(\omega_0)} \tag{0.14}$$

If the stimulating radiation comes from the thermal environment of the atom, then from 0.6 we get

$$\frac{A}{R_{b\to a}} = e^{\hbar\omega_0/k_B T} - 1 \tag{0.15}$$

At room temperature $T = 300$ K and with $k_b = 1.38 \times 10^{-23} \mathrm{m^2 kg\ s^{-2}\ K^{-1}}$ then for a frequency of 5×10^{12} Hz $\Longrightarrow$ $\omega_0 = 3.14 \times 10^{12}\ \mathrm{s^{-1}}$ we get

$$\frac{A}{R_{b\to a}} = 0.083 \tag{0.16}$$

For frequencies much lower than this the exponential gets very close to 1, so the ratio gets very small indicating that stimulated emission dominates. For larger frequencies, spontaneous emission dominates. For visible light, the frequency is in the region of $10^{15}\ \mathrm{s^{-1}}$ so spontaneous emission dominates.

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