D.Rubin
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Sontaneous Emission

Einstein coefficients

Suppose we have a room full of atoms that can make transitions between state ψ_a and state ψ_b and they are in equilibrium with a radiation field with density $\rho(\omega_0)$ where $\omega_0 = (E_b - E_a)/\hbar$. Let N_a be the number of atoms in the lower energy state, and N_b the number in the higher energy state. Atoms can make transitions from the lower to the upper state by absorption of energy from the radiation field and from the upper to the lower state by stimulated emission. They can also make transitions from higher to lower state by spontaneous emission. The spontaneous emission rate is independent of the intensity of radiation in the room. It happens spontaneously.

If A is the spontaneous emission rate then $N_b A$ is the number of particles/second leaving state b by spontaneous emission. $N_b B_{ba}\rho(\omega_0)$ is the rate at which particles are leaving state b by stimulated emission.

$$B_{ba} = \frac{\pi}{3\epsilon_0\hbar} | \langle \psi_b \mid q\vec{r} \mid \psi_a \rangle |^2$$

The atoms in the lower energy state absorb energy and make transitions to the upper energy state at the rate $N_a B_{ab}\rho(\omega_0)$. So the rate of change of the number of particles in the uppe energy state

$$\frac{dN_b}{dt} = -AN_b - N_b B_{ba}\rho(\omega_0) + N_a B_{ab}\rho(\omega_0)$$

The atoms are in equilibrium with the radiation and $\frac{dN_b}{dt} = 0$ We solve for $\rho(\omega_0)$

$$\rho(\omega_0) = \frac{AN_b}{N_a B_{ab} - N_b B_{ba}} = \frac{A}{\frac{N_a}{N_b} B_{ab} - B_{ba}} \tag{1}$$

Meanwhile we learned that the number of particles in states with energy a

$$N_a \propto e^{-E_a/kT}$$

Then

$$\frac{N_a}{N_b} = \frac{e^{-E_a/KT}}{e^{-E_b/kT}} = e^{\hbar\omega_0/kT}$$

Substitution in Equation 1 gives

$$\rho(\omega_0) = \frac{A}{e^{\hbar\omega_0/kT}B_{ab} - B_{ba}} \tag{2}$$

We know that the Plank blackbody radiation distribution is

$$\rho(\omega_0) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/kT} - 1} \tag{3}$$

Equating 1 and 3 we find that $B_{ab} = B_{ba}$, and

$$A = \frac{\omega^3\hbar}{\pi^2 c^3}B = \frac{\omega^3}{3\pi\epsilon_0\hbar c^3}|\langle\psi_f \mid q\vec{r} \mid \psi_i\rangle|^2 \tag{4}$$

and that is the spontaneous emission rate.

Vacuum fluctuations and spontaneous emission

An alternative strategy for determining the spontaneous emission rate is to begin with the expression for the stimulated rate, and then substitute the ground state radiation density of the vacuum. We showed that the stimulated emission rate is

$$R_{b\to a} = \frac{\pi}{3\epsilon_o\hbar^2}|\langle\psi_a \mid q\vec{r} \mid \psi_b\rangle|^2\rho(\omega_0) \tag{5}$$

The spontaneous emission rate is not really spontaneous. It is induced by the energy in the ground state of the radiation field. If we knew the number of photons per unit volume per unit frequency in the ground state of the vacuum, then we could use Equation 5 to compute the spontaneous emission rate. Let's see if we can figure it out.

Suppose that the vacuum is filled with an oscillator at every possible frequency and wave number. In a dark room all of the oscillators are in their ground states. If the energy of each oscillator is assoicated with radiation at that frequency, then if the oscillator is in the ground state it must have the energy of a single photon, namely $\hbar\omega$. That is the smallest unit of energy available. So there is one photon at each frequency. All we need to do now is to count the number of oscillators, namely, the number of different frequencies.

The number of distinct states with wave number k is

$$dN = 2\frac{1}{8}\frac{4\pi k^2 dk}{\pi^3/V} = \frac{Vk^2 dk}{\pi^2}$$

The 2 is because there are two polarization states for photons. The 1/8 is because we only count the phase space volume in the octant with $k_x > 0, k_y > 0$ and $k_z > 0$. The $4\pi k^2 dk$ is the volume of a spherical shell with radius k, and the π^3/V is the volume that each space takes up in the phase space. In terms of ω

$$dN = \frac{V\omega^2 d\omega}{c^3\pi^2}$$

dN is the number of oscillators with frequency between ω and $\omega + d\omega$. If each oscillator is in the ground state, then the total energy in the dN oscillators is

$$dE = dN\hbar\omega = \frac{\hbar V\omega^3 d\omega}{c^3\pi^2}$$

and

$$\frac{1}{V}\frac{dE}{d\omega} = \rho(\omega) = \frac{\hbar\omega^3}{c^3\pi^2}$$

and substitution into Equation 5 gives

$$R_{b\to a} = \frac{\pi}{3\epsilon_0\hbar^2} |\langle\psi_a \mid q\vec{r} \mid \psi_b\rangle|^2 \frac{\hbar\omega^3}{c^3\pi^2} = \frac{\omega^3}{3\pi c^3\epsilon_0\hbar} |\langle\psi_a \mid q\vec{r} \mid \psi_b\rangle|^2 \tag{6}$$

which is the spontaneus emission rate and it agrees with Equation 4