Quantized Radiation Field

Spontaneous emission, like fluorescence, phosphorescence, spontaneous light scattering, Raman scattering, don't come naturally out of a semiclassical treatment of the field-matter interaction. You need to quantize the E.M. field, a treatment that also satisfies energy conservation.

Background

Our treatment of the vector potential has drawn on the monochromatic plane-wave solution to the wave-equation for **A**. The quantum treatment of light as a particle describes the energy of the light source as proportional to the frequency $\hbar\omega$, and the photon of this frequency is associated with a cavity mode with wavevector $|k| = \omega / c$ that describes the number of oscillations that the wave can make in a cube with length **L**. For a very large cavity you have a continuous range of allowed **k**. The cavity is important for considering the energy density of a light field, since the electromagnetic field energy per unit volume will clearly depend on the wavelength $\lambda = 2\pi/|\mathbf{k}|$ of the light.

Boltzmann used a description of the light radiated from a blackbody source of finite volume at constant temperature in terms of a superposition of cavity modes to come up with the statistics for photons. The classical treatment of this problem says that the energy density (modes per unit volume) increases rapidly with increasing wavelength. For an equilibrium body, the energy absorbed has to equal the energy radiated, but clearly as frequency increases, the energy of the radiated light should diverge. Boltzmann used the detailed balance condition to show that the particles that made up light must obey Bose-Einstein statistics. That is the equilibrium probability of finding a photon in a particular cavity mode is given by

$$f(\omega) = \frac{1}{e^{\hbar\omega/kT} - 1}$$

From our perspective (in retrospect), this should be expected, because the quantum treatment of any particle has to follow either Bose-Einstein statistics or Fermi-Dirac statistics, and clearly light energy is something that we want to be able to increase arbitrarily. That is, we want to be able to add mode and more photons into a given cavity mode. By summing over the number of cavity modes in a cubical box (using periodic boundary conditions) we can determine that the density of cavity modes (a photon density of states),

$$g(\omega) = \frac{\omega^2}{\pi^2 c^3}$$

Using the energy of a photon, the energy density per mode is

$$\hbar\omega\, g(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}$$

and so the probability distribution that describes the quantum frequency dependent energy density is

$$u(\omega) = \hbar\omega\, g(\omega)\, f(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/kT}-1}$$

<u>The Quantum Vector Potential</u>

So, for a quantized field, the field will be described by a photon number $N_{\bar{k}j}$, which represents the number of photons in a particular mode ($\bar{k}, j$) with frequency $\omega = ck$ in a cavity of volume v. For light of a particular frequency, the energy of the light will be $N_{\bar{k}j}\hbar\omega$. So, the state of the electromagnetic field can be written:

$$\left|\varphi_{EM}\right\rangle = \left|N_{\bar{k}_1,j_1}, N_{\bar{k}_2,j_2}, N_{\bar{k}_3,j_3}, \ \dots\right\rangle$$

If my matter absorbs a photon from mode $\bar{k}_2$, then the state of my system would be

$$\left|\varphi'_{EM}\right\rangle = \left|N_{\bar{k}_1,j}, \quad {}_{\bar{k}_2,j_2}-1, N_{\bar{k}_3,j}, \dots\right\rangle$$

What I want to do is to write a quantum mechanical Hamiltonian that includes both the matter and the field, and then use first order perturbation theory to tell me about the rates of absorption and stimulated emission. So, I am going to partition my Hamiltonian as a sum of a contribution from the matter and the field:

$$H_0 = H_{EM} + H_M$$

If the matter is described by $\left|\varphi_M\right\rangle$, then the total state of the E.M. field and matter can be expressed as product states:

$$\left|\varphi\right\rangle = \left|\varphi_{EM}\right\rangle\left|\varphi_M\right\rangle$$

And we have eigenenergies

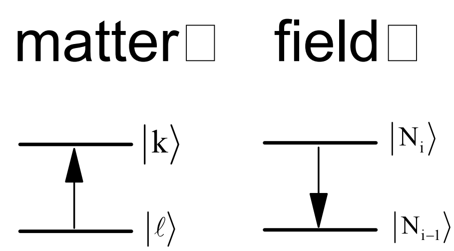
$$E = E_{EM} + E_M$$

Now, if I am watching transitions from an initial state $|\ell\rangle$ to a final state $|k\rangle$, then I can express the initial and final states as:

$$|\varphi_I\rangle = |\ell; N_1, N_2, N_3 \ldots, N_i, \ldots\rangle$$

$$|\varphi_F\rangle = |k; N_1, N_2, N_3, \ldots, N_i \pm 1, \ldots\rangle$$

$$\begin{pmatrix} +: \text{emission} \\ -: \text{absorption} \end{pmatrix}$$



Where I have abbreviated $N_i \equiv N_{\bar{k}_i, j_i}$, the energies of these two states are:

$$E_I = E_\ell + \sum_j N_j \left(\hbar\omega_j\right) \qquad\qquad \omega_j = ck_j$$

$$E_F = E_k + \sum_j N_j \left(\hbar\omega_j\right) \pm \hbar\omega_i$$

So looking at absorption $\begin{pmatrix} |k\rangle & \overline{} \\ & \uparrow \\ |\ell\rangle & \underline{} \end{pmatrix}$, we can write the Golden Rule Rate for transitions between states as:

$$w_{k\ell} = \frac{2\pi}{\hbar} \delta\left(E_k - E_\ell - \hbar\omega\right) \left|\langle \varphi_F | V(t) | \varphi_I \rangle\right|^2$$

Now, let's compare this to the absorption rate in terms of the classical vector potential:

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

If these are to be the same, then clearly $V(t)$ must have part that looks like $\left(\hat{\epsilon} \cdot \bar{p}\right)$ that acts on the matter, but it will also need another part that acts to lower and raise the photons in the field. Based on analogy with our electric dipole Hamiltonian, we write:

$$V(t) = \frac{-q}{m} \frac{1}{\sqrt{v}} \sum_{\bar{k},j} \left(\bar{p}_k \cdot \hat{\epsilon}_j \, \hat{A}_{\bar{k},j} + \bar{p}_k^{\dagger} \cdot \hat{\epsilon}_j^{*} \, \hat{A}_{\bar{k},j}^{\dagger}\right)$$

where $\hat{A}_{\bar{k},j}$ and $\hat{A}^{\dagger}_{\bar{k},j}$ are lowering/raising operators for photons in mode k. These are operators in the field states, whereas $\bar{p}_k$ remains only an operator in the matter states. So, we can write out the matrix elements of V as

$$\left\langle \varphi_F \left| V(t) \right| \varphi_I \right\rangle = -\frac{q}{m} \frac{1}{\sqrt{v}} \left\langle k \left| \bar{p}_k \cdot \hat{\in} \right| \ell \right\rangle \left\langle \ldots, N_i - 1, \ldots \left| \hat{A}_i \right| \ldots, N_i, \ldots \right\rangle$$

$$= \frac{1}{\sqrt{v}} \omega_{k\ell} \left\langle k \left| \hat{\in} \cdot \bar{\mu} \right| \ell \right\rangle \left\langle A_i^{(-)} \right\rangle$$

Comparing with our Golden Rule expression for <u>absorption</u>,

$$w_{k\ell} = \frac{\pi}{2\hbar^2} \delta(\omega_{k\ell} - \omega) \frac{\omega_{k\ell}^2}{\omega^2} E_0^2 \left| \mu_{k\ell} \right|^2$$

We see that the matrix element

$$\left\langle A_i^{(-)} \right\rangle = \sqrt{\frac{E_0^2}{4 v \omega^2}} \qquad \text{but } \frac{E_0^2}{8\pi} = N\hbar\omega$$

$$= \sqrt{\frac{2\pi\hbar}{v\omega}} \sqrt{N}$$

So we can write

$$\hat{A}_{\bar{k},j} = \sqrt{\frac{2\pi\hbar}{v\,\omega}}\, a_{\bar{k},j}$$

$$\hat{A}^{\dagger}_{\bar{k},j} = \sqrt{\frac{2\pi\hbar}{v\,\omega}}\, a^{\dagger}_{\bar{k},j}$$

where $a, a^{\dagger}$ are lowering, raising operators. So

$$\hat{A} = \sum_{\bar{k},j} \sqrt{\frac{2\pi\hbar}{v\,\omega}}\, \hat{\in}_j \left(a_{\bar{k}j}\, e^{i(\bar{k}\cdot\bar{r} - \omega t)} + a^{\dagger}_{\bar{k}j}\, e^{-i(\bar{k}\cdot\bar{r} - \omega t)} \right)$$

So what we have here is a system where the light field looks like an infinite number of harmonic oscillators, one per mode, and the field raises and lowers the number of quanta in the field while the momentum operator lowers and raises the matter:

$$H = H_{EM} + H_M + V(t) = H_0 + V(t)$$

$$H_{EM} = \sum_{\bar{k},j} \hbar\omega_{\bar{k}} \left(a^\dagger_{\bar{k}j} a_{\bar{k}j} + \tfrac{1}{2} \right)$$

$$H_M = \sum_i \frac{p_i^2}{2m_i} + V_i(\bar{r}, t)$$

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

$$= \sum_{\bar{k},j} \frac{q}{m} \sqrt{\frac{2\pi\hbar}{v\,\omega_k}} \left(\hat{\in}_j \cdot \bar{p} \right) \left[a_{\bar{k},j}\, e^{i(k \cdot r - \omega t)} + a^\dagger_{\bar{k},j}\, e^{-i(\bar{k} \cdot \bar{r} - \omega t)} \right]$$

$$= V^{(-)} + V^{(+)}$$

Let’s look at the matrix elements for absorption $(\omega_{k\ell} > 0)$

$$\left\langle k, N_i - 1 \middle| V^{(-)} \middle| \ell, N_i \right\rangle = \frac{-q}{m} \sqrt{\frac{2\pi\hbar}{v\,\omega}} \left\langle k, N_i - 1 \middle| (\hat{\in} \cdot \bar{p}) a \middle| \ell, N_i \right\rangle$$

$$= \frac{-q}{m} \sqrt{\frac{2\pi\hbar}{v\,\omega}} \sqrt{N_i} \left\langle k \middle| \hat{\in} \cdot \bar{p} \middle| \ell \right\rangle$$

$$= -i \sqrt{\frac{2\pi\hbar\omega}{v}} \sqrt{N_i}\;\; \hat{\in} \cdot \bar{\mu}_{k\ell}$$

and for stimulated emission $(\omega_{k\ell} < 0)$

$$\langle k, N_i + 1 | V^{(+)} | \ell, N_i \rangle = \frac{-q}{m}\sqrt{\frac{2\pi\hbar}{v\,\omega}}\langle k, N_i + 1 | (\hat{\epsilon}\cdot\overline{p}) a^\dagger | \ell, N_i \rangle$$

$$= \frac{-q}{m}\sqrt{\frac{2\pi\hbar}{v\,\omega}}\sqrt{N_i + 1}\langle k | \hat{\epsilon}\cdot\hat{p} | \ell \rangle$$

$$= -i\sqrt{\frac{2\pi\hbar\omega}{v}}\sqrt{N_i + 1}\;\hat{\epsilon}\cdot\overline{\mu}_{k\ell}$$

We have spontaneous emission! Even if there are no photons in the mode $(N_k = 0)$, you can still have transitions downward in the matter which creates a photon.

Let's play this back into the summation-over-modes expression for the rates of absorption/emission by isotropic field.

$$w_{k\ell} = \int d\omega \frac{2\pi}{\hbar^2}\frac{\omega^2}{(2\pi^2)^3}\delta(\omega_{k\ell} - \omega)\int d\Omega \sum_j \left|\langle k, N_i + 1 | V^{(+)} | \ell, N_i \rangle\right|^2$$

$$= \underbrace{\frac{2\pi}{\hbar^2}\frac{\omega^2}{(2\pi c)^3}}_{\text{number density per mode}} \quad (2\pi\hbar\omega)(N_i + 1) \quad \underbrace{\frac{8\pi}{3}|\mu_{k\ell}|^2}_{\text{average over polarization}}$$

$$= \frac{4(N_i + 1)\omega^3}{3\hbar c^3}|\mu_{k\ell}|^2$$

$$= B_{k\ell}(N_i + 1)\underbrace{\frac{\hbar\omega^3}{\pi^2 c^3}}_{\substack{\text{energy density}\\ \text{per mode}}}$$

So we have the result we deduced before.