4. INTERACTION OF LIGHT WITH MATTER

One of the most important topics in time-dependent quantum mechanics for chemists is the description of spectroscopy, which refers to the study of matter through its interaction with light fields (electromagnetic radiation). Classically, light-matter interactions are a result of an oscillating electromagnetic field resonantly interacting with charged particles. Quantum mechanically, light fields will act to couple quantum states of the matter, as we have discussed earlier.

Like every other problem, our starting point is to derive a Hamiltonian for the light-matter interaction, which in the most general sense would be of the form

$$H = H_M + H_L + H_{LM}. \tag{4.1}$$

The Hamiltonian for the matter H_M is generally (although not necessarily) time independent, whereas the electromagnetic field H_L and its interaction with the matter H_{LM} are time-dependent. A quantum mechanical treatment of the light would describe the light in terms of photons for different modes of electromagnetic radiation, which we will describe later. However, we will start with a common semiclassical treatment of the problem. For this approach we treat the matter quantum mechanically, and treat the field classically. For the field we assume that he light only presents a time-dependent interaction potential that acts on the matter, but the matter doesn't influence the light. (Quantum mechanical energy conservation says that we expect that the change in the matter to raise the quantum state of the system and annihilate a photon from the field. We won't deal with this right now). In that case, we can really largely ignore H_L, and we have a Hamiltonian that can be solved in the interaction picture representation:

$$\begin{aligned} H &\approx H_M + H_{LM}(t) \\ &= H_0 + V(t) \end{aligned} \tag{4.2}$$

Here, we'll derive the Hamiltonian for the light-matter interaction, the Electric Dipole Hamiltonian. It is obtained by developing a classical Hamiltonian for the interaction of charged particles with an electromagnetic field, and then substituting quantum operators for the matter.

$$\begin{aligned} p &\rightarrow -i\hbar\hat{\nabla} \\ x &\rightarrow \hat{x} \end{aligned} \tag{4.3}$$

In order to get the classical Hamiltonian, we need to work through two steps: (1) We need to describe electromagnetic fields, specifically in terms of a vector potential, and (2) we need to describe how the electromagnetic field interacts with charged particles.

Brief summary of electrodynamics

Let's summarize the description of electromagnetic fields that we will use. A derivation of the plane wave solutions to the electric and magnetic fields and vector potential is described in the appendix. Also, it is helpful to review this material in Jackson[1] or Cohen-Tannoudji, et al.[2]

> Maxwell's Equations describe electric and magnetic fields $\left(\bar{E}, \bar{B}\right)$.

> To construct a Hamiltonian, we must describe the time-dependent interaction potential (rather than a field).

> To construct a potential representation of $\bar{E}$ and $\bar{B}$, you need a vector potential $\bar{A}\left(\bar{r},t\right)$ and a scalar potential $\varphi\left(\bar{r},t\right)$. For electrostatics we normally think of the field being related to the electrostatic potential through $\bar{E} = -\nabla\varphi$, but for a field that varied in time and in space, the electrodynamic potential must be expressed in terms of both $\bar{A}$ and φ.

> In general an electromagnetic wave written in terms of the electric and magnetic fields requires 6 variables (the *x,y,* and *z* components of *E* and *B*). This is an overdetermined problem; Maxwell's equations constrain these. The potential representation has four variables (A_x, A_y, A_z and φ), but these are still not uniquely determined. We choose a constraint – a representation or guage – that allows us to uniquely describe the wave. Choosing a gauge such that $\varphi = 0$ (Coulomb gauge) leads to a plane-wave description of $\bar{E}$ and $\bar{B}$:

$$-\bar{\nabla}^2\bar{A}\left(\bar{r},t\right) + \frac{1}{c^2}\frac{\partial^2\bar{A}\left(\bar{r},t\right)}{\partial t^2} = 0 \tag{4.4}$$

$$\bar{\nabla}\cdot\bar{A} = 0 \tag{4.5}$$

This wave equation allows the vector potential to be written as a set of plane waves:

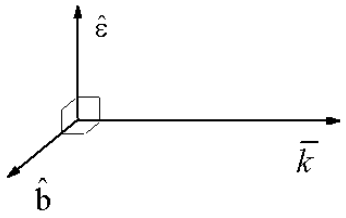
$$\bar{A}(\bar{r},t) = A_0\hat{\varepsilon}\, e^{i(\bar{k}\cdot\bar{r}-\omega t)} + A_0^*\hat{\varepsilon}\, e^{-i(\bar{k}\cdot\bar{r}-\omega t)}. \tag{4.6}$$

This describes the wave oscillating in time at an angular frequency ω and propagating in space in the direction along the wavevector $\bar{k}$, with a spatial period $\lambda = 2\pi/|\bar{k}|$. The wave has an amplitude A_0 which is directed along the polarization unit vector $\hat{\varepsilon}$. Since $\bar{\nabla}\cdot\bar{A} = 0$, we see that $\bar{k}\cdot\hat{\varepsilon} = 0$ or $\bar{k}\perp\hat{\varepsilon}$. From the vector potential we can obtain $\bar{E}$ and $\bar{B}$

$$\begin{aligned}\bar{E} &= -\frac{\partial\bar{A}}{\partial t} \\ &= i\omega A_0\hat{\varepsilon}\left(e^{i(\bar{k}\cdot\bar{r}-\omega t)} - e^{-i(\bar{k}\cdot\bar{r}-\omega t)}\right)\end{aligned} \tag{4.7}$$

$$\begin{aligned}\bar{B} &= \bar{\nabla}\times\bar{A} \\ &= i\left(\bar{k}\times\hat{\varepsilon}\right)A_0\left(e^{i(\bar{k}\cdot\bar{r}-\omega t)} - e^{-i(\bar{k}\cdot\bar{r}-\omega t)}\right)\end{aligned} \tag{4.8}$$

If we define a unit vector along the magnetic field polarization as $\hat{b} = \left(\bar{k}\times\hat{\varepsilon}\right)/|\bar{k}| = \hat{k}\times\hat{\varepsilon}$, we see that the wavevector, the electric field polarization and magnetic field polarization are mutually orthogonal $\hat{k}\perp\hat{\varepsilon}\perp\hat{b}$.



Also, by comparing eq. (4.6) and (4.7) we see that the vector potential oscillates as cos ωt, whereas the field oscillates as sin ωt. If we define

$$\frac{1}{2}E_0 = i\omega A_0 \tag{4.9}$$

$$\frac{1}{2}B_0 = i|k|A_0 \tag{4.10}$$

then,

$$\bar{E}(\bar{r},t) = |E_0|\hat{\varepsilon}\sin\left(\bar{k}\cdot\bar{r}-\omega t\right) \tag{4.11}$$

$$\bar{B}\left(\bar{r},t\right)=\left|B_0\right|\hat{b}\sin\left(\bar{k}\cdot\bar{r}-\omega t\right). \tag{4.12}$$

Note, $E_0/B_0=\omega/\left|k\right|=c$.

Hamiltonian for radiation field interacting with charged particle

Now, let's find a classical Hamiltonian that describes charged particles in field in terms of the vector potential. Start with Lorentz force on a particle with charge q

(1) $$\bar{F} = q\left(\bar{E} + \bar{v} \times \bar{B}\right). \tag{4.13}$$

Here $\bar{v}$ is the velocity of the particle. Writing this for one direction (x) in terms of the Cartesian components of $\bar{E}$, $\bar{v}$ and $\bar{B}$, we have:

(2) $$F_x = q\left(E_x + v_y B_z - v_z B_y\right). \tag{4.14}$$

In Lagrangian mechanics, this force can be expressed in terms of the total potential energy U as

(3) $$F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt}\left(\frac{\partial U}{\partial v_x}\right) \tag{4.15}$$

Using the relationships that describe $\bar{E}$ and $\bar{B}$ in terms of A and φ, inserting into eq. (4.14) and working it into the form of eq. (4.15), we can show that:

(4) $$U = q\varphi - q\bar{v} \cdot \bar{A} \tag{4.16}$$

This is derived in CTDL,[3] and you can confirm by plugging it into eq. (4.15).

Now we can write a Lagrangian in terms of the kinetic and potential energy of the particle

$$L = T - U \tag{4.17}$$

(5) $$L = \frac{1}{2} m\bar{v}^2 + q\bar{v} \cdot \bar{A} - q\varphi \tag{4.18}$$

The classical Hamiltonian is related to the Lagrangian as

(6) $$\begin{aligned} H &= \bar{p} \cdot \bar{v} - L \\ &= \bar{p} \cdot \bar{v} - \tfrac{1}{2} m\bar{v}^2 - q\,\bar{v} \cdot \bar{A} - q\varphi \end{aligned} \tag{4.19}$$

Recognizing $$\bar{p} = \frac{\partial L}{\partial \bar{v}} = m\bar{v} + q\bar{A} \tag{4.20}$$

we write $$\bar{v} = \tfrac{1}{m}\left(\bar{p} - q\bar{A}\right). \tag{4.21}$$

Now substituting (4.21) into (4.19), we have:

$$H = \tfrac{1}{m}\,\bar{p}\cdot\left(\bar{p}-q\bar{A}\right) - \tfrac{1}{2m}\left(\bar{p}-q\bar{A}\right)^2 - \tfrac{q}{m}\left(\bar{p}-q\bar{A}\right)\cdot A + q\varphi \tag{4.22}$$

$$H = \frac{1}{2m}\left[\bar{p}-q\bar{A}\left(\bar{r},t\right)\right]^2 + q\varphi\left(\bar{r},t\right) \tag{4.23}$$

This is the classical Hamiltonian for a particle in an electromagnetic field. In the Coulomb gauge$\left(\varphi = 0\right)$, the last term is dropped.

We can write a Hamiltonian for a collection of particles in the absence of a external field

$$H_0 = \sum_i \left(\frac{\bar{p}_i^2}{2m_i} + V_0\left(\bar{r}_i\right) \right). \tag{4.24}$$

and in the presence of the EM field:

$$H = \sum_i \left(\frac{1}{2m_i}\left(\bar{p}_i - q_i\bar{A}\left(\bar{r}_i\right)\right)^2 + V_0\left(r_i\right) \right). \tag{4.25}$$

Expanding:
$$H = H_0 - \sum_i \frac{q_i}{2m_i}\left(p_i\cdot\bar{A} + \bar{A}\cdot\bar{p}_i\right) + \cancel{\sum_i \frac{q_i}{2m_i}\left|\bar{A}\right|^2} \tag{4.26}$$

Generally the last term is considered small. That is the energy of particles high relative to amplitude of potential. (This term should be considered for extremely high field strength, which significantly distorts the potential binding molecules together). For weak fields we have:

$$H = H_0 + V\left(t\right) \tag{4.27}$$

$$V\left(t\right) = \sum_i \frac{q_i}{2m_i}\left(\bar{p}_i\cdot\bar{A} + \bar{A}\cdot\bar{p}_i\right) \tag{4.28}$$

Now we are in a position to substitute the quantum mechanical momentum for the classical. Here the vector potential remains classical, and only modulates the interaction strength.

$$\bar{p} = -i\hbar\bar{\nabla} \tag{4.29}$$

$$V\left(t\right) = \sum_i \frac{i\hbar}{2m_i} q_i\left(\bar{\nabla}_i\cdot\bar{A} + \bar{A}\cdot\bar{\nabla}_i\right) \tag{4.30}$$

We can show that $\bar{\nabla}\cdot\bar{A}=\bar{A}\cdot\bar{\nabla}$. Notice $\bar{\nabla}\cdot\bar{A}=\left(\bar{\nabla}\cdot\bar{A}\right)+\bar{A}\cdot\bar{\nabla}$ (chain rule). For instance if we are operating on a wavefunction $\bar{\nabla}\cdot\bar{A}\left|\psi\right\rangle=\left(\bar{\nabla}\cdot\bar{A}\right)\left|\psi\right\rangle+\bar{A}\cdot\left(\bar{\nabla}\left|\psi\right\rangle\right)$, but we are working in the Coulomb gauge $\left(\bar{\nabla}\cdot\bar{A}=0\right)$. Now we have:

$$\begin{aligned} V\left(t\right) &= \sum_i \frac{i\hbar q_i}{m_i}\,\bar{A}\cdot\bar{\nabla}_i \\ &= -\sum_i \frac{q_i}{m_i}\,\bar{A}\cdot\bar{p}_i \end{aligned} \tag{4.31}$$

For a single charge particle our interaction Hamiltonian is

$$\begin{aligned} V\left(t\right) &= -\frac{q}{m}\,\bar{A}\cdot\bar{p} \\ &= -\frac{q}{m}\left[A_0\hat{\varepsilon}\cdot\bar{p}\;e^{i\left(\bar{k}\cdot\bar{r}-\omega t\right)}+\text{c.c.}\right] \end{aligned} \tag{4.32}$$

Electric Dipole Approximation

Under most circumstances, we can neglect the wavevector dependence of the interaction potential. If the wavelength of the field is much larger than the molecular dimension $\left(\lambda\to\infty\right)\left(\left|k\right|\to 0\right)$, then $e^{i\bar{k}\cdot\bar{r}}\approx 1$.

We do retain the spatial dependence for certain types of light matter interactions. In that case we define r_0 as the center of mass of a molecule and expand

$$\begin{aligned} e^{i\bar{k}\cdot\bar{r}_i} &= e^{i\bar{k}\cdot\bar{r}_0}\,e^{i\bar{k}\cdot\left(\bar{r}_i-\bar{r}_0\right)} \\ &= e^{i\bar{k}\cdot\bar{r}_0}\left[1+i\bar{k}\cdot\left(\bar{r}_i-\bar{r}_0\right)+\ldots\right] \end{aligned} \tag{4.33}$$

For interactions, with UV, visible, and infrared (but not X-ray) radiation, $\left|k\right|\left|\bar{r}_i-\bar{r}_0\right|<<1$, and setting $\bar{r}_0=0$ means that $e^{i\bar{k}\cdot\bar{r}}\to 1$. We retain the second term for quadrupole transitions: charge distribution interacting with gradient of electric field and magnetic dipole.

4.2 Electric Dipole Hamiltonian

Now, using $A_0 = iE_0/2\omega$,

$$V(t) = \frac{-iqE_0}{2m\omega}\left[\hat{\varepsilon}\cdot\bar{p}\; e^{-i\omega t} - \hat{\varepsilon}\cdot\bar{p}\; e^{+i\omega t}\right] \tag{4.34}$$

$$\begin{aligned} V(t) &= \frac{-qE_0}{m\omega}\left(\hat{\varepsilon}\cdot\bar{p}\right)\sin\omega t \\ &= \frac{-q}{m\omega}\left(\bar{E}(t)\cdot\bar{p}\right) \end{aligned} \tag{4.35}$$

or for a collection of charged particles (molecules):

$$V(t) = -\left(\sum_i \frac{q_i}{m_i}\left(\hat{\varepsilon}\cdot\bar{p}_i\right)\right)\frac{E_0}{\omega}\sin\omega t \tag{4.36}$$

This is known as the electric dipole Hamiltonian (EDH).

Harmonic Perturbation: Matrix Elements

To better interpret this, let's evaluate the transition rates induced by $V(t)$. For a perturbation $V(t) = V_0 \sin\omega t$ the rate of transitions induced by field is

$$w_{k\ell} = \frac{\pi}{2\hbar}\left|V_{k\ell}\right|^2\left[\delta\left(E_k - E_\ell - \hbar\omega\right) + \delta\left(E_k - E_\ell + \hbar\omega\right)\right] \tag{4.37}$$

Let's look at the matrix elements for the EDH.

$$V_{k\ell} = \left\langle k\left|V_0\right|\ell\right\rangle = \frac{-qE_0}{m\omega}\left\langle k\left|\hat{\varepsilon}\cdot\bar{p}\right|\ell\right\rangle \tag{4.38}$$

We can evaluate the matrix element $\left\langle k\left|\bar{p}\right|\ell\right\rangle$ using

$$\left[\bar{r}, H_0\right] = \frac{i\hbar\bar{p}}{m} \tag{4.39}$$

which gives

$$\begin{aligned}\left\langle k\left|\bar{p}\right|\ell\right\rangle &= \frac{m}{i\hbar}\left\langle k\left|\bar{r}\,H_0 - H_0\,\bar{r}\right|\ell\right\rangle \\ &= \frac{m}{i\hbar}\left(\left\langle k\left|\bar{r}\right|\ell\right\rangle E_\ell - E_k\left\langle k\left|\bar{r}\right|\ell\right\rangle\right) \\ &= im\omega_{\ell k}\left\langle k\left|\bar{r}\right|\ell\right\rangle\end{aligned} \tag{4.40}$$

So we have

$$V_{k\ell} = -iqE_0\frac{\omega_{\ell k}}{\omega}\left\langle k\left|\hat{\varepsilon}\cdot\bar{r}\right|\ell\right\rangle \tag{4.41}$$

or for a collection of particles

$$\begin{aligned}V_{k\ell} &= -iE_0\frac{\omega_{\ell k}}{\omega}\left\langle k\left|\hat{\varepsilon}\cdot\left(\sum_i q_i\bar{r}_i\right)\right|\ell\right\rangle \\ &= -iE_0\frac{\omega_{\ell k}}{\omega}\left\langle k\left|\hat{\varepsilon}\cdot\bar{\mu}\right|\ell\right\rangle \\ &= -iE_0\frac{\omega_{\ell k}}{\omega}\bar{\mu}_{kl}\end{aligned} \tag{4.42}$$

$\bar{\mu}$ is the dipole operator. The dipole moment can be expressed more generally as the distribution of charge in the molecule:

$$\bar{\mu} = \int d\bar{r}\;\bar{r}\;\rho\left(\bar{r}\right) \tag{4.43}$$

So
$$V\left(t\right) = -\bar{\mu}\cdot\bar{E}(t) \tag{4.44}$$

Then the rate of transitions between quantum states induced by the electric field is

$$\begin{aligned}w_{k\ell} &= \frac{\pi}{2\hbar}\left|E_0\right|^2\frac{\omega_{k\ell}^2}{\omega^2}\left|\bar{\mu}_{kl}\right|^2\left[\delta\left(E_k - E_\ell - \hbar\omega\right) + \left(E_k - E_\ell + \hbar\omega\right)\right] \\ &= \frac{\pi}{2\hbar^2}\left|E_0\right|^2\left|\bar{\mu}_{kl}\right|^2\left[\delta\left(\omega_{k\ell} - \omega\right) + \delta\left(\omega_{k\ell} + \omega\right)\right]\end{aligned} \tag{4.45}$$

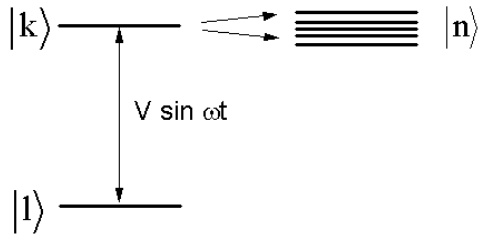
<u>This is an expression for the absorption spectrum</u> since the rate of transitions can be related to the power absorbed from the field. More generally we would express the absorption spectrum in terms of a sum over all initial and final states, the eigenstates of H_0:

$$w_{fi} = \sum_{i,f}\frac{\pi}{\hbar^2}\left|E_0\right|^2\left|\mu_{fi}\right|^2\left[\delta\left(\omega_{fi} - \omega\right) + \delta\left(\omega_{fi} + \omega\right)\right] \tag{4.46}$$

The strength of interaction between light and matter is given by the matrix element $\mu_{fi} \equiv \left\langle f \left| \bar{\mu} \cdot \hat{\varepsilon} \right| i \right\rangle$. The scalar part $\left\langle f \left| \mu \right| i \right\rangle$ says that you need a change of charge distribution between $\left| f \right\rangle$ and $\left| i \right\rangle$ to get effective absorption. This matrix element is the basis of selection rules based on the symmetry of the states. The vector part says that the light field must project onto the dipole moment. This allows information to be obtained on the orientation of molecules, and forms the basis of rotational transitions.

Relaxation Leads to Line-broadening

Let's combine the results from the last two lectures, and describe absorption to a state that is coupled to a continuum. What happens to the probability of absorption if the excited state decays exponentially?



$|k\rangle$ relaxes exponentially

... for instance by coupling to continuum

$P \propto \exp[-\bar{w}\ t]$

We can start with the first-order expression:

$$b_k = \frac{-i}{\hbar}\int_{t_0}^{t} d\tau \left\langle k\middle|V\middle|t\right\rangle \tag{4.47}$$

or equivalently

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell}t}\, V_{k\ell}(t) \tag{4.48}$$

We can add irreversible relaxation to the description of b_k, following our early approach:

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell}t}\, V_{k\ell}(t) - \frac{\bar{w}_{nk}}{2} b_k \tag{4.49}$$

Or using $V(t) = -iE_0\bar{\mu}_{k\ell}\sin\omega t$

$$\begin{aligned}\frac{\partial}{\partial t} b_k &= \frac{-i}{\hbar} e^{i\omega_{k\ell}t}\sin\omega t\, V_{k\ell} - \frac{\bar{w}_{nk}}{2} b_k(t) \\ &= \frac{E_0\,\omega_{k\ell}}{2i\hbar\omega}\left[e^{i(\omega_{k\ell}+\omega)} - e^{i(\omega_{k\ell}-\omega)t}\right]\bar{\mu}_{k\ell} - \frac{\bar{w}_{nk}}{2} b_k(t)\end{aligned} \tag{4.50}$$

The solution to the differential equation

$$\dot{y} + ay = be^{i\alpha t} \tag{4.51}$$

is

$$y(t) = Ae^{-at} + \frac{be^{i\alpha t}}{a + i\alpha}. \tag{4.52}$$

$$b_k(t) = Ae^{-\bar{w}_{nk}t/2} + \frac{E_0\bar{\mu}_{k\ell}}{2i\hbar}\left[\frac{e^{i(\omega_{k\ell}+\omega)t}}{\bar{w}_{nk}/2 + i(\omega_{k\ell}+\omega)} - \frac{e^{i(\omega_{k\ell}-\omega)t}}{\bar{w}_{nk}/2 + i(\omega_{k\ell}-\omega)}\right] \tag{4.53}$$

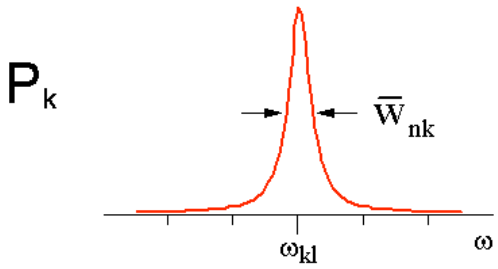
Let's look at absorption only, in the long time limit:

$$b_k(t) = \frac{E_0\bar{\mu}_{k\ell}}{2\hbar}\left[\frac{e^{i(\omega_{k\ell}-\omega)t}}{\omega_{k\ell} - \omega - i\bar{w}_{nk}/2}\right] \tag{4.54}$$

For which the probability of transition to k is

$$P_k = |b_k|^2 = \frac{E_0^2|\mu_{k\ell}|^2}{4\hbar^2}\frac{1}{(\omega_{k\ell}-\omega)^2 + \bar{w}_{nk}^{\,2}/4} \tag{4.55}$$

The frequency dependence of the transition probability has a Lorentzian form:



The linewidth is related to the relaxation rate from k into the continuum n. Also the linewidth is related to the system rather than the manner in which we introduced the perturbation.

Appendix: Review of Free Electromagnetic Field

Maxwell's Equations (SI):

(1) $\bar{\nabla}\cdot\bar{B} = 0$

(2) $\bar{\nabla}\cdot\bar{E} = \rho/\epsilon_0$

(3) $$\overline{\nabla} \times \overline{E} = -\frac{\partial \overline{B}}{\partial t}$$

(4) $$\overline{\nabla} \times \overline{B} = \mu_0 \overline{J} + \in_0 \mu_0 \frac{\partial \overline{E}}{\partial t}$$

$\overline{E}$: electric field; $\overline{B}$: magnetic field; $\overline{J}$: current density; ρ: charge density; $\in_0$: electrical permittivity; μ_0: magnetic permittivity

We are interested in describing $\overline{E}$ and $\overline{B}$ in terms of a scalar and vector potential. This is required for our interaction Hamiltonian.

Generally: A vector field $\overline{F}$ assigns a vector to each point in space. The divergence of the field

(5) $$\overline{\nabla} \cdot \overline{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}$$

is a scalar. For a scalar field ϕ, the gradient

(6) $$\nabla \phi = \frac{\partial \phi}{\partial x}\hat{x} + \frac{\partial \phi}{\partial y}\hat{y} + \frac{\partial \phi}{\partial z}\hat{z}$$

is a vector for the rate of change at on point in space. Here $\hat{x}^2 + \hat{y}^2 + \hat{z}^2 = \hat{r}^2$ are unit vectors.

Also, the curl

(7) $$\overline{\nabla} \times \overline{F} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix}$$

is a vector whose *x*, *y*, and *z* components are the circulation of the field about that component.

Some useful identities from vector calculus are:

(8) $\bar{\nabla}\cdot\left(\bar{\nabla}\times\bar{F}\right)=0$

(9) $\nabla\times\left(\nabla\phi\right)=0$

(10) $\nabla\times\left(\bar{\nabla}\times\bar{F}\right)=\bar{\nabla}\left(\bar{\nabla}\cdot\bar{F}\right)-\bar{\nabla}^2\bar{F}$

We now introduce a vector potential $\bar{A}(\bar{r},t)$ and a scalar potential $\varphi(\bar{r},t)$, which we will relate to $\bar{E}$ and $\bar{B}$

Since $\bar{\nabla}\cdot\bar{B}=0$ and $\bar{\nabla}\left(\bar{\nabla}\times\bar{A}\right)=0$:

(11) $\bar{B}=\bar{\nabla}\times\bar{A}$

Using (3), we have:

$$\bar{\nabla}\times\bar{E}=-\bar{\nabla}\times\frac{\partial\bar{A}}{\partial t}$$

or

(12) $$\bar{\nabla}\times\left[\bar{E}+\frac{\partial\bar{A}}{\partial t}\right]=0$$

From (9), we see that a scalar product exists with:

(13) $$\bar{E}+\frac{\partial\bar{A}}{\partial t}=-\bar{\nabla}\varphi(\bar{r},t)$$

convention

or

(14) $$\bar{E}=\frac{\partial\bar{A}}{\partial t}-\nabla\varphi$$

So we see that the potentials $\bar{A}$ and φ determine the fields $\bar{B}$ and $\bar{E}$:

(15) $\bar{B}(\bar{r},t)=\bar{\nabla}\times\bar{A}(\bar{r},t)$

(16) $$\bar{E}(\bar{r},t)=-\bar{\nabla}\varphi(\bar{r},t)-\frac{\partial}{\partial t}\bar{A}(\bar{r},t)$$

We are interested in determining the wave equation for $\bar{A}$ and φ. Using (15) and differentiating (16) and substituting into (4):

(17) $$\bar{\nabla}\times\left(\bar{\nabla}\times\bar{A}\right)+\in_0\mu_0\left(\frac{\partial^2\bar{A}}{\partial t^2}+\bar{\nabla}\frac{\partial\varphi}{\partial t}\right)=\mu_0\bar{J}$$

Using (10):

(18) $$\left[-\bar{\nabla}^2\bar{A}+\in_0\mu_0\frac{\partial^2\bar{A}}{\partial t^2}\right]+\bar{\nabla}\left(\bar{\nabla}\cdot\bar{A}+\in_0\mu_0\frac{\partial\varphi}{\partial t}\right)=\bar{\mu}_0\bar{J}$$

From (14), we have:

$$\bar{\nabla}\cdot\bar{E}=-\frac{\partial\bar{\nabla}\cdot\bar{A}}{\partial t}-\bar{\nabla}^2\varphi$$

and using (2):

(19) $$\frac{-\partial\bar{V}\cdot\bar{A}}{\partial t}-\bar{\nabla}^2\varphi=\rho/\in_0$$

Notice from (15) and (16) that we only need to specify <u>four</u> field components (A_x, A_y, A_z, φ) to determine all <u>six</u> $\bar{E}$ and $\bar{B}$ components. But $\bar{E}$ and $\bar{B}$ do not uniquely determine $\bar{A}$ and φ. So, we can construct $\bar{A}$ and φ in any number of ways without changing $\bar{E}$ and $\bar{B}$. Notice that if we change $\bar{A}$ by adding $\bar{\nabla}\chi$ where χ is any function of $\bar{r}$ and t, this won't change $\bar{B}$ $\left(\nabla\times\left(\nabla\cdot B\right)=0\right)$. It will change E by $\left(-\frac{\partial}{\partial t}\bar{\nabla}\chi\right)$, but we can change φ to $\varphi'=\varphi-\frac{\partial\chi}{\partial t}$. Then $\bar{E}$ and $\bar{B}$ will both be unchanged. This property of changing representation (gauge) without changing $\bar{E}$ and $\bar{B}$ is gauge invariance. We can transform between gauges with:

(20) $$\bar{A}'\left(\bar{r},t\right)=\bar{A}\left(\bar{r},t\right)+\bar{\nabla}\cdot\chi\left(\bar{r},t\right)$$

<u>gauge transformation</u>

(21) $$\varphi'\left(\bar{r},t\right)=\varphi\left(\bar{r},t\right)-\frac{\partial}{\partial t}\chi\left(\bar{r},t\right)$$

Up to this point, A' and Q are undetermined. Let's choose a χ such that:

(22) $\overline{\nabla} \cdot \overline{A} + \epsilon_0 \mu_0 \frac{\partial \varphi}{\partial t} = 0$ Lorentz condition

then from (17):

(23) $-\nabla^2 \overline{A} + \epsilon_0 \mu_0 \frac{\partial^2 \overline{A}}{\partial t^2} = \mu_0 \overline{J}$

The RHS can be set to zero for no currents.

From (19), we have:

(24) $\epsilon_0 \mu_0 \frac{\partial^2 \varphi}{\partial t^2} - \nabla^2 \varphi = \frac{\rho}{\epsilon_0}$

Eqns. (23) and (24) are wave equations for $\overline{A}$ and φ. Within the Lorentz gauge, we can still arbitrarily add another χ (it must only satisfy 22). If we substitute (20) and (21) into (24), we see:

(25) $\nabla^2 \chi - \epsilon_0 \mu_0 \frac{\partial^2 \chi}{\partial t^2} = 0$

So we can make further choices/constraints on $\overline{A}$ and φ as long as it obeys (25).

For a field far from charges and currents, $J = 0$ and $\rho = 0$.

(26) $-\overline{\nabla}^2 \overline{A} + \epsilon_0 \mu_0 \frac{\partial^2 \overline{A}}{\partial t^2} = 0$

(27) $-\overline{\nabla}^2 \varphi + \epsilon_0 \mu_0 \frac{\partial^2 \varphi}{\partial t^2} = 0$

We now choose $\varphi = 0$ (Coulomb gauge), and from (22) we see:

(28) $\overline{\nabla} \cdot \overline{A} = 0$

So, the wave equation for our vector potential is:

(29) $-\overline{\nabla}^2 \overline{A} + \epsilon_0 \mu_0 \frac{\partial^2 \overline{A}}{\partial t^2} = 0$

The solutions to this equation are plane waves.

(30) $\bar{A} = \bar{A}_0 \sin\left(\omega t - \bar{k}\cdot\bar{r} + \alpha\right)$

α : phase

(31) $= \bar{A}_0 \cos\left(\omega t - \bar{k}\cdot\bar{r} + \alpha'\right)$

$\bar{k}$ is the wave vector which points along the direction of propagation and has a magnitude:

(32) $k^2 = \omega^2 \mu_0 \in_0 = \omega^2 / c^2$

Since (28) $\bar{\nabla}\cdot\bar{A} = 0$

$-\bar{k}\cdot\bar{A}_0 \cos\left(\omega t - \bar{k}\cdot\bar{r} + \alpha\right) = 0$

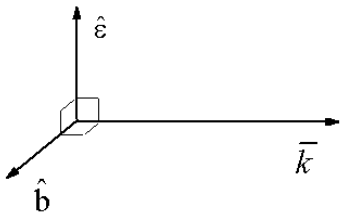
(33) $\therefore \quad \bar{k}\cdot\bar{A}_0 = 0 \qquad\qquad \bar{k} \perp \bar{A}_0$

A_0 is the direction of the potential → polarization. From (15) and (16), we see that for $\varphi = 0$:

$$\bar{E} = -\frac{\partial \bar{A}}{\partial t} = -\omega \bar{A}_0 \cos\left(\omega t - \bar{k}\cdot\bar{r} + \alpha\right)$$

$$\bar{B} = \bar{\nabla}\times\bar{A} = -\left(\bar{k}\times\bar{A}_0\right)\cos\left(\omega t - \bar{k}\cdot\bar{r} + \alpha\right)$$

$\therefore \quad \bar{k} \perp \bar{E} \perp \bar{B}$



4.4 Rate of Absorption and Stimulated Emission

The rate of absorption induced by the field is

$$w_{k\ell}(\omega)=\frac{\pi}{2\hbar^2}\left|E_0(\omega)\right|^2\left|\langle k|\hat{\epsilon}\cdot\bar{\mu}|\ell\rangle\right|^2\delta(\omega_{k\ell}-\omega) \tag{4.1}$$

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

$$\mathrm{S}=\frac{\mathrm{c}}{4\pi}\left(\bar{\mathrm{E}}\times\bar{\mathrm{B}}\right) \tag{4.2}$$

$$\mathrm{I}=\langle\mathrm{S}\rangle=\frac{\mathrm{c}}{4\pi}\langle\bar{\mathrm{E}}^2\rangle=\frac{\mathrm{c}}{8\pi}\mathrm{E}_0^2 \tag{4.3}$$

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

$$\mathrm{U}=\frac{\mathrm{I}}{\mathrm{c}}=\frac{1}{8\pi}\mathrm{E}_0^2 \qquad \text{(for a monochromatic field)} \tag{4.4}$$

Using this we can write

$$\mathrm{w}_{k\ell}=\frac{4\pi^2}{\hbar^2}\mathrm{U}(\omega)\left|\langle\mathrm{k}|\hat{\epsilon}\cdot\bar{\mu}|\ell\rangle\right|^2\delta(\omega_{k\ell}-\omega) \tag{4.5}$$

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

$$\mathrm{w}_{k\ell}=\frac{4\pi^2}{3\hbar^2}\mathrm{U}(\omega)\left|\bar{\mu}_{k\ell}\right|^2\delta(\omega_{k\ell}-\omega) \tag{4.6}$$

or more commonly

$$\mathrm{w}_{k\ell}=\mathrm{B}_{k\ell}\,\mathrm{U}(\omega_{k\ell}) \tag{4.7}$$

$$\mathrm{B}_{k\ell}=\frac{4\pi^2}{3\hbar^2}\left|\mu_{k\ell}\right|^2 \qquad \text{Einstein B coefficient} \tag{4.8}$$

(this is sometimes written as $B_{k\ell} = \left(2\pi/3\hbar^2\right)\left|\mu_{k\ell}\right|^2$ 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

$$N\hbar\omega = \frac{E_0^2}{8\pi} \qquad U = N\frac{\hbar\omega^3}{\pi^2 c^3} \tag{4.9}$$

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

$$\sigma_A = \frac{\text{total energy absorbed / unit time}}{\text{total incident intensity}\left(\text{energy / unit time / area}\right)}$$
$$= \frac{\hbar\omega \cdot w_{k\ell}}{I} = \frac{\hbar\omega \cdot B_{k\ell}\, U\left(\omega_{k\ell}\right)}{c\, U\left(\omega_{k\ell}\right)} \tag{4.10}$$

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

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 $|n\rangle$:

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

$$B_{nm}\, U(\omega_{nm}) = B_{nm}\, U(\omega_{nm}) \qquad since\ U(\omega_{nm}) = U(\omega_{mn}) \tag{4.11}$$

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

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

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.

$$\frac{dI}{I} = -N_n \sigma_A \, dx + N_m \sigma_{SE} \, dx \qquad (4.12) \qquad \text{——————} \; |m\rangle$$

$$\frac{dI}{I} = -(N_n - N_m)\sigma_a \, dx \qquad (4.13) \qquad \text{——————} \; |n\rangle$$

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,

$$N_n = N\left(\frac{e^{-\beta E_n}}{Z}\right) \qquad (4.14)$$

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

Integrating over a pathlength L:

$$\frac{I}{I_0} = e^{-\Delta N \sigma_a L} \qquad \textit{for high freq.} \;\; \Delta N \approx N \qquad (4.15)$$

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

or written as Beer's Law:

$$A = -log\frac{I}{I_0} = C \in L \qquad C : mol/liter \quad \in : liter/mol\,cm \qquad (4.16)$$

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

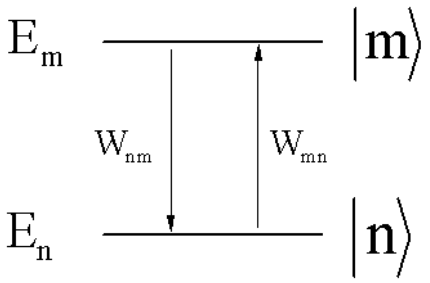
4.5 SPONTANEOUS EMISSION

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.

$$N_m / N_n = e^{-\hbar\omega_{mn}/kT} \tag{4.17}$$

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

$$N_m B_{nm} U(\omega_{mn}) \stackrel{?}{=} N_n B_{mn} U(\omega_{mn}) \tag{4.18}$$

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

$$\begin{gathered} \mathrm{W_{nm}} = \mathrm{W_{mn}} \\ \mathrm{N_m}\left(\mathrm{A_{nm}} + \mathrm{B_{nm}}\,\mathrm{U}(\omega_{mn})\right) = \mathrm{N_n}\,\mathrm{B_{mn}}\,\mathrm{U}(\omega_{mn}) \end{gathered} \tag{4.19}$$

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

$$A_{nm} = B_{nm}\, U(\omega_{mn})\left(e^{\hbar\omega_{mn}/kT} - 1\right) \tag{4.20}$$

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

$$\mathrm{U}(\omega) = \underbrace{\frac{\hbar\omega^3}{\pi^2 c^3}}_{\mathrm{U}_\omega} \underbrace{\frac{1}{e^{\hbar\omega_{mn}/\mathrm{kT}} - 1}}_{\langle \mathrm{N}_\omega \rangle} \tag{4.21}$$

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.

$$\therefore \quad \mathrm{A}_{nm} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{nm} \qquad \text{Einstein A coefficient} \tag{4.22}$$

The total rate of emission from the excited state is

$$\mathrm{w}_{nm} = \mathrm{B}_{nm}\,\mathrm{U}(\omega_{nm}) + \mathrm{A}_{nm} \qquad \text{using } \mathrm{U}(\omega_{nm}) = \mathrm{N}\frac{\hbar\omega^3}{\pi^2 \mathrm{C}^3} \tag{4.23}$$

$$= \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{nm}(\mathrm{N}+1) \tag{4.24}$$

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

$$\mathrm{w}_{nm} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{nm}(\mathrm{N}) \tag{4.25}$$

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

$$\mathrm{w}_{mn} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{mn}\mathrm{N} \tag{4.26}$$

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

$$\tau_{\mathrm{rad}} = \frac{1}{\mathrm{A}} \tag{4.27}$$

4.6 Quantized Radiation Field

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

$$f(\omega) = \frac{1}{e^{\hbar\omega/kT} - 1} \tag{4.1}$$

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),

$$g(\omega) = \frac{\omega^2}{\pi^2 c^3} \tag{4.2}$$

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

$$\hbar\omega\, g(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \tag{4.3}$$

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

$$u(\omega) = \hbar\omega\, g(\omega) f(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1} \tag{4.4}$$

4.6 The Quantum Vector Potential

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:

$$\left|\varphi_{EM}\right\rangle = \left|N_{\bar{k}_1,j_1}, N_{\bar{k}_2,j_2}, N_{\bar{k}_3,j_3}, \ldots\right\rangle \tag{4.5}$$

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

$$\left|\varphi'_{EM}\right\rangle = \left|N_{\bar{k}_1,j}, N_{\bar{k}_2,j_2} - 1, N_{\bar{k}_3,j}, \ldots\right\rangle \tag{4.6}$$

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:

$$H_0 = H_{EM} + H_M \tag{4.7}$$

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:

$$\left|\varphi\right\rangle = \left|\varphi_{EM}\right\rangle\left|\varphi_M\right\rangle \tag{4.8}$$

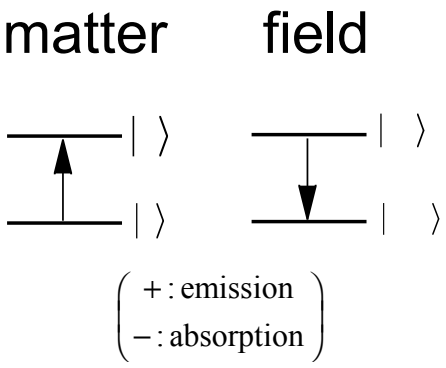
And we have eigenenergies

$$E = E_{EM} + E_M \tag{4.9}$$

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:

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

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



(4.10), (4.11)

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

$$E_I = E_\ell + \sum_j N_j(\hbar\omega_j) \qquad \omega_j = ck_j \qquad (4.12)$$

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

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

$$w_{k\ell} = \frac{2\pi}{\hbar}\delta(E_k - E_\ell - \hbar\omega)\left|\langle\varphi_F|V(t)|\varphi_I\rangle\right|^2 \qquad (4.13)$$

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

$$w_{k\ell} = \frac{2\pi}{v\,\hbar^2}\sum_{\bar{k}j}\delta(\omega_{k\ell} - \omega)\frac{q^2}{m^2}\left|A_{\bar{k},j}\right|^2\left|\langle k|\hat{\epsilon}_j\cdot\bar{p}|\ell\rangle\right|^2 \qquad (4.14)$$

If these are to be the same, then clearly $V(t)$ must have part that looks like $(\hat{\epsilon}\cdot\bar{p})$ 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:

$$V(t)=\frac{-q}{m}\frac{1}{\sqrt{v}}\sum_{\bar{k},j}\left(\bar{p}_k\cdot\hat{\epsilon}_j\,\hat{A}_{\bar{k},j}+\bar{p}_k^{\dagger}\cdot\hat{\epsilon}_j^{*}\,\hat{A}_{\bar{k},j}^{\dagger}\right) \tag{4.15}$$

where $\hat{A}_{\bar{k},j}$ and $\hat{A}_{\bar{k},j}^{\dagger}$ 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

$$\begin{aligned}\left\langle\varphi_F\left|V(t)\right|\varphi_I\right\rangle &= -\frac{q}{m}\frac{1}{\sqrt{v}}\left\langle k\left|\bar{p}_k\cdot\hat{\epsilon}\right|\ell\right\rangle\left\langle\ldots,N_i-1,\ldots\left|\hat{A}_i\right|\ldots,N_i,\ldots\right\rangle \\ &= \frac{1}{\sqrt{v}}\omega_{k\ell}\left\langle k\left|\hat{\epsilon}\cdot\bar{\mu}\right|\ell\right\rangle\left\langle A_i^{(-)}\right\rangle\end{aligned} \tag{4.16}$$

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

$$w_{k\ell}=\frac{\pi}{2\hbar^2}\delta(\omega_{k\ell}-\omega)\frac{\omega_{k\ell}^2}{\omega^2}E_0^2\left|\mu_{k\ell}\right|^2 \tag{4.17}$$

We see that the matrix element

$$\begin{aligned}\left\langle A_i^{(-)}\right\rangle &= \sqrt{\frac{E_0^2}{4v\omega^2}} \qquad \text{but } \frac{E_0^2}{8\pi}=N\hbar\omega \\ &= \sqrt{\frac{2\pi\hbar}{v\omega}}\sqrt{N}\end{aligned} \tag{4.18}$$

So we can write

$$\begin{aligned}\hat{A}_{\bar{k},j} &= \sqrt{\frac{2\pi\hbar}{v\,\omega}}\,a_{\bar{k},j} \\ \hat{A}_{k,j}^{\dagger} &= \sqrt{\frac{2\pi\hbar}{v\,\omega}}\,a_{\bar{k},j}^{\dagger}\end{aligned} \tag{4.19}$$

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

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

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:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

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

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

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

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

So we have the result we deduced before.

Appendix: Rates of Absorption and Stimulated Emission

Here are a couple of more detailed derivations:

Version 1:

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:

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

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

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

and we get ρ_E by integrating over all Ω

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

number density at ω

We can now write the <u>total</u> 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 $d\omega$ $\times$ # of polarization components $\times$ 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.

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

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

The vector potential for a single mode is

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

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

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

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:

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

or for a collection of particles

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

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:

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

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: $d\Omega = \sin\theta\, d\theta\, d\phi$

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

can be written as $\bar{k}$

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

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

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

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

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

For the field

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

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

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

For a broadband source, the energy density of the light

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

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

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 $g(\omega)$

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

4.3 Appendix: Review of Free Electromagnetic Field

Maxwell's Equations (SI):

(1) $\bar{\nabla} \cdot \bar{B} = 0$

(2) $\bar{\nabla} \cdot \bar{E} = \rho / \in_0$

(3) $\bar{\nabla} \times \bar{E} = -\frac{\partial \bar{B}}{\partial t}$

(4) $\bar{\nabla} \times \bar{B} = \mu_0 \bar{J} + \in_0 \mu_0 \frac{\partial \bar{E}}{\partial t}$

$\bar{E}$: electric field; $\bar{B}$: magnetic field; $\bar{J}$: current density; ρ: charge density; $\in_0$: electrical permittivity; μ_0: magnetic permittivity

We are interested in describing $\bar{E}$ and $\bar{B}$ in terms of a scalar and vector potential. This is required for our interaction Hamiltonian.

Generally: A vector field $\bar{F}$ assigns a vector to each point in space. The divergence of the field

(5) $\bar{\nabla} \cdot \bar{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}$

is a scalar. For a scalar field ϕ, the gradient

(6) $\nabla \phi = \frac{\partial \phi}{\partial x} \hat{x} + \frac{\partial \phi}{\partial y} \hat{y} + \frac{\partial \phi}{\partial z} \hat{z}$

is a vector for the rate of change at on point in space. Here $\hat{x}^2 + \hat{y}^2 + \hat{z}^2 = \hat{r}^2$ are unit vectors.

Also, the curl

(7) $$\bar{\nabla}\times\bar{F}=\begin{vmatrix}\hat{x} & \hat{y} & \hat{z}\\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z}\\ F_x & F_y & F_z\end{vmatrix}$$

is a vector whose x, y, and z components are the circulation of the field about that component.

Some useful identities from vector calculus are:

(8) $$\bar{\nabla}\cdot\left(\bar{\nabla}\times\bar{F}\right)=0$$

(9) $$\nabla\times\left(\nabla\phi\right)=0$$

(10) $$\nabla\times\left(\bar{\nabla}\times\bar{F}\right)=\bar{\nabla}\left(\bar{\nabla}\cdot\bar{F}\right)-\bar{\nabla}^2\bar{F}$$

We now introduce a vector potential $\bar{A}(\bar{r},t)$ and a scalar potential $\varphi(\bar{r},t)$, which we will relate to $\bar{E}$ and $\bar{B}$

Since $\bar{\nabla}\cdot\bar{B}=0$ and $\bar{\nabla}\left(\bar{\nabla}\times\bar{A}\right)=0$:

(11) $$\bar{B}=\bar{\nabla}\times\bar{A}$$

Using (3), we have:

$$\bar{\nabla}\times\bar{E}=-\bar{\nabla}\times\frac{\partial\bar{A}}{\partial t}$$

or

(12) $$\bar{\nabla}\times\left[\bar{E}+\frac{\partial\bar{A}}{\partial t}\right]=0$$

From (9), we see that a scalar product exists with:

(13) $$\bar{E}+\frac{\partial\bar{A}}{\partial t}=-\bar{\nabla}\varphi(\bar{r},t)$$

convention

or

(14) $$\bar{E} = \frac{\partial \bar{A}}{\partial t} - \nabla\varphi$$

So we see that the potentials $\bar{A}$ and φ determine the fields $\bar{B}$ and $\bar{E}$:

(15) $$\bar{B}(\bar{r},t) = \bar{\nabla} \times \bar{A}(\bar{r},t)$$

(16) $$\bar{E}(\bar{r},t) = -\bar{\nabla}\varphi(\bar{r},t) - \frac{\partial}{\partial t}\bar{A}(\bar{r},t)$$

We are interested in determining the wave equation for $\bar{A}$ and φ. Using (15) and differentiating (16) and substituting into (4):

(17) $$\bar{\nabla} \times \left(\bar{\nabla} \times \bar{A}\right) + \in_0 \mu_0 \left(\frac{\partial^2 \bar{A}}{\partial t^2} + \bar{\nabla}\frac{\partial \varphi}{\partial t} \right) = \mu_0 \bar{J}$$

Using (10):

(18) $$\left[-\bar{\nabla}^2 \bar{A} + \in_0 \mu_0 \frac{\partial^2 \bar{A}}{\partial t^2} \right] + \bar{\nabla}\left(\bar{\nabla} \cdot \bar{A} + \in_0 \mu_0 \frac{\partial \varphi}{\partial t} \right) = \bar{\mu}_0 \bar{J}$$

From (14), we have:

$$\bar{\nabla} \cdot \bar{E} = -\frac{\partial \bar{\nabla} \cdot \bar{A}}{\partial t} - \bar{\nabla}^2\varphi$$

and using (2):

(19) $$\frac{-\partial \bar{V} \cdot \bar{A}}{\partial t} - \bar{\nabla}^2\varphi = \rho / \in_0$$

Notice from (15) and (16) that we only need to specify <u>four</u> field components (A_x, A_y, A_z, φ) to determine all <u>six</u> $\bar{E}$ and $\bar{B}$ components. But $\bar{E}$ and $\bar{B}$ do not uniquely determine $\bar{A}$ and φ. So, we can construct $\bar{A}$ and φ in any number of ways without changing $\bar{E}$ and $\bar{B}$. Notice that if we change $\bar{A}$ by adding $\bar{\nabla}\chi$ where χ is any function of $\bar{r}$ and t, this won't change $\bar{B}$ $\left(\nabla \times (\nabla \cdot B) = 0\right)$. It will change E by $\left(-\frac{\partial}{\partial t}\bar{\nabla}\chi\right)$, but we can change φ to $\varphi' = \varphi - \frac{\partial \chi}{\partial t}$. Then $\bar{E}$ and $\bar{B}$ will both be unchanged. This property of

changing representation (gauge) without changing $\bar{E}$ and $\bar{B}$ is gauge invariance. We can transform between gauges with:

(20) $$\bar{A}'(\bar{r},t) = \bar{A}(\bar{r},t) + \bar{\nabla}\cdot\chi(\bar{r},t)$$

(21) $$\varphi'(\bar{r},t) = \varphi(\bar{r},t) - \frac{\partial}{\partial t}\chi(\bar{r},t)$$

gauge transformation

Up to this point, A' and Q are undetermined. Let's choose a χ such that:

(22) $$\bar{\nabla}\cdot\bar{A} + \in_0 \mu_0 \frac{\partial \varphi}{\partial t} = 0$$

Lorentz condition

then from (17):

(23) $$-\nabla^2\bar{A} + \in_0 \mu_0 \frac{\partial^2 \bar{A}}{\partial t^2} = \mu_0 \bar{J}$$

The RHS can be set to zero for no currents.

From (19), we have:

(24) $$\in_0 \mu_0 \frac{\partial^2 \varphi}{\partial t^2} - \nabla^2\varphi = \frac{\rho}{\in_0}$$

Eqns. (23) and (24) are wave equations for $\bar{A}$ and φ. Within the Lorentz gauge, we can still arbitrarily add another χ (it must only satisfy 22). If we substitute (20) and (21) into (24), we see:

(25) $$\nabla^2\chi - \in_0 \mu_0 \frac{\partial^2 \chi}{\partial t^2} = 0$$

So we can make further choices/constraints on $\bar{A}$ and φ as long as it obeys (25).

For a field far from charges and currents, $J = 0$ and $\rho = 0$.

(26) $$-\bar{\nabla}^2\bar{A} + \in_0 \mu_0 \frac{\partial^2 \bar{A}}{\partial t^2} = 0$$

(27) $$-\bar{\nabla}^2\varphi+\epsilon_0\,\mu_0\frac{\partial^2\varphi}{\partial t^2}=0$$

We now choose $\varphi=0$ (Coulomb gauge), and from (22) we see:

(28) $$\bar{\nabla}\cdot\bar{A}=0$$

So, the wave equation for our vector potential is:

(29) $$-\bar{\nabla}^2\bar{A}+\epsilon_0\,\mu_0\frac{\partial^2\bar{A}}{\partial t^2}=0$$

The solutions to this equation are plane waves.

(30) $$\bar{A}=\bar{A}_0\sin\left(\omega t-\bar{k}\cdot\bar{r}+\alpha\right)$$

α : phase

(31) $$=\bar{A}_0\cos\left(\omega t-\bar{k}\cdot\bar{r}+\alpha'\right)$$

$\bar{k}$ is the wave vector which points along the direction of propagation and has a magnitude:

(32) $$k^2=\omega^2\mu_0\epsilon_0=\omega^2/c^2$$

Since (28) $\bar{\nabla}\cdot\bar{A}=0$

$$-\bar{k}\cdot\bar{A}_0\cos\left(\omega t-\bar{k}\cdot\bar{r}+\alpha\right)=0$$

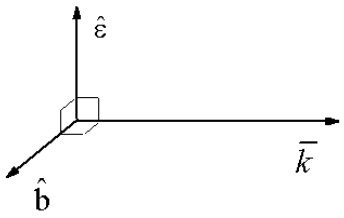
(33) $$\therefore\quad \bar{k}\cdot\bar{A}_0=0 \qquad\qquad \bar{k}\perp\bar{A}_0$$

A_0 is the direction of the potential → polarization. From (15) and (16), we see that for $\varphi=0$:

$$\bar{E}=-\frac{\partial\bar{A}}{\partial t}=-\omega\bar{A}_0\cos\left(\omega t-\bar{k}\cdot\bar{r}+\alpha\right)$$

$$\bar{B}=\bar{\nabla}\times\bar{A}=-\left(\bar{k}\times\bar{A}_0\right)\cos\left(\omega t-\bar{k}\cdot\bar{r}+\alpha\right)$$

$$\therefore\quad \bar{k}\perp\bar{E}\perp\bar{B}$$



Rate of Absorption and Stimulated Emission

The rate of absorption induced by the field is

$$w_{k\ell}(\omega) = \frac{\pi}{2\hbar^2}\left|E_0(\omega)\right|^2 \left|\langle k|\hat{\epsilon}\cdot\bar{\mu}|\ell\rangle\right|^2 \delta(\omega_{k\ell}-\omega) \tag{4.1}$$

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

$$\mathrm{S} = \frac{\mathrm{c}}{4\pi}\left(\bar{\mathrm{E}}\times\bar{\mathrm{B}}\right) \tag{4.2}$$

$$\mathrm{I} = \langle \mathrm{S}\rangle = \frac{\mathrm{c}}{4\pi}\left\langle \bar{\mathrm{E}}^2\right\rangle = \frac{\mathrm{c}}{8\pi}\mathrm{E}_0^2 \tag{4.3}$$

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

$$\mathrm{U} = \frac{\mathrm{I}}{\mathrm{c}} = \frac{1}{8\pi}\mathrm{E}_0^2 \qquad \text{(for a monochromatic field)} \tag{4.4}$$

Using this we can write

$$\mathrm{w}_{k\ell} = \frac{4\pi^2}{\hbar^2}\mathrm{U}(\omega)\left|\langle \mathrm{k}|\hat{\epsilon}\cdot\bar{\mu}|\ell\rangle\right|^2 \delta(\omega_{k\ell}-\omega) \tag{4.5}$$

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

$$\mathrm{w}_{k\ell} = \frac{4\pi^2}{3\hbar^2}\mathrm{U}(\omega)\left|\bar{\mu}_{k\ell}\right|^2 \delta(\omega_{k\ell}-\omega) \tag{4.6}$$

or more commonly

$$\mathrm{w}_{k\ell} = \mathrm{B}_{k\ell}\,\mathrm{U}(\omega_{k\ell}) \tag{4.7}$$

$$\mathrm{B}_{k\ell} = \frac{4\pi^2}{3\hbar^2}\left|\mu_{k\ell}\right|^2 \qquad \text{Einstein B coefficient} \tag{4.8}$$

(this is sometimes written as $\mathrm{B}_{k\ell} = \left(2\pi/3\hbar^2\right)\left|\mu_{k\ell}\right|^2$ 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

$$N\hbar\omega = \frac{E_0^2}{8\pi} \qquad U = N\frac{\hbar\omega^3}{\pi^2 c^3} \tag{4.9}$$

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

$$\sigma_A = \frac{\text{total energy absorbed / unit time}}{\text{total incident intensity } (\text{energy / unit time / area})}$$
$$= \frac{\hbar\omega \cdot w_{k\ell}}{I} = \frac{\hbar\omega \cdot B_{k\ell}\, U(\omega_{k\ell})}{c\, U(\omega_{k\ell})} \tag{4.10}$$

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

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 $|n\rangle$:

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

$$B_{nm}\, U(\omega_{nm}) = B_{nm}\, U(\omega_{nm}) \qquad since\ U(\omega_{nm}) = U(\omega_{mn}) \tag{4.11}$$

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

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

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.

$$\frac{dI}{I} = -N_n \sigma_A \, dx + N_m \sigma_{SE} \, dx \qquad (4.12) \qquad \text{——————} \; |m\rangle$$

$$\frac{dI}{I} = -(N_n - N_m)\sigma_a \, dx \qquad (4.13) \qquad \text{——————} \; |n\rangle$$

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,

$$N_n = N\left(\frac{e^{-\beta E_n}}{Z}\right) \qquad (4.14)$$

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

Integrating over a pathlength L:

$$\frac{I}{I_0} = e^{-\Delta N \sigma_a L} \qquad \textit{for high freq.} \;\; \Delta N \approx N \qquad (4.15)$$

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

or written as Beer's Law:

$$A = -log\frac{I}{I_0} = C \in L \qquad C : mol/liter \quad \in : liter/mol\,cm \qquad (4.16)$$

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

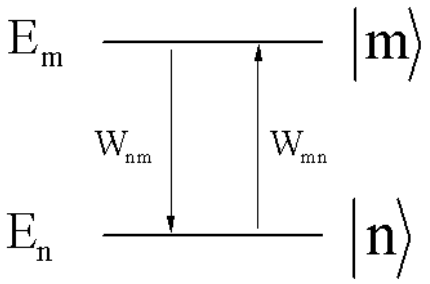
SPONTANEOUS EMISSION

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.

$$N_m / N_n = e^{-\hbar\omega_{mn}/kT} \tag{4.17}$$

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

$$N_m B_{nm} U(\omega_{mn}) \stackrel{?}{=} N_n B_{mn} U(\omega_{mn}) \tag{4.18}$$

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

$$\mathrm{W_{nm}} = \mathrm{W_{mn}}$$

$$\mathrm{N_m}\left(\mathrm{A_{nm}} + \mathrm{B_{nm}}\,\mathrm{U}(\omega_{mn})\right) = \mathrm{N_n}\,\mathrm{B_{mn}}\,\mathrm{U}(\omega_{mn}) \tag{4.19}$$

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

$$A_{nm} = B_{nm}\, U(\omega_{mn})\left(e^{\hbar\omega_{mn}/kT} - 1\right) \tag{4.20}$$

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

$$\mathrm{U}(\omega) = \underbrace{\frac{\hbar\omega^3}{\pi^2 c^3}}_{\mathrm{U}_\omega} \underbrace{\frac{1}{e^{\hbar\omega_{mn}/\mathrm{kT}} - 1}}_{\langle \mathrm{N}_\omega \rangle} \tag{4.21}$$

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.

$$\therefore \quad \mathrm{A}_{nm} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{nm} \qquad \text{Einstein A coefficient} \tag{4.22}$$

The total rate of emission from the excited state is

$$\mathrm{w}_{nm} = \mathrm{B}_{nm}\,\mathrm{U}(\omega_{nm}) + \mathrm{A}_{nm} \qquad \text{using } \mathrm{U}(\omega_{nm}) = \mathrm{N}\frac{\hbar\omega^3}{\pi^2 \mathrm{C}^3} \tag{4.23}$$

$$= \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{nm}(\mathrm{N}+1) \tag{4.24}$$

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

$$\mathrm{w}_{nm} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{nm}(\mathrm{N}) \tag{4.25}$$

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

$$\mathrm{w}_{mn} = \frac{\hbar\omega^3}{\pi^2 c^3}\mathrm{B}_{mn}\mathrm{N} \tag{4.26}$$

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

$$\tau_{\mathrm{rad}} = \frac{1}{\mathrm{A}} \tag{4.27}$$

Quantized Radiation Field

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

$$f(\omega) = \frac{1}{e^{\hbar\omega/kT} - 1} \tag{4.1}$$

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),

$$g(\omega) = \frac{\omega^2}{\pi^2 c^3} \tag{4.2}$$

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

$$\hbar\omega\, g(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \tag{4.3}$$

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

$$u(\omega) = \hbar\omega\, g(\omega) f(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1} \tag{4.4}$$

The Quantum Vector Potential

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:

$$\left|\varphi_{EM}\right\rangle = \left|N_{\bar{k}_1,j_1}, N_{\bar{k}_2,j_2}, N_{\bar{k}_3,j_3}, \ldots\right\rangle \tag{4.5}$$

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

$$\left|\varphi'_{EM}\right\rangle = \left|N_{\bar{k}_1,j}, N_{\bar{k}_2,j_2} - 1, N_{\bar{k}_3,j}, \ldots\right\rangle \tag{4.6}$$

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:

$$H_0 = H_{EM} + H_M \tag{4.7}$$

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:

$$\left|\varphi\right\rangle = \left|\varphi_{EM}\right\rangle\left|\varphi_M\right\rangle \tag{4.8}$$

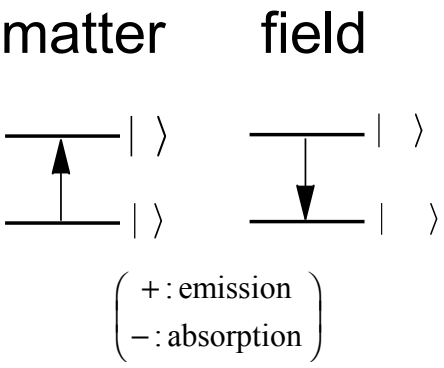
And we have eigenenergies

$$E = E_{EM} + E_M \tag{4.9}$$

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:

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

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



(4.10), (4.11)

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

$$E_I = E_\ell + \sum_j N_j(\hbar\omega_j) \qquad \omega_j = ck_j \qquad (4.12)$$

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

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

$$w_{k\ell} = \frac{2\pi}{\hbar}\delta(E_k - E_\ell - \hbar\omega)\left|\langle\varphi_F|V(t)|\varphi_I\rangle\right|^2 \qquad (4.13)$$

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

$$w_{k\ell} = \frac{2\pi}{v\,\hbar^2}\sum_{\bar{k}j}\delta(\omega_{k\ell} - \omega)\frac{q^2}{m^2}\left|A_{\bar{k},j}\right|^2\left|\langle k|\hat{\epsilon}_j\cdot\bar{p}|\ell\rangle\right|^2 \qquad (4.14)$$

If these are to be the same, then clearly $V(t)$ must have part that looks like $(\hat{\epsilon}\cdot\bar{p})$ 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:

$$V(t)=\frac{-q}{m}\frac{1}{\sqrt{v}}\sum_{\bar{k},j}\left(\bar{p}_k\cdot\hat{\epsilon}_j\,\hat{A}_{\bar{k},j}+\bar{p}_k^{\dagger}\cdot\hat{\epsilon}_j^{*}\,\hat{A}_{\bar{k},j}^{\dagger}\right) \tag{4.15}$$

where $\hat{A}_{\bar{k},j}$ and $\hat{A}_{\bar{k},j}^{\dagger}$ 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

$$\begin{aligned}\left\langle\varphi_F\left|V(t)\right|\varphi_I\right\rangle &= -\frac{q}{m}\frac{1}{\sqrt{v}}\left\langle k\left|\bar{p}_k\cdot\hat{\epsilon}\right|\ell\right\rangle\left\langle\ldots,N_i-1,\ldots\left|\hat{A}_i\right|\ldots,N_i,\ldots\right\rangle \\ &= \frac{1}{\sqrt{v}}\omega_{k\ell}\left\langle k\left|\hat{\epsilon}\cdot\bar{\mu}\right|\ell\right\rangle\left\langle A_i^{(-)}\right\rangle\end{aligned} \tag{4.16}$$

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

$$w_{k\ell}=\frac{\pi}{2\hbar^2}\delta(\omega_{k\ell}-\omega)\frac{\omega_{k\ell}^2}{\omega^2}E_0^2\left|\mu_{k\ell}\right|^2 \tag{4.17}$$

We see that the matrix element

$$\begin{aligned}\left\langle A_i^{(-)}\right\rangle &= \sqrt{\frac{E_0^2}{4v\omega^2}} \qquad \text{but } \frac{E_0^2}{8\pi}=N\hbar\omega \\ &= \sqrt{\frac{2\pi\hbar}{v\omega}}\sqrt{N}\end{aligned} \tag{4.18}$$

So we can write

$$\begin{aligned}\hat{A}_{\bar{k},j} &= \sqrt{\frac{2\pi\hbar}{v\,\omega}}\,a_{\bar{k},j} \\ \hat{A}_{k,j}^{\dagger} &= \sqrt{\frac{2\pi\hbar}{v\,\omega}}\,a_{\bar{k},j}^{\dagger}\end{aligned} \tag{4.19}$$

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

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

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:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

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

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

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

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

So we have the result we deduced before.

Appendix: Rates of Absorption and Stimulated Emission

Here are a couple of more detailed derivations:

Version 1:

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:

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

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

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

and we get ρ_E by integrating over all Ω

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

number density at ω

We can now write the <u>total</u> 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 $d\omega$ $\times$ # of polarization components $\times$ 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.

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

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

The vector potential for a single mode is

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

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

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

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:

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

or for a collection of particles

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

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:

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

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: $d\Omega = \sin\theta\, d\theta\, d\phi$

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

can be written as $\bar{k}$

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

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

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

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

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

For the field

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

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

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

For a broadband source, the energy density of the light

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

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

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 $g(\omega)$

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

Readings

[1] Jackson, J. D. *Classical Electrodynamics* (John Wiley and Sons, New York, 1975).
[2] Cohen-Tannoudji, C., Diu, B. & Lalöe, F. *Quantum Mechanics* (Wiley-Interscience, Paris, 1977), Appendix III.
[3] Cohen-Tannoudji, et al. app. III, p. 1492.