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 $\lambda = 2\pi/|k|$ 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

$$f(\omega) = \frac{1}{e^{\hbar\omega/kT} - 1}$$  (4.83)

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),

$$g(\omega) = \frac{\omega^2}{\pi^2c^3}$$  (4.84)

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

$$\hbar\omega g(\omega) = \frac{\hbar\omega^3}{\pi^2c^3}$$  (4.85)

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

$$u(\omega) = \hbar\omega g(\omega) f(\omega) = \frac{\hbar\omega^3}{\pi^2c^3} \frac{1}{e^{\hbar\omega/kT} - 1}$$  (4.86)
The Quantum Vector Potential

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

$$|\varphi_{EM}\rangle = |N_{\vec{k}_1,j}, N_{\vec{k}_2,j_2}, N_{\vec{k}_3,j_3}, \ldots \rangle \quad (4.87)$$

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

$$|\varphi'_{EM}\rangle = |N_{\vec{k}_1,j}, N_{\vec{k}_2,j_2} - 1, N_{\vec{k}_3,j_3}, \ldots \rangle \quad (4.88)$$

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:

$$H_0 = H_{EM} + H_M \quad (4.89)$$

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

$$|\varphi\rangle = |\varphi_{EM}\rangle |\varphi_M\rangle \quad (4.90)$$

And we have eigenenergies

$$E = E_{EM} + E_M \quad (4.91)$$
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:

\[
|\varphi_i\rangle = |\ell; N_1, N_2, N_3, \ldots, N_i, \ldots\rangle \\
|\varphi_F\rangle = |k; N_1, N_2, N_3, \ldots, N_i \pm 1, \ldots\rangle
\]

\[
\begin{array}{c}
\text{matter} \\
|\ell\rangle
\end{array} \quad \begin{array}{c}
\text{field} \\
|k\rangle \quad |N_i\rangle
\end{array}
\]

\[
\begin{array}{c}
\text{(+: emission)} \\
\text{(-: absorption)}
\end{array}
\]

(4.92), (4.93)

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

\[
E_i = E_\ell + \sum_j N_j (\hbar \omega_j) \\
\omega_j = ck_j
\]

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

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

\[
w_{kr} = \frac{2\pi}{\hbar} \delta(E_k - E_\ell - \hbar \omega) \left| \langle \varphi_F | V(t) | \varphi_i \rangle \right|^2
\]

(4.95)

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

\[
w_{kr} = \frac{2\pi}{\hbar} \sum_{ij} \delta(\omega_{kr} - \omega) \frac{q^2}{m^2} |A_{k,j}|^2 \left| \langle k | \hat{\mathbf{\xi}} \cdot \hat{\mathbf{p}} | \ell \rangle \right|^2
\]

(4.96)

If these are to be the same, then clearly $V(t)$ must have part that looks like $(\hat{\mathbf{\xi}} \cdot \hat{\mathbf{p}})$ 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:
\[ V(t) = \frac{-q}{m} \frac{1}{\sqrt{V}} \sum_{k,j} \left( \vec{p}_k \cdot \vec{e}_j \hat{A}^\dagger_{k,j} + \vec{p}^*_k \cdot \vec{e}^*_j \hat{A}_{k,j} \right) \] 

(4.97)

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

\[
\langle \varphi_f \left| V(t) \right| \varphi_i \rangle = -\frac{q}{m} \frac{1}{\sqrt{V}} \langle k \left| \vec{p}_k \cdot \vec{e} \right| \ell \rangle \langle \ldots, N_i - 1, \ldots \left| \hat{A}_1 \right| \ldots, N, \ldots \rangle 
\]

(4.98)

\[
= \frac{1}{\sqrt{V}} \omega_{k_\ell} \langle k \left| \vec{e} \cdot \vec{p} \right| \ell \rangle \langle \hat{A}_1 \rangle 
\]

Comparing with our Golden Rule expression for absorption,

\[
w_{k_\ell} = \frac{\pi}{2h^2} \delta(\omega_{k_\ell} - \omega) \frac{\omega_{k_\ell}^2 E_0^2}{\omega^2} |\mu_{k_\ell}|^2
\]

(4.99)

We see that the matrix element

\[
\langle \hat{A}_1 \rangle = \sqrt{\frac{E_0^2}{4v\omega^3}} \quad \text{but} \quad \frac{E_0^2}{8\pi} = N\hbar\omega 
\]

(4.100)

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

So we can write

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

(4.101)

\[
\hat{A}^\dagger_{k,j} = \sqrt{\frac{2\pi\hbar}{v\omega}} a^\dagger_{k,j} 
\]

where \( a, a^\dagger \) are lowering, raising operators. So
\[
\hat{A} = \sum_{k,j} \sqrt{\frac{2\pi\hbar}{v\omega}} \hat{\varepsilon}_j \left( a_{kj} e^{i(k\tau-\omega t)} + a_{kj}^\dagger e^{-i(k\tau-\omega t)} \right)
\]

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:

\[
H = H_{EM} + H_M + V(t) = H_0 + V(t)
\]

\[
H_{EM} = \sum_{k,j} h\omega_k \left( a_{kj}^\dagger a_{kj} + \frac{1}{2} \right)
\]

\[
H_M = \sum_i \frac{p_i^2}{2m_i} + V_i(\vec{r}, t)
\]

\[
V(t) = -\frac{q}{m} \vec{A} \cdot \vec{p}
\]

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

\[
= V^{(-)} + V^{(+)}
\]

Let’s look at the matrix elements for absorption \( (\omega_k > 0) \)

\[
\langle k, N_i - 1 | V^{(-)} | \ell, N_i \rangle = -\frac{q}{m} \sqrt{\frac{2\pi\hbar}{v\omega}} \langle k, N_i - 1 | (\hat{\varepsilon} \cdot \vec{p}) a | \ell, N_i \rangle
\]

\[
= -\frac{q}{m} \sqrt{\frac{2\pi\hbar}{v\omega}} \sqrt{N_i} \langle k | \hat{\varepsilon} \cdot \vec{p} | \ell \rangle
\]

\[
= -i \sqrt{\frac{2\pi\hbar\omega}{v}} \sqrt{N_i} \hat{\varepsilon} \cdot \vec{p}_{k\ell}
\]
and for stimulated emission \((\omega_{kl} < 0)\)

\[
\langle k, N_i + 1 | V^{(+)} | \ell, N_i \rangle = -\frac{q}{m} \sqrt{\frac{2\pi \hbar}{\nu \omega}} \langle k, N_i + 1 | (\hat{e} \cdot \hat{p}) a^\dagger | \ell, N_i \rangle \\
= -\frac{q}{m} \sqrt{\frac{2\pi \hbar}{\nu \omega}} \sqrt{N_i + 1} \langle k | \hat{e} | \ell \rangle \\
= -i \sqrt{\frac{2\pi \hbar \omega}{\nu}} \sqrt{N_i + 1} \hat{e} \cdot \hat{\eta}_{kl}
\]

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.

\[
w_{kl} = \int d\omega \frac{2\pi}{\hbar^2} \frac{\omega^2}{(2\pi)^5} \delta(\omega_{kl} - \omega) \int d\Omega \sum_j \left| \langle k, N_i + 1 | V^{(+)} | \ell, N_i \rangle \right|^2
\]

\[
= \frac{2\pi}{\hbar^2} \frac{\omega^2}{(2\pi)^5} (2\pi \nu \omega)(N_i + 1) \frac{8\pi}{3} |\mu_{kl}|^2
\]

\[
\approx \frac{4}{3} \frac{(N_i + 1) \omega^3}{\hbar c^3} |\mu_{kl}|^2
\]

\[
= B_{kl} (N_i + 1) \frac{\hbar \omega^3}{\pi^2 c^3}
\]

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 \( w_{\ell \ell} \) induced by an isotropic, broadband light source

\[
w_{\ell \ell} = \int w_{\ell \ell} (\omega) \rho_E (\omega) d\omega
\]

where, for a monochromatic light source

\[
w_{\ell \ell} (\omega) = \frac{\pi}{2\hbar^3} |E_0 (\omega)|^2 \left| \langle k | \hat{E} | \ell \rangle \right|^2 \delta (\omega_{\ell \ell} - \omega)
\]

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:

\[
A = A_0 \hat{e} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \text{c.c.}
\]

but more generally:

\[
A = \sum_{\mathbf{k}, j} A_{\mathbf{k} j} \hat{e}_j e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \text{c.c.}
\]

where the sum is over the \( \mathbf{k} \) 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

\[
dN = \frac{1}{(2\pi)^3} \frac{\omega^2}{c^3} d\omega d\Omega
\]

and we get \( \rho_E \) by integrating over all \( \Omega \)

\[
\rho_E (\omega) d\omega = \frac{1}{(2\pi)^3} \frac{\omega^2}{c^3} d\omega \int d\Omega = \frac{\omega^2}{2\pi^2 c^3} d\omega
\]

number density at \( \omega \)
We can now write the total transition rate between two discrete levels summed over all frequencies, direction, polarizations

\[ w_{k'} = \int d\omega \frac{\pi}{2\hbar} |E_0(\omega)|^2 \delta(\omega_{k'} - \omega) \frac{1}{(2\pi)^3} \frac{\omega^2}{c^3} \sum_j \int \! d\Omega |\langle k | \hat{\epsilon}_j \cdot \hat{n} | f \rangle|^2 \]

\[ = \frac{|E_0(\omega_{k'})|^2 \omega^2}{6\pi\hbar^2 c^3} |\vec{\mu}_{k'}|^2 \]

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.

\[ U(\omega_{k'}) = \frac{\omega^2}{2\pi^2 c^5} \cdot 2 \cdot \frac{E_0^2}{8\pi} \]

\[ w_{k'} = B_{k'} U(\omega_{k'}) \]

\[ B_{k'} = \frac{4\pi^2}{3\hbar^2} |\vec{\mu}_{k'}|^2 \] 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 \( N \)

\[ N\hbar\omega = \frac{E_0^2}{8\pi} \quad \text{and} \quad U(\omega_{k'}) = N \frac{\hbar \omega^3}{\pi^2 c^5} \]

The golden rule rate for absorption also gives the same rate for stimulated emission. We find for two levels \( |m\rangle \) and \( |n\rangle \):

\[ w_{nm} = w'_{nm} \]

\[ B_{nm} U(\omega_{nm}) = B_{nm} U(\omega_{nm}) \quad \text{since} \quad U(\omega_{nm}) = U(\omega_{mn}) \]

\[ B_{nm} = B_{nm} \]

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 \( k \).

\[
S = \frac{c}{4\pi} \mathbf{E} \times \mathbf{B} = \frac{c \omega^2 A_0^2}{8\pi} \hat{k} = \frac{\omega^2 E_0^2}{2\pi}
\]

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

The vector potential for a single mode is

\[
A = A_0 \hat{\mathbf{e}} e^{i(\mathbf{r} \cdot \mathbf{a} - \omega t)} + c.c.
\]

with \( \omega = c k \). More generally any wave can be expressed as a sum over Fourier components of the wave vector:

\[
A = \sum_{\mathbf{k},j} A_{\mathbf{k},j} \hat{\mathbf{e}}_j e^{i(\mathbf{r} \cdot \mathbf{k} - \omega t)} + c.c.
\]

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:

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

or for a collection of particles

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

Now, the momentum depends on the position of particles, and we can express \( p \) in terms of an integral over the distribution of particles:

\[
p = \int d^3r \ p(r) \quad \quad p(r) = \sum_i p_i \delta(r - r_i)
\]

So if we assume that all particles have the same mass and charge—say electrons:
\[ V(t) = \frac{-q}{m} \int d^3r \mathbf{\bar{A}}(\mathbf{r}, t) \cdot \mathbf{\bar{p}}(r) \]

The rate of transitions induced by a single mode is:

\[ (w_{k\ell})_{\ell,i} = \frac{2\pi}{\sqrt{\hbar^2}} \delta(\omega_{k\ell} - \omega) \frac{q^2}{m^2} |A_{\ell,i}|^2 \left| \langle k | \mathbf{\bar{p}}(\mathbf{r}) | \ell \rangle \right|^2 \]

And the total transition rate for an isotropic broadband source is:

\[ w_{k\ell} = \sum_{\ell,i} (w_{k\ell})_{\ell,i} \]

We can replace the sum over modes for a fixed volume with an integral over \( k \):

\[ \frac{1}{V} \sum_{k} \Rightarrow \int \frac{d^3k}{(2\pi)^3} \rightarrow \int dk \frac{k^2}{(2\pi)^3} \rightarrow \int d\omega \frac{\omega^2}{(2\pi C)^3} \]

So for the rate we have:

\[ d\Omega = \sin \theta d\theta d\phi \]

\[ w_{k\ell} = \int d\omega \frac{2\pi}{\hbar^2} \frac{\omega^2}{(2\pi C)^3} \delta(\omega_{k\ell} - \omega) \frac{q^2}{m^2} \int d\Omega \sum_{j} \left| \langle k | \mathbf{\bar{p}}(\mathbf{r}) | \ell \rangle \right|^2 |A_{\ell,i}|^2 \]

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

\[ \frac{q}{m} \left< k | \mathbf{\bar{p}}(\mathbf{r}) | \ell \right> = \frac{-q}{m} \sum_{i} \left< k | \mathbf{\bar{p}} | \ell \right> \delta(\mathbf{r} - \mathbf{\bar{r}}) \]

\[ = \frac{-i}{\hbar} q \sum_{i} \left< k | [\mathbf{\bar{r}}, H_0] \delta(\mathbf{r} - \mathbf{\bar{r}}) | \ell \right> \]

\[ = -i \omega_{k\ell} \sum_{i} q \mathbf{\bar{e}} \cdot \left< k | \mathbf{\bar{r}} | \ell \right> \]

\[ = -i \omega_{k\ell} \sum_{i} \left< k | \mathbf{\bar{u}} | \ell \right> \quad \text{where} \quad \mathbf{\bar{u}} = \sum_{i} q_i \mathbf{r}_i \]

For the field

\[ \sum_{k\ell} |A_{\ell,i}|^2 = \sum_{k\ell} \left| \frac{E_{k\ell}}{2\omega} \right|^2 = \frac{E_0^2}{4\omega^2} \]
\[ W_{kt} = \int d\omega \frac{2\pi}{4\hbar^2} \frac{\omega^2}{(2\pi c)^3} \delta(\omega_{kt} - \omega) \frac{\partial^2}{\partial \omega^2} E_0^2 \int d\Omega \sum_j \langle k | \hat{\epsilon}_j \cdot \hat{\mu} | t \rangle^2 \] 

\[ = \frac{\omega^2}{6\pi \hbar^2 c^3} |E_0|^2 |\mu_{kt}| \]

For a broadband source, the energy density of the light

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

\[ W_{kt} = B_{kt} U(\omega_{kt}) \quad B_{kt} = \frac{4\pi^3}{3\hbar^2} |\mu_{kt}|^2 \]

We can also write the incident energy density in terms of the quantum energy per photon. For \( N \) photons in a single mode:

\[ N\hbar\omega = B_{kt}N \frac{\hbar\omega^3}{\pi^2 c^3} \]

where \( B_{kt} \) has molecular quantities and no dependence or field. Note \( B_{kt} = B_{ik} \) — ratio of S.E. = absorption.

The ratio of absorption can be related to the absorption cross-section, \( \delta_A \)

\[ \sigma_A = \frac{P}{I} = \frac{\text{total energy absorbed/unit time}}{\text{total intensity (energy/unit time/area)}} \]

\[ P = \hbar\omega \cdot W_{kt} = \hbar\omega B_{kt} U(\omega_{kt}) \]

\[ I = cU(\omega_{kt}) \]

\[ \sigma_A = \frac{\hbar\omega}{c} B_{kt} \]

or more generally, when you have a frequency-dependent absorption coefficient described by a lineshape function \( g(\omega) \)
\[ \sigma_a(\omega) = \frac{\hbar \omega}{c} B_{kr} g(\omega) \quad \text{units of cm}^2 \]
The Boltzmann distribution gives us the number of molecules in each state.

\[ N_m / N_n = e^{-\hbar \omega_m / kT} \]  

(4.102)

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

\[ N_m B_{mn} U(\omega_{mn}) = N_n B_{nm} U(\omega_{nm}) \]  

(4.103)

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

\[ W_{nm} = W_{nn} \]  

(4.104)

\[ N_m (A_{nm} + B_{mn} U(\omega_{mn})) = N_n B_{mn} U(\omega_{mn}) \]

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

\[ A_{nm} = B_{mn} U(\omega_{mn}) \left( e^{\hbar \omega_{mn} / kT} - 1 \right) \]  

(4.105)

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

\[ U(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / kT} - 1} \]  

(4.106)

\( U_\omega \) is the energy density per photon of frequency \( \omega \).

\( \langle N_\omega \rangle \) is the mean number of photons at a frequency \( \omega \).

\[ \therefore A_{nm} = \frac{\hbar \omega^3}{\pi^2 c^3} B_{nm} \]  

Einstein A coefficient  

(4.107)

The total rate of emission from the excited state is

\[ w_{nm} = B_{nm} U(\omega_{nm}) + A_{nm} \]  

using \( U(\omega_{nm}) = N \frac{\hbar \omega^3}{\pi^2 c^3} \)  

(4.108)
\[
\frac{\hbar \omega^3}{\pi^2 c^3} B_{nm} (N+1)
\]

(4.109)

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

\[
w_{nm} = \frac{\hbar \omega^3}{\pi^2 c^3} B_{nm} (N)
\]

(4.110)

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

\[
w_{nm} = \frac{\hbar \omega^3}{\pi^2 c^3} B_{nm} N
\]

(4.111)

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

\[
\tau_{\text{rad}} = \frac{1}{A}
\]

(4.112)

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:

\[
|\phi_i\rangle = |\ell; N_1, N_2, N_3, \ldots, N_i, \ldots\rangle
\]

\[
|\phi_f\rangle = |k; N_1, N_2, N_3, \ldots, N_i \pm 1, \ldots\rangle
\]

\[
|\ell\rangle \quad \text{matter} \quad |k\rangle \quad \text{field}
\]

\[
|N_i\rangle
\]

(\(+\) : emission) (\(-\) : absorption)

(4.113), (4.114)

Where I have abbreviated \(N_i \equiv N_{\ell_i k_i}\), the energies of these two states are:

\[
E_i = E_\ell + \sum_j N_j (\hbar \omega_j)
\]

\[
\omega_j = c k_j
\]

(4.115)
\[ E_r = E_k + \sum_j N_j \left( \hbar \omega_j \right) \pm \hbar \omega_j \]

So looking at absorption \( \left( \begin{array}{c} k \\ \ell \end{array} \right) \rightarrow \left( \begin{array}{c} \uparrow \end{array} \right) \), we can write the Golden Rule Rate for transitions between states as:

\[ w_{k\ell} = \frac{2\pi}{\hbar} \delta(E_k - E_\ell - \hbar \omega) \left| \langle \varphi_r | V(t) | \varphi_\ell \rangle \right|^2 \] (4.116)

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

\[ w_{k\ell} = \frac{2\pi}{v \hbar^2} \sum_{\omega_j} \delta(\omega_k - \omega) \frac{q^2}{m^2} \left| A_{k\ell} \right|^2 \left| \langle k | \vec{p} \cdot \vec{e} | \ell \rangle \right|^2 \] (4.117)

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

\[ V(t) = -\frac{q}{m} \frac{1}{\sqrt{V}} \sum_{\kappa,j} \left( \vec{p}_k \cdot \vec{e}_j \hat{A}_{\kappa,j} + \vec{p}^*_k \cdot \vec{e}^*_j \hat{A}^\dagger_{\kappa,j} \right) \] (4.118)

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

\[ \langle \varphi_r | V(t) | \varphi_\ell \rangle = -\frac{q}{m} \frac{1}{\sqrt{V}} \langle k | \vec{p}_k \cdot \vec{e} | \ell \rangle \langle \ldots, N_i - 1, \ldots | \hat{A}_i | \ldots, N_i, \ldots \rangle \]

\[ = \frac{1}{\sqrt{V}} \omega_k \langle k | \vec{e} | \vec{p} \rangle \langle \ell | \hat{A}^{(-)} \rangle \] (4.119)

Comparing with our Golden Rule expression for absorption,

\[ w_{k\ell} = \frac{\pi}{2\hbar^2} \delta(\omega_k - \omega) \frac{\alpha_k^2}{\omega^2} E_0^2 |\mu_{k\ell}|^2 \] (4.120)
We see that the matrix element

\[
\langle A^{(-)} \rangle = \sqrt{\frac{E_0^2}{4\omega^2}} \quad \text{but} \quad \frac{E_0^2}{8\pi} = N\hbar \omega \\
= \sqrt{\frac{2\pi\hbar}{\nu\omega}} \sqrt{N}
\]

So we can write

\[
\hat{A}_{x,j} = \sqrt{\frac{2\pi\hbar}{\nu\omega}} a_{x,j}
\]

\[
\hat{A}_{x,j}^\dagger = \sqrt{\frac{2\pi\hbar}{\nu\omega}} a_{x,j}^\dagger
\]

where \( a, a^\dagger \) are lowering, raising operators. So

\[
\hat{A} = \sum_{k,j} \sqrt{\frac{2\pi\hbar}{\nu\omega}} \hat{e}_j \left( a_{kj} e^{i(\omega t - \omega x)} + a_{kj}^\dagger e^{-i(\omega t - \omega x)} \right)
\]

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:
\[
H = H_{EM} + H_M + V(t) = H_0 + V(t)
\]

\[
H_{EM} = \sum_{k,j} \hbar \omega_k \left( a_{kj}^{+} a_{kj} + \frac{1}{2} \right)
\]

\[
H_M = \sum_i \frac{p_i^2}{2m_i} + V_i(\vec{r}, t)
\]

\[
V(t) = \frac{-q}{m} \vec{A} \cdot \vec{p}
\]

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

\[
= V(-) + V(^+)
\]

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

\[
\langle k, N_i - 1 | V(-) | \ell, N_i \rangle = \frac{-q}{m} \sqrt{\frac{2\pi \hbar}{v \omega}} \langle k, N_i - 1 | (\hat{\vec{r}} \cdot \vec{p}) a | \ell, N_i \rangle
\]

\[
= \frac{-q}{m} \sqrt{\frac{2\pi \hbar}{v \omega}} \sqrt{N_i} \langle k | \hat{\vec{r}} \cdot \vec{p} | \ell \rangle
\]

\[
= -i \sqrt{\frac{2\pi \hbar \omega}{v}} \sqrt{N_i} \hat{\vec{r}}_{k\ell}
\]

and for stimulated emission \(\omega_{kl} < 0\)
\[ \langle k, N_i + 1 | V^{(\ell)} | \ell, N_i \rangle = \frac{-q}{m} \sqrt{\frac{2\pi \hbar}{v \omega}} \langle k, N_i + 1 | (\varepsilon \cdot \mathbf{p}) a^{\dagger} | \ell, N_i \rangle \]

\[ = \frac{-q}{m} \sqrt{\frac{2\pi \hbar}{v \omega}} \sqrt{N_i + 1} \langle k | \varepsilon \cdot \mathbf{p} | \ell \rangle \]

\[ = -i \sqrt{\frac{2\pi \hbar \omega}{v}} \sqrt{N_i + 1} \varepsilon^{\dagger} \mathbf{p}_{k_\ell} \]

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.

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

\[ = \frac{2\pi}{\hbar^2} \frac{\omega^2}{(2\pi c)^3} \left(2\pi \hbar \omega \right) (N_i + 1) \frac{8\pi}{3} |\mathbf{p}_{k\ell}|^2 \]

\[ = \frac{4(N_i + 1)\omega^3}{3\hbar c^3} |\mathbf{p}_{k\ell}|^2 \]

\[ = B_{k\ell} (N_i + 1) \frac{\hbar \omega^3}{\pi^2 c^3} \]

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

\[
  w_{k\ell} (\omega) = \frac{\pi}{2\hbar^2} |E_0 (\omega)|^2 |\langle k \mid \hat{\epsilon} \cdot \hat{\mathbf{P}} \mid \ell \rangle|^2 \delta (\omega_{k\ell} - \omega)
\]

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:

\[
  A = A_0 \hat{\epsilon} e^{i(\hat{\mathbf{r}} \cdot \mathbf{k} - \omega t)} + \text{c.c.}
\]

but more generally:

\[
  A = \sum_{k,j} A_{k,j} \hat{\epsilon}_j e^{i(\hat{\mathbf{r}} \cdot \mathbf{k} - \omega t)} + \text{c.c.}
\]

where the sum is over the \( \hat{\mathbf{k}} \) 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

\[
  \frac{dN}{d\Omega} = \frac{1}{(2\pi)^3 c^3} \frac{\omega^2}{d\omega} d\omega d\Omega
\]

and we get \( \rho_E \) by integrating over all \( \Omega \)

\[
  \rho_E (\omega) d\omega = \frac{1}{(2\pi)^3 c^3} \frac{\omega^2}{d\omega} \int d\Omega = \frac{\omega^2}{2\pi^2 c^3} d\omega
\]

number density at \( \omega \).
We can now write the total transition rate between two discrete levels summed over all frequencies, direction, polarizations

\[ w_{kk'} = \int d\omega \frac{\pi}{2\hbar} |E_0(\omega)|^2 \delta(\omega_{kk'} - \omega) \frac{\hbar}{c^3} \sum_j \int d\Omega |\langle \kappa | \tilde{e}_j | \mu | \rangle|^2 \]

\[ = \frac{|E_0(\omega_{kk'})|^2 \omega^2}{6\pi \hbar^2 c^3} |\mu_{kk'}|^2 \]

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.

\[ U(\omega_{kk'}) = \frac{\omega^2}{2\pi^2 c^5} \cdot \frac{E_0^2}{8\pi} \]

\[ w_{kk'} = B_{kk'} U(\omega_{kk'}) \]

\[ B_{kk'} = \frac{4\pi^2}{3\hbar^2} |\mu_{kk'}|^2 \] 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 \( N \)

\[ N\hbar\omega = \frac{E_0^2}{8\pi} \quad U(\omega_{kk'}) = N \frac{\hbar \omega^3}{\pi^2 c^5} \]

The golden rule rate for absorption also gives the same rate for stimulated emission. We find for two levels \( |m\rangle \) and \( |n\rangle \):

\[ w_{nm} = w_{nm} \]

\[ B_{nm} U(\omega_{nm}) = B_{nm} U(\omega_{nm}) \quad \text{since} \quad U(\omega_{nm}) = U(\omega_{nm}) \]

\[ B_{nm} = B_{nm} \]

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 $k$.

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

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

The vector potential for a single mode is

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

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

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

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:

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

or for a collection of particles

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

Now, the momentum depends on the position of particles, and we can express $p$ in terms of an integral over the distribution of particles:

$$ p = \int d^3r \ p(r) \quad \quad p(r) = \sum_i p_i \delta(r - r_i) $$

So if we assume that all particles have the same mass and charge—say electrons:
\[ V(t) = -\frac{q}{m} \int d^3 r \overline{A}(\mathbf{r}, t) \cdot \mathbf{p}(r) \]

The rate of transitions induced by a single mode is:

\[ (w_{k\ell})_{\ell,j} = \frac{2\pi}{\sqrt{h^2}} \delta(\omega_{k\ell} - \omega) \frac{q^2}{m^2} |A_{\ell,j}|^2 \left| \left\langle k|\mathbf{\hat{e}} \cdot \mathbf{p}(r)|\ell\right\rangle \right|^2 \]

And the total transition rate for an isotropic broadband source is:

\[ w_{k\ell} = \sum_{k,j} (w_{k\ell})_{\ell,j} \]

We can replace the sum over modes for a fixed volume with an integral over \( k \):

\[ \frac{1}{V} \sum_k \Rightarrow \int \frac{d^3 k}{(2\pi)^3} \rightarrow \int dk \frac{k^2}{(2\pi)^3} \rightarrow \int d\omega \omega^2 \frac{d\Omega}{(2\pi)^3} \]

So for the rate we have:

\[ d\Omega = \sin \theta d\theta d\phi \]

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

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

\[ \frac{q}{m} \langle k|\mathbf{\hat{e}} \cdot \mathbf{p}(r)|\ell\rangle = -\frac{q}{m} \sum_i \langle k|\mathbf{\hat{e}} \cdot \mathbf{p}_i \delta(\mathbf{\bar{r}} - \mathbf{r})|\ell\rangle \]

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

\[ = -i\omega_{k\ell} \sum_i \mathbf{\hat{e}} \cdot \langle k| \mathbf{\bar{r}} |\ell\rangle \]

\[ = -i\omega_{k\ell} \langle k| \mathbf{\bar{r}} |\ell\rangle \quad \text{where } \mathbf{\bar{r}} = \sum_i q_i \mathbf{r}_i \]

For the field

\[ \sum_{k_y} \left| A_{k_y} \right|^2 = \sum_{k_y} \left| \frac{E_{k_y}}{2 \omega} \right|^2 = \frac{E_0^2}{4 \omega^2} \]
\[ W_{kt} = \int d\omega \frac{2\pi}{4\hbar^2} \frac{\omega^2}{(2\pi c)^3} \delta(\omega_{kt} - \omega) \frac{\omega^2}{\omega} E_0^2 \left[ \sum_j |k| \hat{e}_j \cdot \overline{\mu} |\ell|^2 \right] \]

\[ = \frac{\omega^2}{6\pi\hbar^2 c^3} |E_0|^2 |\mu_{kt}| \]

For a broadband source, the energy density of the light

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

\[ W_{kt} = B_{kt} U (\omega_{kt}) \quad B_{kt} = \frac{4\pi^3}{3\hbar^2} |\mu_{kt}|^2 \]

We can also write the incident energy density in terms of the quantum energy per photon. For \( N \) photons in a single mode:

\[ N\hbar\omega = B_{kt} N \frac{\hbar\omega^3}{\pi^2 c^3} \]

where \( B_{kt} \) has molecular quantities and no dependence or field. Note \( B_{kt} = B_{\text{ik}} \) — ratio of S.E. = absorption.

The ratio of absorption can be related to the absorption cross-section, \( \delta_A \)

\[ \sigma_A = \frac{P}{I} = \frac{\text{total energy absorbed/unit time}}{\text{total intensity (energy/unit time/area)}} \]

\[ P = \hbar \omega \cdot W_{k\ell} = \hbar \omega B_{k\ell} U (\omega_{k\ell}) \]

\[ I = c U (\omega_{k\ell}) \]

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

or more generally, when you have a frequency-dependent absorption coefficient described by a lineshape function \( g(\omega) \)
\[ \sigma_{\omega}(\omega) = \frac{\hbar \omega}{c} B_{k'} g(\omega) \quad \text{units of cm}^2 \]

Readings