March 25, 2015
Lecture XXV

Quantization of the E-M field

2.0.1 Electric quadrupole transition

If E1 transitions are forbidden by selection rules, then we consider the next term in the expansion of the spatial dependence of the field operator and the magnetic term in the interaction Hamiltonian. Recall that the $\frac{e}{mc}\mathbf{p}\cdot\mathbf{A}$ term in the interaction, that can connect initial and final states with a difference of a single photon, is write

$$\langle f; n_{k\lambda}-1 \mid H_1 \mid i; n_{k\lambda}\rangle = -\frac{e}{m}\sqrt{\frac{n_k\hbar}{2\omega V}}\left\langle f \mid e^{i(\mathbf{k}\cdot\mathbf{x})}\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda} \mid i\right\rangle e^{-i\omega t}$$

Expanding the exponent to first order, where $\mathbf{x}\cdot\mathbf{x}$ is the small parameter (long wavelength and small atom) gives us

$$\langle f; n_{k\lambda}-1 \mid H_1 \mid i; n_{k\lambda}\rangle = -\frac{e}{m}\sqrt{\frac{n_k\hbar}{2\omega V}}\langle f \mid (1+i(\mathbf{k}\cdot\mathbf{x}))\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda} \mid i\rangle e^{-i\omega t}$$

Typically the first order term contributes only if the zeroth order (dipole) is forbidden. Then

$$\langle f; n_{k\lambda}-1 \mid H_1 \mid i; n_{k\lambda}\rangle = -i\frac{e}{m}\sqrt{\frac{n_k\hbar}{2\omega V}}\langle f \mid (\mathbf{k}\cdot\mathbf{x})\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda} \mid i\rangle e^{-i\omega t}$$

Consider evaluation of the matrix element

$$\langle f \mid (\mathbf{k}\cdot\mathbf{x})\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda} \mid i\rangle$$

We can expand

$$\begin{aligned}\langle f \mid (\mathbf{k}\cdot\mathbf{x})(\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda}) \mid i\rangle &= \frac{1}{2}\langle f \mid (\mathbf{k}\cdot\mathbf{x})(\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda}) + (\mathbf{k}\cdot\mathbf{p})(\epsilon_{\mathbf{k}\lambda}\cdot\mathbf{x}) \mid i\rangle \\ &+\frac{1}{2}\langle f \mid (\mathbf{k}\cdot\mathbf{x})(\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda}) - (\mathbf{k}\cdot\mathbf{p})(\epsilon_{\mathbf{k}\lambda}\cdot\mathbf{x}) \mid i\rangle\end{aligned}$$

The first term

$$\frac{1}{2}\left((\mathbf{k}\cdot\mathbf{x})(\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda}) + (\mathbf{k}\cdot\mathbf{p})(\epsilon_{\mathbf{k}\lambda}\cdot\mathbf{x})\right) = \frac{1}{2}\mathbf{k}\cdot(\mathbf{xp}+\mathbf{px})\cdot\epsilon_{\mathbf{k}\lambda}$$

As before, we can write the operator $\mathbf{p} = \frac{im}{\hbar}[H_0, \mathbf{x}]$ so that

$$\mathbf{xp}+\mathbf{px} = \frac{im}{\hbar}[H_0, \mathbf{xx}].$$

Finally

$$\frac{1}{2}\mathbf{k}\cdot\langle f \mid \mathbf{xp}+\mathbf{px} \mid i\rangle\cdot\epsilon_{\mathbf{k}\lambda} = -\frac{im\omega}{2}\mathbf{k}\cdot\langle f \mid \mathbf{xx} \mid i\rangle\cdot\epsilon_{\mathbf{k}\lambda}.$$

This transition is the electric quadrupole (E2) transition. Since $\mathbf{k}\cdot\epsilon = 0$,

$$k_i\langle x_i x_j\rangle\epsilon_j = k_i\langle T_{ij}\rangle\epsilon_j$$

where

$$T_{ij} = x_i x_j - \frac{\delta_{ij}}{3}|\mathbf{x}|^2.$$

has zero trace and 5 independent components that can be written as a linear combination of Y_2^m (spherical tensor operator). The the WE theorem tells use that the total angular momentum of initial and final states can change by at most 2.

2.0.2 Magnetic dipole transition

The second term can be written

$$\frac{1}{2}\langle f \mid (\mathbf{k}\cdot\mathbf{x})(\mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda}) - (\mathbf{k}\cdot\mathbf{p})(\epsilon_{\mathbf{k}\lambda}\cdot\mathbf{x}) \mid i\rangle \quad = \quad \frac{1}{2}\langle f \mid (\mathbf{k}\times\epsilon_{\mathbf{k}\lambda})\cdot(\mathbf{x}\times\mathbf{p}) \mid i\rangle$$

$\mathbf{k}\times\epsilon_{\mathbf{k}\lambda}$ is the leading term in the plane-wave expansion of the magnetic field $\mathbf{B}$ and $\mathbf{x}\times\mathbf{p}$ is the orbital angular momentum. This term contributes to magnetic dipole M1 transitions. The operator is constructed from Y_1^m and corresponds to transitions between states with $\Delta l < 1$. The M1 transition will be relevant when the E1 transition is zero, perhaps because initial and final states have δl even so no parity change. This might correspond to a spin flip. As stated above, the intrinsic parity of the photon is odd, so if initial and final states of the emitting atom have the same parity, it must be that the photon has some orbital angular momentum with respect to the atomic coordinate system. If the orbital angular momenum is $kr = l = 1$, then the photon would have had to be emitted at $r = 1/k$. But as we determined earlier, $kr \ll 1$ for typical energy differences between levels and so the rate for such a process is low.

The next term in the interaction Hamiltonian is

$$\mu\cdot\mathbf{B} = \frac{e\hbar}{2mc}\sigma\cdot(\mathbf{k}\times\epsilon)\left(\sqrt{\frac{\hbar}{2\omega V}}\right)$$

to be compared to

$$\frac{e}{2mc}\mathbf{L}\cdot(\mathbf{k}\times\epsilon)\left(\sqrt{\frac{\hbar}{2\omega V}}\right)$$

Clearly of the same order.

2.0.3 Forbidden transition

Typical E1 transitions are of order 10^{-8} s. And E2 and M1 10^{-3}s. What about something like $2S$ to $1S$ which is forbiddent for all E and M transitions by angular momentum conservation? Decays by emission of two photons. How about a ball park estimate.

First the E1 transition We have something like

$$\Gamma \quad = \quad \frac{2\pi}{\hbar}\left(\frac{e}{mc}\sqrt{\frac{\hbar c}{2kV}}\langle f \mid \mathbf{p} \mid i\rangle\right)^2 \frac{V\omega^2}{(2\pi)^3\hbar c^3}d\Omega$$

$$
\begin{aligned}
&\sim \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 \frac{\hbar c^2}{2\omega}\left(m\omega \langle f \mid \mathbf{x} \mid i\rangle\right)^2 \frac{\omega^2}{(2\pi)^3\hbar c^3} d\Omega \\
&\sim \frac{2\pi}{\hbar}\left(\frac{e}{m}\right)^2 \frac{\hbar}{2\omega}\left(m\omega a_0\right)^2 \frac{\omega^2}{(2\pi)^3\hbar c^3} d\Omega \\
&\sim \frac{e^2}{\hbar c} a_0^2 \frac{\omega^3}{c^2} \\
&\sim \alpha a_0^2 k^3 c \\
&\sim \alpha a_0^2 \frac{c}{\lambda^3} \\
&\sim \frac{(0.5\times 10^{-10}\mathrm{m})^2}{137}\frac{(3\times 10^8\mathrm{m/s})}{(10^{-7}\mathrm{m})^3} \\
&\sim 10^7 \mathrm{s}^{-1}
\end{aligned}
$$

For an E2 transition, instead of $\langle \mathbf{x} \rangle$ we have $k\langle \mathbf{xx} \rangle$ so the rate will be smaller by

$$
\sim \left(\frac{a_0}{\lambda}\right)^2
$$

Again that 2s to 1s transition. The term H_2 is a candidate. But it cannot couple the atomic states. We need to revisit the time dependent perturbation theory. We started with

$$
\dot{c}_m = \sum_k (1/i\hbar)\langle m \mid H_I(t) \mid k\rangle e^{i(E_m-E_k)t/\hbar} c_k(t).
$$

Then for the first order approximation we assume that $c_k(0) = \delta_{kl}$ to get

$$
c_m^1(t) = \frac{1}{i\hbar}\int_0^t dt' \langle m \mid H_I(t') \mid l\rangle e^{i(E_m-E_l)t'/\hbar}
$$

If we need the next order then substitute c_m^1 into that last equation to get

$$
\begin{aligned}
c_m^2(t) &= \frac{1}{i\hbar}\sum_n \int_0^{t'} dt'' \langle m \mid H_I(t'') \mid n\rangle e^{i(E_m-E_n)t'/\hbar} c_n^1(t'') \\
&= \left(\frac{1}{i\hbar}\right)^2 \sum_n \int_0^t dt'' \int_0^{t''} dt' \langle m \mid H_I(t'') \mid n\rangle e^{i(E_m-E_n)t''/\hbar} \langle n \mid H_I(t') \mid l\rangle e^{i(E_n-E_l)t'/\hbar}
\end{aligned}
$$

If the perturbation has harmonic time dependence we get

$$
\begin{aligned}
c_m^2(t) &= \left(\frac{1}{i\hbar}\right)^2 \sum_n \int_0^t dt'' \int_0^{t''} dt' \langle m \mid H_I \mid n\rangle e^{i(\hbar\omega_{mn}+E_m-E_n)t''/\hbar} \langle n \mid H_I \mid l\rangle e^{i(\hbar\omega_{nl}+E_n-E_l)t'/\hbar} \\
&= \left(\frac{1}{i\hbar}\right)^2 \sum_n \langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle \int_0^t dt'' \int_0^{t''} dt' e^{i(\hbar\omega_{mn}+E_m-E_n)t''/\hbar} e^{i(\hbar\omega_{nl}+E_n-E_l)t'/\hbar}
\end{aligned}
$$

Let's suppose that the perturbation turns on gradually, rather than suddenly at $t = 0$, so that we can integrate from $-\infty$. We add an infinitesimal imaginary term $(-i\epsilon)$, (We choose the sign of

ω and ω' to look like emission and absorption of photons in a scattering process.

$$c_m^2(t) = \left(\frac{1}{i\hbar}\right)^2 \sum_n \langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle \int_{-\infty}^{t} dt'' \int_{-\infty}^{t''} dt' e^{i(-\hbar\omega - i\epsilon + E_m - E_n)t''/\hbar} e^{i(\hbar\omega' - i\epsilon + E_n - E_l)t'/\hbar}$$

Then

$$\begin{aligned} c_m^2(t) &= -\left(\frac{1}{\hbar}\right)^2 \sum_n \langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle \int_{-\infty}^{t} dt'' e^{i(-\hbar\omega - i\epsilon + E_m - E_n)t''/\hbar} \left(\frac{e^{i(\hbar\omega' - i\epsilon + E_n - E_l)t''/\hbar}}{i(\omega' - i\epsilon + (E_n - E_l)/\hbar}\right) \\ &= -\left(\frac{1}{\hbar}\right)^2 \sum_n \langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle \int_{-\infty}^{t} dt'' \left(\frac{e^{i(\hbar(\omega' - \omega) - i\epsilon + E_m - E_l)t''/\hbar}}{i(\omega' + i\epsilon + (E_n - E_l)/\hbar)}\right) \end{aligned}$$

Then let and we have, (where $E_{ml} = E_m - E_l$, etc.),

$$\begin{aligned} c_m^2(t) &= -\left(\frac{1}{\hbar}\right)^2 \sum_n \frac{\langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle}{i(\omega' + (E_{nl})/\hbar)} \int_{-\infty}^{t} e^{i(\omega' - i\epsilon - \omega + E_{ml}/\hbar)t'} \\ &= -\left(\frac{1}{\hbar}\right)^2 \sum_n \frac{\langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle}{i(\omega' + (E_{nl})/\hbar)} \frac{e^{i(\omega' - i\epsilon - \omega + E_{ml}/\hbar)t}}{i(\omega' - i\epsilon - \omega + E_{ml})} \end{aligned}$$

The transition probability

$$|c_m^2(t)|^2 = \left| \left(\frac{1}{\hbar}\right)^2 \sum_n \frac{\langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle}{i(\omega' + (E_{nl})/\hbar)} \right|^2 \frac{e^{2\epsilon t}}{(\omega - \omega + E_{ml})^2 + \epsilon^2}$$

The transition rate

$$\begin{aligned} \frac{d}{dt}|c_m^2(t)|^2 &= \left| \left(\frac{1}{\hbar}\right)^2 \sum_n \frac{\langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle}{i(\omega' + (E_{nl})/\hbar)} \right|^2 \frac{2\epsilon e^{2\epsilon t}}{(\omega - \omega + E_{ml})^2 + \epsilon^2} \\ \to \lim_{\epsilon \to 0} \frac{d|c_m^2|^2}{dt} &= \left| \left(\frac{1}{\hbar}\right)^2 \sum_n \frac{\langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle}{i(\omega' + (E_{nl})/\hbar)} \right|^2 2\pi\delta(\omega' - \omega + E_{ml}/\hbar) \\ &= \frac{2\pi}{\hbar^4} \left| \sum_n \frac{\langle m \mid H_I \mid n\rangle \langle n \mid H_I \mid l\rangle}{(\omega' + (E_{nl})/\hbar)} \right|^2 \delta(\omega' - \omega + E_{ml}/\hbar) \end{aligned}$$