April 6, 2015
Lecture XXVI

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

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

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

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

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

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

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

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

The first term

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

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

$$\mathbf{x}\mathbf{p}+\mathbf{p}\mathbf{x}=\frac{im}{\hbar}[H_0,\mathbf{x}\mathbf{x}].$$

Finally

$$\frac{1}{2}\mathbf{k}\cdot\langle f \mid \mathbf{x}\mathbf{p}+\mathbf{p}\mathbf{x} \mid i\rangle\cdot\epsilon_{\mathbf{k}\lambda} \quad = \quad -\frac{im\omega}{2}\mathbf{k}\cdot\langle f \mid \mathbf{x}\mathbf{x} \mid i\rangle\cdot\epsilon_{\mathbf{k}\lambda}.$$

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.

Spherical tensor operator

Let's examine the tensor operator T_{ij} in more detail. Recall that a cartesian tensor operator can be assembled from cartesian vector operators $\mathbf{U}$ and $\mathbf{V}$ according to

$$W_{ij} = U_i V_j$$

As long as $\mathbf{U}$ and $\mathbf{V}$ transform as vectors under rotations then so will W_{ij}. But the cartesian tensor does not transform irreducibly. We can write

$$U_i V_j = \mathbf{U}\cdot\mathbf{V}\frac{\delta_{ij}}{3} + \frac{1}{2}(U_i V_j - U_j V_i) + \frac{1}{2}(U_i V_j + U_j V_i) - \mathbf{U}\cdot\mathbf{V}\frac{\delta_{ij}}{3}$$

The first term transforms as a scalar, the second as a vector (namely $\mathbf{U}\times\mathbf{V}$) and the third term is a 3X3 symmetric traceless tensor. The 9 real parameters of the 3X3 cartesian tensor correspond to one parameter for the scalar, 3 for the vector and 5 for the symmetric zero trace tensor. We can identify a correspondence between the spherical tensors with spherical harmonics.

$$\begin{aligned}
Y_1^0 &= \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \to T_0^1 = \sqrt{\frac{3}{4\pi}}V_z \\
Y_1^{\pm1} &= \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} = \mp\sqrt{\frac{3}{4\pi}}\frac{x\pm iy}{\sqrt{2}r} \to T_{\pm1}^1 = \mp\sqrt{\frac{3}{4\pi}}\frac{V_x \pm iV_y}{\sqrt{2}} \\
Y_2^{\pm2} &= \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm2i\phi} = \sqrt{\frac{15}{8\pi}}\left(\frac{x\pm iy}{\sqrt{2}r}\right)^2 \to T_{\pm2}^2 = \sqrt{\frac{15}{8\pi}}\left(\frac{V_x \pm iV_y}{\sqrt{2}}\right)^2 \\
Y_2^{\pm1} &= \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi} = \mp\sqrt{\frac{15}{4\pi}}\frac{(x\pm iy)z}{\sqrt{2}r^2} \to T_{\pm1}^2 = \mp\sqrt{\frac{15}{4\pi}}\frac{(V_x \pm iV_y)}{\sqrt{2}}V_z \\
Y_2^0 &= \sqrt{\frac{15}{16\pi}}(3\cos^2\theta - 1) = \sqrt{\frac{15}{16\pi}}2\frac{z^2 - (x+iy)/\sqrt{2}(x-iy)/\sqrt{2}}{r^2} \to T_0^2 = \sqrt{\frac{15}{16\pi}}2\left(V_z^2 - (V_x+iV_y)(V_x-iV_y)/2\right)
\end{aligned}$$

The above is obviously a special case, namely $U = V$ but at least we see that we can write a cartesian tensor in spherical basis. More generally

$$
\begin{aligned}
T^0_0 &= -\frac{\mathbf{U}\cdot\mathbf{V}}{3} = \frac{(U_{+1}V_{-1} + U_{-1}V_{+1} - U_0V_0)}{3} \\
T^1_q &= \frac{(\mathbf{U}\times\mathbf{V})_\mathbf{q}}{i\sqrt{2}} \\
T^2_{\pm 2} &= U_{\pm 1}V_{\pm 1} \\
T^2_{\pm 1} &= \frac{U_{\pm 1}V_0 + U_0V_{\pm 1}}{\sqrt{2}} \\
T^2_0 &= \frac{U_{+1}V_{-1} + 2U_0V_0 + U_{-1}V_{+1}}{\sqrt{6}}
\end{aligned}
$$

Indeed if $X^{k_1}_{q_1}$ and $Y^{k_2}_{q_2}$ are irreducible spherical tensors under rotations then

$$Z^k_q = \sum_{q_1,q_2} \langle kq \mid k_1q_qk_2q_2\rangle X^{k_1}_{q_1}Y^{k_2}_{q_2}$$

wnere $\langle kq \mid k_1q_1k_2q_2\rangle$ is a Clebsch Gordon coefficient. We see that spherical tensors can be combined in the same way as angular momentum states as we can write analogously

$$\mid kq\rangle = \sum_{q_1,q_2} \langle kq \mid k_1q_qk_2q_2\rangle \mid k_1q_1\rangle \mid k_2q_2\rangle$$

Back to the quadrupole operator

$$T_{ij} \rightarrow T^2_{\pm 2,\pm 1,0} = x_ix_j - \frac{1}{3}\delta_{ij} \rightarrow T^{k=2}_{q=\pm 2,\pm 1,0} \rightarrow r^2Y^{m=\pm 2,\pm 1,0}_{l=2}$$

Wigner Ekhart Theorem

We take advantage of the spherical tensor formalism to evaluate the matrix element for the electric quadrupole transition. Suppose the quantum numbers of initial and final state are α, j, m and α', j', m' respectively. Then we need to evaluate

$$\left\langle \alpha', j', m' \mid T^2_q \mid \alpha, j, m \right\rangle$$

The Wiger Ekhart theorem states that

$$\left\langle \alpha', j', m' \mid T^k_q \mid \alpha, j, m \right\rangle = \langle j', m' \mid k, q, j, m\rangle \frac{\langle \alpha' j' || T^k || \alpha j\rangle}{\sqrt{2j+1}}$$

The Clebsch Gordon coefficient is zero unless $j' = m + q$ and $k + j \geq j' \geq |k - j|$ We see that $\Delta l \leq 2$. Parity is conserved in electromagnetic interactions. The quadrupole operator is even under the parity operation. Therefore, initial and final states must have the same parity so $\Delta l = 2, 0$. The wave functions of initial and final atomic states are $R_i(r)Y^m_l(\theta,\phi)$ and $R_f()Y^{m'}_{l'}(\theta,\phi)$ respectively. And we saw above that $T^k_q = r^2Y^q_k(\theta,\phi)$. Therefore

$$\left\langle f \mid T^k_q \mid i \right\rangle = \int R_f(r)R_i(r)r^2r^2dr \int Y^{m'*}_{l'}Y^q_kY^m_l d\Omega$$

We can use the triple integral for spherical harmonics

$$\int d\Omega Y_l^{m*}(\theta,\phi)Y_{l_1}^{m_1}(\theta,\phi)Y_{l_2}^{m_2}(\theta,\phi) = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}}\langle l0 \mid l_1 0 l_2 0\rangle\langle l_1 m_1 l_2 m_2 \mid lm\rangle$$

The last Clebsch Gordon coefficient enforces the Wigner Ekhart selection rules. Note that for any given initial and final state, there will be a non-zero for only one of the five T_q^k. All that remains is the radial integrals.

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 $\Delta l \leq 1$. 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.

2.1 Plank radiation law

Suppoe we have atoms that make transitions between state A and B as follows

$$A \leftrightarrow \gamma + B$$

The higher energy state A decays to state B with emission of a photon. Then state B absorbs a photon and transitions to A. If the system is in equilibrium then

$$N(B)w_{abs} = N(A)w_{emis}$$

where $N(B), N(A)$ are the numbers of atoms in states A and B respectively. *wabs* is the probablity that an atom in the state B absorbs a photon and w_{emis} is the probablity that an atom in state A emits a photon. If the atoms are in thermal equilibrium then

$$\frac{N(B)}{N(A)} = \frac{w_{emis}}{w_{abs}} = \frac{e^{-E_B/kT}}{e^{-E_A/kT}} = e^{\hbar\omega/kT} \tag{2.1}$$

The transition probability from state A and n photons to the state B with $n+1$ photons

$$w_{emis} \propto |\left\langle B, n_\gamma + 1 \mid e^{-i\mathbf{k}\cdot x}\epsilon^\alpha \cdot \mathbf{p}a_k \mid A, n_\gamma \right\rangle|^2 = (n_\gamma + 1)|\left\langle B \mid e^{-i\mathbf{k}\cdot x}\epsilon^\alpha \cdot \mathbf{p} \mid A \right\rangle|^2$$

The probability for transition from state B with n photons to state A with $n-1$ is

$$w_{abs} \propto |\left\langle A, n_\gamma - 1 \mid e^{+i\mathbf{k}\cdot x}\epsilon^\alpha \cdot \mathbf{p}a_k^\dagger \mid A, n_\gamma \right\rangle|^2 = (n_\gamma)|\left\langle A \mid e^{+i\mathbf{k}\cdot x}\epsilon^\alpha \cdot \mathbf{p} \mid B \right\rangle|^2$$

The ratio

$$\frac{w_{emis}}{w_{abs}} = \frac{n+1}{n}$$

Together with Equation 2.1 we find that the number of photons in thermal equilibrium with wave number $\mathbf{k}$ and polarization ϵ is

$$n = \frac{1}{e^{\hbar\omega/kT} - 1}$$

That is, we imagine that there is an oscillator with $omega = c|\mathbf{k}|$ and that it is in equilibrium at temperature T when it is in the n^{th} energy level. Now imagine a box with walls that absorb and emit photons at all wavelengths and polarizations. It is filled with oscillators at every possible frequency. Each oscillator will be at energy

$$E_n = \frac{\hbar\omega_n}{e^{\hbar\omega/kT} - 1}$$

The total number of oscillators per unit frequency is the density of states

$$dN = 2\frac{V4\pi k^2 dk}{(2\pi)^3} = 2\frac{V4\pi\omega^2 d\omega}{(2\pi)^3 c^3}$$

The number of states per unit frequency per unit volume is

$$\rho(\omega) = \frac{8\pi\omega^2}{(2\pi)^3 c^3}$$

The total energy per unit frequency per unit volume is

$$U(\omega) = \rho(\omega)E_n = \frac{8\pi\hbar\omega^3}{(2\pi)^3 c^3 (e^{\hbar\omega/kT} - 1)}$$