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Lecture XXIV

Quantization of the E-M field

2.1 Radiative transitions

We consider the nonrelativistic regime so no pair production or annihilation.The hamiltonian for interaction of fields and sources is

$$H_\gamma + \sum_i \frac{1}{2m_i}(\mathbf{p}_i - \frac{e}{c}\mathbf{A}_i)^2 - \sum \mu_\mathbf{i} \cdot \mathbf{B_i} + \frac{1}{8\pi}\sum_{i\neq j}\frac{e_i e_j}{|\mathbf{r_i} - \mathbf{r_j}|} + \text{everything else.} \tag{2.1}$$

H_γ is the energy of the free field $\sim \sum_k \hbar\omega_k$. μ is the magnetic dipole moment

$$\mu = \frac{e\hbar}{2m_i c} g_i c \mathbf{s_i}$$

and $\mathbf{s_i}$ is the particle spin. "Everything else" contains non-electromagnetic interactions and fine and hyperfine structure. The interaction term in our Hamiltonian has terms linear (H_1) and quadratic (H_2) in the E-B fields.

$$\begin{aligned} H_1 &= \frac{e}{mc}\mathbf{p}\cdot\mathbf{A} - \mu\cdot\mathbf{B} \\ H_2 &= \frac{1}{2m}\left(\frac{e}{c}\right)^2 |\mathbf{A}|^2 \end{aligned}$$

(Coulomb gauge where $\nabla\cdot\mathbf{A} = 0$.) What are the relative strengths of the pieces? We are thinking about atomic transitions so non-relativistic electrons and emssion or absorption of photons with energy characteristic of atomic biniding energy.

$$\frac{e}{mc}\mathbf{p}\cdot\mathbf{A} \sim \frac{e}{mc}mv\sqrt{\frac{E_\gamma}{\lambda}} \sim e\alpha\sqrt{(\alpha^2 mc^2)^2/\hbar c} \sim \sqrt{\alpha}\alpha^3(mc^2) \sim \sqrt{\alpha}\left(\frac{v}{c}\right)^3 mc^2 \tag{2.2}$$

$$\mu\cdot\mathbf{B} \sim \frac{e\hbar}{2mc}kA \sim \frac{e\hbar}{2mc}k\sqrt{\frac{E_\gamma}{\lambda}} \sim \frac{e\hbar}{2mc}\frac{E_\gamma}{\hbar c}\sqrt{\frac{E_\gamma^2}{(\hbar c)}} \sim \frac{\sqrt{\alpha}}{2mc^2}(\alpha^2 mc^2)^2 \sim \sqrt{\alpha}\alpha^4 mc^2 \sim \sqrt{\alpha}\left(\frac{v}{c}\right)^4 mc^2 \tag{2.3}$$

Finally

$$H_2 \sim \frac{e^2}{2mc^2}|\mathbf{A}|^2 \sim \frac{e^2}{2mc^2}\frac{E_\gamma}{\lambda} \sim \alpha\alpha^4 mc^2 \sim \alpha\left(\frac{v}{c}\right)^4 mc^2 \tag{2.4}$$

2.1.1 Emission and absorption of photons

Let's write the vector potential field operator for future reference.

$$\mathbf{A}(\mathbf{x},t) = \sum_{k,\lambda} c\sqrt{\frac{\hbar}{2\omega V}}[a_{k,\lambda}\hat{\epsilon}^\lambda e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + a^\dagger_{k,\lambda}\hat{\epsilon}^\lambda e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}]$$

The creation and annihilation operators connect states that differ by precisely one photon of momentum k and polarization λ. In particular

$$\left\langle n_k + 1 \mid a^\dagger_{k\lambda} \mid n_k \right\rangle = \sqrt{n_k + 1}$$

and

$$\langle n_k - 1 \mid a_{k\lambda} \mid n_k \rangle = \sqrt{n_k}$$

Consider absorption of a photon by an atom transitioning from $\mid i\rangle$ to $\mid f\rangle$. The annihilation operator component of the field operator is the only part that contributes.

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

The annihilation gives zero for all but the photon $\mathbf{k}$ and polarization in the initial state.

2.1.2 Semi-classical description

Let's revisit the semi-classical description. Then we said that $a_{k\lambda}$ was a fourier coefficient of the plane wave expansion of the vector potential, rather than an annihilation operator. We could write the absorption process as

$$\mathbf{A} = c\sqrt{\frac{n_{k\lambda}\hbar}{2\omega V}} \epsilon_\lambda e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}$$

The absorption probability is proportional to $|\mathbf{A}|^2$. In the quantum theory the probablity scales linearly with $n_{k\lambda}$. Works fine and the results are equivalent. What about the emission process. Then we have something like

$$\begin{aligned}
\langle f; n_{k\lambda} + 1 \mid H_1 \mid i; n_{k\lambda} \rangle &= -\frac{e}{mc} \left\langle f; n_k + 1 \mid \sum_i c\sqrt{\frac{\hbar}{2\omega V}} a^\dagger_{k,\lambda} e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega t)} \mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda} \mid i; n_k \right\rangle \\
&= -\frac{e}{m}\sqrt{\frac{(n_k+1)\hbar}{2\omega V}} \left\langle f \mid e^{-i(\mathbf{k}\cdot\mathbf{x})} \mathbf{p}\cdot\epsilon_{\mathbf{k}\lambda} \mid i \right\rangle e^{i\omega t}
\end{aligned}$$

Time dependent perturbation theory

We have a hamiltonian $H = H_0 + H_I$ and state

$$\mid \psi(t)\rangle = \sum_k c_k(t) \mid u_k\rangle e^{-iE_k t/\hbar}$$

where

$$H_0 \mid u_k\rangle = E_k \mid u_k\rangle$$

Then substitution into Schrodinger's equation

$$\begin{aligned}
H|\,\psi\rangle &= i\hbar\frac{\partial}{\partial t}|\,\psi\rangle \\
(H_0+H_I)|\,\psi\rangle &= i\hbar\sum_k\left(\frac{\partial c_k}{\partial t}-i\frac{E_k}{\hbar}c_k|\,u_k\rangle\right)e^{-iE_kt/\hbar} \\
\langle u_m\,|(H_0+H_I)|\,\psi\rangle &= i\hbar\langle u_m\,|\sum_k\left(\frac{\partial c_k}{\partial t}-i\frac{E_k}{\hbar}c_k|\,u_k\rangle\right)e^{-iE_mt/\hbar} \\
\sum_k c_k\,\langle u_m\mid H_I\mid u_k\rangle\,e^{-iE_kt/\hbar} &= i\hbar\frac{\partial c_m}{\partial t}e^{-iE_mt/\hbar} \\
\rightarrow \dot{c}_m = \frac{1}{i\hbar}\sum_k c_k\,\langle m\mid H_I\mid k\rangle\,e^{i(E_m-E_k)t/\hbar}
\end{aligned}$$

If at $t=0$ the system is in the state l and if the perturbation is weak so that $c_l(0)=1$ and all others are small, then

$$\dot{c}_m = \frac{1}{i\hbar}\,\langle m\mid H_I\mid l\rangle\,e^{i(E_m-E_l)t/\hbar}$$

and

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

If the time dependence of H_I is sinusoidal then $H_I(t')=H_Ie^{\pm i\omega t}$ and

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

Then

$$\begin{aligned}
|c_m|^2 &= \frac{1}{\hbar^2}|\,\langle m\mid H_I\mid l\rangle\,|^2\frac{\sin^2((E_m-E_l\mp\hbar\omega)/\hbar)t/2}{t[(E_m-E_l\mp\hbar\omega)/2/\hbar]^2} \\
&= \frac{1}{\hbar^2}|\,\langle m\mid H_I\mid l\rangle\,|^2t\pi\delta((E_m-E_l\mp\hbar\omega)/2)
\end{aligned}$$

where we use

$$\lim_{\alpha\rightarrow\infty}\frac{\sin^2\alpha x}{\alpha x^2}=\delta(x)$$

Finally

$$|c_m|^2=\frac{1}{\hbar^2}|\,\langle m\mid H_I\mid l\rangle\,|^2 2\pi t\hbar\delta(E_m-E_l\mp\hbar\omega)$$

and the transition rate is

$$\frac{d}{dt}|c_m|^2=\frac{2\pi}{\hbar}|\,\langle m\mid H_I\mid l\rangle\,|^2\;\delta(E_m-E_l\mp\hbar\omega)$$

To turn it into a real measureable rate we need to sum over all of the final states. For photons there are

$$\rho=\frac{V|k^2|d\mathbf{k}d\Omega}{(2\pi)^3d(\hbar\omega)}$$

states per unit energy $\hbar\omega$ in the interval $\hbar\omega \to \hbar\omega + d(\hbar\omega)$. Then

$$\rho = \frac{V\omega^2 d\Omega}{(2\pi)^3 \hbar c^3}.$$

So the transition probability per unit time into $d\Omega$ is

$$w = \frac{2\pi}{\hbar} |\langle m \mid H_I \mid l \rangle|^2 \rho$$

where ρ must satisfy the delta function.

2.1.3 Density of States

For spontaneous emission, we multiply by the density of states, that is the number of states per unit energy available to the final state photon with energy $\hbar\omega$. Then

$$\rho(E) = \frac{Vd^3k}{(2\pi)^3 d(\hbar\omega)} = \frac{Vk^2 d\omega d\Omega}{(2\pi)^3 c\hbar d\omega} = \frac{Vk^2 d\Omega}{(2\pi)^3 \hbar c}$$

What about absorption? Suppose the atom is in a cavity with modes with frequencies corresponding to the interesting transition. Now put a single photon into each mode. There is one and only one mode (and photon) that can excite the transition and be absorbed. Now put a second photon into every mode. The absorption rate will increase by a factor of two. The number of photons per unit energy is

$$\rho = \frac{Vk^2 d\Omega}{(2\pi)^3 \hbar c} n_k$$

2.1.4 Quantum mechanical one photon transitions

The lowest order interaction hamiltonian for single photon transitions is

$$H_1 = \frac{e}{mc} c \sqrt{\frac{\hbar}{2\omega V}} \mathbf{p} \cdot \hat{\epsilon}^\lambda(\mathbf{k}) e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \tag{2.5}$$

The transition rates are given by the Golden rule

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} |\frac{e}{mc} c \sqrt{\frac{\hbar}{2\omega V}} \left\langle f \mid \mathbf{p} \cdot \hat{\epsilon}^\lambda(\mathbf{k}) e^{-i(\mathbf{k}\cdot\mathbf{r})} \mid i \right\rangle|^2 \delta(E_i - E_f) \tag{2.6}$$

and

$$d\Gamma_{i\to f} = \frac{2\pi}{\hbar} \frac{e^2}{m^2} \frac{\hbar}{2\omega V} |\left\langle f \mid \mathbf{p} \cdot \hat{\epsilon}^\lambda(\mathbf{k}) e^{-i(\mathbf{k}\cdot\mathbf{r}} \mid i \right\rangle|^2 \frac{V}{(2\pi)^3} \frac{k^2 d\Omega}{\hbar c}$$

Spontaneous emission

Here the initial state is $\mid i; 0\rangle = \mid i\rangle_{atom} \mid 0\rangle_\gamma$ and the final state is $\mid f, 1\rangle = \mid f\rangle_{atom} \mid 1_{k\lambda}\rangle = \mid f\rangle a^\dagger_{k\lambda} \mid 0\rangle$. The differential transition rate is

$$d\Gamma = \frac{2\pi}{\hbar} |\langle f; 1_{k\lambda} \mid H_1 \mid i; 0\rangle|^2 \rho_f(k)$$

where the density of fnal photon states is

$$\rho_f = \frac{V}{(2\pi)^3}\frac{d^3k}{\hbar d\omega} = \frac{V}{\hbar c(2\pi)^3}k^2 d\Omega$$

Only the part of the interaction hamiltonian proportional to the creation operator contributes. And that contribution is a single photon.

2.1.5 Electric Dipole transition

We will need to evaluate

$$\left\langle f \mid \mathbf{p}\cdot\hat{\epsilon}^\lambda(\mathbf{k})e^{-i(\mathbf{k}\cdot\mathbf{r})} \mid i\right\rangle$$

. The energy of a photon emitted in an atomic transition is of order the binding energy $\sim \alpha^2 mc^2$. The wavelength $\lambda = \frac{\hbar c}{\alpha^2 mc^2}$. The size of the atom is of order $a_0 = \frac{\hbar^2}{me^2} = \frac{\hbar}{mc\alpha}$. Therefore $\lambda/a_0 \sim \frac{1}{\alpha}$, that is, the wavelength is much bigger than the atom so that we can expand

$$e^{i(\mathbf{k}\cdot\mathbf{r})} \sim 1 + i\mathbf{k}\cdot\mathbf{r} + \dots$$

and keep only the lowest order term, namely 1. This is the dipole approximation. Then

$$\left\langle f \mid \mathbf{p}\cdot\hat{\epsilon}^\lambda(\mathbf{k})e^{-i(\mathbf{k}\cdot\mathbf{r})} \mid i\right\rangle = \left\langle f \mid \mathbf{p}\cdot\hat{\epsilon}^\lambda(\mathbf{k}) \mid i\right\rangle$$

We use the fact that

$$[H_0, \mathbf{r}] = \frac{1}{2m}[\mathbf{p}^2, \mathbf{r}] = -i\frac{\mathbf{p}}{m}\hbar$$

to rewrite

$$\langle f \mid \mathbf{p} \mid i\rangle \cdot \hat{\epsilon}^\lambda(\mathbf{k}) = \frac{m}{\hbar}\langle f \mid [H_0, \mathbf{r}] \mid i\rangle \cdot \hat{\epsilon}^\lambda(\mathbf{k})$$

and since initial and final states are eigenkets of H_0 with $E_i - E_f = \hbar\omega$

$$\langle f \mid [H_0, \mathbf{r} \mid i\rangle \cdot \hat{\epsilon}^\lambda(\mathbf{k}) = im\omega\langle f \mid \mathbf{r} \mid i\rangle \cdot \hat{\epsilon}^\lambda(\mathbf{k})$$

Spherical tensor

Let's work in the spherical basis with unit vectors $\hat{\epsilon}_\pm = \mp\frac{1}{\sqrt{2}}(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}})$, $\hat{\epsilon}_0 = \hat{\mathbf{z}}$. and write $\mathbf{r}$ as a spherical tensor

$$V_1^{\pm 1} = \mp\frac{1}{\sqrt{2}}(x \pm iy) = r\sqrt{\frac{4\pi}{3}}Y_1^{\pm 1}, \qquad V_1^0 = z = r\sqrt{\frac{4\pi}{3}}Y_1^0$$

Let's consider $\lambda = +1$ and $\mathbf{k}$ in the θ direction with respect to the z-axis of the atom, and the matrix element

$$\left\langle n_f, l_f, m_f \mid V_1^1 \mid n_i, l_i, m_i\right\rangle \hat{\epsilon}_+^* \cdot \hat{\epsilon}_{\lambda=+1}(\mathbf{k})$$

The polarization vector $\hat{\epsilon}_{+1}(\mathbf{k}) = -\frac{1}{\sqrt{2}}(\hat{\mathbf{x}}' + i\hat{\mathbf{y}}')$ where $\hat{\mathbf{x}}'$ and $\hat{\mathbf{y}}'$ are the unit vectors in the coordinate system with $\hat{\mathbf{z}} \parallel \mathbf{k}$. Then $\hat{\epsilon}_{+1}(\mathbf{k}) = -\frac{1}{\sqrt{2}}(\hat{\mathbf{x}}\cos\theta + \hat{\mathbf{z}}\sin\theta + i\hat{\mathbf{y}})$. (We assume that the angle θ is about the $\hat{\mathbf{y}}$ axis.) Now

$$\left\langle n_f, l_f, m_f \mid V_1^1 \mid n_i, l_i, m_i\right\rangle \hat{\epsilon}_+^* \cdot \hat{\epsilon}_{\lambda=+1}(\mathbf{k}) \quad = \quad \left\langle n_f, l_f, m_f \mid V_1^1 \mid n_i, l_i, m_i\right\rangle \frac{1}{2}(1+\cos\theta)$$

Similarly

$$\begin{aligned}\left\langle n_f, l_f, m_f \mid V_1^0 \mid n_i, l_i, m_i \right\rangle \hat{\epsilon}_0^* \cdot \hat{\epsilon}_{\lambda=+1}(\mathbf{k}) &= \left\langle n_f, l_f, m_f \mid V_1^0 \mid n_i, l_i, m_i \right\rangle \frac{1}{\sqrt{2}} \sin\theta \\ \left\langle n_f, l_f, m_f \mid V_1^{-1} \mid n_i, l_i, m_i \right\rangle \hat{\epsilon}_0^* \cdot \hat{\epsilon}_{\lambda=+1}(\mathbf{k}) &= \left\langle n_f, l_f, m_f \mid V_1^{-1} \mid n_i, l_i, m_i \right\rangle \frac{1}{2}(1-\cos\theta)\end{aligned}$$

The total rate from $\mid n_i, l)i, m_i\rangle$ to final state $\mid n_f, l_f, m_f\rangle$ with a photon into angle θ with polarization $+1$ is proportional to

$$\begin{aligned}\frac{d\Gamma}{d\Omega} \propto & \mid \left\langle n_f, l_f, m_f \mid V_1^1 \mid n_i, l_i, m_i \right\rangle \frac{1}{2}(1+\cos\theta)\mid +^2 + \mid \left\langle n_f, l_f, m_f \mid V_1^0 \mid n_i, l_i, m_i \right\rangle \frac{1}{\sqrt{2}} \sin\theta\mid^2 \\ & + \mid \left\langle n_f, l_f, m_f \mid V_1^{-1} \mid n_i, l_i, m_i \right\rangle \frac{1}{2}(1-\cos\theta)\mid^2 \end{aligned} \tag{2.7}$$

Remembering the Wigner Ekhart theorem

$$\left\langle n_f, j_f, m_f \mid V_q^k \mid n_i, j_i, m_i \right\rangle = \langle j_f, m_f | q, k, j_i, m_i\rangle \left\langle n_f, j_f \mid V_1 \mid n_i, j_i \right\rangle$$

where $\langle j_f, m_f | q, k, j_i, m_i\rangle$ is a Clebsch-Gordon coefficient. The C-G coefficient is zero unless $m_f = k + m_i$ and $|j_i + q| \geq j_f \geq |j_i - q|$. Evidently only one term in Equation 2.7 is non-zero for any given choice of initial and final state. Also, the dipole operator has odd parity so the expectation value is nonzero only if initial and final states have opposite parity. We conclude that $\Delta l = \pm 1$. Let's suppose $m_f = m_i + 1$. Then only the first term in Equation 2.7 contributes. Sum over photon polarizatons,

$$\frac{d\Gamma}{d\Omega} \propto \mid \left\langle n_f, l_i \pm 1, m_i + 1 \mid V_1^1 \mid n_i, l_i, m_i \right\rangle \mid^2 \frac{1}{4}\left((1+\cos\theta)^2 + (1-\cos\theta)^2\right) \sin\theta d\theta$$

and integrate over photon directions $\mathbf{k}$.

$$\Gamma \propto \mid \left\langle n_f, l_i \pm 1, m_i + 1 \mid V_1^1 \mid n_i, l_i, m_i \right\rangle \mid^2 \frac{8\pi}{3} \tag{2.8}$$

Next we might sum over all $2m_f + 1$ possible final states. That will involve the other terms in Equ. 2.7. But they are all related (according to WignerEkhart) by Clebsch-Gordon coefficients so it won't be too painful. And if the inital state is ^2P and the final state ^1S, the only final state is $m_f = 0$. We might also average over initial states. But if the final state has $l = 0$, then by symmetry the rate from $l = 1, m_i = 0, \pm 1$ must all be the same.

Matrix element

Next we want to evaluate

$$\left\langle n_f, l_f, m_f \mid V_q^k \mid n_i, l_i, m_i \right\rangle$$

Initial and final atomic states are $\langle \mathbf{x} \mid n_i\rangle = R_{n_i}(r) Y_{l_i}^{m_i}(\theta, \phi)$, and $\langle \mathbf{x} \mid n_f\rangle = R_{n_f}(r) Y_{l_f}^{m_f}(\theta, \phi)$ and $V_q^k = r\sqrt{\frac{4\pi}{3}} Y_q^k(\theta, \phi)$. Then

$$\left\langle n_f, l_f, m_f \mid V_q^k \mid n_i, l_i, m_i \right\rangle = \int_0^\infty r^3 R_{n_i}(r) R_{n_f}^*(r) dr \int Y_{l_f}^{m_f\,*}(\theta, \phi) Y_q^k(\theta, \phi) Y_{l_i}^{m_i}(\theta, \phi) d\Omega \tag{2.9}$$

$$= \int_0^\infty r^3 R_{n_i}(r) R^*_{n_f}(r) dr \sqrt{\frac{(2q+1)(2l_i+1)}{4\pi(2l_f+1)}} \langle l_i q; 00 \mid l_i q : l_f 0\rangle \langle l_i q; m_i k \mid l_i q; l_f m_f\rangle \tag{2.10}$$

Note that the triple product of spherical harmonics enforces the Wigner-Ekhart selection rules. Again if the initial state is $l_i = 1, m_i = -1$ and the final state $l_f = 0, m_f = 0$ then $k = 1$ and

$$\begin{aligned}
\left\langle n_f, 0, 0 \mid V_1^1 \mid n_i, 1, -1\right\rangle &= \int_0^\infty r^3 R_{n_i}(r) R^*_{n_f}(r) dr \sqrt{\frac{4\pi}{3}} \sqrt{\frac{(3)(3)}{4\pi(1)}} \langle 11; 00 \mid 00\rangle \langle 11; -11 \mid 00\rangle \\
&= \int_0^\infty r^3 R_{n_i}(r) R^*_{n_f}(r) dr \sqrt{\frac{4\pi}{3}} \sqrt{\frac{(3)(3)}{4\pi(1)}} \sqrt{\frac{1}{3}} \sqrt{\frac{1}{3}} \\
&= \sqrt{\frac{1}{3}} \int_0^\infty r^3 R_{n_i}(r) R^*_{n_f}(r) dr
\end{aligned}$$

where $\langle 11; -11 \mid 00\rangle = \langle 00 \mid 11; -11\rangle = \sqrt{\frac{1}{3}}$
Note that if the atom were in a magnetic field, then it would be polarized and the levels might be split there would be a correlation between direction, energy, and polarization.