Lecture 45

Relevant sections in text: §

Spontaneous Emission

We now study transitions of a single atomic electron in which, initially, there is no electromagnetic radiation (photons). Given that the interaction between photons and the electron is weak compared to the interaction between the electron and the nucleus we can study the transition probability via first-order time dependent perturbation theory.

Our first task is to identify the unperturbed system and the perturbation. We wrote the Hamiltonian for the electron-photon system as

$$H = \frac{1}{2m}\left(\vec{P} - \frac{q}{c}\vec{A}\right)^2 + V_0(\vec{X}) + \frac{1}{8\pi}\int d^3x\,(E^2 + B^2),$$

where V_0 represents the potential binding the electron to the nucleus. We identify the unperturbed Hamiltonian

$$H_0 = \frac{P^2}{2m} + V_0(\vec{X}) + \frac{1}{8\pi}\int d^3x\,(E^2 + B^2),$$

and the perturbation

$$V = -\frac{q}{mc}\vec{A}\cdot\vec{P} + \frac{q^2}{2mc^2}A^2.$$

(Here we used the fact that the vector potential operator is divergence free.) Giving a rigorous mathematical meaning to the A^2 term is actually somewhat tricky. I'll spare you the details except to say that in order to have a chance of making the A^2 term well-defined we must define it using "normal ordering" in which all annihilation operators are put to the right of all creation operators.

Next we need to get a hold of the unperturbed stationary states. If we use a spherically symmetric atomic potential V_0 we can denote the eigenvectors of H_0 as vectors of the form

$$|E\rangle = |n, l, m\rangle \otimes |\text{photon}\rangle,$$

where the photon states are the states discussed in the last lecture – states representing a collection of photons with given frequencies. The energy of this state is obtained by adding the energy determined by n to that obtained by summing up $\hbar\omega$ for all the different photons.

Let us now use first-order perturbation theory to get an expression for the probability for an atomic electron in an energy level n_i with no photons present at $t = 0$ to make a transition to a state in which the atomic electron is in the state n_f and there is one

photon present at time t. This is a spontaneous transition since no stimulating radiation is present. The initial state vector is then of the form

$$|i\rangle = |n_i, l_i, m_i\rangle \otimes |0\rangle,$$

and has energy E_i, and the final state vector is of the form

$$|f\rangle = |n_f, l_f, m_f\rangle \otimes |1_{\mathbf{k},\sigma}\rangle$$

with energy E_f. Since the final state is part of the continuous spectrum (because k is continuously variable), the transition probability $P(i \to f)$ is really a transition probability density. We have

$$\begin{aligned} P(i \to f) &\approx |\frac{1}{\hbar}\int_0^t dt' e^{\frac{i}{\hbar}(E_f - E_i)t'}\langle f|V|i\rangle|^2 \\ &\approx \frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2 \delta(E_f - E_i)t. \end{aligned}$$

As usual we see that "energy conserving" transitions dominate. In this case "energy conserving" means that the final energy of electron plus photon is equal to the initial energy of the electron. This means in particular that only spontaneous *emission* can occur because the photon vacuum state is the state of lowest photon energy. Thus (using unperturbed energy accounting) the final electronic energy is lower than the initial electronic energy with the difference in energy appearing in the photon. Of course, all of this is contingent upon the non-vanishing of the matrix element, which we now investigate.

Recall that the vector potential operator takes the form

$$\vec{A} = \frac{1}{(2\pi)^{3/2}}\int d^3k\, \vec{A}_{\vec{k}} e^{i\vec{k}\cdot\vec{X}},$$

where

$$\vec{A}_{\vec{k}} = \sum_{\sigma=1}^{2}\sqrt{\frac{\hbar c}{k}}(a_{\vec{k},\sigma}\epsilon_{\vec{k},\sigma} + a^{\dagger}_{-\vec{k},\sigma}\epsilon_{-\vec{k},\sigma}).$$

Here $\vec{X}$, $a_{\vec{k},\sigma}$ and $a^{\dagger}_{\vec{k},\sigma}$ are all operators. First let us focus on the part of the matrix element involving the photons. The perturbation involves terms linear in the creation/annihilation operators (from the $\vec{A}\cdot\vec{P}$ term) and terms quadratic in the creation/annihilation operators (from the A^2 term). If you recall how such terms behave for harmonic oscillator matrix elements between stationary states you will easily see that the matrix element of the A^2 term vanish (keeping in mind we defined this term using normal ordering). Thus we only need to figure out what to do with the matrix element of

$$\vec{A}\cdot\vec{P} = \frac{1}{(2\pi)^{3/2}}\int d^3k \sum_{\sigma=1}^{2}\sqrt{\frac{\hbar c}{k}}e^{i\vec{k}\cdot\vec{X}}(a_{\vec{k},\sigma}\epsilon_{\vec{k},\sigma}\cdot\vec{P} + a^{\dagger}_{-\vec{k},\sigma}\epsilon_{-\vec{k},\sigma}\cdot\vec{P}).$$

Because the annihilation operator sets the vacuum state to the zero vector, only the term with the creation operator is relevant. The creation term only gives a non-zero result when its wave vector and polarization are the same as that appearing in $|f\rangle$. We then get

$$\langle f|V|i\rangle = \frac{1}{(2\pi)^{3/2}}\sqrt{\frac{\hbar c}{k}}\langle n_f, l_f, m_f|e^{i\vec{k}\cdot\vec{X}}(\epsilon_{\vec{k},\sigma}\cdot\vec{P})|n_i, l_i, m_i\rangle.$$

Notice this expression is exactly what we arrived at when treating the electromagnetic field as a classical, externally prescribed field! Thus all our results pertaining to electric dipole transitions come into play. In particular, we again have electric dipole selection rules

$$\Delta l = \pm 1, \quad \Delta m = 0, \pm 1$$

and we have a correspondence between the change of the angular momentum quantum number m and the polarization of the emitted photon.

To get the transition rate (*a la* Fermi's Golden Rule) we should sum over all possible final state photon wave vectors (with the given magnitude) and polarization states, as well as insert the density of states factor. I will not go through all this. But I will point out that, with the transition rate in hand, we can easily compute the lifetime (half-life) of a state which decays by this process. Imagine many atoms all prepared in the same initial state. The transition rate determines how many atoms have decayed at any given time. The reciprocal of the transition rate can then be used to compute the lifetime. For example, the $n_i = 2, l_i = 1$ hydrogen energy level decays to the ground state ($n_f = 0, l_f = 0$) by electric dipole radiation; the lifetime is $1.6 \times 10^{-9} s$, in agreement with experiment.

One final comment: if we consider transitions between initial and final stationary states which both contain a large number of photons (so that the initial and final photon numbers are approximately equal) we can recover the transition rates we computed earlier for stimulated emission/absorption where we had a classical, prescribed radiation field. Thus the "classical, prescribed radiation field" in this context can be interpreted in terms of states containing many photons.