Radiative Transitions

From static atoms we now move to their response when perturbed by an electromagnetic wave. We are going to use a semiclassical approximation, in which the atom is treated quantum mechanically but the radiation is treated classically. Recall that the classical approximation is one in which the discrete nature of photons does not matter. **Ask class:** given that, which of the Einstein coefficients should we be able to get in this way? The B coefficients (absorption and stimulated emission), which depend on the external radiation field. The A coefficient, for spontaneous emission, requires a full quantum treatment and the inclusion of virtual quanta.

In an electromagnetic potential $\phi = \phi_{\rm atom} + \phi_{\rm ext}$, where $\phi_{\rm atom}$ is the scalar potential for the atom, and $\phi_{\rm ext}$ is the external scalar potential, the nonrelativistic Hamiltonian is

$$H = \mathbf{P}^2/2m + e\phi \ . \tag{1}$$

Note that here $\mathbf{P}$ is the mechanical momentum, not the conjugate momentum $\mathbf{p}$ that becomes $-i\hbar\nabla$ in the coordinate representation. The relation between the two is $\mathbf{P} = \mathbf{p} - e\mathbf{A}/c$, where $\mathbf{A}$ is the external vector potential. As always with the potentials, we have a choice of gauge; in this case, a convenient one is the "Coulomb gauge" in which $\nabla \cdot \mathbf{A} = \phi_{\rm ext} = 0$, because then $\mathbf{A}$ commutes with $\mathbf{p}$ in their product. In this gauge,

$$H = p^2/2m - (e/mc)\mathbf{A}\cdot\mathbf{p} + e^2A^2/(2mc^2) + e\phi_{\rm atom} \ . \tag{2}$$

This can be thought of as the sum of the original (non-perturbed) Hamiltonian plus perturbations: $H = H_0 + H_1 + H_2$, where $H_0 = p^2/2m + e\phi_{\rm atom}$, $H_1 = (e/mc)\mathbf{A}\cdot\mathbf{p}$, and $H_2 = e^2A^2/(2mc^2)$. Do we have to include both H_1 and H_2? We can take their ratio to find out.

$$H_1/H_2 = (epA/mc)/(e^2A^2/2mc^2) = (2ev/c)/(\alpha^2 a_0 A) \ , \tag{3}$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant and $a_0 = \hbar^2/me^2 = 5.3\times10^{-9}$ cm is the Bohr radius. What is the order of magnitude of the velocity? For a typical energy $E = -m_e Z^2 e^4/2\hbar^2$, setting $E = -\frac{1}{2}m_e v^2$ gives $v/c = Ze^2/\hbar c = Z\alpha$. That gives

$$\eta \equiv H_1/H_2 \sim 2Ze/(\alpha a_0 A) \ . \tag{4}$$

What is the magnitude of A? We know that $B = \nabla\times A$, so with $E \sim B$ we can estimate $A \sim \lambda E$, where λ is the wavelength of the electromagnetic wave. Note that in doing this we're doing the "cancelling the d's" approach to derivatives. This will be justified after the fact when we discover that $H_1 \gg H_2$, meaning that real precision isn't necessary most of the time. For the energies of interest, $\lambda \sim a_0/\alpha$. A few algebraic manipulations then produce

$$\eta^2 \sim \frac{4\hbar\omega}{2\pi\alpha a_0^2\lambda E^2} \ . \tag{5}$$

What do we do with the E^2? We know that the electromagnetic energy density is something like E^2 or B^2 (with factors of 8π, but at this level of inaccuracy we don't care). For a typical photon energy $\hbar\omega$, that means that the photon number density is $n_{\rm ph} \sim E^2/\hbar\omega$. Putting this together, the ratio of H_1 to H_2 is

$$\eta \sim (n_{\rm ph}a_0^3)^{-1/2} \ . \tag{6}$$

Ask class: can we argue that in most circumstances this ratio is much larger than unity, so that H_2 may be ignored? The idea is that if there are typically far fewer than one photon in a cubic Bohr radius, then $\eta \gg 1$. One photon per cubic Bohr radius would be roughly 10^{25} cm^{-3}. **Ask class:** for a blackbody, how do we estimate the photon number density? We could take the radiation energy density and divide by kT, for example. Or, if we happened to remember that there are about $20T^3$ photons per cubic centimeter for a temperature of T Kelvin, that works as well. Either way, if $T \ll 10^8$ K our assumption that $H_1 \gg H_2$ is okay.

Let's look at this from another perspective. It turns out that the $\mathbf{A}\cdot\mathbf{p}$ term represents single-photon transitions, whereas the A^2 term represents two-photon transitions. Therefore, the H_2 term is only important if there is a reasonable probability that "near" the atom (within a volume a_0^3) there is more than one photon. From a statistical standpoint, this only is likely if the average number of photons in that volume is greater than or comparable to unity. As we'll see, however, there are times when a single-photon transition is forbidden, meaning that the comparatively rare two-photon transitions are needed to go from one state to another.

So let's consider only H_1. What does this do? If the Hamiltonian of a system is explicitly time-independent (e.g., the Hamiltonian of a static atom in the nonrelativistic limit), then once the system is in an eigenstate of that Hamiltonian it stays that way until there is some perturbation. The wave function is then $\psi(t) = \phi_i(\mathbf{r})\exp(-iE_it/\hbar)$, where E_i is the energy of the ith eigenstate ϕ_i. Since the global phase factor $\exp(iE_it/\hbar)$ does not change measurable quantities, the system is stationary. **Ask class:** what does that imply about spontaneous emission in this picture? It wouldn't happen; that's why perturbations from virtual fields are necessary.

When the time-dependent perturbation H_1 is included, things change. In particular, the original wave function of the system is no longer an eigenstate of the full Hamiltonian. Thus the wave function is a mixture of energy eigenstates, each of which has a phase factor that evolves at a different rate (related to their separate energy eigenvalues). The system therefore evolves. Another way to look at this is that the original set of eigenstates $|\phi_i\rangle$ forms a complete set of basis states, so any wave function of the system can be expressed in terms of them. Therefore, one can write the true wave function as

$$\psi(t) = \sum a_k(t)\phi_k \exp(-iE_kt/\hbar) \tag{7}$$

where the $a_k(t)$ are time-dependent coefficients. Thus, the state of the system evolves in a period of time from the pure state ϕ_i (before the perturbation) to a mixture of pure states after the perturbation. The probability of a transition from state i to state f is the overlap between the final state and state i. In formulae, the probability per unit time w_{fi} for a transition from state i to state f due to a perturbation that acts over time T is

$$\begin{array}{rl} w_{fi} & = \frac{4\pi^2}{\hbar^2 T}|H^1_{fi}(\omega_{fi})|^2 \\ H^1_{fi}(\omega) & \equiv (2\pi)^{-1}\int_0^T H^1_{fi}(t')e^{i\omega t'}\,dt' \\ H_{fi}(t) & \equiv \int \phi_f^* H^1 \phi_i\,d^3x \\ \omega_{fi} & \equiv (E_f - E_i)/\hbar\ . \end{array} \tag{8}$$

We assume that $\mathbf{A}(\mathbf{r},t)$ has the form

$$\mathbf{A}(\mathbf{r},t) = \mathbf{A}(t)\exp(i\mathbf{k}\cdot\mathbf{r}) \tag{9}$$

and that $\mathbf{A}(t)$ vanishes outside the interval $(0,T)$. For an atom with several electrons, the perturbation is the sum of the perturbations of each electron singly:

$$H^1 = -\frac{e}{mc}\sum \mathbf{A}\cdot\mathbf{p}_j = \frac{ie\hbar}{mc}\mathbf{A}\cdot\sum\nabla_j\ . \tag{10}$$

Absorption and induced (or stimulated) emission are intimately related, and in fact $w_{fi} = w_{if}$ (as is shown in Rybicki and Lightman, pages 270-271). This is the principle of detailed balance.

The resulting integrals contain a factor of $\exp(i\mathbf{k}\cdot\mathbf{r})$. It would simplify things greatly if we could expand this as a power series

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} + \frac{1}{2}(i\mathbf{k}\cdot\mathbf{r})^2 + \ldots \tag{11}$$

and take the lowest order terms. Can we do that? We need an estimate of the magnitude of $\mathbf{k}\cdot\mathbf{r}$. **Ask class:** how can we estimate this? We know that $r \sim a_0$, and since the wavelength is $\lambda \sim a_0/(Z\alpha)$ we have $kr \sim Z\alpha \ll 1$. **Ask class:** suppose, then, that we are interested in the inner shell electrons of atoms. Roughly at what point do we need to consider higher order terms in the expansion? Around $Z \sim 100$, the next order term becomes comparable to the first term. **Ask class:** for nuclear transitions, the energies are $\sim 10^6$ times higher, and the dimensions are $\sim 10^4$ times lower, than for atomic transitions. How good is the expansion then? You've got to keep many terms, since $\mathbf{k}\cdot\mathbf{r} \sim 1$. We'll find out that the first term (the 1) gives dipole transitions, the second ($i\mathbf{k}\cdot\mathbf{r}$) gives quadrupole, and so on. For atoms, dipole transitions are much stronger than higher-order transitions. One therefore speaks of "allowed" (dipole) and "forbidden" (higher-order) transitions for atomic spectroscopy. No such clean hierarchy exists for nuclear transitions.

With the approximation $\exp(i\mathbf{k}\cdot\mathbf{r}) \approx 1$, we get

$$w_{fi} \approx (4\pi^2/\hbar^2 c)|(\mathbf{1}\cdot\mathbf{d})_{fi}|^2\mathcal{J}(\omega_{fi})\ , \tag{12}$$

where $\mathbf{d} \equiv e\sum_j r_j$ is the dipole operator and $\mathcal{J}(\omega) = (\omega^2/cT)|\mathbf{A}(\omega)|^2$. Also, $\mathbf{1}$ is a unit vector giving the polarization: $\mathbf{A} = A\mathbf{1}$. Averaging over unpolarized radiation gives a factor of 1/3, since $\langle\cos^2\theta\rangle = 1/3$.

We can now take these answers and use them to compute one of the Einstein coefficients. Then, from the Einstein relations, we can get the other two.

Let u and l refer to the upper and lower states. Then, for unpolarized radiation, we have

$$\langle w_{lu}\rangle = B_{lu}J_{\nu_{ul}} \ , \tag{13}$$

from the definition of the first B coefficient. For unidirectional radiation, $J_{\nu_{ul}} = (4\pi)^{-1}\mathcal{J}(\nu_{ul})$. Since $\omega = 2\pi\nu$ we also have $\mathcal{J}(\nu_{ul}) = 2\pi\mathcal{J}(\omega_{ul})$. Therefore,

$$\langle w_{lu}\rangle = \frac{1}{2}B_{lu}\mathcal{J}(\omega_{ul}) \ . \tag{14}$$

Solving, and using the previous expressions, we get

$$B_{lu} = \frac{32\pi^4|d_{lu}|^2}{3ch^2} \ . \tag{15}$$

Let's assume that the levels are nondegenerate. Then the Einstein relations give

$$\begin{aligned} B_{lu} &= B_{ul} \\ A_{ul} &= 64\pi^4\nu_{ul}^3|d_{ul}|^2/(3c^3h) \ . \end{aligned} \tag{16}$$

To get the transition rate for degenerate levels, one averages over initial states and sums over final states (see 10.28b in Rybicki and Lightman).

Instead of carrying around the entire formula, it is usual to quote an *oscillator strength* for a transition. We hinted at this before: if you take a classical model of a transition line and integrate the cross section over the frequency, you get

$$\int_0^\infty \sigma(\nu)d\nu = \pi e^2/(mc) = B_{lu}^{\rm classical}(h\nu_{lu}/4\pi) \ , \tag{17}$$

where $B_{lu}^{\rm classical} = 4\pi^2e^2/(h\nu_{lu}mc)$. Then in general we can write

$$\begin{aligned} B_{lu} &= B_{lu}^{\rm classical}f_{lu} \ , \\ f_{lu} &= \tfrac{2m}{3\hbar^2 g_l e^2}(E_u - E_l)\sum|d_{lu}|^2 \ . \end{aligned} \tag{18}$$

Here g_l is the multiplicity of the lower state, and one sums over the final (upper) state, over all states with the same energy E_u. One can similarly define an emission oscillator strength, except that we find the oscillator strength is *negative.*

We have talked about oscillator strengths assuming discrete states, but in many cases (e.g., when talking about bound-free transitions), the final state is in a continuum. In that case, it's meaningless to think of the oscillator strength to one precisely defined energy, so instead one talks about a probability per frequency range of the upper state. Then the continuum oscillator strength is the total to all continuum states.

Remarkably, even though individual oscillator strengths can be complicated to compute, there is a simple rule that governs the sum of the oscillator strengths of all transitions from a given state. Suppose we have an atom with N electrons. Let n represent the initial state, and n' represent some final state. Then the sum of f over all final states is given by the Thomas-Reiche-Kuhn sum rule:

$$\sum_{n'} f_{nn'} = N \; . \tag{19}$$

Note that since emission oscillator strengths are negative, in general the sum over just absorption oscillator strengths is greater than or equal to N.

We will close by mentioning some aspects of selection rules. If one considers only dipole transitions, then it's only a single electron that is affected (since only a single photon is involved). One can then ask, for a given (n, l, m) initially, what limits are there on (n', l', m')? The way to do this is to examine the integrals for dipole mixing of states. The radial integral, which relates to the n quantum number, is of the form $\int r R_{nl} R_{n'l'} dr$. Examination of these functions reveals that such integrals can be nonzero for any n and n'. That means that, say, a transition from $n = 1$ to $n = 7$ is just as possible as $n = 1$ to $n = 2$. But the l and m quantum numbers are different. For them, it is found that in electric dipole transitions $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$. Two states not related in this way cannot have a direct electric dipole transition. The higher order terms in the series for $\exp(i\mathbf{k} \cdot \mathbf{r})$ contribute different selection rules, but the transitions are much weaker. That's why electric dipole transitions are often called allowed, versus the forbidden transitions that have to take other paths. There are some transition rules that apply to all single-photon transitions. One is that since photons carry off a single unit of angular momentum, it is impossible to go from one state with zero total (spin plus orbital) angular momentum to another zero total angular momentum state. To do that, one must have a transition to an intermediate state or a collision. Consider for example helium in a $1s2s$ state instead of its ground $1s^2$ state. A spontaneous transition to the ground state is extremely forbidden, since it needs to happen via a two-photon transition. For example, in hydrogen the $2s \rightarrow 1s$ transition happens with a spontaneous emission coefficient of 8.4 s^{-1}, versus about $6.2 \times 10^8 \text{ s}^{-1}$ for $2p \rightarrow 1s$. Some people have thought about this as a good way to store energy for, e.g., rocket fuel, but the helium would be highly explosive since collisions will rapidly depopulate the excited states.