May 15

# Absorption and Emission of Photons

We are now ready to work out the matrix elements for photon absorption and emission from atoms. We begin from the Hamiltonian

$$H = \frac{1}{2m}(\vec{p} - q\vec{A})^2 - g\frac{q}{2m}\vec{B}\cdot\vec{S} + V$$

and expand to first order in $\vec{A}$. This gives

$$\Delta H = -\frac{q}{2m}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) - g\frac{q}{2m}\vec{B}\cdot\vec{S}$$

We next insert into this expression the forms of $\vec{A}$ and $\vec{B}$ derived in the previous lecture for a classical electromagnetic plane wave.

$$\vec{A} = \mathrm{Re}\left[-iA_0\vec{\epsilon}\, e^{-i(\omega t - \vec{k}\cdot\vec{x})}\right]$$

$$\vec{B} = \mathrm{Re}\left[A_0\,\vec{k}\times\vec{\epsilon}\, e^{-i(\omega t - \vec{k}\vec{x})}\right]$$

In the derivation to follow, I will assume for simplicity that $\vec{\epsilon}$ is real-valued, that is, that the wave is linearly polarized. It is not difficult to check that the final result is correct also for circularly polarized light waves. I will also treat $A_0$ as real. This will also not affect the final result.

We have, then,

$$\Delta H = -\frac{q}{2m}\{\vec{p},\ \vec{\epsilon}A_0\sin(\omega t - \vec{k}\cdot\vec{x})\}$$

$$-g\frac{q}{2m}\,\vec{k}\times\vec{\epsilon}\,A_0\cos(\omega t - \vec{k}\cdot\vec{x})\cdot\vec{S}$$

This expression looks complicated, but there is a manipulation that simplifies it greatly. Take $\vec{x} = 0$ to be the center of the atom. Then the typical size of $x$ is

$$x \sim 1\,\text{Å}$$

Typical atomic resonances are in the ultraviolet, for which

$$k \sim \frac{2\pi}{\lambda} \sim \frac{2\pi}{1000\,\text{Å}} \sim 10^{-2}/\text{Å}$$

So $kx \sim 10^{-2}$ or smaller.

This is not an accident. For a photon of energy $\omega$, the wavenumber of the photon is

$$k_\gamma \sim \frac{\omega}{c} \quad \text{or} \quad \omega \sim k \cdot c$$

For a nonrelativistic electron in an atom, a kinetic energy $\omega$ leads to a much smaller wavenumber,

$$\omega \sim E \sim \frac{k_e^2}{2m} \sim k_e \cdot v$$

Since $v/c \sim 10^{-2}$ in atoms, we find

$$k_\gamma / k_e \sim v/c \sim 10^{-2}$$

We can take advantage of this by expanding the electromagnetic plane wave in a Taylor series about $\vec{x} = 0$. Then

$$\Delta H = -\frac{q}{2m}\{\vec{p}\cdot\vec{\varepsilon}A_0\}\sin\omega t$$
$$-\frac{q}{2m}\{\vec{p}\cdot\vec{\varepsilon}A_0(-\vec{k}\cdot\vec{x})\}\cos\omega t$$
$$-g\frac{q}{2m}\vec{k}\times\vec{\varepsilon}\,A_0\cdot\vec{S}\cos\omega t + \cdots$$

The second and third terms are smaller than the first term by a factor of $10^{-2}$. The next two terms are smaller by another factor of $10^{-2}$. This gives a systematic expansion of the amplitude in powers of $\langle kx\rangle$. The rates are the squares of amplitudes, and so a process induced by a term in the amplitude with one power of $\langle kx\rangle$ is suppressed by a factor $10^{-4}$.

In this lecture and the next, I will restrict my attention to the leading term in this series. Later, I will discuss the systematic properties of the higher terms in the series.

Take the first term in $\Delta H$, then, and evaluate it between states $|a\rangle$ and $|b\rangle$ that are eigenstates of the Hamiltonian $H_0$ for an electron in an atom

$$H_0|a\rangle = E_a|a\rangle \qquad H_0|b\rangle = E_b|b\rangle \qquad E_b > E_a$$

We find

$$\langle b|\Delta H|a\rangle = -\frac{q}{m}\vec{\varepsilon}\,A_0\cdot\langle b|\vec{p}|a\rangle\sin\omega t$$

A convenient way to evaluate this is to notice that, since $H_0 = p^2/2m + \cdots$,

$$\frac{\vec{p}}{m} = \frac{1}{i}[\vec{r}, H_0]$$

Then

$$\langle b|\Delta H|a\rangle = iqA_0\vec{\varepsilon}\cdot\langle b|[\vec{r},H_0]|a\rangle \sin\omega t$$
$$= -iqA_0\vec{\varepsilon}\,(E_b - E_a)\langle b|\vec{r}|a\rangle \sin\omega t$$

If one photon mediates the transition, its energy is

$$\omega = E_b - E_a$$


Then

$$\langle b|\Delta H|a\rangle = -iqA_0\omega\langle b|\vec{\varepsilon}\cdot\vec{r}|a\rangle \sin\omega t$$

The matrix element of $\Delta H$ is proportional to the matrix element of the electric dipole operator. Thus, the leading-order absorption or emission process is called an *electric dipole transition.*

To compute the rate of transitions from $|a\rangle$ to $|b\rangle$ induced by the electromagnetic plane wave, convert $\Delta H$ to the interaction picture and insert it into the formula for first-order time-dependent perturbation theory. If we take as our initial condition

$$|\Psi_I(t=0)\rangle = |a\rangle$$

and ask for the amplitude for this state to transition to $|b\rangle$ in time $t$, that is given by

$$\langle b|\Psi_I(t)\rangle = -i\int_0^t dt_1\ \langle b|\Delta H_I(t_1)|a\rangle$$
$$= -i\int_0^t dt_1\ e^{iE_bt_1}e^{-iE_at_1}(-iqA_0\omega)\langle b|\vec{\varepsilon}\cdot\vec{r}|a\rangle \sin\omega t_1$$

I will keep only the term in $\sin\omega t$ that resonantly excites the transition,

$$\sin \omega t \rightarrow \frac{-1}{2i} e^{-i\omega t}$$

Then

$$\langle b|\psi_I(t)\rangle \cong -i\frac{q A_0 \omega}{2} \int_0^t dt_1 \, e^{i(E_b - E_a - \omega)t} \langle b|\vec{\varepsilon}\cdot\vec{r}|a\rangle$$

$$= -i\frac{q A_0 \omega}{2} \frac{1}{i(E_b - E_a - \omega)} \left(e^{i(E_b - E_a - \omega)t} - 1\right) \langle b|\vec{\varepsilon}\cdot\vec{r}|a\rangle$$

The probability of the transition is

$$\langle b|\psi_I(t)\rangle = \frac{q^2 |A_0|^2 \omega^2}{4} \left|\langle b|\vec{\varepsilon}\cdot\vec{r}|a\rangle\right|^2 \delta_t(E_b - E_a - \omega)$$

For times $t \gg (E_b - E_a)^{-1}$, the last factor becomes

$$\delta_t(E_b - E_a - \omega) \longrightarrow 2\pi t \, \delta(E_b - E_a - \omega)$$

and we find

$$\frac{\text{transitions}}{\text{sec}} = \frac{q^2 \omega^2 |A_0|^2}{4} \left|\langle b|\vec{\varepsilon}\cdot\vec{r}|a\rangle\right|^2 2\pi \, \delta(E_b - E_a - \omega)$$

For the electromagnetic wave that we are considering, we computed the density and flux of photons in the previous lecture. We found for the flux

$$\Phi = \frac{\varepsilon_0 \omega |A_0|^2 c}{2}$$

Dividing the rate of transitions by the flux to obtain the cross section, we find

$$\sigma(\gamma + a \to b) = \frac{q^2}{2\epsilon_0 c} \omega \left| \langle b | \vec{\epsilon} \cdot \vec{r} | a \rangle \right|^2 2\pi \delta(E_b - E_a - \omega)$$

By following the same steps with a complex-valued polarization vector $\vec{\epsilon}$, one sees that the same result is correct in that more general situation.

We can put this formula into a more convenient form by noting that, for an electron, $q = -e$, so $q^2$ is related to the *fine structure constant*

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.036\ldots}$$

Finally, then,

$$\sigma(\gamma + a \to b) = 2\pi\alpha(\hbar\omega) \left| \langle b | \vec{\epsilon} \cdot \vec{r} | a \rangle \right|^2 2\pi \delta(E_b - E_a - \omega)$$

You can check that, with the one power of $\hbar$, the units are correct. The constant $\alpha$ is dimensionless. The delta function has the units of (energy)$^{-1}$. Then

$$\sigma \sim \alpha \langle r^2 \rangle \sim \alpha \cdot a_0^2 \sim m^2$$

This result for $\sigma$ suggests the form of the quantum mechanical matrix element for a photon to induce an electric dipole transition from $a$ to $b$. From the matrix element

$$\langle b | \Delta H | a + \gamma \rangle$$

we could immediately use Fermi's Golden Rule to compute the cross section for the process

$$a + \gamma \rightarrow b$$

There are no particles in the final state except for the atomic state $|b\rangle$, so phase space is simply

$$\int d\Pi = 2\pi\,\delta(E_b - E_a - \omega)$$

Then

$$\sigma = \frac{1}{v}\; 2\pi\,\delta(E_b - E_a - \omega)\left|\langle b|\,\Delta H\,|a+\gamma\rangle\right|^2$$

where, for an initial state photon, $v = c$. Comparing this to the expression above, we can identify

$$\langle b|\,\Delta H\,|a\gamma\rangle = q\left(\frac{\omega}{2\epsilon_0}\right)^{\frac{1}{2}}\langle b|\,\vec{\varepsilon}\cdot\vec{r}\,|a\rangle$$

Since the Hamiltonian is Hermitian, we have also

$$\langle a\gamma|\,\Delta H\,|b\rangle = q\left(\frac{\omega}{2\epsilon_0}\right)^{\frac{1}{2}}\langle a|\,\vec{\varepsilon}^{\,*}\cdot\vec{r}\,|b\rangle$$

These are indeed the correct amplitudes that can be derived using a full quantum treatment of the electromagnetic field. For interaction of photons with a a particle of

charge $q$, the amplitudes are proportional to $q$. Thus, these amplitudes change sign when we switch from the case of a photon interacting with an electron to that of a photon interacting with a proton or a positron.

Now that we have the relevant matrix element, we can apply Fermi's Golden Rule to compute the decay rate of an excited atomic state. For $b \to a + \gamma$,

$$\Gamma = \int d\Pi \; |\langle a\gamma | \Delta H | b \rangle|^2$$

Using the matrix element above and the expression for photon phase space derived in an earlier lecture, this gives

$$\Gamma = \frac{k^2}{\pi c} \int \frac{d\Omega}{4\pi} \cdot e^2 \frac{\omega}{2\epsilon_0} \left| \langle b | \vec{\varepsilon}^* \cdot \vec{r} | a \rangle \right|^2$$

$$= e^2 \frac{\omega^3}{2\pi\epsilon_0 c^3} \int \frac{d\Omega}{4\pi} \left| \langle b | \vec{\varepsilon}^* \cdot \vec{r} | a \rangle \right|^2$$

or

$$\Gamma = 2\alpha \frac{\omega^3}{c^2} \int \frac{d\Omega}{4\pi} \left| \langle b | \vec{\varepsilon}^* \cdot \vec{r} | a \rangle \right|^2$$

If $\omega$ is a frequency, this expression has units of 1/sec. To express it as a width of a resonance, we multiply it by $\hbar$ to put it into energy units. This width is called the *natural width* of an unstable atomic state. Recall that the basic unit of atomic energies is the Rydberg, the bound state energy of Hydrogen,

$$Ry = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{1}{2} \alpha \frac{\hbar c}{a_0}$$

We can estimate $\Gamma$ in units of the Rydberg

$$\Gamma \sim \alpha \frac{(Ry)^3}{c^2} a_0^2$$

or

$$\Gamma \sim \alpha^3 Ry$$

For a Hydrogen atom, the bound state energies and energy splittings are of the order

$$\text{bound state energies} \sim Ry$$

$$\text{fine structure} \sim \alpha^2 Ry$$

$$\text{hyperfine structure} \sim \frac{m_e}{m_p} \alpha^2 Ry$$

Then the natural width of an atomic resonance is smaller than the fine-structure splittings but larger than the hyperfine structure splittings. I will return to this point in the next lecture.

It is instructive to work through an example of an atomic lifetime calculation explicitly. A simple example is given by the 2P state of Hydrogen, which is unstable with respect to emission of the photon and decay to the 1S state. In the remainder of this lecture, I will compute the lifetime of this state. For simplicity, I will ignore the electron spin; we will come back to the effect of spin in the next lecture.

To compute the decay rate of the 2P state, we need to compute the matrix element

$$\langle 1S | \vec{\epsilon}^* \cdot \vec{r} | 2P, m \rangle$$

To do this, recall the structure of Hydrogen atom bound states

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\phi)$$

For the case at hand, we need

$$R_{10} = 2 a_0^{-3/2} e^{-r/a_0} \qquad R_{21} = \frac{1}{\sqrt{24}} \frac{r}{a_0^{5/2}} e^{-r/2a_0}$$

and

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \qquad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta \qquad Y_{1\pm1} = \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi}$$

Consider first the case $m = 0$. In this case,

$$\langle 1s | \vec{r} | 2\ell\, m=0 \rangle = \int \frac{dr\, r^2\, d\cos\theta\, d\phi}{a_0^3} \frac{1}{\sqrt{6}} e^{-r/a_0} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \cdot \sqrt{\frac{3}{4\pi}} \cos\theta \cdot \vec{r}$$

Let

$$\vec{r}^{\,a} = (r) \cdot (\sin\theta\cos\phi,\ \sin\theta \sin\phi,\ \cos\theta)^a$$

Then the integral over $d\phi$ gives zero for the $\hat{1}$ and $\hat{2}$ components of $\vec{r}$, so the only nonzero term is the $\hat{3}$ component.

$$\langle 1s | r^a | 2\ell\, m=0 \rangle = \delta^{a3} \int \frac{dr\, r^2 r^2}{a_0^4} e^{-3/2\, r/a_0} \frac{1}{\sqrt{6}} \int_{-1}^{1} \frac{d\cos\theta}{2} \cos^2\theta\, \sqrt{3}$$

$$= \delta^{a3} \frac{4!}{\sqrt{6}} \left(\frac{2}{3}\right)^5 \sqrt{3} \cdot \frac{1}{3} a_0 = \delta^{a3} \frac{1}{\sqrt{2}} \frac{2^8}{3^5} a_0$$

Then

$$\left|\langle 1S|\vec{\varepsilon}^{*}\cdot\vec{r}\,|2P\,m=0\rangle\right|^2 = \frac{2^{15}}{3^{10}}\,a_0^2\,\left|\vec{\varepsilon}^{*}\cdot\hat{3}\right|^2$$

and

$$\Gamma(2P\,m=0\to 1S+\gamma(\varepsilon)) = 2\alpha\frac{\omega^3}{c^2}\,\frac{2^{15}}{3^{10}}\,a_0^2\int\frac{d\Omega}{4\pi}\left|\vec{\varepsilon}^{*}\cdot\hat{3}\right|^2$$

We can clean up the prefactor a little using

$$\omega = \tfrac{3}{4}R_y \qquad \frac{a_0}{\hbar c} = \frac{1}{2}\frac{\alpha}{R_y}$$

Then,

$$\Gamma(2P\,m=0\to 1S+\gamma) = \alpha^3 R_y\cdot\frac{2^8}{3^7}\cdot\int\frac{d\Omega}{4\pi}\left|\vec{\varepsilon}^{*}\cdot\hat{3}\right|^2$$

The last integral here has some additional physics in it. The polarization $\vec{\epsilon}$ is must be transverse to the direction of motion of the photon, so not every choice of $\vec{\epsilon}$ is allowed for each photon direction. For a photon with momentum

$$\vec{k} = k\,(\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$$

the allowed directions of polarization are

$$\vec{\varepsilon} = (\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta) \quad , \quad \vec{\varepsilon} = (-\sin\phi, \cos\phi, 0)$$

For these choices, the quantity $\vec{\epsilon}^{*} \cdot \hat{3}$ that appears in the matrix element is

$$\vec{\epsilon}^{*} \cdot \hat{3} = -\sin\theta \quad , \quad \vec{\epsilon}^{*} \cdot \hat{3} = 0$$

so the total decay rate is

$$\sum_{\varepsilon} \Gamma(2P_{m=0} \rightarrow 1S + \gamma(\varepsilon)) = \alpha^3 Ry \frac{2^8}{3^7} \cdot \int \frac{d\Omega}{4\pi} \sin^2\theta$$

Our final result is, then,

$$\Gamma(2P_{m=0} \rightarrow 1S + \gamma) = \alpha^3 Ry \cdot \frac{2^9}{3^8} = 0.078\,\alpha^3 Ry$$

Since $Ry = 13.6$ eV,

$$\Gamma(2P(m=0) \rightarrow 1S + \gamma) = 4.1 \times 10^{-7} \text{ eV}$$

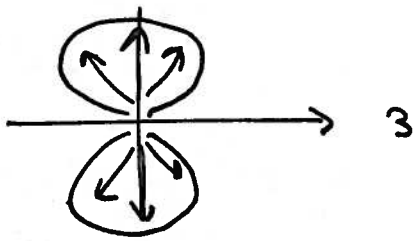
In units of 1/sec,

$$\Gamma/\hbar = 0.63 \times 10^9 \text{/sec} \qquad \tau = \frac{\hbar}{\Gamma} = 1.6 \times 10^{-9} \text{ sec}$$

Notice that, for a 2P $m = 0$ state, the decay photons are not emitted isotropically. Instead, we have found

$$\frac{d\Gamma}{d\cos\theta} \sim \sin^2\theta$$

This is a radiation pattern




of the same form as the classical radiation from a charge oscillating in the $\hat{3}$ direction. In particular, the photon cannot be emitted in the $\hat{3}$ direction, because the emission process requires that the polarization vector have a component parallel to $\vec{3}$.

Let's go back now and consider the decay of the 2P $m = \pm 1$ states. We hope that these states would have the same lifetime as the $m = 0$ state; this must be true by rotational invariance. For $m = +1$, the emission matrix element is

$$\langle 1s|\vec{r}^{\,a}|2P_{m=+1}\rangle = \int \frac{dr\, r^2 r^2}{a^4} \frac{e^{-3/2\, r/a_0}}{\sqrt{6}} \int \frac{d\cos\theta}{2} \frac{d\phi}{2\pi} \cdot \sqrt{3/2} \cdot \sin\theta e^{i\phi} \cdot (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)^a$$

$$= \frac{4!}{\sqrt{6}}\left(\frac{2}{3}\right)^5 \cdot \sqrt{\frac{3}{2}} \cdot \frac{2}{3} \cdot \left(\frac{1}{2}, \frac{+i}{2}, 0\right)^a = \frac{1}{\sqrt{2}} \frac{2^8}{3^5} \cdot \epsilon_+^a$$

where

$$\vec{\epsilon}_+ = \frac{1}{\sqrt{2}}(\hat{1} + i\hat{2}) \qquad \vec{\epsilon}_- = \frac{1}{\sqrt{2}}(\hat{1} - i\hat{2})$$

This expression has the same normalization as the $m = 0$ case, but now the matrix element picks out polarization vectors with overlap with $\vec{\epsilon}_+$. The polarization vector

$\vec{\epsilon}_+$ signals a photon carrying angular momentum $+1 \cdot \hbar$ about the $\hat{3}$ axis. The spin of the photon thus carries away the angular momentum of the $m = +1$ 2P state. In a similar way, we find for the $m = -1$ state,

$$\langle 1S | r^a | 2P\ m=-1 \rangle = \frac{1}{\sqrt{2}} \frac{2^8}{3^5} \cdot \varepsilon_-^a$$

For these states, I would like to introduce an easier trick to work out the radiation pattern. If we are interested in the total decay rate, we can sum over squared matrix elements involving the two polarization vectors orthogonal to the photon momentum $\vec{k}$. This sum is given by

$$\sum_{\varepsilon} \varepsilon^a \varepsilon^{b*} = \delta^{ab} - \hat{k}^a \hat{k}^b$$

Then, for the $m = 0$ case,

$$\sum_{\varepsilon} |\vec{\varepsilon}^* \cdot \hat{3}|^2 = \hat{3}^a (\delta^{ab} - \hat{k}^a \hat{k}^b) \hat{3}^b = 1 - \cos^2\theta = \sin^2\theta$$

and, for the $m = +1$ case,

$$\sum_{\varepsilon} |\vec{\varepsilon}^* \cdot \vec{\varepsilon}_+|^2 = \varepsilon_-^a (\delta^{ab} - \hat{k}^a \hat{k}^b) \varepsilon_+^b = 1 - |\varepsilon_+ \cdot \hat{k}|^2$$

Since

$$\vec{\varepsilon}_+ \cdot \hat{k} = \frac{1}{\sqrt{2}} (\sin\theta \cos\phi + i \sin\theta \sin\phi) = \frac{1}{\sqrt{2}} \sin\theta\, e^{i\phi}$$

this gives

$$\sum_{\varepsilon} \left| \vec{\varepsilon}^{\,*} \cdot \vec{\varepsilon}_{+} \right|^2 = 1 - \tfrac{1}{2}\sin^2\theta = \tfrac{1}{2}(1+\cos^2\theta)$$

The case $m = -1$ gives the same result. All three sums have the same average over solid angle, in all cases

$$\sum_{\varepsilon} \int \frac{d\Omega}{4\pi} \left| \vec{\varepsilon}^{\,*} \cdot \hat{3} \right|^2 = \sum_{\varepsilon} \int \frac{d\Omega}{4\pi} \left| \vec{\varepsilon}^{\,*} \cdot \vec{\varepsilon}_{\pm} \right|^2 = 2/3$$

Then we find

$$\Gamma(2P\ m=1) = \Gamma(2P\ m=0) = \Gamma(2P\ m=-1) = \frac{2^9}{3^8}\alpha^3 R_y$$

with

$$\frac{1}{\Gamma}\frac{d\Gamma}{d\cos\theta} = \begin{cases} 3/8\,(1+\cos^2\theta) & m=+1 \\ 3/4\ \sin^2\theta & m=0 \\ 3/8\,(1+\cos^2\theta) & m=-1 \end{cases}$$

If we consider an ensemble of 2P states with each of the $m$ state equally populated,the distribution of the emitted photons will be isotropic, as we might have expected.

In a realistic experiment, we might not have a randomly oriented ensemble of 2P states. Consider an experiment in which we shine unpolarized light along the $\hat{3}$ axis onto atoms of Hydrogen in their ground states.

Because $\vec{\epsilon} \cdot \hat{3} = 0$, the photons will have a random collection of polarizations

$\vec{\epsilon}_+$ and $\vec{\epsilon}_-$

but never $\vec{\epsilon} = \hat{3}$. Then, the incoming photons will excite only the $m = \pm 1$ 2P states. These states will then decay in a non-isotropic fashion, and we will find

$\frac{d\sigma}{d\cos\theta} \sim (1 + \cos^2\theta)$ $\rightsquigarrow$ 


for the complete process.