# Photon Interactions

In this section, we will treat interactions between photons and atoms, using the interaction representation. For simplicity, the atom discussed in detail is a hydrogen atom with the nucleus regarded as infinitely heavy. The Hamiltonian of the atom plus photons is

$$H = \frac{1}{2m}(\frac{\hbar\vec{\nabla}}{i} + \frac{e\vec{A}}{c})^2 - \frac{e^2}{r} + \frac{e\hbar}{mc}\vec{S}\cdot(\vec{\nabla}\times\vec{A}) + H_\gamma,$$

where

$$H_\gamma = \sum_{\vec{k},\lambda}\hbar\omega_{\vec{k}}(a^\dagger_{\vec{k},\lambda}a_{\vec{k},\lambda} + \frac{1}{2}),$$

In the interaction representation, we break the Hamiltonian into two parts,

$$H = H_0 + V.$$

In our case,

$$H_0 = H_{at} + H_\gamma,$$

were $H_{at}$ is just the hydrogen atom Hamiltonian,

$$H_{at} = \frac{1}{2m}(\frac{\hbar\vec{\nabla}}{i})^2 - \frac{e^2}{r}$$

The interaction between the atom and the photons is $V$, given by

$$V = \frac{e\vec{A}}{mc}\cdot\vec{P} + \frac{e^2\vec{A}^2}{2mc^2} + \frac{e\hbar}{mc}\vec{S}\cdot(\vec{\nabla}\times\vec{A}),$$

where $\vec{P} = \hbar\vec{\nabla}/i$. Note that because $\vec{\nabla}\cdot\vec{A} = 0$, we do not have to apply $\vec{P}$ to $\vec{A}$.

**States** In the interaction picture, the states are eigenstates of $H_0$, and $V$ causes transitions between these eigenstates. Eigenstates of $H_0$ are in a *product space,* composed of eigenstates of $H_{at}$ and $H_\gamma$. Eigenstates of $H_{at}$ are simply hydrogen atom wave functions, $\Psi_{nlms}(\vec{x})$, where $s$ is the $z$ component of electron spin. Eigenstates of $H_\gamma$ are built using the fact that $H_\gamma$ is the sum of independent harmonic oscillators. So if $|0>$ is the ground state of all oscillators or the no photon state, we have for eigenstates of $H_\gamma$,

$$|0>, \text{ no photons}$$

$$a^\dagger_{\vec{k}\lambda}|0>, \text{ one photon}$$

$$a^\dagger_{\vec{k}\lambda}a^\dagger_{\vec{k}\lambda}|0>, \text{ two photons}$$

$$\vdots$$

So putting the atomic eigenstates together with photon eigenstates, we have for eigenstates of $H_0$,

1. atom and no photons
$$\Psi_{nlms}(\vec{x})|0>=|0>\Psi_{nlms}(\vec{x})$$

2. atom and one photon
$$\Psi_{nlms}(\vec{x})a^\dagger_{\vec{k}\lambda}|0>=a^\dagger_{\vec{k}\lambda}|0>\Psi_{nlms}(\vec{x})$$

3. etc

In writing out these examples, we have emphasized that $\Psi_{nlms}(\vec{x})$ is just a function, multiplying the ket describing the photons.

**Decay Rate** Let us now set up the calculation of a decay rate where a hydrogen atom starts in a state $nlms$ and ends up in a state $n'l'm's'$ along with emission of a photon. Our *initial* state is
$$|i>=\Psi_{nlms}(\vec{x})|0>,$$
and our *final* state is
$$|f>=\Psi_{n'l'm's'}(\vec{x})a^\dagger_{\vec{k}\lambda}|0>,$$
where in order for the decay to occur, we must have $n'<n$.

We will calculate this matrix element to first order, so we need
$$\frac{-i}{\hbar}<f|\int_{-\infty}^{\infty}V_I(t)dt|i>$$

Now with no photon initially, and one photon finally, only the terms in $V$ which are *linear* in $\vec{A}$ can give a non-zero matrix element. Of these, the term involving the electron spin operator coupled to $\vec{\nabla}\times\vec{A}$ will turn out to be very small compared to the term in $\vec{A}\cdot\vec{P}$, so we concentrate on the latter. For the photonic part of the matrix element, we must calculate
$$<0|a_{\vec{k}\lambda}\vec{A}(\vec{x},t)|0>.$$

The only term in $\vec{A}$ which will give a non-zero matrix element is the one which contains $a^\dagger_{\vec{k}\lambda}$. We have
$$<0|a_{\vec{k}\lambda}\vec{A}(\vec{x},t)|0>=(\sqrt{\frac{4\pi c^2\hbar}{2\omega_{\vec{k}}V}})\vec{\epsilon^*_\lambda}(\vec{k})\exp(-i\vec{k}\cdot\vec{x}+i\omega_{\vec{k}}t).$$

A factor like this will occur whenever there is a *final* photon. This takes care of the photonic part of the matrix element. The atomic part will involve
$$\frac{e}{mc}\Psi^*_{n'l'm's'}(\vec{x})\frac{\hbar\vec{\nabla}}{i}\Psi_{nlms}(\vec{x})\exp(\frac{i}{\hbar}(E_{n'}-E_n)t).$$

The time dependent factors arise from the fact that the momentum operator is in the interaction representation,

$$\vec{P}_I(t) = \exp(\frac{i}{\hbar}H_{at}t)\vec{P}\exp(-\frac{i}{\hbar}H_{at}t)$$

We can now write our matrix element. We have

$$< f|U_I^{(1)}(\infty,-\infty)|i >= -\frac{i}{\hbar}\int_{-\infty}^{\infty} dt \exp(\frac{i}{\hbar}(E_{n'} + \hbar\omega_{\vec{k}} - E_n)t)) \tag{1}$$

$$\cdot(\sqrt{\frac{4\pi c^2\hbar}{2\omega_{\vec{k}}V}})(\frac{e}{mc})\int d\vec{x}\exp(-i\vec{k}\cdot\vec{x})\vec{\epsilon}^*_\lambda \cdot \Psi^*_{n'l'm's'}(\vec{x})\frac{\hbar\vec{\nabla}}{i}\Psi_{nlms}(\vec{x})$$

The time integral is very simple and gives a factor

$$-\frac{2\pi i}{\hbar}\delta(\omega_{\vec{k}} + (\frac{E_{n'} - E_n}{\hbar}))$$

**Dipole Approximation** The dipole approximation stems from the fact that the wavelength of the photon emitted in any atomic transition is very large compared to the size of the atom. For the case we are considering where the transition is from $n = 2$ to $n' = 1$, we have the energy of the photon is

$$\hbar\omega_{\vec{k}} = \frac{3}{4}13.6\,eV.$$

The corresponding wavelength is

$$\lambda = \frac{hc}{\hbar\omega_{\vec{k}}} = \frac{12,400\ \mathring{A}\ eV}{\frac{3}{4}13.6\,eV} = 1215\ \mathring{A},$$

so $\lambda >> a_0$. This has the consequence that the factor $\exp(-i\vec{k}\cdot\vec{x})$ is essentially constant over the atom. The *dipole approximation* replaces this factor by unity. The atomic matrix element simplifies to

$$(\frac{e}{mc})\int d\vec{x}\vec{\epsilon}^*_\lambda \cdot \Psi^*_{n'l'm's'}(\vec{x})\frac{\hbar\vec{\nabla}}{i}\Psi_{nlms}(\vec{x})$$

The term "dipole approximation" becomes clearer if we use the equation of motion for the electron momentum operator. We have

$$\vec{P} = m\frac{d\vec{X}}{dt} = m\frac{i}{\hbar}[H_{at}, \vec{X}].$$

Inserted in the atomic matrix element, the commutator will generate a factor

$$\frac{i(E_{n'} - E_n)}{\hbar} = -i\omega_{\vec{k}}$$

We now have

$$< f|U_I^{(1)}(\infty,-\infty)|i >= -\frac{2\pi}{\hbar}\delta(\omega_{\vec{k}} + (\frac{E_{n'} - E_n}{\hbar}))(\sqrt{\frac{4\pi c^2\hbar}{2\omega_{\vec{k}}V}})\frac{\omega_{\vec{k}}}{c} < n'l'm's'|e\vec{X}|nlms > \cdot\vec{\epsilon}^*_\lambda$$

We see that the matrix element is proportional to the matrix element of the dipole moment operator $(e\vec{X})$ between the initial and final atomic states.

**Transition Rate** The next step is to turn the expression for $< f|U_I^{(1)}(\infty,-\infty)|i >$ into one for the *transition rate*. This is done as usual in using time dependent perturbation theory. We imagine that the interval of time integration was finite; $[-T/2, T/2]$. We square the results, and then divide by the total time interval $T$. This amounts to "Fermi's Golden Rule." The result for the rate $\mathcal{R}$ is

$$\mathcal{R} = \sum_{\vec{k},\lambda} \frac{(2\pi)^2}{\hbar}\delta(\omega_{\vec{k}} + (\frac{E_{n'} - E_n}{\hbar}))\frac{\omega_{\vec{k}}}{V}| < n'l'm's'|e\vec{X}|nlms > \cdot\vec{\epsilon}^*_\lambda|^2$$

At this point, we take the box size to infinity, so

$$\sum_{\vec{k}} \to \frac{V}{(2\pi)^3}\int d\vec{k}$$

Using $\omega_{\vec{k}} = |\vec{k}|c$, we can write the rate as

$$\mathcal{R} = \sum_\lambda \int d\Omega_{\vec{k}} d\omega \frac{\omega^3}{(2\pi c)^3}\frac{(2\pi)^2}{\hbar}\delta(\omega + (\frac{E_{n'} - E_n}{\hbar}))| < n'l'm's'|e\vec{X}|nlms > \cdot\vec{\epsilon}^*_\lambda|^2$$

Using $\omega/(2\pi c) = 1/\Lambda$, and consuming the Dirac $\delta$function, we have

$$\hbar\mathcal{R} = \sum_\lambda \frac{1}{(\Lambda)^3}\int d\Omega_{\vec{k}}|2\pi < n'l'm's'|e\vec{X}|nlms > \cdot\vec{\epsilon}^*_\lambda|^2.$$

Here $\Lambda$ is the wavelength of the emitted photon, given by

$$\Lambda = \frac{hc}{(E_n - E_{n'})}$$

The quantity $\hbar\mathcal{R}$ is an energy. We may get its order of magnitude by estimating that the matrix element of $e\vec{X}$ is $O(ea_0)$. So omitting factors of $2\pi$ etc, we have

$$\hbar\mathcal{R} \sim \frac{e^2}{a_0}(\frac{a_0}{\Lambda})^3$$

The typical value of $\Lambda$ is several thousand $\overset{\circ}{A}$. As we saw, its value for the $n = 2 \to n = 1$ transition in hydrogen is 1215 $\overset{\circ}{A}$. The factor $\hbar\mathcal{R}$ can be thought of as the uncertainty or "width" of the upper state, the lower one being stable in hydrogen. The factor $(a_0/\Lambda)^3$ makes this very small compared to the atomic energy scale itself. In more qualitative terms, the excited states are all unstable. However, their decay rates are relatively slow, so the uncertainty in the energy of an excited state is tiny compared to the energy itself.

**Beyond The Electric Dipole Approximation** The electric dipole approximation is usually good, but there are important cases where an electric dipole transition is forbidden because of selection rules. The full set of selection rules will be stated later. In this section we explore the next terms that occur beyond the electric dipole. The situation is somewhat similar to the multipole expansion in electrostatics. Recall that the electric potential of localized charge distribution can be exapnded as

$$\phi(\vec{x}) = \frac{q}{r} + \frac{\vec{p}\cdot\vec{x}}{r^3} + \ldots,$$

where $q$ is the total charge of the distibution, $\vec{p}$ is its total electric dipole moment, etc.

In the present case we are not expanding the potential, but instead the transition rate, which is basically a probability. Thus there is no expansion in $1/r$, rather an expansion in $1/\Lambda$, where again $\Lambda$ is the wavelength of light emitted in the transition.

Returning to Eq.(1), we expand $\exp(-i\vec{k}\cdot\vec{x})$ and keep the linear term in $\vec{k}$. We now have the matrix element

$$\frac{-ie}{mc}\int d\vec{x}\Psi^*_{n'l'm's'}(\vec{x})x_j p_l \Psi_{nlms}(\vec{x})k_j(\epsilon^*_\lambda)_l, \tag{2}$$

where $p_l = \hbar(\vec{\nabla})_l/i$ . What we will do next is transform this matrix element into electric quadrupole and magnetic dipole moments. For simplicity of writing, we make the following notational replacements

$$nlms \rightarrow\ a,\ \ n'l'm's' \rightarrow\ b,$$

and use a bra-ket notation, so the atomic matrix element Eq.(2) will be written as

$$< b|x_j p_l|a > .$$

Our first move will be to replace $< b|x_j p_l|a >$ as follows

$$< b|x_j p_l|a > \rightarrow \frac{1}{2}(< b|x_j p_l|a > + < b|p_l x_j|a >).$$

This is not an equality because $[x_j, p_l] = i\hbar\delta_{jl}$. However the commutator term will vanish because

$$\delta_{jl}k_j(\epsilon^*_\lambda)_l = \vec{k}\cdot\vec{\epsilon}^*_\lambda = 0.$$

Next we will use

$$\vec{p} = m\frac{d\vec{x}}{dt} = \frac{im}{\hbar}[H, x],$$

and write

$$\frac{1}{2} < b|x_j p_l + p_l x_j|a >= \frac{im}{2\hbar} < b|x_j[H, x_l] + [H, x_l]x_j|a > \tag{3}$$

$$= \frac{im}{2\hbar}\left(< b|x_j H x_l - x_l H x_j|a > +(E_b - E_a) < b|x_j x_l|a >\right)$$

The term in this expression with $H$ sandwiched in between two coordinates is manifestly antisymmetric. It will contribute to the magnetic dipole matrix element. The second term is manifestly symmetric, and will contribute to the electric quadrupole matrix element.

**Symmetric Term** In this section we will work out the symmetric term. We have

$$\frac{-ie}{mc} < b|x_j p_l|a > k_j(\epsilon^*_\lambda)_l \ \ (symmetric)$$

$$= \frac{e}{2c}\omega_{ba} < b|x_j x_l|a > k_j(\epsilon^*_\lambda)_l,$$

where $\omega_{ba} = (E_b - E_a)/\hbar$. Now the quadrupole moment of a localized charge distribution is

$$Q_{jl} = \int d\vec{x}(3x_j x_l - r^2\delta_{jl})\rho(\vec{x}).$$

The $\delta_{jl}$ will not contribute in our case because it generates a $\vec{k}\cdot\vec{\epsilon}^*_\lambda = 0$. We finally have

$$\frac{-ie}{mc} < b|x_j p_l|a > k_j(\epsilon^*_\lambda)_l \ \ (symmetric)$$

$$= \frac{\omega_{ba}}{6c} < b|Q_{jl}|a > k_j(\epsilon^*_\lambda)_l.$$

**Antisymmetric Term** Returning to Eq.(3) we have

$$< b|x_j H x_l - x_l H x_j|a >=< b|x_j[H, x_l] - x_l[H, x_j]|a >,$$

since the added terms cancel. We now have

$$\frac{im}{2\hbar} < b|x_j[H, x_l] - x_l[H, x_j]|a >= \frac{1}{2} < b|x_j p_l - x_l p_j|a > .$$

Attaching the wave vector and polarization vector, our matrix element is now

$$\frac{-ie}{2mc} < b|x_j p_l - x_l p_j|a > k_j(\vec{\epsilon}^*_\lambda)_l = \frac{-ie\hbar}{2mc} < b|\vec{L}|a > \cdot(\vec{k}\times\vec{\epsilon}^*_\lambda),$$

where $\vec{L}$ is measured in units of $\hbar$. Combining this with the spin dependent term we finally have for the magnetic dipole term,

$$\frac{-ie\hbar}{2mc} < b|\vec{L} + 2\vec{S}|a > \cdot(\vec{k}\times\vec{\epsilon}^*_\lambda)$$

**Summary and Selection Rules** Our matrix element including electric quadrupole and magnetic dipole terms is

$$\frac{-ie}{mc} < b|x_j p_l|a > k_j(\vec{\epsilon}^*_\lambda)_l = \frac{\omega_{ba}}{6c} < b|Q_{jl}|a > k_j(\vec{\epsilon}^*_\lambda)_l - \frac{ie\hbar}{2mc} < b|\vec{L} + 2\vec{S}|a > \cdot(\vec{k}\times\vec{\epsilon}^*_\lambda)$$

It is easy to estimate the rough size of these terms compared to the electric dipole term. We have an extra power of $x$ in the atomic matrix element, and an extra overall power of $k$. This is roughly $O(a_0/\Lambda)$ smaller than the electric dipole in the matrix element, and $O(a_0/\Lambda)^2$ in the rate. Nevertheless for cases where the electric dipole matrix vanishes,

these terms can and do play an important role. The selection rules for the various cases are as follows:

| | | |
|---|---|---|
| electric dipole | $\Delta J = 0, \pm 1$ | parity change |
| magnetic dipole | $\Delta J = 0, \pm 1$ | no parity change |
| electric quadrupole | $\Delta J = 0, \pm 1, \pm 2$ | no paritychange |

In all these cases $J = 0 \rightarrow J = 0$ is forbidden by angular momentum conservation.