

Lecture 37

Relevant sections in text: §5.7

Electric dipole transitions

Our transition probability (to first order in perturbation theory) is

$$P(i \rightarrow f) \approx \frac{4\pi^2\alpha}{m^2\hbar\omega_{fi}^2} N(\omega_{fi}) |\langle n_f, l_f, m_f | e^{-i|\omega_{fi}| \frac{1}{c} \hat{n} \cdot \vec{X}} \hat{e} \cdot \vec{P} | n_i, l_i, m_i \rangle|^2,$$

where

$$\alpha = \frac{q^2}{\hbar c} \approx \frac{1}{137}$$

is the *fine structure constant* and

$$N(\omega) = \frac{\omega^2}{c} |A(\omega)|^2$$

is the energy per unit area per unit frequency carried by the EM pulse characterized by the vector potential in the radiation gauge with frequency components $A(\omega)$.

We now want to analyze the matrix element which appears. This factor reflects the atomic structure and characterizes the response of the atom to the electromagnetic wave.

Let us begin by noting that the wavelength of the radiation absorbed/emitted is on the order of $2\pi c/\omega_{fi} \sim 10^{-6}m$, while the atomic size is on the order of the Bohr radius $\sim 10^{-8}m$. Thus one can try to expand the exponential in the matrix element:

$$\langle n_f, l_f, m_f | e^{-i|\omega_{fi}| \frac{1}{c} \hat{n} \cdot \vec{X}} \hat{e} \cdot \vec{P} | n_i, l_i, m_i \rangle = \langle n_f, l_f, m_f | (1 - ip|\omega_{fi}| \frac{1}{c} \hat{n} \cdot \vec{X} + \dots) \hat{e} \cdot \vec{P} | n_i, l_i, m_i \rangle.$$

The first term in this expansion, if non-zero, will be the dominant contribution to the matrix element. Thus we can approximate

$$\langle n_f, l_f, m_f | e^{-i|\omega_{fi}| \frac{1}{c} \hat{n} \cdot \vec{X}} \hat{e} \cdot \vec{P} | n_i, l_i, m_i \rangle \approx \langle n_f, l_f, m_f | \hat{e} \cdot \vec{P} | n_i, l_i, m_i \rangle,$$

which is known as the *electric dipole approximation*. Transitions for which this matrix element is non-zero have the dominant probability; they are called *electric dipole transitions*. We shall see why in a moment. Transitions for which the dipole matrix element vanishes are often called “forbidden transitions”. This does not mean that they cannot occur, but only that the probability is much smaller than that of transitions of the electric dipole type, so they do not arise at the level of the approximation we are using.

If we restrict attention to the electric dipole approximation, the transition probability is controlled by the matrix element $\langle n_f, l_f, m_f | \vec{P} | n_i, l_i, m_i \rangle$. To compute it, we use the fact that

$$[\vec{X}, H_0] = i\hbar \frac{\vec{P}}{m},$$

and that

$$H_0|n, l, m\rangle = E_n|n, l, m\rangle.$$

We get

$$\begin{aligned}\langle n_f, l_f, m_f | \vec{P} | n_i, l_i, m_i \rangle &= \frac{m}{i\hbar} \langle n_f, l_f, m_f | \vec{X} H_0 - H_0 \vec{X} | n_i, l_i, m_i \rangle \\ &= im\omega_{fi} \langle n_f, l_f, m_f | \vec{X} | n_i, l_i, m_i \rangle.\end{aligned}$$

Now perhaps you can see why this is called a dipole transition: the transition only occurs according to whether or not the matrix elements of the (component along \hat{e} of the) dipole moment operator, $q\vec{X}$, are non-vanishing.

Selection rules for Electric Dipole Transitions

We have seen that the dominant transitions are of the electric dipole type. We now consider some details of the dipole matrix elements

$$\langle n_f, l_f, m_f | q\hat{e} \cdot \vec{X} | n_i, l_i, m_i \rangle.$$

In particular, we derive necessary conditions on l and m such that the dipole matrix element is non-zero and hence electric dipole transitions can occur. These conditions are usually called *selection rules* for the (first-order) electric dipole transitions. Transitions which do not obey these selection rules are usually called “forbidden transitions”. Of course they are only forbidden insofar as our approximations are valid. The forbidden transitions may very well occur, but they will be far less likely than the (first-order) electric dipole transitions being considered here.

The selection rules we shall derive are determined solely by the angular momentum properties of the unperturbed stationary states. Thus, the selection rules rely upon the fact that the stationary states can be chosen to be orbital angular momentum eigenstates, which requires that the atomic potential V_0 be a central potential: $V_0 = V_0(|\vec{X}|)$ (see below). On the other hand, the selection rules do not depend upon any further properties of this potential.

Digression: Rotational Symmetry

Here we briefly explain how angular momentum conservation is tied to rotational symmetry. Recall the unitary rotation operator:

$$U(\hat{n}, \theta) = e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{J}}.$$

For a spinless particle (which is how we are modeling the electron) we have

$$\vec{J} = \vec{L} = \vec{X} \times \vec{P}.$$

On position/momentum eigenvectors $|\vec{x}\rangle, |\vec{p}\rangle$ we have

$$e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{J}}|\vec{x}\rangle = |R(\hat{n}, \theta)\vec{x}\rangle, \quad e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{J}}|\vec{p}\rangle = |R(\hat{n}, \theta)\vec{p}\rangle$$

where $R(\hat{n}, \theta)$ is the 3-d orthogonal transformation rotating about the axis \hat{n} by the angle θ . From this it follows that (exercise)

$$e^{\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}}\vec{X}e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}} = R(\hat{n}, \theta)\vec{X}, \quad e^{\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}}\vec{P}e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}} = R(\hat{n}, \theta)\vec{P}.$$

From this it follows that

$$e^{\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}}P^2e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}} = P^2,$$

and

$$e^{\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}}V(\vec{X})e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}} = V(R(\hat{n}, \theta)\vec{X}).$$

(The last relation can be seen using the spectral decomposition of $V(\vec{X})$, or by verifying this relation in the position basis.)

If the potential is rotationally invariant, *i.e.*, is spherically symmetric, *i.e.*, depends only upon the distance from the center of rotation, *i.e.*, describes a central force, then

$$e^{\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}}V(|X|)e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}} = V(|X|).$$

The Hamiltonian is then rotationally invariant:

$$e^{\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}}\left(\frac{P^2}{2m} + V(|X|)\right)e^{-\frac{i}{\hbar}\theta\hat{n}\cdot\vec{L}} = \frac{P^2}{2m} + V(|X|).$$

By considering an infinitesimal transformation it easily follows that

$$[H, \vec{L}] = 0.$$

This is just infinitesimal rotation invariance. But it also means that angular momentum is conserved — its probability distribution is unchanged in time. This is because stationary states can be chosen to be angular momentum eigenstates. Thus we see how a symmetry corresponds to a conservation law. For us, however, the key thing here is that for a central potential the energy eigenvectors can be chosen to be also angular momentum eigenvectors.

Selection rules involving m

We now consider restrictions on m_i and m_f needed so that the three components of \vec{X} have non-vanishing matrix elements. Our main identity arises because \vec{X} is a vector operator; we have that

$$[R_i, L_j] = i\hbar\epsilon_{ijk}R_k.$$

In particular,

$$[X, L_z] = -i\hbar Y, \quad [Y, L_z] = i\hbar X, \quad [Z, L_z] = 0.$$

These formulas simply give the infinitesimal change of the position vector under rotations (exercise) and are the infinitesimal versions of the formulas given above. You can easily check them explicitly.

From these identities we have

$$0 = \langle n_f, l_f, m_f | [Z, L_z] | n_i, l_i, m_i \rangle = (m_i - m_f) \hbar \langle n_f, l_f, m_f | Z | n_i, l_i, m_i \rangle,$$

so that the z matrix element vanishes unless $m_i = m_f$. Next we have

$$(m_i - m_f) \hbar \langle n_f, l_f, m_f | X | n_i, l_i, m_i \rangle = \langle n_f, l_f, m_f | [X, L_z] | n_i, l_i, m_i \rangle = -i\hbar \langle n_f, l_f, m_f | Y | n_i, l_i, m_i \rangle$$

and

$$(m_i - m_f) \hbar \langle n_f, l_f, m_f | Y | n_i, l_i, m_i \rangle = \langle n_f, l_f, m_f | [Y, L_z] | n_i, l_i, m_i \rangle = i\hbar \langle n_f, l_f, m_f | X | n_i, l_i, m_i \rangle$$

from which it follows that either

$$(m_i - m_f)^2 = 1,$$

or

$$\langle n_f, l_f, m_f | Y | n_i, l_i, m_i \rangle = \langle n_f, l_f, m_f | X | n_i, l_i, m_i \rangle = 0.$$

Thus, for the X and Y matrix elements to be non-vanishing we must have

$$m_f = m_i \pm 1.$$

In short, no electric dipole transitions occur unless

$$\Delta m = 0, \pm 1.$$

If $\Delta m = 0$, then only radiation with polarization with a component along z will stimulate a transition (in this approximation). If $\Delta m = \pm 1$, then polarization in the $x - y$ plane will stimulate transitions. Likewise, these are the polarizations that feature in the respective emission processes, that is, the emitted radiation will have this polarization structure.

Selection rules involving l

We have seen how the electric dipole transitions require $\Delta m = 0, \pm 1$. We can get selection rules involving l by playing a similar game as above, but now using the commutator

$$[L^2, [L^2, \vec{X}]] = 2\hbar^2(L^2\vec{X} + \vec{R}L^2).$$

Take the initial-final matrix element of both sides of this equation and use the fact that vectors defining the matrix element are L^2 eigenvectors. You will find that this identity implies (exercise)

$$2[l_f(l_f + 1) + l_i(l_i + 1)] - [l_f(l_f + 1) - l_i(l_i + 1)]^2 \langle n_f, l_f, m_f | \vec{X} | n_i, l_i, m_i \rangle = 0.$$

Therefore, if

$$\langle n_f, l_f, m_f | \vec{X} | n_i, l_i, m_i \rangle \neq 0,$$

then

$$[l_f(l_f + 1) + l_i(l_i + 1)] - [l_f(l_f + 1) - l_i(l_i + 1)]^2 = 0.$$

This condition can be factored into the form (exercise)

$$[(l_f + l_i + 1)^2 - 1][(l_f - l_i)^2 - 1] = 0.$$

Keeping in mind that l is non-negative, you can see that the first term vanishes if and only if $l_i = l_f = 0$. The second term vanishes if and only if $l_f - l_i = \pm 1$. We conclude that the transition is forbidden unless

$$\Delta l = \pm 1$$

or

$$l_f = l_i = 0,$$

In fact, the second case is excluded: an explicit calculation easily shows that the dipole matrix element actually vanishes if the initial and final states are zero angular momentum states. To see this, simply recall that each of (X, Y, Z) is a linear combination of $l = 1$ spherical harmonics. If $l_f = l_i = 0$, then the angular integrals in the inner products vanish by orthogonality of $l = 1$ spherical harmonics with $l = 0$ spherical harmonics (exercise).

To summarize, the electric dipole selection rules are

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

These conditions are necessary for a transition to occur, given our approximations. These selection rules are compatible with an interpretation in terms of emission and absorption of photons by the atom. Using this point of view, the photon will have frequency $\omega \approx |\omega_{fi}|$ (interpretable as “conservation of energy”) and the photon carries angular momentum $\sqrt{2}\hbar$, or as one says, the photon must have spin-1 (by conservation of angular momentum). Indeed, if the photon carries spin-1, then our previous discussion of addition of angular momentum coupled with an assumption of conservation of angular momentum for the atom-photon system imply that the angular momentum of the atom after the transition must be $l, l \pm 1$ (exercise). The first possibility doesn’t occur in the electric dipole approximation.

This is all true, but it is a mistake to think that this picture can be obtained from our treatment of an atom in a radiation field. There are two reasons why our current description is inadequate. First, we have not treated the electromagnetic field as dynamical – we have simply postulated its form. Because the electromagnetic field configuration is specified once and for all, there is no way to describe emission and/or absorption of energy and angular momentum from the electromagnetic field, which is not allowed to change. This is reflected in the fact that the Hamiltonian we have been using does not give the total energy of the combined system of electron and electromagnetic field, rather it just gives the non-conserved energy of the electron. Similarly, the angular momentum $\vec{L} = \vec{X} \times \vec{P}$ that we are speaking of is not the total, conserved angular momentum of the charge and electromagnetic field, but rather just the unconserved angular momentum of the charge alone. To include the electromagnetic field in the bookkeeping of conservation laws we must include the electromagnetic degrees of freedom into the system and include suitable terms in the Hamiltonian to describe the dynamics of these degrees of freedom and their coupling to the charge. This leads us to the second difficulty with our previous treatment. Our model was “semi-classical” since the charge was given a quantum treatment but the electromagnetic field was given a classical treatment. It does not appear possible to have a consistent theory of charges and electromagnetic fields in which the former are described via quantum mechanics and the latter treated via classical physics. This was realized early on in the history of quantum mechanics. What is needed, then, is a method for incorporating electromagnetic degrees of freedom into the system using the rules of quantum mechanics. It was (I think) Dirac who first showed a way to “quantize” the electromagnetic field and then consider a quantum dynamical system of charges and fields. Thus QED was born. A healthy dividend was paid for this quantum description of electrodynamics: one could now explain *spontaneous emission*, which is the phenomenon where an atom (or other quantum system) in an excited bound state will spontaneously emit radiation and drop to a lower energy state – even in the absence of a perturbation.