Lecture 42

Relevant sections in text: §5.7

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. To understand the orgin of the selection rules we digress for a moment to consider symmetries and conservation laws.

Digression on Symmetries and Conservation Laws

Consider a system described by a (time-independent, for simplicity) Hamiltonian H. We say that a unitary transformation U is a *symmetry* of the system if

$$U^\dagger H U = H \quad \Longleftrightarrow \quad [H, U] = 0.$$

One way to understand the utility of this definition is to note that if U is a symmetry then for any given state vector $|\psi\rangle$ there will always be another state vector $U|\psi\rangle$ which has the same probability distribution for H. To prove this it is sufficient to note for any function of one variable $F(x)$ (*e.g.,* a characteristic function for some energy or energies) we have

$$\langle \psi | F(H) | \psi \rangle = \langle \psi | F(U^\dagger H U) | \psi \rangle = \langle \psi | U^\dagger F(H) U | \psi \rangle.$$

If $U(\lambda)$ is a *continuous symmetry*, *i.e.,* a 1 parameter family of unitary transformations satisfying

$$U^\dagger(\lambda) H U(\lambda) = H, \quad \forall\ \lambda,$$

then we get a conservation law. To see this, write

$$U(\lambda) = \exp\left\{-\frac{i}{\hbar}\lambda G\right\},$$

where G is a Hermitian operator, the infinitesimal generator. The symmetry condition, when expanded in powers of λ, shows that the infinitesimal change in H is given by $\frac{\lambda}{i\hbar}[H, G]$ and this must vanish:

$$[G, H] = 0.$$

This means that the probability distribution of G does not change in time, which you can see, *e.g.,* in the Heisenberg picture. Thus we have the very important result: *To each continuous symmetry there is associated a conservation law. The conserved quantity is the infinitesimal generator of the symmetry.* An important corollary of this result is that if G generates a symmetry, then stationary states can also be chosen to be G eigenstates.

Rotational Symmetry

Here we apply the above considerations to 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 $|\vec{X}|$ from the center of rotation, *i.e.,* describes a central force, then

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

The Hamiltonian is then rotationally invariant:

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

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. Moreover, we see that for a central potential the energy eigenvectors can be chosen to be also angular momentum eigenvectors.

Selection rules involving m

We now return to the electric dipole matrix element between stationary states – also taken to be angular momentum eigenstates. We begin by obtaining 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 $\vec{X}$ changes under rotations like a vector. Infinitesimally we have that

$$[X_i, L_j] = i\hbar\epsilon_{ijk}X_k.$$

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

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

and

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

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 summary, 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.