Lecture 43

Relevant sections in text: §5.7

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 (good exercise)

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

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 factor vanishes if and only if $l_i = l_f = 0$. The second factor 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, use coordinate wave functions to compute the matrix element. Then recall that each of (x, y, z) is a linear combination of $l = 1$ spherical harmonics. If $l_f = l_i = 0$, then the position wave functions have no angular dependence. 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).

While the foregoing interpretation in terms of emission and absorption of photons is correct, it is a mistake to think that this picture can be rigorously 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 define photons. This is the birth of quantum electrodynamics. In this quantum dynamical system of charges and fields the transitions we have been studying can indeed be viewed in terms of emission and absorption of photons.

A healthy dividend was paid for this fully quantum description of electrodynamics: one could now explain *spontaneous emission*, which is the phenomenon where an atom (or other quantum system) in an exited bound state may spontaneously emit a photon and drop to a lower energy state – even in the absence of a perturbation.* The usual,

* For example, the $2P$ state of Hydrogen will spontaneously decay by electric dipole radiation

purely quantum mechanical model of an atom in terms of electrons bound to the nucleus by a potential cannot account for spontaneous emission. After all, in this description the energy levels of an atom are stationary states – you will recall that nothing ever happens in a stationary state. Somehow the correct description of an atomic electron coupled to photons is such that the usual energy levels of an atom are not in fact stationary states – even in the absence of any radiation to stimulate transitions. In the following we give some details of all this.

Harmonic Oscillators again

Our first goal will be to describe the photon without considering its interaction with other (charged) particles. This is a quantum version of considering the EM field in the absence of sources. Indeed, our strategy for describing photons will be to extract them from a "quantization" of the source-free electromagnetic field. The key idea that allows this point of view is that the EM field can be viewed as an infinite collection of coupled harmonic oscillators. We know how to describe harmonic oscillators quantum mechanically, and we can try to carry this information over to the EM field. First, let us quickly review the key properties of the harmonic oscillator.

Recall that the energy of a classical oscillator with displacement $x(t)$ is given by

$$E = \frac{m}{2}\dot{x}^2 + \frac{1}{2}m\omega^2 x^2.$$

Indeed, this energy function completely characterizes the oscillator (exercise). In the quantum description we view the energy in terms of coordinate and momentum operators:

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2,$$

where

$$[X, P] = i\hbar\mathbf{1},$$

with "$\mathbf{1}$" being the identity operator. Let us recall the definition of the "ladder operators":

$$a = \sqrt{\frac{m\omega}{2\hbar}}(X + i\frac{P}{m\omega}), \quad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(X - i\frac{P}{m\omega}),$$

satisfying the commutation relations (exercise)

$$[a, a^\dagger] = 1.$$

– emission of a photon – to the ground state ($1S$). The lifetime of the $2P$ state is about 10^{-9} s.

The Hamiltonian takes the form (exercise)

$$H = \hbar\omega(a^\dagger a + \frac{1}{2}\mathbf{1}).$$

We can drop the the second term (with the "$\frac{1}{2}$") if we want; it just defines the zero point of energy. The stationary states are labeled by a non-negative integer n,

$$H|n\rangle = E_n|n\rangle, \quad E_n = (n + \frac{1}{2})\hbar\omega.$$

The ground state $|0\rangle$ satisfies

$$a|0\rangle = 0.$$

Excited states are obtained via the identity (exercise)

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle.$$

We also have

$$a|n\rangle = \sqrt{n}|n-1\rangle.$$

It is easy to generalize this treatment to a system consisting of a number of uncoupled harmonic oscillators with displacements X_i and momenta P_i, masses m_i and frequencies ω_i, $i = 1, 2, \ldots, N$, . The Hilbert space is the tensor product of N 1-d oscillator Hilbert spaces. The Hamiltonian is (exercise)

$$H = \sum_i \frac{1}{2}\left(\frac{P_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2 X_i^2\right) = \sum_i \left(a_i^\dagger a_i + \frac{1}{2}I\right).$$

Even with a set of coupled oscillators, if the couplings are themselves harmonic, we can pass to the normal mode coordinates and momenta. In this case the Hamiltonian again takes the form given above. So, this description is quite general.

Fourier components of an EM field

To find a quantum description of the EM field we need some elementary results from classical electromagnetic theory. To begin with, we introduce the EM potentials. Recall that the homogeneous subset of the Maxwell equations

$$\nabla \times \mathbf{E} + \frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} = 0$$

and

$$\nabla \cdot \mathbf{B} = 0$$

are equivalent to the existence of a vector field, the *vector potential* $\mathbf{A}$ and a scalar field, the *scalar potential* ϕ such that

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} - \nabla\phi, \quad \mathbf{B} = \nabla \times \mathbf{A}.$$

This is the general solution to the homogeneous subset of the Maxwell equations.

The potentials are far from uniquely defined. If $(\phi, \mathbf{A})$ are a set of potentials for a given EM field $(\mathbf{E}, \mathbf{B})$, then so are (exercise)

$$\phi' = \phi - \frac{1}{c}\frac{\partial \Lambda}{\partial t},$$

$$\mathbf{A}' = \mathbf{A} + \nabla\Lambda,$$

where Λ is *any* (well-behaved) function of space and time. This transformation between two sets of potentials for the same EM field is called a *gauge transformation*, for historical reasons that we shall not go into. The notion of gauge invariance, which just seems like a technical detail in Maxwell theory, is actually pretty profound in physics. However, for our purposes, we just note that the freedom to redefine potentials via a gauge transformation means that we can try to make a convenient choice of potentials. Our choice will be always to put the potentials in the *radiation gauge*. What this means is as follows. Any electromagnetic field can be described by a set of potentials such that

$$\phi = 0, \quad \nabla \cdot \mathbf{A} = 0.$$

This should amuse you (at least a little). In electrostatics it is conventional to work in a gauge in which $\mathbf{A} = 0$ and then the static electric field is (minus) the gradient of the scalar potential. This is certainly the most convenient way to analyze electrostatics, but one *could* opt to use a time-dependent (and curl-free) vector potential if so-desired (exercise).

The Hamiltonian of the electromagnetic field

To use the harmonic oscillator paradigm to "quantize" the EM field, we first express the total energy of the field in terms of the potentials:

$$H = \frac{1}{8\pi}\int_{\text{all space}} d^3x\,(E^2 + B^2) = \frac{1}{8\pi}\int_{\text{all space}} d^3x\,[\frac{1}{c^2}\left(\frac{\partial \mathbf{A}}{\partial t}\right)^2 + (\nabla \times \mathbf{A})^2]\,.$$

You can think of the first integral in the sum as the kinetic energy of the field and the second integral as the potential energy. This is something more than an analogy. It is possible to think of the electromagnetic field as a Hamiltonian dynamical system with the vector potential playing the role of (an infinite number of) generalized coordinate(s) and the electric field as its "canonically conjugate momentum".

Next we make a Fourier decomposition of $\mathbf{A}$:

$$\mathbf{A}(\mathbf{x},t) = \frac{1}{(2\pi)^{3/2}} \int d^3k\, \mathbf{A}_\mathbf{k}(t) e^{i\mathbf{k}\cdot\mathbf{x}}.$$

Note that (exercises)

$$(A_\mathbf{k})^* = A_{-\mathbf{k}},$$

$$\nabla\cdot\mathbf{A} = 0 \Longleftrightarrow \mathbf{k}\cdot\mathbf{A}_\mathbf{k} = 0,$$

$$\frac{\partial\mathbf{A}}{\partial t} = \frac{1}{(2\pi)^{3/2}} \int d^3k\, \dot{\mathbf{A}}_\mathbf{k}(t) e^{i\mathbf{k}\cdot\mathbf{x}},$$

$$\nabla\times\mathbf{A} = \frac{i}{(2\pi)^{3/2}} \int d^3k\, [\mathbf{k}\times\mathbf{A}_\mathbf{k}(t)] e^{i\mathbf{k}\cdot\mathbf{x}}.$$

We can simplify our form of the Hamiltonian using (1) a vector identity for the dot product of a pair of cross products, and (2) the radiation gauge condition. We get (exercise)

$$\begin{aligned} H &= \int d^3k \left\{ \frac{1}{c^2} |\dot{\mathbf{A}}_\mathbf{k}|^2 + |\mathbf{k}\times\mathbf{A}_\mathbf{k}|^2 \right\} \\ &= \int d^3k \left\{ \frac{1}{c^2} |\dot{\mathbf{A}}_\mathbf{k}|^2 + k^2 |A_\mathbf{k}|^2 \right\}. \end{aligned}$$

Let's compare this with the harmonic oscillator Hamiltonian. Think of the integrand as the energy of a single oscillator, labeled by $\mathbf{k}$, and the integral as a sum over these labels. Then we have (exercise)

$$\omega \longrightarrow \omega(k) = kc,$$

and

$$m \longrightarrow \frac{1}{c^2}.$$

The frequency correspondence is perfectly reasonable; it describes the frequency-wave number dispersion relation of an EM wave. The mass analogy is ok mathematically, but shouldn't be taken too literally in a physical sense; there is no particularly meaningful way to ascribe a rest mass to the electromagnetic field.