

Lecture 36

Relevant sections in text: §5.7

What happens when you shine light on an atom?

You will have noticed that up to this point in our discussion of time-dependent perturbation theory I have assiduously avoided much in the way of concrete, specific applications of our results. This was partially because you will do the relatively easy applications in your homework, while the more involved applications would distract too much from the general features of the perturbative approach. Also, I wanted to use the perturbative point of view not just to solve this or that example situation, but rather to give a general point of view on quantum dynamics that is available whenever the perturbative approximation is valid. Now, though, we should have a look at a good example where this technology is useful.

We shall study the perturbative dynamics of an atomic electron when exposed to a (weak) plane electromagnetic wave. This is a simple model which can be used to answer (at least in part) the question posed in the title of this section. The story is a little long, but I think it is useful and instructive.

We are principally interested in the case where the electron is, in the absence of the perturbation, in a “bound stationary state” of some potential, with the electromagnetic field serving to stimulate transitions between the bound or ionized states. Our strategy is as follows. We model the atom as a spinless particle bound by some potential V_0 . Of course, more sophisticated models of the atom are available. We could specialize V_0 to be a central potential, or even the Coulomb potential, but we won't have to make any such choices for a while. Thus, the unperturbed Hamiltonian is of the form

$$H_0 = \frac{P^2}{2m} + V_0(\vec{R}).$$

The unperturbed stationary states are just the energy eigenstates of H_0 — these are the “energy levels” of the atom.

Now we want to introduce the electromagnetic radiation. The total electromagnetic field that the particle interacts with will then be the superposition of the field represented by V_0 (*e.g.*, an electrostatic field) with the field of the incident radiation. Let us describe the radiation using the vector potentials $(\phi(\vec{r}, t), \vec{A}(\vec{r}, t))$. It is a standard result of electromagnetic theory that, in regions of space free of electromagnetic sources, it is always possible to choose the electromagnetic potentials so that they are in the “radiation gauge”:

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

In this gauge the electric and magnetic fields are determined by the potentials according to

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

We wish to use this description to incorporate the electromagnetic perturbation only. We could, if desired, use this description also to include the V_0 contribution to the total electromagnetic field. In this case, though, one is not easily able to make the split between the unperturbed system and the perturbation.

Note that we are using a physical model in which the EM radiation is specified once and for all, ignoring all electromagnetic sources in our system. Of course, the atomic electron itself also serves as a source of an EM field. Thus we are in an approximation where this effect can be ignored. Nonetheless, at the end of the day we will interpret the dynamics as energy level transitions accompanied by absorption or emission of radiation by the electron! This is a typical “physical” analysis in which we make suitable approximations but use our knowledge of physical behavior to interpret the results, even if our interpretation goes beyond the validity of the mathematical model. In physics, this kind of reasoning is something akin to an art form.

Next, I remind you of the form of the Hamiltonian for a particle of charge q and mass m moving in a *given* electromagnetic field. We have

$$H = \frac{1}{2m} (\vec{P} - \frac{q}{c} \vec{A})^2 + q\phi,$$

where (ϕ, \vec{A}) are operators, possibly depending upon time, obtained by taking the scalar and vector potentials $(\phi(\vec{r}, t), \vec{A}(\vec{r}, t))$ and viewing them as operators via

$$\phi = \phi(\vec{R}, t), \quad \vec{A} = \vec{A}(\vec{R}, t).$$

The radiation field has $\phi = 0$. If you like, you can think of V_0 as being obtained from the $q\phi$ contribution to H . In any case, the perturbation comes from the terms involving \vec{A} . We are, of course, assuming that the components of the vector potential are suitably small so that their contribution to the matrix elements of H are small compared to the matrix elements of H_0 . Since the vector potential is to be “small”, in a first approximation we can neglect the term quadratic in \vec{A} in the above Hamiltonian. We are left with the following (approximate) Hamiltonian:

$$H = H_0 + V,$$

where

$$V = -\frac{q}{mc} \vec{A} \cdot \vec{P}.$$

We will use this Hamiltonian, in the context of perturbation theory, to investigate the behavior of an atomic electron in the presence of an electromagnetic wave.

The radiation field

We have seen that we can describe the radiation field by a vector potential. The Maxwell equations determine the vector potential, in the radiation gauge, according to

$$\nabla^2 \vec{A} - \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2} = 0, \quad \nabla \cdot \vec{A} = 0.$$

It is easy to write down the general solution to this equation. We will specialize to a solution representing a plane electromagnetic wave traveling in the direction of the unit vector \hat{n} :

$$\vec{A}(\vec{r}, t) = \hat{e} \int_{-\infty}^{\infty} d\omega A(\omega) e^{-i\omega(t - \frac{1}{c}\hat{n}\cdot\vec{r})},$$

where $A(\omega) = A^*(-\omega)$ determines the frequency composition of the wave. Because the vector potential is “transverse”, $\nabla \cdot \vec{A} = 0$, we have that

$$\hat{e} \cdot \hat{n} = 0.$$

Evidently, the vector \hat{e} determines the plane polarization.

A general radiation field can be viewed as a superposition of plane waves of the type shown above. The superposition is over the propagation directions and polarizations. If we have time, later we will consider this case. For now we will stick with plane waves of a fixed polarization and propagation direction.

Transitions

Let us now compute the probability $P(i \rightarrow f)$ for transition from an initial state, assumed to be an unperturbed stationary state at time t_0 , to a final (unperturbed stationary) state at time t . To keep things a little more concrete, we can suppose that the atomic electron is bound by a central force so that the unperturbed stationary states can be described by a “principal quantum number” n labeling the energies along with the usual orbital angular momentum quantum numbers l and m . The initial and final states are $|n_i, l_i, m_i\rangle$ at $t = 0$ $|n_f, l_f, m_f\rangle$ at time t . The final state is labeled as if it is a bound state, but it will be straightforward to adjust our results to apply to unbound final states whose energy lies in a continuum. Also, you will easily see that most of what we do is insensitive to the details of the particular model we use for the atomic electron. We have

$$P(i \rightarrow f) \approx \left| \left\{ \frac{1}{\hbar} \int_{t_0}^t dt' \int_{-\infty}^{\infty} d\omega e^{i\omega_f t'} [V_{fi}(\omega) e^{i\omega t'} + V_{if}^*(\omega) e^{-i\omega t'}] \right\} \right|^2$$

Here

$$V_{fi}(\omega) = \frac{q}{mc} A(\omega) \langle n_f, l_f, m_f | e^{-i\omega \frac{1}{c} \hat{n} \cdot \vec{R}} \hat{e} \cdot \vec{P} | n_i, l_i, m_i \rangle.$$

The frequency ω_{fi} depends upon our model of the atom, *i.e.*, our choice for V_0 . If we choose the Coulomb potential (so that we have a hydrogenic atom), then

$$\omega_{fi} = \frac{1}{\hbar}(E_f - E_i) = \frac{Z^2 q^2}{2a} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right),$$

with Z the nuclear charge number, a the Bohr radius, and $n = 1, 2, \dots$ is the principal quantum number labeling the energy levels. (But, again, this particular formula for ω_{fi} formula is contingent upon the simplest model of a hydrogenic atom.)

Let us suppose that the electromagnetic radiation is a pulse of some finite duration such that t_0 is before the pulse arrives and t is after the pulse has passed. We can then easily compute the transition probability by letting the range of time integration run from $-\infty$ to ∞ . In this limit the time integral yields a delta function in frequency space. This lets us perform the frequency integral. We get

$$P(i \rightarrow f) \approx \left| \frac{2\pi q}{\hbar m c} A(|\omega_{fi}|) \langle n_f, l_f, m_f | e^{-i|\omega_{fi}| \frac{1}{c} \hat{n} \cdot \vec{R}} \hat{e} \cdot \vec{P} | n_i, l_i, m_i \rangle \right|^2.$$

This formula applies to either stimulated emission and absorption.

Note that the only Fourier component of the radiation field that contributes to the transition is at the frequency ω_{fi} of the transition. If the wave has no frequency component at ω_{fi} then the transition probability vanishes (in this approximation). This jibes with the picture of transitions being accompanied by emission or absorption of discrete “quanta” of size $\hbar\omega_{fi}$. Indeed, let us express the transition probability in terms of the net energy delivered by the pulse. It is not hard to see that the energy contained in the wave per unit area orthogonal to the wave propagation (the Poynting flux) is given by

$$\mathcal{E} = \int_{-\infty}^{\infty} dt \frac{c}{4\pi} (\vec{E} \times \vec{B}) \cdot \vec{n} = \frac{1}{c} \int_0^{\infty} d\omega \omega^2 |A(\omega)|^2.$$

Let us define $N(\omega)$ as the energy carried by the wave (for all time) through unit area per unit frequency:

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

In terms of $N(\omega)$ we have

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

where

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

is the *fine structure constant*.

This probability comes as the product of 3 factors: (1) the intensity of the electromagnetic radiation (embodied in $N(\omega)$), which reflects the adjustable role of the outside influence that stimulates the transitions; (2) the fine structure constant, which characterizes the strength (fixed by nature) of the electromagnetic interaction; (3) the matrix element between the initial and final states, which reflects the role played by the atomic structure itself. We next spend some time analyzing this matrix element.