Lecture 41

Relevant sections in text: §5.7

Transitions

We are exposing an atomic electron to a plane-polarized electromagnetic wave traveling in the direction of the unit vector $\hat{n}$:

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

where $A(\omega) = A^*(-\omega)$ determines the frequency composition of the wave. We also have that

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

The vector $\hat{e}$ determines the polarization.

Using first order perturbation theory, let us now compute the probability $P(i \to f)$ 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 (see below for more on this). 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 were 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 potential we use for the atomic electron. We have

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

Here

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

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

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

with q the charge on the electron, Z the nuclear charge number, a the Bohr radius, and $n = 1, 2, \ldots$ 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

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

This formula applies to either stimulated emission or 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 $\hbar\omega_{fi}$.

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

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

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

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

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.

Electric dipole transitions

We now want to analyze the matrix element which appears in the transition probability. 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:

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

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 elements $\langle n_f, l_f, m_f|\vec{P}|n_i, l_i, m_i\rangle$. To compute them, 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.