

Lecture 35

Relevant sections in text: §5.6

Fermi's Golden Rule

First order perturbation theory gives the following expression for the transition probability:

$$P(i \rightarrow n, i \neq n) = \frac{4|V_{ni}|^2}{(E_n - E_i)^2} \sin^2 \left\{ \frac{(E_n - E_i)t}{2\hbar} \right\}.$$

We have seen that the “energy conserving” transitions (if there are any available) become dominant after a sufficiently large time interval. Indeed, the probabilities for energy non-conserving transitions are bounded in time, while the probability for energy conserving transitions grow quadratically with time (for as long as the approximation is valid). Here “large time” means that the elapsed time is much larger than the period of oscillation of the transition probability for energy-non-conserving transitions

$$T := \frac{2\pi\hbar}{|E_n - E_i|}.$$

Note that the typical energy scale for atomic structure is on the order of electron-volts. This translates into a typical time scale $T \sim 10^{-15}$ s, so “large times” is often a very good approximation.

In the foregoing we have been tacitly assuming the final state is an energy eigenstate coming from the discrete part of the energy spectrum. If the final state energies lie in a continuum (at least approximately) we get a qualitatively similar picture, but the details change. We shall see that the transition probability at “large times” still favors energy conserving transitions, but it will only grow linearly with time because the width of the probability distribution about such transitions is becoming narrower with time. We can see this by supposing the probability is a continuous function of $\Delta E = E_n - E_i$ (see discussion below) and considering the large t limit via the identities

$$\lim_{\alpha \rightarrow \infty} \frac{\sin^2(\alpha x)}{\alpha x^2} = \pi \delta(x), \quad \delta(ax) = \frac{1}{|a|} \delta(x)$$

Then we have (exercise)

$$P(i \rightarrow n, i \neq n) \approx \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(\Delta E) t, \quad t \gg T.$$

This implies that in this case (quasi-continuum of final states) the *transition rate* $\frac{dP}{dt}$ is constant at late times:

$$\frac{d}{dt} P(i \rightarrow n, i \neq n) \approx \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(\Delta E), \quad t \gg T.$$

a result which is one version of *Fermi's Golden Rule*.

An example of a continuum of final states appears in the Auger ionization of a Helium atom. Here two electrons in the 2S (unperturbed) stationary state make a transition (thanks to their electrostatic repulsion) to a state in which one electron is in the 1S state and the other is ejected. Another example would be elastic scattering of an electron off of an ion. In such situations there is a continuum (or near continuum) of (nearly) degenerate states that can serve as the state denoted by $|n\rangle$. In this case one will have a “density of states” factor $\rho(E)$. The quantity $\rho(E)dE$ is the number of states with energies between E and $E + dE$. The transition rate from the initial state $|i\rangle$ into states with energy $E \in \mathcal{E}$ is then

$$\frac{d}{dt}P(i \rightarrow \mathcal{E}) = \int_{\mathcal{E}} dE_n \rho(E_n) \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_i, E_n) = \frac{2\pi}{\hbar} \rho(E_i) |V_{ni}|^2.$$

This is probably the most commonly used version of Fermi's Golden Rule. We will consider an example of this a bit later.

Harmonic Perturbations

We now consider perturbations which depend upon time. Usually we can Fourier analyze the time dependence and view the perturbation as a superposition of many perturbations that each depend harmonically on the time. Therefore, the next thing to consider are such harmonically varying perturbations. As a good example, which we shall consider later, consider the effect of an electromagnetic wave incident upon an atomic electron. If the wave is nearly monochromatic then one can model the time dependence of the associated perturbation as harmonic.

Suppose, then, that the perturbation is of the form

$$V(t) = \mathcal{V}e^{i\omega t} + \mathcal{V}^\dagger e^{-i\omega t},$$

where \mathcal{V} is some time-independent operator and ω is a given frequency. (Note that there are now two time scales in the problem: that associated with the perturbation, and that naturally defined by the difference in unperturbed energies.) We again suppose that at the initial time $t = 0$ the system is in an eigenstate $|i\rangle$ of H_0 . We ask what is the probability for finding the system in the state $|n\rangle$ at time t ($n \neq i$). Using our previous results we have that (exercise)

$$P(i \rightarrow n; i \neq n) = \left| \frac{1}{\hbar} \int_0^t dt' (\mathcal{V}_{ni} e^{i\omega t'} + \mathcal{V}_{ni}^\dagger e^{-i\omega t'}) e^{i\omega_{ni} t} \right|^2, \quad \omega_{ni} := \frac{E_n - E_i}{\hbar}.$$

The integral is the sum of two terms, where each is of the form encountered in the time-independent perturbation case, except that now the frequency in the exponents is shifted via

$$\omega_{ni} \rightarrow \omega_{ni} \pm \omega.$$

This allows us to use our previous analysis for the late time transition rates, provided the frequencies are modified as shown above in order to handle the current situation.

In detail, after taking the absolute-square in the above formula for the probability, we have 3 terms: two “direct terms” and a cross term. Each has a vanishing denominator “on resonance”, that is, when the initial and final states are such that $\omega_{ni} \pm \omega = 0$. As before, the limit as the denominator vanishes for each of these terms is finite and grows with time. Thus, as before, the principal transitions at “late times” are such that one of these frequency combinations vanishes. For a given initial and final state only one of these two options (\pm) can occur. The direct terms have the square of the growing probability, while the cross term only involves this quantity linearly. The cross term can therefore be ignored compared to the direct terms.

In summary, at large enough times, the only transitions with appreciable probability will be those for which either

$$\omega_{ni} + \omega = 0$$

or

$$\omega_{ni} - \omega = 0.$$

Of course, only one of these two situations can occur for a given choice of frequency ω and for a given initial and final state. In the first case we have

$$\omega_{ni} + \omega = 0 \iff E_n = E_i - \hbar\omega,$$

and in the second case we have

$$\omega_{ni} - \omega = 0 \iff E_n = E_i + \hbar\omega.$$

So, using the unperturbed energy observable to interpret these results, we have the following situation. When $E_n = E_i - \hbar\omega$ we speak of *stimulated emission*, since the perturbation has (from the unperturbed point of view) caused the system to “emit” a quantum of energy $\hbar\omega$. When $E_n = E_i + \hbar\omega$ we speak of *stimulated absorption*, since the perturbation has (from the unperturbed point of view) caused the system to “absorb” a quantum of energy $\hbar\omega$.

To get a formula for the late time transition rates we simply have to make the appropriate shift

$$\omega_{ni} \rightarrow \omega_{ni} \pm \omega$$

in our previous formulas. In the case of a (quasi-)continuum of final states we get

$$\frac{d}{dt}P(i \rightarrow n, i \neq n) = \frac{2\pi}{\hbar} \left[|\mathcal{V}_{ni}|^2 \delta(E_n - E_i + \hbar\omega) + |\mathcal{V}_{ni}^\dagger|^2 \delta(E_n - E_i - \hbar\omega) \right].$$

This is yet another version of Fermi's Golden Rule. Note that, since

$$|\mathcal{V}_{ni}|^2 = \mathcal{V}_{ni}^* \mathcal{V}_{ni} = \mathcal{V}_{in}^\dagger (\mathcal{V}_{in}^\dagger)^* = |\mathcal{V}_{in}^\dagger|^2$$

the transition rate (per unit energy) for $i \rightarrow n$ is the same as that for $n \rightarrow i$, a phenomenon often called "detailed balancing".