Lecture 38

Relevant sections in text: §5.6

Fermi's Golden Rule

First order perturbation theory gave us the following expression for the transition probability:

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

We have seen that the "energy conserving" transitions (if there are any available) become dominant after a sufficiently large time interval. Indeed, the probabilties 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 for atomic systems.

In the foregoing we have been tacitly assuming the final state is an energy eigenstate coming from the discrete part of the energy spectrum. In many important examples the final state energies lie in a continuum (at least approximately). In this case we get a qualitatively similar picture, but the details change in significant ways. 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 final state, which we now denote by $|\gamma\rangle = |E, \alpha\rangle$, is part of a continuum of states labeled by the continuous energy E and possibly some additional variables α corresponding to the spectra of a CSCO. The transition probability is now a probability density (at least in energy space) and is to be integrated/summed over some range in the (E, α) variables to get a transition probability. The late time limit of the probability density can be computed via the identities

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

Then we have for the transition *density* (exercise)

$$P(i \to \gamma) \approx \frac{2\pi}{\hbar}|V_{\gamma i}|^2 \delta(E - E_i)t, \quad t >> T.$$

This implies that in this case (quasi-continuum of final states) at late times the *transition rate density* $\frac{dP}{dt}$ is non-negligible for energy conserving transitions and is constant in time:

$$\frac{d}{dt}P(i \to \gamma) \approx \frac{2\pi}{\hbar}|V_{\gamma i}|^2 \delta(E - E_i), \quad t >> T.$$

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

In situations where there is a continuum (or near continuum) of final energies we often are just interested in the transition rate to final states with energy in some range $\mathcal{E}$. We then need to integrate the transition rate density over $\mathcal{E}$ and sum/integrate over the remaining "quantum numbers" to get a transition rate. The result will involve 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 w from the initial state $|i\rangle$ into states with energy $E \in \mathcal{E}$ is then expressible in the form

$$w = \int d\alpha \int_{\mathcal{E}} dE \rho(E) \frac{2\pi}{\hbar}|V_{\gamma i}|^2 \delta(E - E_i) = \frac{2\pi}{\hbar}\rho(E_i) \int d\alpha \, |V_{\gamma i}|^2,$$

where in the last expression it is understood that $\gamma = (E_i, \alpha)$. This is probably the most commonly used version of Fermi's Golden Rule.

Example: Auto-ionization of Helium

An example of a continuum of final states appears in the auto-ionization (also called radiationless or Auger transition) 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. The ejected electron has a continuum of final energies hence the final state of the two electrons does as well. Let us have a brief look at this.

First we give a naive argument based upon energy considerations to see why auto-ionization is potentially viable. Using the formula for a single electron energy in a hydrogenic atom:

$$E_n = -\frac{Z^2}{n^2} \times 13.6\, eV,$$

we can give a naive estimate of the energy of a Helium atom in which both electrons are in the 2S state, namely $-27.2\, eV$, which is $81.6\, eV$ above the naive ground state energy. I say "naive" because I am ignoring the energy due to electrostatic repulsion of the electrons. On the other hand, consider the (naive) energy of the atom when one electron is in the hydrogenic ground state and one is ionized with zero energy. The energy is $-54.4\, eV$, considerably lower than the case with two electrons in the 2S state. Energetically then, it is conceivable that the electrostatic repulsion—which removes the hydrogenic states' status

as stationary states—could induce transitions to this lower energy state with the energy difference appearing in the kinetic energy of the ionized electron. This phenomenon has in fact been observed. Here we give a quick study of it from the point of view of Fermi's Golden Rule.

To be continued...