

Lecture 34

Relevant sections in text: §5.6

Time-dependent perturbation theory (cont.)

We are constructing an approximation scheme for solving

$$i\hbar \frac{d}{dt} c_n(t) = \sum_m e^{\frac{i}{\hbar}(E_n - E_m)t} V_{nm}(t) c_m(t), \quad V_{nm} = \langle n | V(t) | m \rangle.$$

For simplicity we shall suppose (as is often the case) that the initial state is an eigenstate of H_0 . Setting $|\psi(0)\rangle = |i\rangle$, *i.e.*, taking the initial state to be one of the *unperturbed* energy eigenvectors, we get as our zeroth-order approximation:

$$c_n(t) \approx c_n^{(0)} = \delta_{ni}.$$

We get our “first-order approximation” $c_n^{(1)}(t)$ by improving our approximation of the right-hand side of the differential equations to be accurate to first order. This we do by using the zeroth order approximation of the solution, $c_n^{(0)}$ in the right hand side of the equation. So, we now approximate the differential equation as

$$i\hbar \frac{d}{dt} c_n(t) \approx e^{\frac{i}{\hbar}(E_n - E_i)t} V_{ni}(t),$$

with solution

$$c_n(t) \approx c_n^{(0)} + c_n^{(1)}(t) = \delta_{ni} + \frac{1}{i\hbar} \int_0^t dt' e^{\frac{i}{\hbar}(E_n - E_i)t'} V_{ni}(t').$$

Successive approximations are obtained by iterating this procedure. We shall only deal with the first non-trivial approximation, which defines *first-order time-dependent perturbation theory*.

We assumed that the system started off in the (formerly stationary) state $|i\rangle$ defined by H_0 . Of course, generally the perturbation will be such that $|i\rangle$ is not a stationary state for H , so that at times $t > 0$ the state vector will change. We can still ask what is the probability for finding the system in an eigenstate $|n\rangle$ of H_0 . Assuming that $n \neq i$ this is

$$P(i \rightarrow n, i \neq n) = \left| \frac{1}{\hbar} \int_0^t dt' e^{\frac{i}{\hbar}(E_n - E_i)t'} V_{ni}(t') \right|^2.$$

This is the *transition probability* to first-order in TDPT. The probability for no transition is, in this approximation,

$$P(i \rightarrow i) = 1 - \sum_{n \neq i} P(i \rightarrow n, i \neq n).$$

TDPT is valid so long as the transition probabilities are all much less than unity. Otherwise, our approximation begins to fail.

The transition probability for $i \rightarrow n$ is only non-zero if there is a non-zero matrix element V_{ni} “connecting” the initial and final states. Otherwise, we say that the transition is “forbidden”. Of course, it is only forbidden in the leading order approximation. If a particular transition $i \rightarrow n$ is forbidden in the sense just described, then physically this means that the transition may occur with very small probability compared to other, non-forbidden transitions. To calculate this very small probability one would have to go to higher orders in TDPT.

Example: time-independent perturbation

As our first application of TDPT we consider what happens when the perturbation V does not in fact depend upon time. This means, of course, that the true Hamiltonian H_0+V is time independent, too (since we assume H_0 is time independent). If we can solve the energy eigenvalue problem for H_0+V we can immediately write down the exact solution to the Schrödinger equation and we don’t need to bother with approximation methods. But we are assuming, of course, that the problem is not exactly soluble. Now, in the current example of a time-independent perturbation, we could use the approximate eigenvalues and eigenvectors from time independent perturbation theory to get approximate solutions to the Schrödinger equation. This turns out to be equivalent to the results we will obtain below using time dependent perturbation theory. It’s actually quite a nice exercise to prove this, but we won’t bother.

Assuming V is time independent, the integral appearing in the transition probability can be easily computed and we get (exercise)

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

Assuming this matrix element V_{ni} does not vanish, we see that the transition probability oscillates in time. The amplitude of this oscillation is small provided the magnitude of the transition matrix element of the perturbation is small compared to the unperturbed energy difference between the initial and final states. This number had better be small or the perturbative approximation is not valid.

Let us consider the energy dependence of the transition probability. The amplitude of the temporally oscillating transition probability decreases quickly as the energy of the final state differs from the energy of the initial state. The dominant transition probabilities occur when $E_n = E_i$, $i \neq n$. For this to happen, of course, the states $|n\rangle$ and $|i\rangle$ must correspond to a degenerate or nearly degenerate eigenvalue. When $E_n \approx E_i$ we have

$$P(i \rightarrow n, i \neq n, E_n = E_i) = \frac{1}{\hbar^2} |V_{ni}|^2 t^2.$$

Because of the growth in time, our approximation breaks down eventually in this case. Still, you can see that the transition probability is peaked about those states such that $E_n \approx E_i$, with the peak having height proportional to t^2 and width proportional to $1/t$. Thus as the time interval becomes large enough the principal probability is for transitions of the “energy conserving type”, $E_n \approx E_i$. For shorter times the probabilities for “energy non-conserving” transitions are less negligible. Indeed, the probability for a transition with an energy difference ΔE at time t is appreciable once the elapsed time satisfies

$$t \sim \frac{\pi \hbar}{\Delta E},$$

as you can see by inspecting the transition probability. This is just a version of the time-energy uncertainty principle expressed in terms of the unperturbed stationary states. One sometimes characterizes the situation by saying that one can “violate energy conservation by an amount ΔE provided you do it over a time interval Δt such that $\Delta t \Delta E \sim \hbar$ ”.

All this talk of “energy non-conservation” is of course purely figurative. The *true* energy, represented by $H_0 + V$ is conserved, as always in quantum mechanics when the Hamiltonian is time independent. It is only because we are considering the dynamics in terms of the unperturbed system, using the unperturbed “energy” defined by H_0 , that we can speak of energy non-conservation from the unperturbed point of view. You can see, however, why slogans like “you can violate conservation of energy if you do it over a short enough time” might arise and what they really mean. You can also see that such slogans can be very misleading.