

## Lecture 37

Relevant sections in text: §5.6

### Time Dependent Perturbation Theory (cont.)

Last time we supposed we could write the Hamiltonian in the form

$$H(t) = H_0 + V(t),$$

and then we wrote the Schrödinger equation in the form

$$i\hbar \frac{d}{dt} c_n(t) = \sum_m e^{\frac{i}{\hbar}(E_n - E_m)t} V_{nm}(t) c_m(t),$$

where

$$H_0|n\rangle = E_n|n\rangle, \quad V_{nm}(t) = \langle n|V(t)|m\rangle.$$

Now we suppose that the matrix elements  $V_{nm}$  are suitably small and we develop a scheme to approximate the solutions of the Schrödinger equation as written above. To do this we again introduce a parameter  $\lambda \in [0, 1]$  and replace  $V \rightarrow \lambda V$ . We then suppose the solutions to the equations can be expressed as

$$c_n(t) = c_n^{(0)} + \lambda c_n^{(1)} + \dots$$

Again, assuming the perturbation is “small”, we can approximate the solution by truncating the series.

Substituting this into the equations above, and equating powers of  $\lambda$  we get to first order in  $\lambda$  (exercise):

$$i\hbar \frac{d}{dt} c_n^{(0)}(t) = 0,$$

$$\frac{d}{dt} c_n^{(1)}(t) = \sum_m e^{\frac{i}{\hbar}(E_n - E_m)t} V_{nm}(t) c_m^{(0)}(t).$$

The zeroth order equation recovers the result that the expansion coefficients are constant in time when the perturbation is ignored. As in TIPT, the higher order equations involve solutions to the lower order equations. To first order in perturbation theory the solutions are easily obtained once initial conditions are selected.

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:

$$c_n(t) \approx c_n^{(0)} = \delta_{ni} + \mathcal{O}(V).$$

Using this in the first order equation we get

$$c_n(t) \approx c_n^{(0)} + c_n^{(1)}(t) = \delta_{ni} + \frac{1}{i\hbar} \int_0^t dt' e^{\frac{i}{\hbar}(E_n - E_i)t'} V_{ni}(t') + \mathcal{O}(V^2).$$

We shall only deal with this 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 the 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. At any fixed time  $t > 0$  the amplitude of the transition probability involves a central peak at  $E_n = E_i$ , which can occur only if this energy is degenerate since we assume the initial and final states are distinct. Away from the central peak the probability decreases quickly (in an oscillatory fashion) as the energy of the final state differs from the energy of the initial state.

The height of the central peak of the transition probability is proportional to  $t^2$  as you can see via l'Hospital's rule with  $E_n = E_i$ ; we have

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

This means that – if there are states with  $E_n = E_i$  – we cannot use this formula for an arbitrary time interval: eventually the transition probability exceeds unity (let alone remaining small).

The width of the central peak is proportional to  $1/t$  as you can see by noting that the boundaries of the central peak occur at energy differences where the transition probability vanishes:

$$(E_n - E_i)/\hbar = \pm \frac{2\pi}{t}.$$

Thus as the time interval becomes large enough (but not so large the approximation breaks down) 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  $\Delta E$  at time  $t$  is appreciable once the elapsed time satisfies

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

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  $\Delta E$  provided you do it over a time interval  $\Delta t$  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.

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\* It’s worth noting that the often heard description of the vacuum involving spontaneous creation and destruction of particle-antiparticle pairs is an artifact of a similar perturbative analysis.