A Review of Perturbation Theory

April 17, 2002

Most quantum mechanics problems are not solvable in closed form with analytical techniques. To extend our repetoire beyond just particle-in-a-box, a number of approximation techniques have been developed. A large class of these fall under the heading of "perturbation theory", in which we consider our system to obey Hamiltonian H that may be written as

$$H = H^0 + \lambda H^1 + \lambda^2 H^2 + ..., \tag{1}$$

where H^0 is an exactly solvable Hamiltonian, λ is a small parameter, and the other terms may therefore be taken as small corrections.

These notes are a quick review of how to deal with systems that obey such Hamiltonians. We'll be using Dirac notation and the Schrödinger formalism, in which the states are time-dependent. We begin with time-independent perturbation theory, and will then move on to consider time-dependent problems. For now, we'll only deal with single-particle problems, too.

1 Time-independent

We're going to use the time-independent Schrödinger equation, and look for the energy eigenvalues and eigenstates of H. First, suppose that our *unperturbed* problem,

$$H^0|\psi^0\rangle = E^0|\psi^0\rangle \tag{2}$$

may be solved exactly, giving an energy eigenvalue spectrum E_j^0 with corresponding eigenstates $|\psi_j^0\rangle$. Remember, because H^0 is a Hermitian operator, its eigenvalues are real, and its eigenvectors $|\psi_j^0\rangle$ form a complete set.

The strategy we're going to take is straightforward. We're going to assume that our perturbative corrections to the Hamiltonian, $\lambda H^1 + \lambda^2 H^2 + ...$, lead to corresponding perturbative corrections to the eigenvalues and eigenstates. That is,

$$\begin{aligned} E_j &= E_j^0 + \lambda E_j^1 + \lambda^2 E_j^2 + ..., \\ |\psi_j\rangle &= |\psi_j^0\rangle + \lambda|\psi_j^1\rangle + \lambda^2|\psi_j^2\rangle + ... \end{aligned} \tag{3}$$

For now, we'll plug into the time-independent Schrödinger equation, and use some linear algebra to solve for terms of interest.

First, we need to check normalization. Taking the inner product of the proposed eigenstate $|\psi_j\rangle$ with itself and setting equal to 1, and grouping terms by orders in λ, we see

$$\begin{aligned} \langle\psi_j^0|\psi_j^0\rangle &= 1 \\ \langle\psi_j^1|\psi_j^0\rangle + \langle\psi_j^0|\psi_j^1\rangle &= 0, \text{ etc.} \end{aligned} \tag{4}$$

So, we can take $\langle\psi_j^1|\psi_j^0\rangle = 0$ without any problems.

1.1 Nondegenerate, 1st and 2nd order

Plugging into the Schrödinger equation up to second order,

$$(H^0 + \lambda H^1 + \lambda^2 H^2)(|\psi^0\rangle + \lambda|\psi^1\rangle + \lambda^2|\psi^2\rangle) = (E_j^0 + \lambda E_j^1 + \lambda^2 E_j^2)(|\psi^0\rangle + \lambda|\psi^1\rangle + \lambda^2|\psi^2\rangle). \quad (5)$$

For simpicity's sake, let's assume initially that our original, unperturbed eigenvalue spectrum is nondegenerate. That is,

$$E_j^0 \neq E_k^0 \quad (6)$$

for all $j \neq k$.

Now let's take the inner product of Eq. 5 with $\langle\psi_j^0|$. Again, let's look order by order in λ. To zeroth order, we get

$$\langle\psi_j^0|H^0|\psi_j^0\rangle = \langle\psi_j^0|E^0|\psi_j^0\rangle, \quad (7)$$

which we know is true because $|\psi_j^0\rangle$ is the solution to the unperturbed problem with eigenvalue E_j^0.

To first order, we find

$$\langle\psi_j^0|H^1|\psi_j^0\rangle = E_j^1. \quad (8)$$

So, the first order correction to the energy eigenvalue of state j is the matrix element of the first order perturbation Hamiltonian between the unperturbed states.

Now we want to find $|\psi_j^1\rangle$, the first order correction to the state $|\psi_j^0\rangle$. Take the inner product of Eq. 5 with $\langle\psi_k^0|$ this time, with $k \neq j$. The zeroth order term vanishes. The first order term gives:

$$\langle\psi_k^0|H^1|\psi_j^0\rangle = (E_k^0 - E_j^0)\langle\psi_k^0|\psi_j^1\rangle. \quad (9)$$

Rearranging,

$$\langle\psi_k^0|\psi_j^1\rangle = \frac{\langle\psi_k^0|H^1|\psi_j^0\rangle}{(E_k^0 - E_j^0)} \quad (10)$$

Since the unperturbed eigenfunctions form a complete set, we can write the correction to the eigenfunction as

$$\begin{aligned} |\psi_j^1\rangle &= \sum_k |\psi_k^0\rangle\langle\psi_k^0|\psi_j^1\rangle \\ &= \sum_{k\neq j} |\psi_k^0\rangle \frac{\langle\psi_k^0|H^1|\psi_j^0\rangle}{(E_k^0 - E_j^0)}. \end{aligned} \quad (11)$$

Now that we have an expression for $|\psi_j^1\rangle$, we can plug that into Eq. 5, take the inner product of both sides with $\langle\psi_j^0|$ as before, and look at the second order terms.

$$\begin{aligned} E_j^2 &= \langle\psi_j^0|H^1|\psi_j^1\rangle \\ &= \sum_{k\neq j} \langle\psi_j^0|H^1|\psi_k^0\rangle \frac{\langle\psi_k^0|H^1|\psi_j^0\rangle}{(E_k^0 - E_j^0)} \\ &= \sum_{k\neq j} \frac{|\langle\psi_k^0|H^1|\psi_j^0\rangle|^2}{(E_k^0 - E_j^0)}. \end{aligned} \quad (12)$$

We've now found the first and second order corrections to the unperturbed energy spectrum, and the first order correction to the unperturbed states.

1.2 Degeneracies

If the unpertrubed system has degenerate levels, things can get messy. The perturbation can "lift the degeneracy", meaning that two unperturbed states with *identical* unperturbed energies can end up getting *different* perturbation corrections to their energies and the states themselves. A classical example: a compass in zero magnetic field has all orientations degenerate. However, an external magnetic field in the plane of the compass needle breaks the degeneracy, and picks out a unique ground state of the perturbed system.

Suppose we start out with two unperturbed degenerate states, $|\xi_f^0\rangle$ and $|\xi_g^0\rangle$. Rather than just using $|\xi_f^0\rangle$ and $|\xi_g^0\rangle$ as the basis for our perturbation calculation, we want to find linear combinations of the two to use instead. Ideally we want the perturbation to not mix the originally degenerate states. That is, we want to find a combination of coefficients c_f, c_g and use $c_f|\xi_f^0\rangle + c_g|\xi_g^0\rangle$ (and the combination orthogonal to that) as the starting points for our perturbation calculation. We determine the values of c_f, c_g by requiring that the perturbation be diagonal in the new basis.

1.3 Summary

We've seen that perturbation theory may be used to solve problems that are *close* to exactly solvable unperturbed problems. The perturbation changes the energy eigenvalues from their unperturbed values. It also alters a particular unperturbed state by mixing it with the other unperturbed states by an amount related to the matrix element of the perturbation; see Eq. 8. That change to the states leads to a higher order correction to the energy, Eq. 12.

There are systematic approaches to carry out perturbation theory to higher orders. The most well-known example is the diagrammatic technique developed in quantum field theory by Richard Feynman.

2 Time-dependent

What happens if we have an explicitly time-dependent Hamiltonian? The classic example of this is behavior of a system under the influence of electromagnetic radiation. Here the time-dependence of the electric and magnetic fields is harmonic, and the results can be profound (Stokes shifts in Raman spectroscopy; lasing; etc.).

Here we briefly introduce a few ways of dealing with time-dependent problems. We discuss the sudden and adiabatic approximations, and time-dependent perturbation theory. We end with a derivation of Fermi's Golden Rule, an expression used commonly for determining rates of processes in solid state systems.

2.1 Sudden and adiabatic approximations

Suppose we consider turning on some perturbing Hamiltonian, H', in addition to our unperturbed Hamiltonian, H^0. Suppose further that the system was initially in a state $|\psi(0)\rangle$.

Consider the case where the perturbation is turned on *instantaneously* at $t = 0$ and is left on for all future times. This is a time when we can apply the sudden approximation. If the eigenfunctions of the new Hamitonian $H^0 + H'$ are labeled $|\phi'_j\rangle$ with energies E'_j, then we can write down the state for all future times:

$$\phi(t > 0) = \sum_j |\phi'_j\rangle\langle\phi'_j|\psi(0)\rangle e^{-iE'_j t/\hbar}. \tag{13}$$

We project the original state onto the new eigenstates, and time-evolve those new eigenstates according to the new Hamiltonian. This approximation is valid provided the turn-on time of H' is short compared to the relevant time scales of $\sim \hbar/E'_j$.

Similarly, we consider the adiabatic limit, in which H' is turned on infinitesmally slowly (or at least slowly compared to all relevant energy scales, given by $\hbar/\Delta E_{jk}$, where ΔE_{jk} is the energy spacing between any two adjacent levels). If the adiabatic approximation is a good one, then the turn-on of the perturbation may be sufficiently gentle that each old eigenstate $|\phi^0_j\rangle$ smoothly evolves into a new eigenstate $|\phi'_j\rangle$. If the perturbation would've caused old levels to cross, instead one generally finds an "avoided crossing". The detailed analysis of the probability of ending up in the "other" level after an avoided crossing as a function of perturbation rate was done be Landau and Zener back in the 1930s. See Landau and Lifschitz QM text, or Rubbermark *et al.*, PRA **23**, 3107 (1981).

2.2 Transition probabilities

What if the time dependence is more subtle than just turning on a perturbation and leaving it there? Then we need time-dependent perturbation theory. Begin with our unperturbed Hamiltonian, H^0, and again assume a nondegenerate eigenvalue spectrum E^0_j (As above, the degenerate case is a reasonably straightforward development from the nondegenerate case). At time $t = 0$ we consider beginning to perturb our system with some $H'(t)$.

At any time t we can expand the true, unknown $|\Psi(t)\rangle$ in the time-evolved versions of the unperturbed eigenstates, $|\psi^0_j\rangle$. That is:

$$|\Psi(t)\rangle = \sum_j c_j(t) e^{-iE^0_j t/\hbar}|\psi^0_j\rangle, \tag{14}$$

where the $c_j(t)$ are the time-dependent coefficients of the expansion. We can interpret this as saying that, if we turned the perturbation H' off instantly at time t, the probability of finding the system in state $|\psi^0_j\rangle$ is given by $|c_j(t)|^2$. Note (without proof) that this expansion automatically preserves normalizalization as long as the perturbation $H'(t)$ is real.

Plug the state given in Eq. 14 into the time-dependent Schrödinger equation, using the total Hamiltonian, $H^0 + H'$:

$$i\hbar\sum_j \dot{c}_j(t)e^{-iE^0_j t/\hbar}|\psi^0_j\rangle + i\hbar\sum_j \frac{-i}{\hbar}E^0_j c_j(t)e^{-iE^0_j t/\hbar}|\psi^0_j\rangle = \sum_j (H^0 + H'(t))c_j(t)e^{-iE^0_j t/\hbar}|\psi^0_j\rangle. \tag{15}$$

Drop identical terms from both sides after using the H^0 operator on the right hand side. Then take the inner product of both sides with $\langle\psi^0_k|e^{iE^0_k t/\hbar}$, and get

$$i\hbar\dot{c}_k(t) = \sum_j c_j(t)\langle\psi^0_k|H'(t)|\psi^0_j\rangle e^{i(E^0_k - E^0_j)t/\hbar}. \tag{16}$$

This is exact, so far. Define

$$\begin{aligned}\omega_{kj} &\equiv \frac{E^0_k - E^0_j}{\hbar}, \\ H'_{kj} &\equiv \langle\psi^0_k|H'(t)|\psi^0_j\rangle. \end{aligned} \tag{17}$$

One can now try writing $H'(t)$ as a power series in some small parameter λ, and parallel our earlier analysis. However, a more common and useful approach is an interative one, described below. Let's assume that at $t = 0$ the system was in a particular unperturbed eigenstate, $|\psi_a^0\rangle$. Therefore, $c_a(t=0) = 1$, and $c_{j\neq a}(t=0) = 0$. That is, $c_a(t=0) = \delta_{ja}$. Plug this into Eq. 16, and we get

$$
\begin{aligned}
c_a(t) &= \frac{1}{i\hbar}\int_0^t H'_{aa}(\tau)d\tau + 1, \qquad j = a, \\
c_j(t) &= \frac{1}{i\hbar}\int_0^t H'_{ja}(\tau)e^{i\omega_{ja}\tau}d\tau, \qquad j \neq a.
\end{aligned} \tag{18}
$$

We can define a transition probability, the probability of finding the system in (approximately) state j at time t after starting out in state a, as

$$P_{ja}(t) = |c_j(t)|^2 = \frac{1}{\hbar^2}|\int_0^t H'_{ja}(\tau)e^{i\omega ja\tau}d\tau|^2. \tag{19}$$

From this expression it is already possible to see where selection rules come from: if the matrix element of the perturbation between the initial and (approximate) final states, H'_{ja}, is zero, then to first order the transition is forbidden.

Consider something like our sudden approximation case from before, where H' is turned on at $t = 0$. In particular, let's assume

$$H'(t) = V_0\cos(\omega_r t) = V_0\left[\frac{e^{i\omega_r t} + e^{-i\omega_r t}}{2}\right]. \tag{20}$$

for $t > 0$. Now we're representing the true new eigenstates approximately by the old unperturbed states.

If we actually plug this into our probability expression, we find, first for $\omega_r = 0$,

$$P_{ja} = \frac{|V_{0,ja}|^2}{\hbar^2}\frac{\sin^2(\omega_{ja}t/2)}{(\omega_{ja}/2)^2}. \tag{21}$$

Remember, $\sin^2(x)/x^2$ is strongly peaked around $x = 0$. That implies that *transitions between initial and final states are favored if energy is conserved*, that is, if $\omega_{ja} \approx 0$. Let's define:

$$F(t, \omega_{ja}) \equiv \frac{2\sin^2\omega_{ja}t/2}{\omega_{ja}^2}. \tag{22}$$

This quantity will be useful in a bit.

If we do the $\omega_r \neq 0$ case, we find:

$$c_j(t) = -i\frac{|V_{0,ja}|^2}{\hbar^2}\left[\frac{e^{i(\omega_{ja}+\omega_r)t} - 1}{i(\omega_{ja} + \omega_r)} + \frac{e^{i(\omega_{ja}-\omega_r)t} - 1}{i(\omega_{ja} - \omega_r)}\right] \tag{23}$$

If we take the magnitude-squared of this to find P_{ja}, we get

$$P_{ja}(t) = F(t, \omega_{ja} + \omega_r)|V_{0,ja}|^2 + F(t, \omega_{ja} - \omega_r)|V_{0,ja}|^2 + \quad \text{crossterms}. \tag{24}$$

The function $F(t, \omega)$ has some interesting properties. For fixed $\omega \neq 0$, it's t-dependence is just $\sim \sin^2$. However, at fixed t, it's peak at $\omega = 0$ is $t^2/2$, and its half-width is $2\pi/t$. So, as t increases, $F(t, \omega)$ becomes more and more strongly peaked around $\omega = 0$. In fact,

$$\int_{-\infty}^{+\infty} F(t, \omega)d\omega = \pi t, \tag{25}$$

and one can show that $F(t, \omega) \to \pi t \delta(\omega)$ as $t \to \infty$.

For us, this means that at long times (but not times so long that the initial state gets depleted!) transitions only occur to states that conserve energy. For our $\omega_r \neq 0$ case above, we find transitions are probable between states j and a only if they differ in energy by an amount $\hbar\omega_r$. These two processes correspond to absorption and stimulated emission.

2.3 Fermi's Golden Rule

Consider the $\omega_r \neq 0$ case from above, and suppose that there are a number of states $\nu(E)$ that satisfy the conservation of energy condition between initial and final states. Also, suppose those final states also share the same matrix element with the initial state, $V_{0,ja}$. In that case, the *rate* at which transitions occur is given by:

$$\frac{dP_{ja}(t)}{dt} = \frac{2\pi}{\hbar}|V_{0,ja}|^2 \nu(E). \tag{26}$$

This relation is called *Fermi's Golden Rule*, and is commonly used to determine the rates of many quantum mechanical processes.

Remember that we're doing perturbation theory here, and asking the question, if a system starts out in (unperturbed) state a, what is the probability of finding it later in (approximately) unperturbed state p. The key to our approximations is that the time-dependent perturbation is small, that we wait long enough for our F functions to act like energy-conserving delta functions, but not so long that the initial state's population is changed much. These are conditions for the validity of Fermi's Golden Rule, which is fundamentally a first-order time dependent perturbation theory result.

Note that:

- If the initial and final states in question are not connected by the perturbing potential (that is, the matrix element in question is zero), the rate of the process is also zero. This is an example of the origin of selection rules.
- If the number of available final states is zero, the rate of the process is also zero. The importance of this point can't be overestimated. As we'll see, it's the reason that semiconductors are semiconductors, that band insulators are band insulators, etc.

3 Conclusion

This concludes our review of perturbation theory. The main results to take away from this are the first and second order corrections to the energies in time-independent problems, and Fermi's Golden Rule.

For a more complete discussion of perturbation methods, most quantum mechanics textbooks will be useful references. Particularly valuable are Cohen-Tannoudji's and Sakurai's texts.