Perturbation Theory Liboff Chap. 13 (9.1)

We've long since run out of problems where we can solve the Schrödinger eq'n exactly to find energy eigenstates. But we believe that QM describes all physics on small scales, regardless of whether we can ourselves solve the problems analytically.

Now we don't throw up our hands and go home; instead we devise approximation methods that, while they don't give us exact sol'ns, get us pretty darn close. Perturbation theory is one such method.

To keep it simple, we'll start w/ time independent, nondegenerate perturbation theory.

We want to solve

$$\hat{H}\psi_n = E_n\psi_n \qquad (*)$$

where $\hat{H}$ is some Hamiltonian operator where we don't have an analytic solution. Well, if $\hat{H}$ is close to a Hamitonian $\hat{H}_0$ where we do know the eigenfunctions, then we can find the ψ_n in $(*)$ by doing a perturbative expansion.

To make all this more concrete, suppose

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

Where

$\hat{H}$ = total Hamiltonian, for which we want to find eigenfunctions + eigenvalues

$\hat{H}_0$ = "unperturbed Hamiltonian" whose eigenfns + eigenvalues we know:

$$\underset{\uparrow}{\hat{H}_0 \varphi_n^{(0)}} = \underset{\uparrow}{E_n^{(0)}}\, \underset{\uparrow}{\varphi_n^{(0)}}$$

we know these.

$\hat{H}'$ = "perturbation Hamiltonian" which is small compared to $\hat{H}_0$.

[Reality check: It's pretty meaningless to describe one operator as being small compared to another. In fact we mean something more specific, which we will see below. But this assumption of smallness is crucial for perturbation theory to work.]

and we want to find approximate sol'ns to

$$\hat{H} \underset{\uparrow}{\varphi_n} = \underset{\uparrow}{E_n} \varphi_n$$

we want approximations to these.

The first thing to notice is that if $\hat{H}'$ is small compared to $\hat{H}_0$, then φ_n and E_n are probably not very different from $\varphi_n^{(0)}$ and $E_n^{(0)}$, which means we can expand about the unperturbed values, i.e. we expect (9.3)

$$\varphi_n = \varphi_n^{(0)} + \Delta\varphi_n \qquad \text{with } \Delta\varphi_n, \Delta E_n \text{ small.}$$
$$E_n = E_n^{(0)} + \Delta E_n$$

So for bookkeeping purposes, let's write $\hat{H}'$ as $\lambda \hat{H}'$ where λ is a small parameter. The sole purpose of introducing λ is to keep track of the "smallness" of various terms; Powers of λ will correspond to orders of corrections.

(Note $\lambda \to 0$ gives the unperturbed problem and $\lambda \to 1$ is the exact problem we're trying to solve.)

Then we expand $\varphi_n + E_n$ about $\varphi_n^{(0)} + E_n^{(0)}$ in powers of λ:

$$\varphi_n = \varphi_n^{(0)} + \lambda\varphi_n^{(1)} + \lambda^2\varphi_n^{(2)} + \cdots$$
$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

and we want to solve for the $\varphi_n^{(i)}$ and $E_n^{(i)}$.

Now substitute into $(\hat{H}_0 + \lambda\hat{H}')\varphi_n = E\varphi_n$ and collect orders of λ:

$$(\hat{H}_0 + \lambda \hat{H}')\left[\varphi_n^{(0)} + \lambda \varphi_n^{(1)} + \lambda^2 \varphi_n^{(2)} + \cdots\right]$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}\right)\left[\varphi_n^{(0)} + \lambda \varphi_n^{(1)} + \lambda^2 \varphi_n^{(2)} + \cdots\right]$$

and keeping terms up to order λ^2 we get

$$\left[\hat{H}_0 \varphi_n^{(0)} - E_n^{(0)} \varphi_n^{(0)}\right]$$

$$+ \lambda\left[\hat{H}' \varphi_n^{(0)} + \underbrace{\hat{H}_0 \varphi_n^{(1)} - E_n^{(0)} \varphi_n^{(1)}}_{\text{not necessarily } = 0!} - E_n^{(1)} \varphi_n^{(0)}\right]$$

$$+ \lambda^2\left[\hat{H}_0 \varphi_n^{(2)} + \hat{H}' \varphi_n^{(1)} - E_n^{(0)} \varphi_n^{(2)} - E_n^{(1)} \varphi_n^{(1)} - E_n^{(2)} \varphi_n^{(0)}\right]$$

$$+ \cdots$$

$$= 0$$

Now λ is arbitrary, and in particular suppose λ is very small (say 10^{-15}). For the preceding eq'n to be true, each term in square brackets must separately be equal to zero.

So we get a bunch of separate eq'ns, one for each power of λ. Notice that the power of λ corresponds to the highest order of φ and E in the eq'n. That means if we solve the eq'ns sequentially we get the sol'ns for succeeding orders, until our patience runs out.

λ^0: 0th order sol'n

$$\hat{H}_0 \varphi_n^{(0)} = E_n^{(0)} \varphi_n^{(0)}$$

We knew that; $\varphi_n^{(0)}$ + $E_n^{(0)}$ are the unperturbed solution. This serves as a consistency check

λ^1: 1st order sol'n

$$\hat{H}' \varphi_n^{(0)} + \underbrace{\hat{H}_0 \varphi_n^{(1)} - E_n^{(0)} \varphi_n^{(1)}} - E_n^{(1)} \varphi_n^{(0)} = 0 \qquad (**)$$

At first sight these terms look like they might cancel. But no, the wave function in there is $\varphi_n^{(1)}$, not $\varphi_n^{(0)}$, so we can't say. But if $\varphi_n^{(1)}$ has a piece that's proportional to $\varphi_n^{(0)}$, then that piece cancels in those two terms. Another way of making this point is to note that for any sol'n $\varphi_n^{(1)}$ to this eq'n,

$$\varphi_n^{(1)} + a\,\varphi_n^{(0)}$$

is also a solution for any a. We don't want or need to muck up the works by including $\varphi_n^{(0)}$ in the higher order sol'ns; the unperturbed sol'n is already taken care of in the zero order term. So to get rid of this problem, let's just <u>require</u> that the higher order →

sol'ns don't contain $\varphi_n^{(0)}$, by which we mean they're orthogonal:

require $\quad \langle \varphi_n^{(i)} | \varphi_n^{(0)} \rangle = 0 \quad$ for all $i > 0$ and all n

Okay, we still have to solve the 1st order eq'n. Note the $\hat{H}_0 \varphi_n^{(1)}$ term. We don't know what $\hat{H}_0$ does to $\varphi_n^{(1)}$ directly, but we do know what $\hat{H}_0$ does to the $\varphi_n^{(0)}$ and that they form a complete set, so we can expand $\varphi_n^{(1)}$ in terms of the $\varphi_n^{(0)}$: *

$$|\varphi_n^{(1)}\rangle = \sum_j c_{nj} |\varphi_j^{(0)}\rangle$$

Then we substitute this expansion into the 1st order eq'n (**) on p. 9.5 and we get

$$\left(\hat{H}_0 - E_n^{(0)}\right) \sum_j c_{nj} |\varphi_j^{(0)}\rangle = \left(E_n^{(1)} - \hat{H}'\right) |\varphi_n^{(0)}\rangle$$

and now our task is to solve for the c_{nj}. We do it by multiplying on the left w/ $\langle \varphi_\ell^{(0)}|$

$$\Rightarrow \quad \sum_j c_{nj}\Big[\underbrace{\langle \varphi_\ell^{(0)} | \hat{H}_0 | \varphi_j^{(0)}\rangle}_{E_\ell^0 \delta_{j\ell}} - E_n^{(0)} \underbrace{\langle \varphi_\ell^{(0)} | \varphi_j^{(0)}\rangle}_{\delta_{j\ell}} = E_n^{(1)} \overbrace{\langle \varphi_j^{(0)} | \varphi_n^{(0)}\rangle}^{\delta_{jn}}$$
$$- \underbrace{\langle \varphi_\ell^{0} | \hat{H}' | \varphi_n^{0}\rangle}_{H'_{\ell n}}$$

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* We are assuming that $\varphi_n^{(1)}$ (and the other $\varphi_n^{(i)}$) lie in a Hilbert space spanned by the $\varphi_n^{(0)}$. This is usually – but not always – the case.

which gives us

$$\left[E_l^{(0)} - E_n^{(0)}\right] c_{nl} + H'_{ln} = E_n^{(1)} \delta_{ln} \qquad (***)$$

with $\quad H'_{ln} = \langle \psi_l^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$

= the ln matrix element of the perturbation Hamiltonian in the unperturbed basis.

Now we need to solve (***) for c_{nl} and $E_n^{(1)}$. For $l \neq n$, $E_n^{(1)}$ drops out and we get

$$c_{nl} = \frac{H'_{ln}}{E_n^{(0)} - E_l^{(0)}} \qquad n \neq l$$

and since we require $\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 0$, then $c_{nn} = 0$.

So plugging in to the expansion for $\psi_n^{(1)}$, we have

$$\psi_n^{(1)} = \sum_{j \neq n} \frac{H'_{jn}}{E_n^{(0)} - E_j^{(0)}} \psi_j^{(0)}$$

Now to find $E_n^{(1)}$, go back to (***) and take $l = n$;

$$E_n^{(1)} = H'_{nn}$$

Kind of a pretty result: the 1st correction to the energy is the corresponding diagonal matrix element of the perturbation Hamiltonian

So we've got our approximate sol'n to 1st order (we set $\lambda = 1$ in the expansions for φ_n and E_n):

$$\boxed{\begin{aligned} \varphi_n &= \varphi_n^0 + \sum_{j \neq n} \frac{H'_{jn}}{E_n^{(0)} - E_j^{(0)}} \varphi_j^{(0)} \\ E_n &= E_n^{(0)} + H'_{nn} \end{aligned}}$$

1st order

and now we see what it means for H' to be small. The expansion coeff's in φ_n must be small which means the H' matrix elements must be small compared to the corresp. unperturbed energy levels:

$$|H'_{jn}| \ll |E_n^{(0)} - E_j^{(0)}|$$

and from E_n, the diagonal elements of H' must be small compared to the unperturbed energies:

$$|H'_{nn}| \ll E_n^{(0)}$$

Now let's move on to the 2nd order solution. To find it, we need to look at the λ^2 terms on p. 9.4; we must have the term multiplying λ^2 be equal to zero, so putting all the $\varphi_n^{(2)}$ terms on the LHS we have

$$(\hat{H}_0 - E_n^{(0)})\varphi_n^{(2)} = (E_n^{(1)} - \hat{H}')\varphi_n^{(1)} + E_n^{(2)}\varphi_n^{(0)}$$

we know these now

As we did above, let's expand $\varphi_n^{(2)}$ in the $\hat{H}_0$ eigenstates:

$$\varphi_n^{(2)} = \sum_i d_{ni}\, \varphi_i^{(0)}$$

(We won't substitute for $E_n^{(1)}$ + $\varphi_n^{(1)}$ just yet.)

we get

$$(\hat{H}_0 - E_n^{(0)}) \sum_i d_{ni}\, \varphi_i^{(0)} = (E_n^{(1)} - \hat{H}')\varphi_n^{(1)} + E_n^{(2)}\varphi_n^{(0)}$$

or $$\sum_i (E_i^{(0)} - E_n^{(0)})\, d_{ni} |\varphi_i^{(0)}\rangle = E_n^{(1)}|\varphi_n^{(1)}\rangle - \hat{H}'|\varphi_n^{(1)}\rangle + E_n^{(2)}|\varphi_n^{(0)}\rangle$$

Taking the inner product with $\langle\varphi_j^{(0)}|$ we get

$$(E_j^{(0)} - E_n^{(0)})\, d_{nj} = E_n^{(1)}\langle\varphi_j^{(0)}|\varphi_n^{(1)}\rangle - \underbrace{\langle\varphi_j^{(0)}|\hat{H}'|\varphi_n^{(1)}\rangle}_{H_{jn}} + E_n^{(2)}\delta_{nj}$$

(*)

We can find $E_n^{(2)}$ by noting that the LHS cancels when $n=j$, so setting $n=j$ we have

$$E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(1)} \rangle - E_n^{(1)} \cancelto{0}{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}$$

and substituting (see p. 9.7) $\psi_n^{(1)} = \sum_{i \neq n} \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} \psi_i^{(0)}$

$$= \sum_{i \neq n} \frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} \underbrace{\langle \psi_n^{(0)} | \hat{H}' | \psi_i^{(0)} \rangle}_{H'_{ni}}$$

and noting that H' must be hermitian so that

$$H'_{in} = (H'_{ni})^*,$$

$$= \sum_{i \neq n} \frac{|H'_{ni}|^2}{E_n^{(0)} - E_i^{(0)}}$$ (+ notice it has dimensions of energy)

Now going back to eq'n (*) at the bottom of p. 9.9, we don't need to substitute this expression for $E_n^{(2)}$ to find the d_{nj}. We'll take $n \neq j$ because recall that $\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 0$ for all i (p. 9.5 - 9.6) so $d_{nn} = 0$.

We'll substitute for $E_n^{(1)}$ & $|\psi_n^{(1)}\rangle$ in terms of the zero-order quantities.

So the eq'n becomes

$$\left(E_j^{(0)} - E_n^{(0)}\right) d_{nj} = \overbrace{H'_{nn}}^{E_n^{(1)}} \sum_{k \neq n} \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} \overbrace{\langle \varphi_j^{(0)} | \varphi_k^{(0)} \rangle}^{\delta_{jk}}$$

$$- \sum_{k \neq n} \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} \underbrace{\langle \varphi_j^{(0)} | H' | \varphi_k^{(0)} \rangle}_{H'_{jk}}$$

+ dividing by $(E_n^{(0)} - E_j^{(0)})$ (watch sign!)

$$d_{nj} = \frac{1}{E_n^{(0)} - E_j^{(0)}} \sum_{k \neq n} \frac{H'_{jk} H'_{kn}}{E_n^{(0)} - E_k^{(0)}}$$

$$- \frac{H'_{nn} H'_{jn}}{\left(E_n^{(0)} - E_j^{(0)}\right)^2}$$

So combining all orders through 2nd, we have

$$\boxed{\begin{aligned} E_n &= E_n^{(0)} + H'_{nn} + \sum_{i \neq n} \frac{|H'_{ni}|^2}{E_n^{(0)} - E_i^{(0)}} \\ \varphi_n &= \varphi_n^{(0)} + \sum_{i \neq n} \left[\frac{H'_{in}}{E_n^{(0)} - E_i^{(0)}} - \frac{H'_{nn} H'_{in}}{\left(E_n^{(0)} - E_i^{(0)}\right)^2} + \sum_{k \neq n} \frac{H'_{ik} H'_{kn}}{\left(E_n^{(0)} - E_i^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} \right] \varphi_i^{(0)} \end{aligned}}$$

through 2nd order

As you can see, things get pretty complicated (9.12)
pretty quickly, and it gets worse with each higher order. (The same problems plagues perturbative expansions in particle physics.)

So we'll stop here, and do an example.

EX

Find the ground state energy for the 1-D potential energy

$$V_1 = \begin{cases} gx & 0 \le x \le a \\ \infty & x < 0,\ x > a \end{cases}$$

This looks like a particle in a box plus a perturbing Hamiltonian $H' = gx$. The unperturbed H_0 is

$$H_0 = \frac{p^2}{2m} + V \quad , \quad V = \begin{cases} 0 & 0 \le x \le a \\ \infty & x < 0,\ x > a \end{cases}$$

and the unperturbed eigenstates and energies are

$$\varphi_n^{(0)} = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad , \quad E_n^{(0)} = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \qquad n = 1, 2, 3 \ldots$$

(9.13)

The $1^{\underline{st}}$ order correction to each of the energies is

$$E_n^{(1)} = H'_{nn} = \int_0^\infty \psi_n^{(0)*}\, gx\, \psi_n^{(0)}\, dx$$

$$= g\frac{2}{a}\underbrace{\int_0^a x\sin^2\frac{n\pi x}{a}\,dx}_{\frac{a^2}{4}}$$

$$= \frac{ga}{2}$$

same for all energy levels (and note that it has units of energy). For perturbation theory to be applicable, we must have

$$H'_{nn} \ll |E_n^{(0)} - E_j^{(0)}|$$

and since $E_1^{(0)}$ is the lowest energy, this translates to

$$\frac{ga}{2} \ll \frac{\pi^2\hbar^2}{2ma^2} \quad \text{or} \quad g \ll \frac{\pi^2\hbar^2}{ma^3} = \frac{E_1^{(0)}}{a/2}$$

Now for the $2^{\underline{nd}}$ order correction, we have

$$E_1^{(2)} = \sum_{i\neq 1}\frac{|H'_{1i}|^2}{E_1^{(0)} - E_i^{(0)}}$$

so we need the matrix elements H'_{1i}

9.14

$$H'_{1i} = \frac{2g}{a}\int_0^a x \sin\frac{\pi x}{a} \sin\frac{i\pi x}{a}\, dx$$

$$= \begin{cases} 0 & \text{if } i \text{ is odd} \\ -\dfrac{8ga}{\pi^2}\dfrac{m}{(m^2-1)^2} & \text{if } m \text{ is even} \end{cases}$$

Now we also need $E_1^{(0)} - E_i^{(0)} = \dfrac{\pi^2 \hbar^2}{2ma^2}(1-i^2)$

So combining,

$$E_1^{(2)} = \sum_{\text{even } i>0} \frac{\left[\dfrac{8ga}{\pi^2}\dfrac{i}{(i^2-1)^2}\right]^2}{\underbrace{\left(\dfrac{\pi^2\hbar^2}{2ma^2}\right)}_{E_1^{(0)}}(1-i^2)}$$

$$= -\left(\frac{8ga}{\pi^2 E_1^{(0)}}\right)\sum_{\text{even } i>0}\frac{i^2}{(i^2-1)^5}$$

This is an infinite series, but it converges pretty quickly: to 5 sig. digits the sum is 0.016483 and the $i=2$ and $i=4$ terms give 0.016482

Combining everything, we get for the ground state energy

→

9.15

$$E_1 = E_1^{(0)}\left[1 + \frac{ga}{2E_1^{(0)}} - 0.01083\left(\frac{ga}{E_1^{(0)}}\right)^2\right]$$

to 2nd order

Notice that the expansion contains successively higher powers of the small parameter g.