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Daily 12.M Monday 11/17 Griffiths **6.1** Time-independent Perturbations, non-degenerate

These next few days, we'll be looking at ways to get approximate solutions to problems that are too difficult to exactly solve.

2. Time-Independent Perturbation Theory

The idea of perturbation theory is that, if you change the Hamiltonian only a little bit, you'd expect the wavefunctions and their energies to change only a little bit too. Now, we're used to using a Taylor series to expand out a complicated function around some given point, and only using as many terms as we need for the level of accuracy desired. So in the same way, we can imagine that the new wavefunctions and energies should be expressible in terms of a series of subsequently less significant corrections.

2.1 Non-degenerate Perturbation Theory

6.1.1 General Formulation

Imagine you had a system, to be concrete, say a particle in a box, and initially the box floor was perfectly smooth. So you have your simple Hamiltonian ,

$$\hat{H}^o,$$

and your simple wavefunctions that go with it,

$$\psi_n^o,$$

Which have their easily found energies,

E_n^o

Then you go and mess it all up by pushing up a dent in the middle of the well's floor.

Now, the *new* Hamiltonian will be the old one plus a new term for the addition of the dent,

$$\hat{H} = \hat{H}^o + \hat{H}'$$

1. *Conceptual*: What is the point of λ in equation 6.8?

Conceptually, these next few steps are easy to understand if you think of this dynamically; as you push up, the Hamiltonian slowly changes, it'll end up as $\hat{H} = \hat{H}^o + \hat{H}'$, but along the way it's

$$\hat{H} = \hat{H}^o + \lambda(t)\hat{H}'$$

Where $\lambda(t)$ starts out as 0 (so you've not yet started pushing) and ends up as 1 (when you've finished making the dent.)

How does the new wavefunction depend on this 'turning on'? Who knows, but in principle, it *does* depend on it, and we can write out its dependence as a power series:

$$\psi_n = \psi_n^o + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + \ldots$$

Where the ψ's are the corrections (if it make you feel more comfortable, $\psi_n^{(j)} = \frac{1}{j!}\frac{\partial^j \psi_n}{\partial \lambda^j}$, but we won't really be using that fact.)

"Some of the notation, mainly the superscripts and subscripts, went over my head a bit. Their presence made the section hard to follow and differentiate the useful information from the rest." Bradley W

Similarly, the new energy must depend upon how 'turned on' the perturbation is; how, who knows? But presumably that too can be expressed as a power series:

$$E_n = E_n^o + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \ldots$$

Again, if it makes you feel more comfortable, you can imagine we've got a Taylor series here and $E_n^{(j)} = \frac{1}{j!}\frac{\partial^j E_n}{\partial \lambda^j}$, but we won't use that fact.

The fact we will use is this the old familiar:

$$\hat{H}\psi_n = E_n\psi_n$$

But if we rephrase this in terms of our perturbation factor, λ, and all the correction terms,

$$\left(\hat{H}^o + \lambda\hat{H}'\right)\left(\psi_n^o + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + ...\right) = \left(E_n^o + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + ..\right)\left(\psi_n^o + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \lambda^3\psi_n^{(3)} + ..\right.$$

Multiplying this out, we get

$$\left(\hat{H}^o\psi_n^o + \lambda\hat{H}^o\psi_n^{(1)} + \lambda^2\hat{H}^o\psi_n^{(2)} + \lambda\hat{H}'\psi_n^o + \lambda^2\hat{H}'\psi_n^{(1)} + \lambda^3\hat{H}'\psi_n^{(2)} + ...\right) =$$
$$\left(E_n^o\psi_n^o + \lambda E_n^o\psi_n^{(1)} + \lambda^2 E_n^o\psi_n^{(2)} + \lambda E_n^{(1)}\psi_n^o + \lambda^2 E_n^{(1)}\psi_n^{(1)} + \lambda^3 E_n^{(1)}\psi_n^{(2)} + \lambda^2 E_n^{(2)}\psi_n^o + \lambda^3 E_n^{(2)}\psi_n^{(1)} + \lambda^4 E_n^{(2)}\psi_n^{(2)} ...\right)$$

Collecting terms by powers in λ,

$$\left(\hat{H}^o\psi_n^o - E_n^o\psi_n^o\right) + \lambda\left(\left(\hat{H}^o\psi_n^{(1)} + \hat{H}'\psi_n^o\right) - \left(E_n^o\psi_n^{(1)} + E_n^{(1)}\psi_n^o\right)\right) + \lambda^2\left(\left(\hat{H}^o\psi_n^{(2)} + \hat{H}'\psi_n^{(1)}\right) - \left(E_n^o\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^o\right)\right) + ... = 0$$

Now, this is a polynomial in λ and it must sum up to 0 regardless of the value of λ. So, what must be true of each individual coefficient of λ? Each must be individually equal to 0.

$$\hat{H}^o\psi_n^o = E_n^o\psi_n^o$$
$$\hat{H}^o\psi_n^{(1)} + \hat{H}'\psi_n^o = E_n^o\psi_n^{(1)} + E_n^{(1)}\psi_n^o$$
$$\hat{H}^o\psi_n^{(2)} + \hat{H}'\psi_n^{(1)} = E_n^o\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^o$$
...

6.1.2 First-Order Theory

So, the 0th-order equation is the one we already knew:

$$\hat{H}^o\psi_n^o = E_n^o\psi_n^o$$

if there *were no* perturbation, we'd have the original Hamiltonian which is solved by the original wavefunctions with their original energies.

The 1st-order equation though,

$$\hat{H}^o\psi_n^{(1)} + \hat{H}'\psi_n^o = E_n^o\psi_n^{(1)} + E_n^{(1)}\psi_n^o$$

is news. Let's see what we can get from it.

1st-order Energy $E_n^{(1)}$ Correction.

If we inner-product it with the known ψ_n^o, we have

$$\left\langle\psi_n^o\middle|\hat{H}^o\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\middle|\hat{H}'\psi_n^o\right\rangle = \left\langle\psi_n^o\middle|E_n^o\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\middle|E_n^{(1)}\psi_n^o\right\rangle$$

Of course, the energies are just numbers, so we have

$$\left\langle\psi_n^o\middle|\hat{H}^o\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\middle|\hat{H}'\psi_n^o\right\rangle = E_n^o\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle + E_n^{(1)}\left\langle\psi_n^o\middle|\psi_n^o\right\rangle$$

But $\left\langle\psi_n^o\middle|\psi_n^o\right\rangle = 1$, and the original Hamiltonian is most assuredly Hermitian, so we have

$$\left\langle\hat{H}^o\psi_n^o\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\middle|\hat{H}'\psi_n^o\right\rangle = E_n^o\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle + E_n^{(1)}$$

And we know that the original Hamiltonian operating on the original energy eigenstate returns E_n^o, so

$$E_n^o\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle+\left\langle\psi_n^o\middle|\hat{H}'\psi_n^o\right\rangle=E_n^o\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle+E_n^{(1)}$$

Now we can cancel the first term from left and right to be left with

$$\boxed{\left\langle\psi_n^o\middle|\hat{H}'\psi_n^o\right\rangle=E_n^{(1)}}$$

Viola! We now know the first-order correction to the energy.

Why Perturbation theory?

Now you may well say 'but wait, is this result of any *use?* After all, we posited that

$$E_n=E_n^o+\lambda E_n^{(1)}+\lambda^2E_n^{(2)}+\lambda^3E_n^{(3)}+\ldots$$

And we're *really* interested in the case when the perturbation is completely turned on, so λ =1, and that means all correction terms are equally important!

That could indeed be the case; and in that case, perturbation theory wouldn't be the way to tackle the problem. Then again, if it's not just that λ was once-upon-a-time small (when we first started 'turning on' the perturbation to the Hamiltonian), but it's that the *perturbation* is itself small, then we can hope that the 1st-order term will be bigger than the 2nd-order which will be bigger than…

Then a Perturbation approach is useful.

Exercise: This works just as well whether we're talking about a Hamiltonian operator expressed in differentials and wavefunctions as *functions* or the Hamiltonian as matrix and the wavefunctions as *vectors.*

$$\hat{H}=\hat{H}^o+\hat{H}'=\begin{pmatrix}V_o&0&0\\0&-2V_o&0\\0&0&3V_o\end{pmatrix}+\begin{pmatrix}-\varepsilon&\varepsilon&0\\\varepsilon&-\varepsilon&0\\0&0&0\end{pmatrix}$$

First off, what are the original Hamiltonian's eigenvectors?

$$\left|\psi_1^o\right\rangle=\begin{pmatrix}1\\0\\0\end{pmatrix}\quad\left|\psi_2^o\right\rangle=\begin{pmatrix}0\\1\\0\end{pmatrix}\text{ and }\quad\left|\psi_3^o\right\rangle=\begin{pmatrix}0\\0\\1\end{pmatrix}$$

Then what's the 1st-order correction to the energy for each?

$$E_1^{(1)}=\left\langle\psi_1^{(o)}\middle|\hat{H}'\middle|\psi_1^{(o)}\right\rangle=\begin{pmatrix}1&0&0\end{pmatrix}\begin{pmatrix}-\varepsilon&\varepsilon&0\\\varepsilon&-\varepsilon&0\\0&0&0\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix}=-\varepsilon$$

So the energy of the first state is, to 1st-order correction,

$$E_n\approx E_n^{(o)}+E_n^{(1)}=V_o-\varepsilon$$

"Could we go over the second part of example 6.1" Antwain The following exercise is *like* the second part of example 6.1, but with a little more meat.

Exercise: A little more complicated, Let's go back to that infinite square well and tackle the same scenario we'd considered last time with the WKB: an electron in a 1-D solid with a voltage applied, i.e., a sloped bottom.

$$\hat{H}'(x) = -e\Delta V \tfrac{x}{a}$$

$$E_n^{(1)} = \left\langle \psi_n^{(o)} \middle| \hat{H}' \middle| \psi_n^{(o)} \right\rangle = \int_0^a \left(\sqrt{\tfrac{2}{a}} \sin\left(\tfrac{n\pi}{a} x\right)\right)\left(-e\Delta V \tfrac{x}{a}\right)\left(\sqrt{\tfrac{2}{a}} \sin\left(\tfrac{n\pi}{a} x\right)\right)dx = -e\Delta V \tfrac{2}{a^2} \int_0^a x \sin^2\left(\tfrac{n\pi}{a} x\right)dx$$

$$= -e\Delta V \tfrac{2}{a^2} \int_0^a x \tfrac{1}{2}\left(1 - \sin\left(\tfrac{n2\pi}{a} x\right)\right)dx = -e\Delta V \tfrac{1}{a^2}\left(\int_0^a x dx - \int_0^a x \sin\left(\tfrac{n2\pi}{a} x\right)dx\right)$$

$$= -e\Delta V \tfrac{1}{a^2}\left(\tfrac{1}{2}a^2 - \left(\left(\tfrac{a}{n2\pi}\right)^2 \sin\left(\tfrac{n2\pi}{a} x\right) - \tfrac{ax}{n2\pi} \cos\left(\tfrac{n2\pi}{a} x\right)\right)\Big|_0^a\right) = -e\Delta V \tfrac{1}{a^2}\left(\tfrac{1}{2}a^2 + \tfrac{a^2}{n2\pi}\right)$$

$$E_n^{(1)} = -\frac{e\Delta V}{2}\left(1 + \tfrac{1}{n\pi}\right)$$

So, the energy for each state, to first order correction, is

$$E_n \approx E_n^{(o)} + E_n^{(1)} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 - \frac{e\Delta V}{2}\left(1 + \tfrac{1}{n\pi}\right)$$

3. *Starting Weekly HW*: Griffiths 6.1 for part a) you do this, but with a delta-potential in the middle of the well.

1st-order Wavefunction $\psi_n^{(1)}$

Alright, so we've gotten a little practice finding the first-order correction to the energy. What about the wavefunction, how is that messed up because of a perturbation?

"I'm confused why griffiths uses equation 6.11 in the derivation?" Jessica

I'd also like to know how Griffiths uses 6.11 for the rest of the derivation. Spencer

Ditto Jonathan

Mmm...same. I follow the notation and such, but I'm still confused. Gigja

Now, the trick is that our *old* solutions formed a complete basis set for this space, so the correction should be expressible in terms of that basis set. However, one caveat – since this is supposed to be a correction term in $\psi_n = \psi_n^o + \psi_n^{(1)} + \psi_n^{(2)} + \psi_n^{(3)} + \ldots$, that's a correction *on top of* the 0th order term, ψ_n^o, our sum will step over this member of the basis set.

$$\psi_n^{(1)} = \sum_{m \neq n} c_{n,m} \psi_m^{(o)}$$

Of course, as usual, $\left\langle \psi_m^{(o)} \middle| \psi_n^{(1)} \right\rangle = c_{n,m}$

So, we'll use the 1st-order equation to get a relation for the 1st-order wavefunction which we can then inner-product to get the coefficients. It goes like this. The 1st-order equation is

$$\hat{H}^o\psi_n^{(1)} + \hat{H}'\psi_n^o = E_n^o\psi_n^{(1)} + E_n^{(1)}\psi_n^o$$

Rewriting with the things we know on the right-hand side

$$\left(\hat{H}^o - E_n^o\right)\psi_n^{(1)} = \left(E_n^{(1)} - \hat{H}'\right)\psi_n^o$$

Inner producting that with $\psi_m^{(o)}$,

$$\left\langle \psi_m^o \middle| \left(\hat{H}^o - E_n^o\right)\psi_n^{(1)} \right\rangle = \left\langle \psi_m^o \middle| \left(E_n^{(1)} - \hat{H}'\right)\psi_n^o \right\rangle$$

$$\left\langle \psi_m^o \middle| \hat{H}^o\psi_n^{(1)} \right\rangle - \left\langle \psi_m^o \middle| E_n^o\psi_n^{(1)} \right\rangle = \left\langle \psi_m^o \middle| E_n^{(1)}\psi_n^o \right\rangle - \left\langle \psi_m^o \middle| \hat{H}'\psi_n^o \right\rangle$$

$$\left\langle \hat{H}^o\psi_m^o \middle| \psi_n^{(1)} \right\rangle - E_n^o\left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle = E_n^{(1)}\left\langle \psi_m^o \middle| \psi_n^o \right\rangle - \left\langle \psi_m^o \middle| \hat{H}'\psi_n^o \right\rangle$$

$$E_m^o\left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle - E_n^o\left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle = E_n^{(1)}0 - \left\langle \psi_m^o \middle| \hat{H}'\psi_n^o \right\rangle$$

$$\left\langle \psi_m^o \middle| \psi_n^{(1)} \right\rangle = \frac{\left\langle \psi_m^o \middle| \hat{H}'\psi_n^o \right\rangle}{E_n^o - E_m^o}$$

And that is $\left\langle \psi_m^{(o)} \middle| \psi_n^{(1)} \right\rangle = c_{n,m}$

So

$$\psi_n^{(1)} = \sum_{m\neq n} \frac{\left\langle \psi_m^o \middle| \hat{H}'\psi_n^o \right\rangle}{E_n^o - E_m^o}\psi_m^{(o)}$$

note: not so useful if two original states have the same energy as the state you're interested in. Wednesday's reading is about handling *that* kind of situation.

1. *Conceptual*: Can we use equation 6.13 to determine wavefunctions for the Helium atom based on a perturbation to a Hydrogen atom? Why or why not?

"Im a bit confused about the second homework question, mainly with what exactly a "perturbation to a hydrogen atom" actually entails." Sean M

Well, as a first step, you'd want to make the simple change that Z=2, and we'd need to generalize the wavefunction to be a two-electron wavefunction. That's all easy enough (and was done in Chapter 4) but then the question is, can we treat the electron-electron interaction terms as a perturbation?
We could go after the ground state since, in the unperturbed case, this is not degenerate. However, after that, there would be degeneracies in the other states. For example, the n = 2, l =1 and the n = 2, l = 0 have the same energies in the un-perturbed potential, so you couldn't go after corrections for ether without the sum blowing up when the other one was added to the sum.

Another issue is that the "perturbation" of the electron-electron interaction isn't so small; if I remember, it's maybe $1/5^{th}$ of the electron-proton interaction, so 1^{st} order may not be enough to satisfactorily accommodate for adding in this "perturbation."

Let's give it spin.

Exercise: Returning to our matrix Hamiltonian, what's the first-order correction to the first eigenvector?

$$\hat{H} = \hat{H}^o + \hat{H}' = \begin{pmatrix} V_o & 0 & 0 \\ 0 & -2V_o & 0 \\ 0 & 0 & 3V_o \end{pmatrix} + \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

First off, we have

$$\left|\psi_1^o\right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \text{ with } E_1^{(o)} = V_o \quad \left|\psi_2^o\right\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \text{ with } E_1^{(o)} = -2V_o \text{ and } \quad \left|\psi_3^o\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \text{ with } E_1^{(o)} = 3V_o$$

So the two inner products are

$$\left\langle \psi_2^{(o)} \middle| \hat{H}' \middle| \psi_1^{(o)} \right\rangle = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -\varepsilon \\ \varepsilon \\ 0 \end{pmatrix} = \varepsilon$$

$$\left\langle \psi_3^{(o)} \middle| \hat{H}' \middle| \psi_1^{(o)} \right\rangle = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -\varepsilon & \varepsilon & 0 \\ \varepsilon & -\varepsilon & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -\varepsilon \\ \varepsilon \\ 0 \end{pmatrix} = 0$$

So, the sum is

$$\psi_1^{(1)} = \sum_{m \neq 1} \frac{\left\langle \psi_m^o \middle| \hat{H}' \psi_1^o \right\rangle}{E_1^o - E_m^o} \psi_m^{(o)} = \frac{\left\langle \psi_2^o \middle| \hat{H}' \psi_1^o \right\rangle}{E_1^o - E_2^o} \psi_2^{(o)} + \frac{\left\langle \psi_3^o \middle| \hat{H}' \psi_1^o \right\rangle}{E_1^o - E_3^o} \psi_2^{(o)} = \frac{\varepsilon}{V_o - (-2V_o)} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \frac{0}{V_o - 3V_o} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{\varepsilon}{3V_o} \\ 0 \end{pmatrix}$$

Then, to first order,

$$\left|\psi_1\right\rangle \approx \left|\psi_1^o\right\rangle + \left|\psi_1^{(1)}\right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ \frac{\varepsilon}{3V_o} \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ \frac{\varepsilon}{3V_o} \\ 0 \end{pmatrix}$$

Exercise: Or, for the more complicated, differential-Hamiltonian case, with the sloped bottom in a square well,

$$\hat{H}'(x) = -e\Delta V\,\tfrac{x}{a}, \qquad \left|\psi_n^o\right\rangle = \sqrt{\tfrac{2}{a}}\sin\left(\tfrac{n\pi}{a}x\right), \text{ and } \qquad E_n^{(o)} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2$$

So, $\left\langle\psi_m^{(o)}\left|\hat{H}'\right|\psi_n^{(o)}\right\rangle = \int_0^a \left(\sqrt{\tfrac{2}{a}}\sin\left(\tfrac{m\pi}{a}x\right)\right)\left(-e\Delta V\,\tfrac{x}{a}\right)\left(\sqrt{\tfrac{2}{a}}\sin\left(\tfrac{n\pi}{a}x\right)\right)dx = -e\Delta V\,\tfrac{2}{a^2}\int_0^a x\sin\left(\tfrac{m\pi}{a}x\right)\sin\left(\tfrac{n\pi}{a}x\right)dx$

Where $\sin\left(\tfrac{m\pi}{a}x\right)\sin\left(\tfrac{n\pi}{a}x\right) = \frac{1}{2}\left(\cos\left(\tfrac{(m-n)\pi}{a}x\right) - \cos\left(\tfrac{(m+n)\pi}{a}x\right)\right)$

$$\left\langle\psi_m^{(o)}\left|\hat{H}'\right|\psi_n^{(o)}\right\rangle = -e\Delta V\,\tfrac{1}{a^2}\left(\int_0^a x\cos\left(\tfrac{(m-n)\pi}{a}x\right)dx - \int_0^a x\cos\left(\tfrac{(m+n)\pi}{a}x\right)dx\right)$$

$$= -e\Delta V\,\tfrac{1}{a^2}\left(\left(\tfrac{a}{(m-n)\pi}\right)^2\cos\left(\tfrac{(m-n)\pi}{a}x\right) + \tfrac{ax}{(m-n)\pi}\sin\left(\tfrac{(m-n)\pi}{a}x\right) - \left(\tfrac{a}{(m+n)\pi}\right)^2\cos\left(\tfrac{(m+n)\pi}{a}x\right) - \tfrac{ax}{(m+n)\pi}\sin\left(\tfrac{(m+n)\pi}{a}x\right)\right)_0^a$$

$$= -e\Delta V\,\tfrac{1}{\pi^2}\left(\left(\tfrac{1}{(m-n)}\right)^2\left(\cos\left((m-n)\pi\right)-1\right) - \left(\tfrac{1}{(m+n)}\right)^2\left(\cos\left((m+n)\pi\right)-1\right)\right)$$

For even m±n, the cosines are 1 which kills the whole thing; for odd m±n, they're -1, so

$$\left\langle\psi_m^{(o)}\left|\hat{H}'\right|\psi_n^{(o)}\right\rangle = -e\Delta V\,\tfrac{1}{\pi^2}\left(\left(\tfrac{1}{(m-n)}\right)^2(-2) - \left(\tfrac{1}{(m+n)}\right)^2(-2)\right) = e\Delta V\,\tfrac{2}{\pi^2}\left(\left(\tfrac{1}{(m-n)}\right)^2 - \left(\tfrac{1}{(m+n)}\right)^2\right) = e\Delta V\,\tfrac{2}{\pi^2}\,\tfrac{(m+n)^2-(m-n)^2}{\left(m^2-n^2\right)}$$

$$\left\langle\psi_m^{(o)}\left|\hat{H}'\right|\psi_n^{(o)}\right\rangle = e\Delta V\,\tfrac{2}{\pi^2}\,\tfrac{m^2+n^2+2mn-m^2-n^2+2mn}{\left(m^2-n^2\right)} = e\Delta V\,\tfrac{8}{\pi^2}\,\tfrac{mn}{\left(m^2-n^2\right)}$$

for m±n odd;
0 for m±n even.

Then

$$\psi_n^{(1)} = \sum_{m\neq n}\frac{\left\langle\psi_m^o\left|\hat{H}'\psi_n^o\right\rangle}{E_n^o - E_m^o}\psi_m^{(o)} = \sqrt{\tfrac{2}{a}}\sum_{\substack{m\neq n\\ odd\,m+n}}\frac{e\Delta V\,\frac{8}{\pi^2}\frac{mn}{\left(m^2-n^2\right)}}{\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 - \frac{\hbar^2}{2m}\left(\frac{m\pi}{a}\right)^2}\sin\left(\tfrac{m\pi}{a}x\right) = \sqrt{\tfrac{2}{a}}\,\frac{16ma^2}{\hbar^2\pi^4}e\Delta V\sum_{\substack{m\neq n\\ odd\,m+n}}\frac{mn\sin\left(\frac{m\pi}{a}x\right)}{\left(m^2-n^2\right)^2}$$

Not pretty, but there it is.

1. *Starting Weekly HW*: Griffiths 6.1 for part b) you do this, but with a delta-potential in the middle of the well.

6.1.3 Second-Order Theory

Now, in practice, if using a power series expansion is a good idea at all, it's because the higher order terms are negligible, so you only need a few terms; i.e., in this context, if you're dealing with a mere perturbation (thus the name). So, we'll go after the 2nd-order expression for the energy, but leave off there.

Looking at the 2nd-order equation that we'd originally generated,

$$\hat{H}^o\psi_n^{(2)} + \hat{H}'\psi_n^{(1)} = E_n^o\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^o$$

2st-order Energy $E_n^{(2)}$ Correction.

Once we've got the 1'st order energy correction and the 1st-order wave correction, then we know most everything in this expression. Taking the inner product of this with ψ_n^o will isolate the energy correction:

$$\left\langle\psi_n^o\middle|\hat{H}^o\psi_n^{(2)}\right\rangle + \left\langle\psi_n^o\middle|\hat{H}'\psi_n^{(1)}\right\rangle = \left\langle\psi_n^o\middle|E_n^o\psi_n^{(2)}\right\rangle + \left\langle\psi_n^o\middle|E_n^{(1)}\psi_n^{(1)}\right\rangle + \left\langle\psi_n^o\middle|E_n^{(2)}\psi_n^o\right\rangle$$

$$\left\langle\hat{H}^o\psi_n^o\middle|\psi_n^{(2)}\right\rangle + \left\langle\psi_n^o\middle|\hat{H}'\psi_n^{(1)}\right\rangle = E_n^o\left\langle\psi_n^o\middle|\psi_n^{(2)}\right\rangle + E_n^{(1)}\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle + E_n^{(2)}$$

$$E_n^o\left\langle\psi_n^o\middle|\psi_n^{(2)}\right\rangle + \left\langle\psi_n^o\middle|\hat{H}'\psi_n^{(1)}\right\rangle = E_n^o\left\langle\psi_n^o\middle|\psi_n^{(2)}\right\rangle + E_n^{(1)}\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle + E_n^{(2)}$$

The left most terms on both sides are equal and so cancel

$$\left\langle\psi_n^o\middle|\hat{H}'\psi_n^{(1)}\right\rangle = E_n^{(1)}\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle + E_n^{(2)}$$

But we already decided that the one member of our complete basis set of original solutions that *doesn't* go into building the higher order corrections for ψ_n is $\psi_n^{(0)}$. Formally, we could express $\psi_n^{(1)} = \sum_{m\neq n} c_{n,m}\psi_m^{(o)}$. So $\left\langle\psi_n^o\middle|\psi_n^{(1)}\right\rangle = 0$.

$$\left\langle\psi_n^o\middle|\hat{H}'\psi_n^{(1)}\right\rangle = E_n^{(2)}$$

We can leave off there, since we've already found $\psi_n^{(1)} = \sum_{m\neq n}\frac{\left\langle\psi_m^o\middle|\hat{H}'\psi_n^o\right\rangle}{E_n^o - E_m^o}\psi_m^{(o)}$, then again, subbing that in, we get

$$\left\langle\psi_n^o\middle|\hat{H}'\sum_{m\neq n}\frac{\left\langle\psi_m^o\middle|\hat{H}'\psi_n^o\right\rangle}{E_n^o - E_m^o}\psi_m^{(o)}\right\rangle = E_n^{(2)}$$

$$\sum_{m\neq n}\frac{\left\langle\psi_m^o\middle|\hat{H}'\psi_n^o\right\rangle}{E_n^o - E_m^o}\left\langle\psi_n^o\middle|\hat{H}'\psi_m^{(o)}\right\rangle = E_n^{(2)}$$

$$\boxed{\sum_{m\neq n}\frac{\left|\left\langle\psi_m^o\middle|\hat{H}'\psi_n^o\right\rangle\right|^2}{E_n^o - E_m^o} = E_n^{(2)}}$$

1. *Starting Weekly HW*: Griffiths 6.4. 2nd-order energy corrections for the delta-spike potential and for the perturbed harmonic oscillator (changed *k*)
   Note: you are *not* expected to prove Griffiths' comment on part (a).
   For part b) Hint: You shouldn't have to actually *do* any integrals if you recall that $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}_+ + \hat{a}_-\right)$ and equations 2.66 tell you the result of the raising and lowering operators operating on a wavefunction. In fact, you should find that, in some old, chapter 2 homework you've already solved most of the key integrals.