Chem 549 Assignment 4

Using the Mathematica Symbolic Integrator
Go to:
http://www.wolframalpha.com/widgets/gallery/view.jsp?id=8ab70731b1553f17c11a3bbc87e0b605
Note that it is linked on the web site.
The first thing you see is this:

Let’s use the definite symbolic calculator to determine whether our particle-in-a-box wavefunctions are normalized or not. I know the ground state is:

\[ \Psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \]

and the normalization condition is:

\[ \int_{0}^{a} \Psi(x)^2 = \int_{0}^{a} \frac{2}{a} \sin^2\left(\frac{\pi x}{a}\right) = 1 \]

To check this with the symbolic integrator, I do the following:
Hit submit and:

The part on top (the Definite integral) is the only part you care about.

Obviously, we have correctly calculated that the wavefunction is properly normalized.

Now as another example, let’s calculate the example from the book concerning perturbation theory. The particle in the box Hamiltonian is:

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \]

Where \( V(x) = 0 \) if \( 0 < x < a \) and \( V(x) = \infty \) if \( x < 0 \) or \( x > a \). The perturbation from the book (the problem I call the “slanty shanty”) is to make \( V(x) = V \cdot \frac{x}{a} \) where \( V \) is a scalar (just a number). The first order correction is:

\[ \langle \Psi_0(x) | \left( \hat{H}^{\dagger} \right) | \Psi_0(x) \rangle \]  

which is actually: \[ \int_0^a \Psi_0^*(x)(\hat{H}^{\dagger})\Psi_0(x) \, dx \]

Inserting the integral and perturbation yields:

\[ \int_0^a \sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right) \left( V \frac{x}{a} \right) \sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right) \, dx = \int_0^a \frac{2}{a} \sin^2 \left( \frac{\pi x}{a} \right) \left( V \frac{x}{a} \right) \, dx \]

If I plug this into the symbolic integrator (sorry you can’t see the whole thing):

I get the following:
Let's try the excited state: 

$$\Psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$$

I will just skip to the answer:

Same answer just like in the book. Note that you can’t quite use: 

$$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

because the symbolic integrator doesn’t know that n is an integer.

Now for the perturbed wavefunctions, we just covered the fact that the first order correction to the ground state is:

$$|\Psi_0^1(x)\rangle = \sum_{j=1}^{\infty} \frac{\langle \Psi_j^0(x)|\hat{H}^1|\Psi_0^0(x)\rangle}{E_0^0 - E_j^0} |\Psi_j^0(x)\rangle$$

So let’s figure out how much the first excited state weighs into the new, perturbed ground state:
\[
\frac{\langle \Psi_1^0(x)|\left(\hat{H}^\dagger\right)\Psi_0^0(x)\rangle}{E_0^0 - E_j^0} = \frac{\int_0^a \sqrt{\frac{2}{a} \sin \left(\frac{2\pi x}{a}\right)} \left|V \frac{x}{a}\right| \sqrt{\frac{2}{a} \sin \left(\frac{\pi x}{a}\right)}}{\hbar^2 \frac{8m a^2}{8m a^2} - \frac{4h^2}{8m a^2}}.
\]

The top part is evaluated with the symbolic integrator:

\[
\int_0^a \frac{2 \left(\frac{V x}{a}\right) \sin \left(\frac{2\pi x}{a}\right) \sin \left(\frac{\pi x}{a}\right)}{a} dx = -\frac{16V}{9\pi^2}
\]

Making the whole thing:

\[
-\frac{16V}{9\pi^2} = \frac{128m a^2 V}{27h^2 \pi^2}.
\]

It’s interesting to note that as the perturbation gets stronger (V is bigger), then the first state couples into the ground state more. If V was 0, then the ground state is unperturbed.

Now the same for the 2\textsuperscript{nd} excited state:

\[
\frac{\langle \Psi_2^0(x)|\left(\hat{H}^\dagger\right)\Psi_0^0(x)\rangle}{E_0^0 - E_j^0} = \frac{\int_0^a \sqrt{\frac{2}{a} \sin \left(\frac{3\pi x}{a}\right)} \left|V \frac{x}{a}\right| \sqrt{\frac{2}{a} \sin \left(\frac{\pi x}{a}\right)}}{\hbar^2 \frac{8m a^2}{8m a^2} - \frac{9h^2}{8m a^2}}.
\]

Again with the symbolic integrator I get the following:
So it doesn’t contribute.
The 3rd excited state contributes as:
\[
\int_{0}^{a} \frac{2}{a} \sin \left( \frac{4\pi x}{a} \right) \sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right) \, dx
\]
\[
\int_{0}^{a} \frac{2}{a} \sin \left( \frac{\pi x}{a} \right) \sin \left( \frac{\pi x}{a} \right) \, dx
\]
\[
\int_{0}^{a} \frac{2}{a} \sin \left( \frac{\pi x}{a} \right) \sin \left( \frac{\pi x}{a} \right) \, dx = 0
\]

We have:
\[
\int_{0}^{a} \frac{2}{a} \sin \left( \frac{4\pi x}{a} \right) \sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right) \, dx = -\frac{32V}{225\pi^2} = -\frac{256ma^2V}{3375h^2\pi^2}
\]
\[
\frac{h^2}{8ma^2} - \frac{16h^2}{8ma^2} = \frac{256ma^2V}{3375h^2\pi^2}
\]
You can double check that the 4th excited state does not contribute. Let’s stop here and reassess.
The perturbed ground state is now:
\[
\Psi_0(x) = \frac{2}{a} \sin \left( \frac{\pi x}{a} \right) + \frac{128ma^2V}{27h^2\pi^2} \sqrt{\frac{2}{a}} \sin \left( \frac{2\pi x}{a} \right) + \frac{256ma^2V}{3375h^2\pi^2} \sqrt{\frac{2}{a}} \sin \left( \frac{4\pi x}{a} \right)
\]

Now to plot this with Matlab. Let’s make \( a = 1 \) nm = \( 1 \times 10^{-9} \) m, \( h = 6.62606957 \times 10^{-34} \) m\(^2\) kg/s, \( m = 9.11 \times 10^{-31} \) kg (an electron’s mass), and for the heck of it let’s make the potential go from 0 to 4 electron volts (1 eV = \( 1.60217657 \times 10^{-19} \) J. Plugging all of this into a Matlab script yields:

```matlab
a=1e-9;
h=6.62606957e-34;
m=9.11e-31;
for j=1:5
    V=(j-1)*1.602e-19;
    c1(j)=sqrt(2/a)*128*m*a*a*V/28/h/pi/pi;
    c2(j)=sqrt(2/a)*256*m*a*a*V/3375/h/pi/pi;
    for i=1:1001
        x=(i-1)*1e-12;
        psi(i,j)=sqrt(2/a)*sin(pi*x/a)+c1*sin(2*pi*x/a)+c2*sin(4*pi*x/a);
    end;
end;
```

Note the function of \( x \) is to go from 0 to 1 nm. When I plot all 5 wavefunctions I get the following:
You can see that the effect of the potential rising to the right is to push the wavefunction to the left.
1. Here is your problem. Let’s center the particle in a box as so:

What are the first five eigenstates of the Hamiltonian (i.e. ground → 4\textsuperscript{th} excited state) and their energies? 
Hint: Draw out what you know the states should look like and match them to some functional form. It isn’t as straightforward as when the box runs from 0 to a.

2. Now tell me what is the first order correction to the ground state energy if the following perturbation is added: \( \hat{H}^1 = V \sqrt{x/a} \)?

3. Now tell me what is the first order correction to the ground state energy if the following perturbation is added: \( \hat{H}^1 = V \frac{x}{a} \)? Also do the same for the 1\textsuperscript{st}, 2\textsuperscript{nd}, and 3\textsuperscript{rd} excited states.

4. Hopefully you see that the perturbation energy increased significantly going from the ground state to the 1\textsuperscript{st} excited state. Why do you think that is?

5. Now expand the ground state wavefunction into the first four excited states and plot the perturbed ground state wavefunction for \( V = 0, 1, 2, 3, 4 \text{ eV} \).