We have been studying the use of perturbation theory to calculate the ‘fine structure’ of the energy spectrum of Hydrogen. As an historical issue, calculating the Hydrogen atom electronic structure was consistently a target for application of quantum mechanics. As the experiments got better, the Hydrogen spectrum (and the spectra of other atoms and molecules) provided a consistent opportunity to test quantum mechanics and for quantum calculations to try to beat experiment to the punch with new predictions.

1. **Feynman-Hellmann Theorem.** (25 points)

Suppose we lived in a world where instead of the electron and proton always having a charge of magnitude $e$, that the fundamental charge magnitude might have small variations. True, for a particular hydrogen atom the electron and proton would have a reason to have equal and opposite charge, so the atom is charge neutral, but maybe one hydrogen atom might vary from the next, by having slightly different value of $e$.

Could you tell from any experiment that such a thing was true or not?

a) Start with the Coulomb potential of the hydrogen atom problem. Assume that there is a small change, $\delta e$, in the fundamental charge unit. Do a first order Taylor expansion of the potential energy in this small change. You have now predicted a small change in the hydrogen atom Hamiltonian. Do you think that this change might cause the energy levels to change too?

b) Use an argument similar to that used for first order non-degenerate perturbation theory to prove that the shift in the hydrogen energy level for the $n$th energy eigen state is, due to this small variation in the fundamental charge, is given by:

$$\frac{\partial E_n}{\partial e} \delta e = \langle \psi_{nlm}^0 | \frac{\partial H^0}{\partial e} \delta e | \psi_{nlm}^0 \rangle \tag{1}$$

In this result, the zeroth-order Hamiltonian is just the usual hydrogen Hamiltonian. As a fine point, you can assume that the zeroth-order state vectors have already been chosen as the ‘good’ state vector linear combinations so we can use non-degenerate perturbation theory without any problem.

c) Now adjust your outlook to imagine that the Hamiltonian might depend on a wide variety of parameters, not just the fundamental charge, say, but lots of different things. It’s not even necessary that the Hamiltonian describe the hydrogen atom. It could be any Hamiltonian for any system. Could you tell by experiments on the energy eigen values if the parameter changed? Generalize your approach in parts a) and b) to prove the Feynman-Hellmann theorem, which states that for a Hamiltonian that depends on any parameter, $\lambda$, that:

$$\frac{\partial E_n}{\partial \lambda} = \langle \psi_n^0 | \frac{\partial H^0}{\partial \lambda} | \psi_n^0 \rangle \tag{2}$$
d) Now, let’s go back to the calculation of the relativistic correction to the energy eigen values described in Griffiths in Section 6.3.1. The discussion takes a clever path through the first-order perturbation theory to come up with a first-order relativistic shift that looks like:

\[ E_{rel,n}^{(1)} = - \left( \frac{E_n^0}{mc^2} \right)^2 \left[ \frac{4n}{l+1/2} - 3 \right] \]  

(3)

To get this result, Griffiths needed to know two expectation values, which he simply stated as his equations 6.55 and 6.56. They are:

\[ \langle \frac{1}{r} \rangle = \langle \psi_{nlm}^0 | \frac{1}{r} | \psi_{nlm}^0 \rangle = \frac{1}{n^2 a} \]  

(4)

and similarly:

\[ \langle \frac{1}{r^2} \rangle = \frac{1}{(l+1/2)n^2 a^2} \]  

(5)

Aren’t you glad that he just quoted the results? Wouldn’t it be a bummer to have to actually CALCULATE these expectation values?? Don’t you have that creepy fear of pulling out the hydrogenic wave functions for the arbitrary zeroth-order state, tossing them into a 3-d polar integral with a 1/r or 1/r^2, and having to prove these results?? Bummer…

But wait! Go back to your results in parts a) and b). Rewrite your result for equation (1) to show how to calculate \( \langle 1/r \rangle \) by just taking a derivative of the zeroth-order energy with respect to the fundamental charge. Prove equation (4) without doing any 3-d polar integrals.

You have just learned that expectation values can often be determined via derivatives of energy eigen values. This idea is similar to how we determine thermodynamic quantities by derivatives of free energies, etc. It suggests new ways to think about what we’re doing in quantum mechanics, but that’s something to ponder on your own.

e) Equation (5) can be proved similarly, but it requires a bit more effort. Start with the radial wave equation for hydrogen, Griffiths Eq. 4.53:

\[ H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \left[ -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] \]  

(6)

Use the Feynman-Hellmann theorem with the angular momentum quantum number, \( l \), as a ‘small parameter’ and prove equation (5) above. To do this, you will pretty clearly need to take derivatives of the zeroth-order energy with respect
to angular momentum quantum number, but apparently, the energy does not depend upon \( l \), only on \( n \). Don’t be fooled: There is a hidden dependence between the two numbers as \( n = j_{\max} + l + 1 \), where the maximum \( j \) quantum number is a constant. In other words, if I tell you the maximum \( j \) for some state, and the angular momentum quantum number, then you can tell me which principal quantum number the state has.

2. **Uncertainty principle for the harmonic oscillator.** (10 pts.)

Let’s continue with the same theme of the Feynman-Hellmann dodge and try it on the one-dimensional harmonic oscillator.

a) Imagine how the harmonic oscillator Hamiltonian changes if you change the spring constant by a small amount. Use the Feynman-Hellmann theorem to determine the expectation value of the squared position, \( \langle x^2 \rangle_n \), for the \( n \)th harmonic oscillator state. You will need to recall the hidden dependence between frequency and spring constant.

b) Use the Feynman-Hellmann theorem with Planck’s constant as the changing parameter to get the expectation value of the squared momentum, \( \langle p^2 \rangle_n \), for the \( n \)th harmonic oscillator state. What do your results from parts a) and b) say about the Uncertainty Principle relationship for position and momentum in the \( n \)th harmonic oscillator state?

2. **The dc Stark effect.** (15 pts.)

If you put an atom into an electric field, the nucleus is pulled one direction and the electron clouds are pulled in the other direction. The distortion shows up as a change in the eigen energies of the atom. Let’s calculate what an applied electric field is expected to do to a hydrogen atom. We will assume that the electric field is a static dc applied field so we can use time-independent techniques. The full ac Stark effect with a time-varying field will come later in the course when we know time-dependent perturbation theory. In any case, the shift in the atomic energy levels with applied electric field is referred to as the Stark Effect.

The applied electric field causes a new term to appear in the Hamiltonian. Let’s consider a field applied in the \( z \)-direction, so that:

\[
H' = eE_0 z = eE_0 r \cos \theta
\]  

(7)

We will treat this term as a small perturbation to the original Hamiltonian and think about what happens to the \( n = 1 \) and \( n = 2 \) states of the hydrogen atom.
a) Show that the Stark shift of the ground state of hydrogen is zero to first order.

b) Next, think about the first excited state, where \( n = 2 \). This state is four-fold degenerate. No point in being clever here. Write down the spatial representations of the four eigen state wave functions for hydrogen. Set up the first-order degenerate perturbation theory and calculate which of the energy levels are shifted by the electric field to first order, how much are these levels shifted by, and what are the new ‘good’ eigen states?