Quantum Physics III (8.06) Spring 2005
Assignment 6

March 8, 2005 **Due March 15, 2005**

Readings

The reading assignment for this problem set is:

- Griffiths all of Chapter 6.
- Cohen-Tannoudji Chapter XI including Complements A-D. Also, Chapter XII. (I could really have put CT Ch. XII on the reading list already last week. It provides more detail (as always with CT!) on a number of classic examples of the application of perturbation theory in atomic physics.)

Problem Set 6

1. **The Feynman-Hellmann Theorem (8 points)**

   Do Griffiths problems 6.32. (That's 6.27 in Griffiths' 1st Ed.)

   [At the end of Problem 6.32, Griffiths asks you to "Compare your answers to Problem 2.12 and the virial theorem predictions." You can skip the comparison to Problem 2.12, but you must do the comparison to what the virial theorem predicts.]

   [Aside: Feynman figured out the Feynman-Hellmann theorem as part of his undergraduate senior thesis, done at MIT in the late 1930's. His senior thesis advisor was Slater, he of the determinant. Note that at MIT we do not *expect* that our undergraduates write senior theses which become part of the standard undergraduate physics curriculum a few decades later. Of course, we don't mind when it happens!

   So, who was Hellmann? I did not know the answer, and have put this question to several former 8.06 classes. Two years ago, a student found the answer for me on the following web page: http://www.tc.chemie.uni-siegen.de/hellmann/hellbioe.html (Thanks to Michael Mortonson for finding this.) Hans Hellmann was a German quantum chemist, born in 1903. He derived the theorem in 1933. Feynman derived it later, independently of Hellmann. Hellmann's wife was Jewish, and for this reason he was fired as an assistant professor in Hannover in late 1933. He fled to Russia, and in the next several years he wrote pioneering papers on quantum chemistry, and the first text book on the subject. Alas, in 1938 he was one of the millions "liquidated" during Stalin's "Great Terror". Now that I know the story, I am saddened that he is not now well-known, although since his career was cut so short this is perhaps not surprising. At the least, you and future 8.06 students will hear of him.]

2. **Energy Shift Due to Finite Nuclear Size (8 points)**

   When you studied the hydrogen atom last semester, you assumed that the Coulomb potential extended all the way to the origin. In reality, the proton's charge is smeared out over a sphere of roughly 10^{-13} cm in radius. This has a small effect on the energy levels of the hydrogen atom. Let's find out how small...

   Model the electric charge distribution of the proton as a uniformly charged sphere of radius R.

   (a) Find the electrostatic potential energy of the electron for all r.

   [Hint: Use Gauss's law $\vec{\nabla} \cdot \vec{E} = 4\pi\rho$ to find the electric field everywhere and then integrate $\vec{F} = -e\vec{E}$ to obtain the potential energy.]

[Answer: $V(r) = -e^2/r$ for $r > R$ and

$$V(r) = -e^2 \left[\frac{1}{2R^3} \left(R^2 - r^2 \right) + \frac{1}{R} \right]$$

for $r < R$.]

(b) Use lowest order perturbation theory to calculate the shift in the energy of the ground state of hydrogen due to this modification of the potential. Evaluate your answer numerically, taking $R = 10^{-13}$ cm, and express your answer as a fraction of the binding energy of the ground state (13.6 eV). [Hint: You can simplify the integrals by noticing that the unperturbed wave function varies only slowly over the range $0 < r < R$.]

(c) Why is this effect most important for states with orbital angular momentum zero? Without doing any calculation, make an estimate of the factor by which this effect is smaller for an $\ell = 1$ state as compared to an $\ell = 0$ state.

3. **Weak-Field Zeeman Effect (18 points)**

When an atom is placed in a uniform external magnetic field $\vec{B}$, the energy levels are shifted. This Zeeman effect is described by the Hamiltonian

$$H'_Z = \frac{e}{2m} \vec{B} \cdot \left(\vec{L} + 2\vec{S} \right) = \frac{e}{2m} \vec{B} \cdot \left(\vec{J} + \vec{S} \right) \tag{1}$$

In this problem, we shall assume that $\vec{B}$ is small enough that the fine structure effects on the energy levels (discussed in lecture and in Section 6.3 of Griffiths) are larger than the Zeeman effects.

Because we are assuming that the fine structure effects (including the spin-orbit coupling) are "big", we'd better use the $|n\ell j m_j\rangle$ basis. These also turn out to be the "good" states with which to analyze the Zeeman effect. We seek to evaluate the first-order Zeeman correction to the energy:

$$E^1_Z \equiv \langle n\ell j m_j | H'_Z | n\ell j m_j \rangle = \frac{e}{2m} \vec{B} \cdot \langle \vec{J} + \vec{S} \rangle \tag{2}$$

(a) Lets begin, though, with some numerical estimates, so that you understand the regime in which the calculation you are doing is valid. Use Griffiths equation 6.66 (which you will have seen in lecture also) to evaluate the fine structure corrections to all eight $n = 2$ levels of the hydrogen atom. Give the energies (and degeneracies) of these levels. (Energies in electron-Volts.)

(b) Now, let's make an order of magnitude estimate of the Zeeman effect. Pretend (only in this part of the problem) that the gyromagnetic ratio for the electron is $g = 1$ instead of $g = 2$. This should be good enough for

an order of magnitude estimate, but will of course not yield the correct dimensionless factors in the results. Write the Zeeman Hamiltonian in this case, and evaluate E_Z^1. Explain why this is much easier than the real ($g = 2$) calculation. Use this simple calculation to estimate the order of magnitude of the Zeeman shifts to the energy levels. Then, by comparison to the fine structure splitting between levels which you found in part (a), estimate for what values of $|\vec{B}|$ (in gauss or Tesla) the Zeeman corrections are smaller than the fine structure corrections.

[Your answer should tell you that while there are certainly experimental circumstances in which the weak-field approximation we are using here is valid, it is also possible to apply fields which are strong enough that the "strong-field" or "intermediate-field" analyses described in Griffiths become appropriate. In the strong field analysis, which I recommend you read in Griffiths, you treat the Zeeman effects as "big" and then add the fine structure effects on as a further perturbation. Ie the opposite order to the way we are handling the present weak-field analysis.]

(c) Suppose that the magnetic field is in the z-direction. Evaluate E_Z^1 for a state with $j = \ell + 1/2$ and for a state with $j = \ell - 1/2$.

[Hint: in order to evaluate $\langle S_z \rangle$, you will have to use Clebsch-Gordan coefficients to write the state $|n\ell j m_j\rangle$ as a linear combination of several $|n\ell m_\ell m_s\rangle$ states. You should look up the Clebsch-Gordan coefficients you need in a table.]

(d) Consider once again the eight $n = 2$ states $|2\ell j m_j\rangle$. Make an energy level diagram (like Griffiths Fig. 6.11) to show how the energies change as $|\vec{B}|$ is increased. Label each line clearly, and indicate its slope and its degeneracy, if any.

(e) Show that if $|n\ell_1 j m_{j1}\rangle$ and $|n\ell_2 j m_{j2}\rangle$ are two different states with the same Bohr and fine structure energies (and therefore the same n and j but not necessarily the same ℓ and m_j) then $\langle n\ell_1 j m_{j1}|J_z + S_z|n\ell_2 j m_{j2}\rangle$ is zero unless $\ell_1 = \ell_2$ and $m_{j1} = m_{j2}$. This is the demonstration that the states $|n\ell j m_j\rangle$ are the "good" unperturbed states upon which the effects of the Zeeman perturbation can be calculated using our perturbation theory formalism.

(f) Griffiths analyzes the weak-field Zeeman effect differently. Let us see how he does it. Griffiths argues (on page 245) that because the operator $\vec{S}$ precesses *rapidly* around the operator $\vec{J}$ (which itself precesses slowly around $\vec{B}$), we can replace $\vec{S}$ by

$$\vec{S}_{\text{ave}} = \frac{(\vec{S} \cdot \vec{J})}{J^2} \vec{J} \, .$$

Under this approximation, show that

$$E_Z^1 = \frac{e}{2m} g(\ell, j) m_j$$

where $g(\ell, j)$ is called the Landé g-factor and is given by

$$g(\ell, j) = \left[1 + \frac{j(j+1) - \ell(\ell+1) + 3/4}{2j(j+1)} \right] .$$

[Showing this means reproducing a paragraph of Griffiths, with details filled in.]

Upon first reading, you may think this derivation sounds fishy. To make you feel better about it, check that for both $j = \ell + 1/2$ and $j = \ell - 1/2$ the result you obtain in this part of the problem agrees with that you found in part (c), by straightforward use of degenerate perturbation theory.

[You may also use the Landé g-factor to check the figure you drew in part (d). I will not ask you to hand in this check.]

4. **Stark Effect for $n = 3$ States of Hydrogen (12 points)**

Consider a hydrogen atom placed in an electric field ε, oriented in the z-direction. The associated perturbation to the Hamiltonian, called the Stark Hamiltonian, is

$$H'_S = -e\varepsilon z = -e\varepsilon r \cos\theta \tag{3}$$

In this problem, you may ignore all fine structure effects, and pretend that the electron has no spin. Ie just think of H'_S as a perturbation to the Bohr Hamiltonian.

We will discuss the first order corrections to the energies of the ground state ($n = 1$) and the first excited states ($n = 2$) in lecture.

In this problem, I ask you to work out the first order corrections to the energies of the $n = 3$ states. In the absence of an electric field, these are 9 degenerate states, so I am asking you to do degenerate perturbation theory with a 9×9 degenerate subspace.

(a) Evaluate the 81 matrix elements of H'_S in the degenerate subspace, but be smart about it.

First of all, use symmetries (and various properties of the spherical harmonics) to argue that many matrix elements are zero. Symmetries also relate some matrix elements to others. If you are sufficiently clever, you can show without calculation that there are only 3 different nonzero matrix elements to calculate. (You may not quite be able to get it down to 3, but you should be able to get it down to a lot fewer than 81.)

Once you have boiled the problem down to the evaluation of a few matrix elements, you will need to look up the unperturbed $n = 3$ hydrogen wave functions in one of your books, and do the integrals. Reduce each integral to a combination of dimensionful constants times a dimensionless integral. Do the dimensionless integral by hand if you wish (!), but I would recommend using Matlab/Maple/Mathematica.

Even if you were not able to argue your way all the way down to only 3 different nonzero matrix elements without calculation, once you have done the explicit calculations that is what you should find, regardless. See whether (after the fact) you can construct the symmetry arguments that could have told you before the fact that there are only 3 different nonzero matrix elements.

(b) Find the eigenvalues of the 9×9 matrix you have constructed in part (a), and determine the energies of the 9 states in an electric field, to first order. I will not ask you to list the zeroth order "good" states (ie the eigenstates of the matrix constructed in part (a)). However, show that each of these nine "good" eigenstates (in addition to being an eigenstate of H'_S) is an eigenstate of L_z with eigenvalue m_ℓ, even though many of them are superpositions of states with different values of ℓ and are therefore not eigenstates of L^2. Make a separate energy-level diagram for the states with each value of m_ℓ. Put these five energy level diagrams next to each other on your page, for $m_\ell = -2, -1, 0, 1, 2$ from left to right.

[The resulting level diagram has several symmetries, all of which can be understood and related to the symmetries you (may have) used to boil your calculational task down to the calculation of three matrix elements. I leave the task of working out how to understand the symmetries of this level diagram for you to do on your own, as I do not see how to pose the required questions without first telling you what the level diagram looks like, and you are supposed to figure that out!]

5. **Van der Waals Interaction between two "toy-model atoms" (14 points)**

Do Griffiths' problem 6.31. (This problem does not occur in Griffiths' 1st Edition.) Note that you should use Gaussian cgs units, as we do in 8.06. That means you should set $4\pi\epsilon_0$ to 1 in Eq. (6.97) and in many subsequent expressions.