Physics 492: Quantum Mechanics II
Problem Set #9
EXTRA CREDIT
Due: Thursday, April 25, 2019 (@ 5PM in TA mailbox)

Problem 1: The Stark effect (35 points)
We have seen how energy levels can shift in the presence of an external magnetic field. This is known as the *Zeeman effect*, which arises due to the interaction between the atom's magnetic dipole moment and the perturbing magnetic field.
Energy levels will also shift in the presence of an externally applied electric fields. The is known as the *Stark effect*, which arises due to the interaction of the atom's electric dipole moment with a perturbing electric field.

Consider the Stark effect in Hydrogen (ignore spin). The total Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

where $\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{r}$ is the Hamiltonian for the relative motion of the electron to the proton, with the usual (zeroth order) bound states $\hat{H}_0|n,l,m\rangle = E_n^{(0)}|n,l,m\rangle$, $E_n^{(0)} = -\frac{1}{2n^2}\frac{e^2}{a_0}$. The perturbation is $\hat{H}_1 = -\hat{\mathbf{d}}\cdot\mathcal{E}$, where $\mathcal{E}$ is the externally applied electric and $\hat{\mathbf{d}} = -e\hat{\mathbf{r}}$ is the electric dipole operator. We will take the electric field in the *z*-direction.

(a) Consider the ground state, 1*s*. Show that the first order shift in the energy vanishes.

(b) Show that the second order shift on the ground state, 1*s*, is

$$\Delta E_{1s}^{(2)} = 2a_0\mathcal{E}^2 \sum_{n,l,m} \frac{\left|\langle n,l,m|\hat{z}|1,0,0\rangle\right|^2}{-1+\frac{1}{n^2}} \quad \text{(sum excludes } n=1\text{)}.$$

(c) Show that this can be simplified to

$$\Delta E_{1s}^{(2)} = \frac{2}{3}a_0^3\mathcal{E}^2 \sum_{n\neq 1} \frac{\left[I(n)\right]^2}{-1+\frac{1}{n^2}}, \text{ where } I(n) = \int_0^\infty d\bar{r}\; \bar{r}\, u_{n,1}(\bar{r})\, u_{1,0}(\bar{r}) \text{ is the radial integral.}$$

(d) This sum can actually be done (you need not do it). The answer is $\Delta E_{1s}^{(2)} = -\frac{9}{4}a_0^3\mathcal{E}^2$. This is known as the "quadratic Stark shift." What is the frequency shift (in Hz) per Volt/cm of electric field? (note the units are crazy here. The energy shift is in cgs units. You need to convert volts to statvolts).

(e) Now consider the Stark shift on the first excited state n=2. As this is four-fold degenerate, (one 2s and three 2p states) we must use *degenerate perturbation theory.* Show that the 4X4 matrix representation of the Hamiltonian in the ordered basis $\{|2,0,0\rangle, |2,1,0\rangle, |2,1,1\rangle, |2,1,-1\rangle\}$ is

$$\hat{H} = \begin{bmatrix} E_2^{(0)} & \varepsilon & 0 & 0 \\ \varepsilon & E_2^{(0)} & 0 & 0 \\ 0 & 0 & E_2^{(0)} & 0 \\ 0 & 0 & 0 & E_2^{(0)} \end{bmatrix}, \text{ where } \varepsilon = -3ea_0\mathcal{E}.$$

(f) The form of this matrix shows that the states $\{|2,1,1\rangle, |2,1,-1\rangle\}$ are not shifted in first order; they remain eigenstates of the Hamiltonian. On the order hand the states $\{|2,0,0\rangle, |2,1,0\rangle\}$ are coupled in a 2X2 block. Diagonalize this block to find that new energy eigenvalues and eigenvectors are "hybrid" s and p states, with corresponding first order shift

$$|2,\pm\rangle = \frac{1}{\sqrt{2}}\left(|2,0,0\rangle \pm |2,1,0\rangle\right), \quad \Delta E_{2,\pm}^{(1)} = \pm\varepsilon = \mp 3ea_0\mathcal{E}$$

This is known as the "linear Stark shift." What is the frequency shift (in Hz) per Volt/cm of electric field? Sketch the energy levels in n=2 as a function of $\mathcal{E}$.

Problem 2: Addition of spin and orbital angular momentum (20 Points)

Consider an electron with orbital angular momentum quantum number $l = 1$ and spin quantum number $s = 1/2$. The total angular momentum operator, is $\hat{\vec{\mathbf{j}}} = \hat{\vec{\mathbf{l}}} + \hat{\vec{\mathbf{s}}}$.

(a) Find the simultaneous eigenvectors of $\hat{\mathbf{j}}^2, \hat{j}_z, \hat{\mathbf{s}}^2, \hat{\mathbf{l}}^2$ (i.e. direct diagonalization of $\hat{\mathbf{j}}^2$).
Hint: Order your basis so that your matrices are block diagonal.

(b) Find the matrix elements of $\hat{\vec{\mathbf{l}}} \cdot \hat{\vec{\mathbf{s}}}$ in the coupled basis.

Hint: Consider $\hat{\vec{\mathbf{j}}}^2 = \left|\hat{\vec{\mathbf{l}}} + \hat{\vec{\mathbf{s}}}\right|^2$.