3. *Quantum Mechanics* (Spring 2006)

A hydrogen atom is placed in a constant weak electric field of strength ε. Ignoring spin, what are the energies of the $n = 1$ and $n = 2$ levels including effects to first order in ε (but ignoring second order effects)?

Note: You may want to use some of the following:

Radial Wave Functions $R_{nl}(r)$ (a is the Bohr radius):

$$R_{10}(r) = \frac{1}{a^{3/2}} 2e^{-r/a} \qquad R_{21}(r) = \frac{1}{a^{3/2}}\frac{1}{2\sqrt{6}}\frac{r}{a}e^{-r/2a}$$
$$R_{20}(r) = \frac{1}{a^{3/2}}\frac{1}{\sqrt{2}}\left(1-\frac{r}{2a}\right)e^{-r/2a}$$

Spherical Harmonics $Y_l^m(\theta,\phi)$:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$$

An integral:

$$\int_0^\infty x^n e^{-x/a}dx = a^{n+1}n!$$

The unperturbed energy is $E_n = -\frac{mZ^2e^4}{2\hbar^2 n^2}$ where $Z=1$.

Assume $\vec{E} = \mathcal{E}\hat{z}$ so the perturbation is $H' = eV = -e\mathcal{E}z$

First order perturbation theory says $\Delta_n^{(1)} = H'_{nn} = \langle \Psi_n | H' | \Psi_n \rangle$

$$\Delta^{(1)}_{100} = -e\mathcal{E}\int R^*_{10}(r)Y^*_{00}(\theta,\phi)\, r\cos(\theta)\, R_{10}(r)Y_{00}(\theta,\phi)\, r^2\sin(\theta)\,dr\,d\theta\,d\phi$$
$$= -e\mathcal{E}\int_0^\infty R^*_{10}(r)R_{10}(r)r^3dr\int_0^\pi \frac{1}{4\pi}\cos(\theta)\sin(\theta)d\theta\int_0^{2\pi}d\phi$$
$$= -\frac{1}{2}e\mathcal{E}\int_0^\infty R^*_{10}(r)R_{10}(r)r^3dr\,\overbrace{\int_0^\pi \frac{1}{2}\sin(2\theta)d\theta}^{0} = 0$$

The $n=2$ states are degenerate, so we use degenerate perturbation theory.

Let V be the 4 by 4 matrix for H' in the basis of the 4 degenerate states: $|200\rangle, |210\rangle, |211\rangle, |21{-1}\rangle$, so elements are of the form $\langle a|H'|b\rangle$ where a and b are from this set of 4.

The selection rules from the Wigner-Eckart Theorem help us evaluate the matrix V. The operator z is the 0^{th} spherical component of a rank 1 tensor $\vec{X}$. So $\Delta l = k = 1$ and $m' = m+q = m$.

$$V = -e\mathcal{E}\begin{pmatrix}\langle 200|z|200\rangle & \langle 200|z|210\rangle & \langle 200|z|211\rangle & \langle 200|z|21{-1}\rangle\\ \langle 210|z|200\rangle & \langle 210|z|210\rangle & \langle 210|z|211\rangle & \langle 210|z|21{-1}\rangle\\ \langle 211|z|211\rangle & \langle 211|z|210\rangle & \langle 211|z|211\rangle & \langle 211|z|21{-1}\rangle\\ \langle 21{-1}|z|21{-1}\rangle & \langle 21{-1}|z|210\rangle & \langle 21{-1}|z|211\rangle & \langle 21{-1}|z|21{-1}\rangle\end{pmatrix} = \begin{pmatrix}0 & \alpha & 0 & 0\\ \alpha^* & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}$$

$$\alpha = -e\mathcal{E}\langle 200|z|210\rangle = -e\mathcal{E}\int R^*_{20}(r)Y^*_{00}(\theta\phi)\, r\cos(\theta)\, R_{21}(r)Y_{10}(\theta,\phi)\, r^2\sin(\theta)\,dr\,d\theta\,d\phi$$
$$= -e\mathcal{E}\int a^{-3/2}\frac{1}{\sqrt{2}}\left(1-\frac{r}{2a}\right)e^{-r/2a}\frac{1}{\sqrt{4\pi}}\, r\cos(\theta)\, a^{-3/2}\frac{1}{2\sqrt{6}}\frac{r}{a}e^{-r/2a}\sqrt{\frac{3}{4\pi}}\cos(\theta)\, r^2\sin(\theta)\,dr\,d\theta\,d\phi$$
$$= -\frac{e\mathcal{E}}{16\pi}a^{-4}\int_0^\infty r^4\left(1-\frac{r}{2a}\right)e^{-r/a}dr\int_0^\pi\cos^2(\theta)\sin(\theta)\,d\theta\int_0^{2\pi}d\phi$$
$$= -\frac{e\mathcal{E}}{8}a^{-4}\left(a^5 4! - \frac{1}{2a}a^6 5!\right)\left(\frac{2}{3}\right) = -\frac{e\mathcal{E}}{12}a(24-60) = 3e\mathcal{E}a$$

Now we diagonalize V to find the energy eigenvalues, but we only need the first quarter.

$$\begin{pmatrix}0 & 3e\mathcal{E}a\\ 3e\mathcal{E}a & 0\end{pmatrix}\begin{pmatrix}\langle 200|\Psi\rangle\\ \langle 210|\Psi\rangle\end{pmatrix} = 3e\mathcal{E}a\begin{pmatrix}\langle 210|\Psi\rangle\\ \langle 200|\Psi\rangle\end{pmatrix} = \lambda\begin{pmatrix}\langle 200|\Psi\rangle\\ \langle 210|\Psi\rangle\end{pmatrix} \Rightarrow \begin{matrix}|\Psi_+\rangle = \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle)\\ |\Psi_-\rangle = \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle)\end{matrix}$$

$$\begin{vmatrix}-\lambda & 3e\mathcal{E}a\\ 3e\mathcal{E}a & -\lambda\end{vmatrix} = 0 \Rightarrow \lambda^2 - (3e\mathcal{E}a)^2 = 0 \Rightarrow \lambda = \pm 3e\mathcal{E}a$$

Therefore, to first order $E_{n=1} = \frac{me^4}{2\hbar^2}$ and $E_{n=2} = \frac{me^4}{8\hbar^2} \pm 3e\mathcal{E}a$