Fall 1999 #8

A hydrogen atom is placed in a constant weak electric field of strength $\mathcal{E}$. Ignoring spin, what are the energies of the $n=1$ and $n=2$ levels including effects to first order in $\mathcal{E}$?

Useful information:

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

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

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

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

→ The unperturbed energies of Hydrogen are given by:

$$E_n = \frac{-\alpha^2 mc^2}{2n^2} = \frac{-13.6\,eV}{n^2} \qquad (n=1,2,3\cdots)$$

The perturbing Hamiltonian is $H' = e\mathcal{E}z$

the shift in the ground state ($\Delta E_{100}^{(1)}$) is thus:

$$\Delta E_{100}^{(1)} = \langle \overset{n}{1}\,\overset{\ell}{0}\,\overset{m}{0}|H'|1\,0\,0\rangle = e\mathcal{E}\langle 1\,0\,0|z|1\,0\,0\rangle$$

since z is an odd function, the integral equals zero, and

$\boxed{\Delta E_{100}^{(1)} = 0}$ ← there is no shift of the ground state

For the $n=2$ state, we must use degenerate perturbation theory, construct the matrix of the perturbing Hamiltonian on the basis states $|2\,0\,0\rangle$, $|2\,1\,0\rangle$, $|2\,1\,1\rangle$, $|2\,1\,-1\rangle$:

recall $z = T_{k=1}^{q=0}$, and the selection rules tell us

(1) $\langle \alpha', j', m'|T_k^q|\alpha, j, m\rangle = 0$ unless $m' = m+q$

(2) $\langle \alpha', j', m'|T_k^q|\alpha, j, m\rangle = 0$ unless j, j', K form a triangle

by inspection, elements with $j'=j=1$ are zero (integrals of $\sin^3\theta\cos\theta$, or $\sin\theta\cos\theta$)

from rule (1), the only nonzero matrix elements will be

$$\langle 2\,1\,0|T_1^0|2\,0\,0\rangle \quad \text{and} \quad \langle 2\,0\,0|T_1^0|2\,1\,0\rangle$$

(the triangle formed by j, j', K has a side of length zero)

∴ it is sufficient to write the matrix using only the basis vectors

$|2\,0\,0\rangle, \; |2\,1\,0\rangle$

evaluating $e\mathcal{E}\langle 210|z|200\rangle = e\mathcal{E}\langle 2\,1\,0|r\cos\theta|2\,0\,0$

$$= e\mathcal{E}\iiint R_{21}^{*} Y_{10}^{*}\; r\cos\theta\; R_{20} Y_{00}\, d^3r$$

$$= e\mathcal{E}\iiint \frac{1}{2\sqrt{6}} a^{-3/2} \frac{r}{a} e^{-r/2a} \sqrt{\frac{3}{4\pi}} \cos\theta \; r\cos\theta \frac{1}{\sqrt{2}} a^{-3/2}\left(1-\frac{r}{2a}\right) e^{-r/2a}$$

$$= e\mathcal{E} \frac{1}{2\sqrt{6}}\left(\frac{1}{a^{3/2}}\right)\left(\frac{1}{a}\right)\sqrt{\frac{3}{4\pi}} \frac{1}{\sqrt{2}}\left(\frac{1}{a^{3/2}}\right)\sqrt{\frac{1}{4\pi}} \iiint r^4 e^{-r/a}\left(1-\frac{r}{2a}\right)\cos^2\theta\sin\theta$$

$$= e\mathcal{E}\left(\frac{1}{a}\right)^4\left(\frac{1}{4\pi}\right)\left(\frac{1}{4}\right)\int_0^\infty dr\left[r^4 e^{-r/a} - \frac{r^5}{2a} e^{-r/a}\right] 2\pi \int_0^\pi \cos^2\theta \sin\theta \, d\theta$$

$$= e\mathcal{E}\left(\frac{1}{a}\right)^4\left(\frac{1}{8}\right)\left[a^5 4! - \frac{1}{2a} a^6 5!\right]\left[-\int_{+1}^{-1} u^2 du\right]$$

$$= e\mathcal{E}a\left(\frac{1}{8}\right)\left[24 - 60\right](-1)\left[-\frac{1}{3} - \left(+\frac{1}{3}\right)\right]$$

$$= \frac{e\mathcal{E}a}{8}(-36)\left(\frac{2}{3}\right) = -3e\mathcal{E}a$$

so the Hamiltonian matrix is

$$H' = \begin{array}{c c} & \begin{array}{cc} |200\rangle & |210\rangle \end{array} \\ \begin{array}{c} |200\rangle \\ |210\rangle \end{array} & \begin{pmatrix} 0 & -3e\mathcal{E}a \\ -3e\mathcal{E}a & 0 \end{pmatrix} \end{array}$$

solving for energy:

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

$$E = \pm 3e\mathcal{E}a$$

So the energies of the $n=2$ states are

$$\boxed{-\frac{13.6}{4}eV, \; -\frac{13.6}{4}eV, \; -\frac{13.6}{4} + 3e\mathcal{E}a, \; -\frac{13.6}{4} - 3e\mathcal{E}a}$$