STARK EFFECT

PROB: Hydrogen atom in an electric field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$. Find 1^{st} order energies of the gnd state and first excited state.

Sol: $\Rightarrow$ $H = -q\mathcal{E}\hat{z}\cdot\vec{r} = -q\mathcal{E}z$

From non degenerate perturbation theory on the ground state atom...

$$E_0' = \langle \psi_{100} | H' | \psi_{100} \rangle$$

$$= -q\mathcal{E}\langle \psi_{100} | z | \psi_{100} \rangle$$

$$= 0$$

Since z is odd & $\psi_{100}(r,\theta,\phi)$ is even

or, alternatively, from the selection rule:

$\langle n'\ell'm' | z | n\ell m \rangle \neq 0$ if $|\Delta m| = 0$ and $|\Delta \ell| = 1$.

Thus there is no first order energy shift on the ground state

For the first excited state $n=2$, there is a four-fold degeneracy initially: $E = \dfrac{-Z^2 e^2}{2a(2)^2}$ for $\ell = 0, 1 \langle {M=0 \atop M=\pm 1}$, ($\ell=0$: $m=0$)

We thus use degenerate perturbation theory.

$$H' = -q\mathcal{E}\begin{pmatrix} \langle 200|z|200\rangle & \langle 200|z|210\rangle & \langle 200|z|211\rangle & \langle 200|z|21{-1}\rangle \\ \langle 210|z|200\rangle & \langle 210|z|210\rangle & \langle 210|z|211\rangle & \langle 210|z|21{-1}\rangle \\ \langle 211|z|200\rangle & \langle 211|z|210\rangle & \langle 211|z|211\rangle & \langle 211|z|21{-1}\rangle \\ \langle 21{-1}|z|200\rangle & \langle 21{-1}|z|210\rangle & \langle 21{-1}|z|211\rangle & \langle 21{-1}|z|21{-1}\rangle \end{pmatrix}$$

Selection rules give

$\langle 210|z|200\rangle = \langle 200|z|210\rangle \neq 0$, all other matrix elements vanish. We are given

$$\psi_{200} = R_{20} Y_{00} = \frac{1}{\sqrt{2a^3}}\left(1-\frac{r}{2a}\right)e^{-r/2a}\frac{1}{\sqrt{4\pi}}$$

$$\psi_{210} = R_{21} Y_{10} = \frac{1}{2\sqrt{6a^3}}\frac{r}{a}e^{-r/2a}\sqrt{\frac{3}{4\pi}}\cos\theta$$

$$\langle 210|z|200\rangle = \langle 210|r\cos\theta|200\rangle$$

$$= \frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{2a^3}}\frac{\sqrt{3}}{\sqrt{4\pi}}\frac{1}{2\sqrt{6a^3}}\int_0^{2\pi}d\phi\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta$$

$$\times\int_0^{\infty}\frac{r}{a}\left(1-\frac{r}{2a}\right)e^{-2r/2a}r^3\,dr$$

$$= \frac{1}{8a^4}\underbrace{\int_{-1}^{1}\cos^2\theta\,d(\cos\theta)}_{\frac{2}{3}}\int_0^{\infty}\left[r^4e^{-r/a}-\frac{1}{2a}r^5e^{-\frac{r}{a}}\right]dr$$

$\left\{\int_0^{\infty}r^n e^{-r/b}dr = b^{n+1}n!\right\}\Rightarrow$ We can use this given integral

$$= \frac{1}{12a^4}\left[a^5 4! - a^5\frac{5!}{2}\right]$$

$$= a\left[2-5\right] = -3a$$

Therefore we can explicitly write the Hamiltonian matrix...

$$H' = -q\mathcal{E}\begin{pmatrix} 0 & -3a & [0] \\ -3a & 0 & \\ [0] & [0] & \end{pmatrix}$$

Diagonalization of this matrix gives the energy eigenvalues $\Rightarrow \det|H - E_1 I| = 0$

$$\det\begin{vmatrix} -E_1' & -3aq\mathcal{E} & 0 & 0 \\ -3aq\mathcal{E} & -E_1' & 0 & 0 \\ 0 & 0 & -E_1' & 0 \\ 0 & 0 & 0 & -E_1' \end{vmatrix} = E_1^2(E_1^2 - 9a^2) = 0$$

So $E_1' = 0, 0, \pm 3aq\mathcal{E}$

Two of the levels have been lifted of their degeneracy (the $|211\rangle$ & $|21{-1}\rangle$ states remain unchanged by the electric field).

Conclusion: In the ground state the energies are unchanged to first order $\Rightarrow E_0 = -\dfrac{e^2}{2a}$

In the excited state the energies become

$$E_1^{(i)} = E_1^{(ii)} = -\frac{e^2}{8a}, \quad E_1^{(iii)} = \frac{-e^2}{8a} + 3aq\mathcal{E}$$

$$E_1^{(iv)} = \frac{-e^2}{8a} - 3aq\mathcal{E}.$$