1.12 Problem 64

External electric field $\vec{\mathcal{E}}$ is applied to a hydrogen atom. Find the splitting of the level $n = 2,\ l = 1$ up to a linear order in $\mathcal{E}$.

Hydrogen has a linear Stark effect since it is accidentally degenerate. First realize that for $n = 2$, the states $|2s\rangle, |2p, m = 0\rangle, |2p, m = 1\rangle$ and $|2p, m = -1\rangle$ all have the same energy. By Stark effect we mean that the atomic energy levels change when we apply an external electric field, if this change is proportional to the electric field, then we say it is a linear Stark effect.

Supposing we take the electric field along the z-axis $\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{z}$, then the perturbation is $V = e\mathcal{E}z$. Now, since we are perturbing the system, we no longer consider it to be spherically symmetric, rather, due to the influence of the electric field the problem becomes axially symmetric. Why? Because rotation around the z-axis leaves the perturbation unchanged. As a consequence of the axial symmetry, the angular momentum along z is conserved, i.e., m is a good quantum number. Therefore, only states with the same m can mix, which leaves us with $|2s\rangle$ and $|2p, m = 0\rangle$ as the only possible mixing. In degenerate perturbation theory, the first order shifts are the eigenvalues of the perturbation matrix $V_{ij} = \langle i|V|j\rangle$. We have to compute $\langle 2s|z|2p, m = 0\rangle$, where the wave functions are $\psi_{200} = \frac{1}{4\sqrt{2\pi}\, a_B^{3/2}} \left(2 - \frac{r}{a_B}\right) e^{-r/(2a_B)}$ and $\psi_{210} = \frac{1}{4\sqrt{2\pi}\, a_B^{3/2}} \left(\frac{r}{a_B}\right) e^{-r/(2a_B)} \cos\theta$. So,

$$\langle 2s|z|2p, m = 0\rangle = \int \psi_{200}^{\dagger} z \psi_{210}\, d^3r$$

$$= \left(\frac{1}{4\sqrt{2\pi}\, a_B^{3/2}}\right)^2 \int_0^{\infty} \left(2 - \frac{r}{a_B}\right)\left(\frac{r}{a_B}\right) r^3 e^{-r/a_B} \int_0^{\pi} \cos^2\theta \sin\theta\, d\theta \int_0^{2\pi} d\phi \tag{24}$$

$$= \left(\frac{1}{4\sqrt{2\pi}\, a_B^{3/2}}\right)^2 * \frac{2}{3} * 2\pi * (-72 a_B) = -3a_B$$

In the basis $\{\, |2s\rangle,\ |2p, 0\rangle,\ |2p, 1\rangle,\ |2p, -1\rangle \,\}$, the perturbation matrix is then

$$V = \begin{pmatrix} 0 & -3e\mathcal{E}a_B & 0 & 0 \\ -3e\mathcal{E}a_B & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{25}$$

with eigenvalues $\pm 3e\mathcal{E}a_B$. The diagonal elements vanish because z is odd under parity. In total we had 4 different states, so the electric field splits these into:

$$E = E_2 + 3e\mathcal{E}a_B, E = E_2 - 3e\mathcal{E}a_B, E = E_2, E = E_2 \tag{26}$$

since for the $m = \pm 1$ p-states the electric field gives zero contribution to the first order.