STARK EFFECT IN HYDROGEN FOR N = 1 AND N = 2

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.36.

The Zeeman effect occurs when an atom is placed in an external magnetic field, resulting in the interaction between field and the magnetic dipole moments of the atom causing splitting of the energy levels. The electrical analogue of the Zeeman effect, when an atom is placed in an external electric field, is called the Stark effect. We can use perturbation theory to analyze the effect on the energy levels of the electron.

The perturbation hamiltonian is, assuming the electric field points in the z direction:

$$H'_S = eE_{ext}z = eE_{ext}r\cos\theta \tag{0.1}$$

To use perturbation theory, we'll need the wave functions for unperturbed hydrogen, which are given in Griffiths as equation 4.89. For the ground state $n = 1$, we have

$$|100\rangle = \frac{2}{a^{3/2}}\frac{1}{\sqrt{4\pi}}e^{-r/a} \tag{0.2}$$

Since the ground state is non-degenerate, we can use non-degenerate perturbation theory:

$$E_{100,1} = \langle 100|H'_S|100\rangle \tag{0.3}$$

Rather than writing out the integral, we observe that $\langle 100|H'_S|100\rangle$ contains the integral of $\cos\theta\sin\theta = \frac{1}{2}\sin 2\theta$ over $\theta = 0,..,\pi$ which is zero, so $E_{100,1} = 0$.

To analyze $n = 2$, we need the four wave functions:

$$|200\rangle = R_{20}(r)\,Y_0^0(\theta,\phi) \tag{0.4}$$

$$= \frac{1}{\sqrt{2}a^{3/2}}\left(1-\frac{r}{2a}\right)\frac{1}{\sqrt{4\pi}}e^{-r/2a} \tag{0.5}$$

$$|211\rangle = R_{21}(r)\,Y_1^1(\theta,\phi) \tag{0.6}$$

$$= -\left(\frac{3}{8\pi}\right)^{1/2}\frac{1}{\sqrt{24}a^{5/2}}re^{-r/2a}\sin\theta e^{i\phi} \tag{0.7}$$

$$|210\rangle = R_{21}(r)\,Y_1^0(\theta,\phi) \tag{0.8}$$

$$= \left(\frac{3}{4\pi}\right)^{1/2}\frac{1}{\sqrt{24}a^{5/2}}re^{-r/2a}\cos\theta \tag{0.9}$$

$$|21-1\rangle = R_{21}(r)\,Y_1^{-1}(\theta,\phi) \tag{0.10}$$

$$= \left(\frac{3}{8\pi}\right)^{1/2}\frac{1}{\sqrt{24}a^{5/2}}re^{-r/2a}\sin\theta e^{-i\phi} \tag{0.11}$$

Since all four of these states have the same unperturbed energy, we need to use degenerate perturbation theory, so we'll need to find the matrix W with elements

$$W_{a,b} = \langle a|H_S'|b\rangle \tag{0.12}$$

where a and b represent one of the four states above.

First, we'll look at the θ integrals. All matrix elements involve integrals of the form (remember that H_S' always contributes a $\cos\theta$ and the spherical volume element always contributes a $\sin\theta$):

$$I_{nm} = \int_0^\pi \sin^n\theta\cos^m\theta d\theta \tag{0.13}$$

For the possible values of n and m in this problem, the only non-zero integrals of this form are

$$I_{12} = \frac{2}{3} \tag{0.14}$$

$$I_{22} = \frac{\pi}{8} \tag{0.15}$$

I_{12} arises in $\langle 200|H_S'|210\rangle$ (and its transpose) and I_{22} arises in $\langle 211|H_S'|210\rangle$ and $\langle 210|H_S'|21-1\rangle$ (and their transposes). Thus these are the only possible non-zero entries in W. However, $\langle 211|H_S'|210\rangle$ and $\langle 210|H_S'|21-1\rangle$

involve integrating $e^{\pm i\phi}$ over $\phi = 0..2\pi$ which gives zero. Thus the only non-zero matrix elements are $\langle 200|\, H'_S\, |210\rangle$ (and its transpose). This gives

$$\langle 200|\, H'_S\, |210\rangle = \frac{1}{\sqrt{2}a^{3/2}}\left(\frac{3}{4\pi}\right)^{1/2}\frac{1}{\sqrt{24}a^{5/2}}\frac{1}{\sqrt{4\pi}}eE_{ext}\times$$

$$\int_0^\infty\int_0^\pi\int_0^{2\pi}\left(1-\frac{r}{2a}\right)re^{-r/a}\,(r\cos\theta)\cos\theta r^2\sin\theta d\phi d\theta dr \tag{0.16}$$

$$= -3aeE_{ext} \tag{0.17}$$

(The integral can be done with software, or by hand using integration by parts.) The matrix W is therefore

$$W = \begin{bmatrix} 0 & 0 & -3aeE_{ext} & 0 \\ 0 & 0 & 0 & 0 \\ -3aeE_{ext} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{0.18}$$

The eigenvalues are 0, 0, $\pm 3aeE_{ext}$ so the $n = 2$ state splits into 3 states, one with energy $E_{2,0}$ (degeneracy 2) and two with energies $E_{2,0} \pm 3aeE_{ext}$ (each with degeneracy 1). The eigenvectors are $[0,1,0,0]$ and $[0,0,0,1]$ for eigenvalue 0, $[-1,0,1,0]$ for $3aeE_{ext}$ and $[1,0,1,0]$ for $-3aeE_{ext}$. Thus the 'good' states are

$$|211\rangle, |21-1\rangle, \frac{1}{\sqrt{2}}\left(-|200\rangle + |210\rangle\right), \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right) \tag{0.19}$$

The electric dipole moment of hydrogen is (treating the proton and electron as point charges):

$$\mathbf{p} = -e\mathbf{r} \tag{0.20}$$

$$= -er\left(\sin\theta\cos\phi\,\hat{\mathbf{x}} + \sin\theta\sin\phi\,\hat{\mathbf{y}} + \cos\theta\hat{\mathbf{z}}\right) \tag{0.21}$$

We can work out the expectation value of $\mathbf{p}$ in each of the 'good' states by straightforward integration: $\langle\mathbf{p}\rangle = \langle a|\,\mathbf{p}\,|a\rangle$ where a stands for one of the 'good' states. Note that if $a = |211\rangle$ or $a = |21-1\rangle$, then $\langle a|\,\mathbf{p}\,|a\rangle$ has only a z component that is non-zero, since the complex exponentials in ϕ cancel out and the integral of $\sin\phi$ or $\cos\phi$ in the x or y components is zero. Similarly, if $a = \frac{1}{\sqrt{2}}\left(-|200\rangle + |210\rangle\right)$ or $a = \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right)$, the x and y components are again zero, since these wave functions are independent of ϕ so the integral of $\sin\phi$ or $\cos\phi$ in the x or y components gives zero again. Therefore, $\langle\mathbf{p}\rangle$ is always in the z direction, and can be calculated from

$$\langle \mathbf{p} \rangle = -e \langle a | r \cos\theta | a \rangle \hat{\mathbf{z}} \tag{0.22}$$

Doing the integrals results in

$$\langle \mathbf{p} \rangle = 0, 0, 3a\hat{\mathbf{z}}, -3a\hat{\mathbf{z}} \tag{0.23}$$

respectively.

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