The Stark effect in hydrogen

When an atom is placed in a uniform external electric field (e.g. in between the plates of a charged capacitor) its energy levels are shifted. In most practical situations the external field is weak (compared to the fields due to nuclei that electrons experience). Thus, the perturbation theory can be applied to find these shifts.

Let us consider the ground and first excited states of hydrogen atom. The Hamiltonian of this system in a constant, uniform electric field is

$$H = \underbrace{\frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}}_{H^0} \underbrace{+ eE_{ext} z}_{H'}$$ (assume E_{ext} to be along z-axis)

which can be splitted into the unperturbed part, H^0, and the perturbation, H'.

First let us consider what happens to the ground state, which is non-degenerate:

$$\psi^{(0)}_{100} = |100\rangle = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}} \qquad a = \frac{4\pi\varepsilon_0 \hbar^2}{Zme^2}$$

The first order correction to the energy is

$$E^{(1)}_{100} = \langle 100|H'|100\rangle = eE_{ext}\frac{1}{\pi a^3}\int e^{-\frac{2r}{a}} \cdot z\, d\vec{r} =$$

$$= \frac{eE_{ext}}{\pi a^3}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{\infty} e^{-\frac{2r}{a}} \cdot r\cos\theta \cdot r^2 \sin\theta\, dr$$

$$\int_0^{\pi} \cos\theta \sin\theta\, d\theta = \frac{\sin^2\theta}{2}\Big|_0^{\pi} = 0 \qquad \text{Thus, } E^{(1)}_{100} = 0$$

In first order the ground state energy is not affected by the uniform electric field. It turns out that in the second order the correction to the energy is (we'll skip the derivation here as it is rather long)

$$E_{100}^{(2)} = -m\left(\frac{3a^2 e E_{ext}}{2\hbar}\right)^2$$

Now let us turn to the first excited state, $n=2$. This energy level is $n^2=4$-times degenerate. The related wave functions are

$$\underbrace{|200\rangle}_{\ell=0}, \quad \underbrace{|211\rangle, \quad |210\rangle, \quad |21-1\rangle}_{\ell=1, \; m_\ell=-1,0,+1}$$

Let us use the following notation:

$$|1\rangle \equiv \psi_{200} = \frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\left(1-\frac{r}{2a}\right)e^{-\frac{r}{2a}}$$

$$|2\rangle \equiv \psi_{211} = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}\, r e^{-\frac{r}{2a}} \sin\theta\, e^{i\phi}$$

$$|3\rangle = \psi_{210} = \frac{1}{\sqrt{2\pi a}}\frac{1}{4a^2}\, r e^{-\frac{r}{2a}} \cos\theta$$

$$|4\rangle = \psi_{21-1} = \frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}\, r e^{-\frac{r}{2a}} \sin\theta\, e^{-i\phi}$$

To compute the first-order correction to the energy we must solve the secular equation

$$\begin{vmatrix} H'_{11}-\varepsilon & H'_{12} & H'_{13} & H'_{14} \\ H'_{21} & H'_{22}-\varepsilon & H'_{23} & H'_{24} \\ H'_{31} & H'_{32} & H'_{33}-\varepsilon & H'_{34} \\ H'_{41} & H'_{42} & H'_{43} & H'_{44}-\varepsilon \end{vmatrix} = 0$$

where $H'_{ij} \equiv \langle i | H' | j \rangle$

Fortunately most integrals in this determinant vanish. All elements with different m_e vanish by orthogonality of the $|nlm_e\rangle$ states

$$H'_{11} = C_{11}\int_0^{\pi} \cos\theta \sin\theta \, d\theta = 0$$

$$H'_{22} = C_{22}\int_0^{\pi} \sin^2\theta \cos\theta \sin\theta \, d\theta = 0$$

$$H'_{33} = C_{33}\int_0^{\pi} \cos^2\theta \cos\theta \sin\theta = 0$$

$$H'_{44} = C_{44}\int_0^{\pi} \sin^2\theta \cos\theta \sin\theta \, d\theta = 0$$

$$H'_{12} = C_{12}\int_0^{2\pi} e^{i\phi} d\phi = 0 \qquad H'_{14} = C_{14}\int_0^{2\pi} e^{-i\phi} d\phi = 0$$

$$H'_{23} = C_{23}\int_0^{2\pi} e^{-i\phi} d\phi = 0 \qquad H'_{24} = C_{24}\int_0^{2\pi} e^{-2i\phi} d\phi = 0$$

$$H'_{34} = C_{34}\int_0^{2\pi} e^{-i\phi} d\phi = 0$$

$$H'_{13} = eE_{ext}\frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\frac{1}{\sqrt{2\pi a}}\frac{1}{4a2}\int \left(1-\frac{r}{2a}\right)e^{-\frac{r}{2a}}\, r e^{-\frac{r}{2a}} \cos\theta\,(r\cos\theta)\, r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$= \frac{eE_{ext}}{16\pi a^4}\cdot 2\pi \underbrace{\int_0^{\pi}\cos^2\theta \sin\theta\, d\theta}_{2/3} \int_0^{\infty}\left(1-\frac{r}{2a}\right)e^{-\frac{r}{a}} r^4\, dr =$$

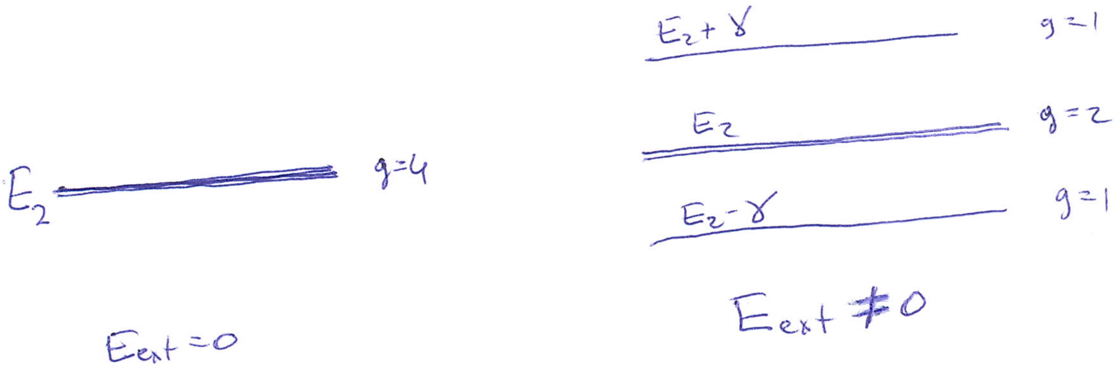
$$= \frac{eE_{ext}}{12a^4}\left[\underbrace{\int_0^{\infty} r^4 e^{-\frac{r}{a}} dr}_{4!\,a^5} - \frac{1}{2a}\underbrace{\int_0^{\infty} r^5 e^{-\frac{r}{a}} dr}_{5!\,a^6}\right] = \frac{eE_{ext}}{12} a\left[24-60\right] = -3eE_{ext}a$$

if $\gamma \equiv 3eE_{ext}a$ then our secular equation looks as follows

$$\begin{vmatrix} -\varepsilon & 0 & -\gamma & 0 \\ 0 & -\varepsilon & 0 & 0 \\ -\gamma & 0 & -\varepsilon & 0 \\ 0 & 0 & 0 & -\varepsilon \end{vmatrix} = 0 \quad \text{or} \quad -\varepsilon \begin{vmatrix} -\varepsilon & 0 & -\gamma \\ 0 & -\varepsilon & 0 \\ -\gamma & 0 & -\varepsilon \end{vmatrix} = 0$$

$$\text{or} \quad \varepsilon\left(\varepsilon^3 - \varepsilon\gamma^2\right) \Rightarrow \begin{array}{l} \varepsilon_{3,4} = 0, 0 \\ \varepsilon_{1,2} = +\gamma, -\gamma \end{array}$$

Thus we find that to terms of lowest order in the electric field E_{ext}, the degenerate $n=2$ level separates into three:



To calculate the new $n=2$ wavefunctions

$$\phi_n^{(0)} = \sum_i c_{ni} \psi_i^{(0)}$$

we substitute $\varepsilon_{1,2,3,4}$ into the original matrix and solve for eigenvectors

$$\begin{pmatrix} -\varepsilon & 0 & -\gamma & 0 \\ 0 & -\varepsilon & 0 & 0 \\ -\gamma & 0 & -\varepsilon & 0 \\ 0 & 0 & 0 & -\varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

The results are:

$$\phi_1^{(0)} = \frac{1}{\sqrt{2}}\left(|1\rangle - |3\rangle\right) \qquad \varepsilon_1 = +\gamma$$

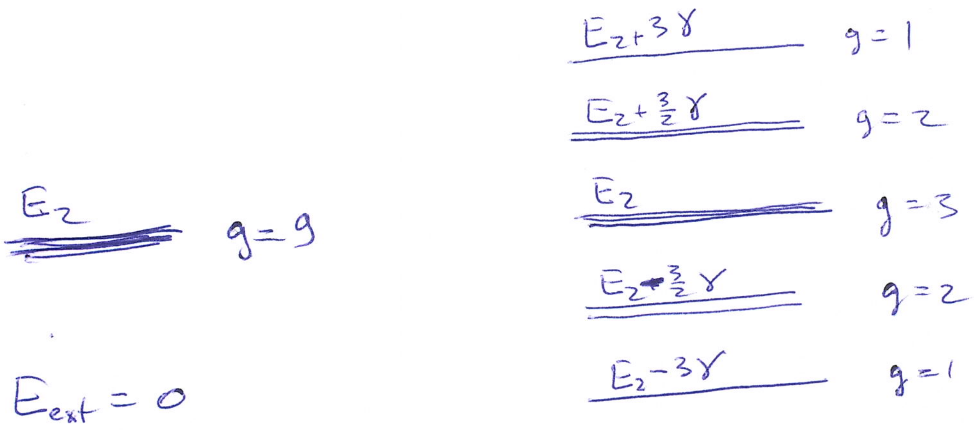
$$\phi_2^{(0)} = \frac{1}{\sqrt{2}}\left(|1\rangle + |3\rangle\right) \qquad \varepsilon_2 = -\gamma$$

$\phi_3^{(0)} = |2\rangle \qquad \varepsilon_3 = 0$

$\phi_4^{(0)} = |4\rangle \qquad \varepsilon_4 = 0$

It turns out that the perturbation mixes the $m_\ell = 0$ states while $m_\ell = 1, -1$ states remain degenerate

In a similar manner we can, in principle, consider all other energy levels. Say, for $n=3$ level we would need to construct a 9×9 matrix and solve the corresponding eigenvalue problem. It turns out that $n=3$ level is also partially splitted when the perturbation is turned on!



and, again, levels with the same value of m_ℓ are mixed.