

## First Order Degenerate Perturbation Theory The Stark Effect for the Hydrogen Atom

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The  $n = 2$  level of the hydrogen atom is 4-fold degenerate with energy  $-1.25 E_h$ . In terms of the  $|nlm\rangle$  quantum numbers these states are  $|200\rangle$ ,  $|210\rangle$ ,  $|211\rangle$ , and  $|21-1\rangle$ .

An electric field in the  $z$ -direction splits the degeneracy because it mixes the  $2s$  and the  $2p_z$  orbitals creating one linear combination polarized in the direction of the field and another polarized against the field. The Hamiltonian for this perturbation in atomic units is:  $H' = \epsilon z$ , which in spherical polar coordinates is:  $H' = \epsilon r \cos(\theta)$ , where  $\epsilon$  is the electric field strength.

In this perturbation method treatment the hydrogen atom eigenfunctions are used to evaluate the matrix elements associated with the total Hamiltonian,  $H^0 + H'$ . Since the results for  $H^0$  are known ( $-1.25 E_h$ ) only the matrix elements for  $H'$  need to be evaluated and most of these are zero.

Below we show that  $\langle 200 | H' | 210 \rangle = \langle 210 | H' | 200 \rangle = -3\epsilon$  and that the other matrix elements involving the  $n = 2$  orbitals are equal to zero.

$$\Psi_{2s}(r) := \frac{1}{\sqrt{32\pi}} \cdot (2 - r) \cdot \exp\left(-\frac{r}{2}\right)$$

$$\Psi_{2p_z}(r, \theta) := \frac{1}{\sqrt{32\pi}} \cdot r \cdot \exp\left(-\frac{r}{2}\right) \cdot \cos(\theta)$$

$$\Psi_{2p_x}(r, \theta, \phi) := \frac{1}{\sqrt{32\pi}} \cdot r \cdot \exp\left(-\frac{r}{2}\right) \cdot \sin(\theta) \cdot \cos(\phi)$$

$$\Psi_{2p_y}(r, \theta, \phi) := \frac{1}{\sqrt{32\pi}} \cdot r \cdot \exp\left(-\frac{r}{2}\right) \cdot \sin(\theta) \cdot \sin(\phi)$$

$$\langle 2s | H' | 2s \rangle = 0 \quad \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}(r) \cdot \epsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\langle 2p_z | H' | 2p_z \rangle = \langle 2p_y | H' | 2p_y \rangle = \langle 2p_x | H' | 2p_x \rangle = 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_z}(r, \theta) \cdot \epsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2p_z}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_y}(r, \theta, \phi) \cdot \epsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2p_y}(r, \theta, \phi) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_x}(r, \theta, \phi) \cdot \epsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2p_x}(r, \theta, \phi) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\langle 2s | H' | 2p_z \rangle = -3\varepsilon \quad \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}(r) \cdot \varepsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2pz}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow (-3) \cdot \varepsilon$$

$$\langle 2s | H' | 2p_x \rangle = \langle 2s | H' | 2p_y \rangle = 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}(r) \cdot \varepsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2px}(r, \theta, \phi) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}(r) \cdot \varepsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2py}(r, \theta, \phi) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\langle 2p_x | H' | 2p_y \rangle = \langle 2p_x | H' | 2p_z \rangle = \langle 2p_y | H' | 2p_z \rangle = 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2px}(r, \theta, \phi) \cdot \varepsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2py}(r, \theta, \phi) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2px}(r, \theta, \phi) \cdot \varepsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2pz}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2py}(r, \theta, \phi) \cdot \varepsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{2pz}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

The matrix elements of the 4x4 perturbation matrix are  $\langle \Psi_i | H_0 + H' | \Psi_j \rangle$ , where the  $\Psi$ 's are the 2s, 2p<sub>z</sub>, 2p<sub>x</sub>, and 2p<sub>y</sub> hydrogen atomic orbitals. Using the values of the integrals evaluated above the perturbation matrix is formed and its eigenvalues and eigenvectors found.

$$\begin{pmatrix} -0.125 - E & -3 \cdot \varepsilon & 0 & 0 \\ -3 \cdot \varepsilon & -0.125 - E & 0 & 0 \\ 0 & 0 & -0.125 - E & 0 \\ 0 & 0 & 0 & -0.125 - E \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

This 4x4 energy matrix is clearly one 2x2 and two 1x1 energy matrices. In other words, as we learned from evaluating the matrix elements, the 2p<sub>x</sub> and 2p<sub>y</sub> are not perturbed by the electric field to first order and have energy -0.125 E<sub>h</sub>.

The eigenvectors and eigenvalues of the 2x2 are found as follows.

$$\left[ \begin{array}{l} (-0.125 - E) \cdot c_1 - 3 \cdot \varepsilon \cdot c_2 = 0 \\ -3 \cdot \varepsilon \cdot c_1 + (-0.125 - E) \cdot c_2 = 0 \\ c_1^2 + c_2^2 = 1 \end{array} \right] \left| \begin{array}{l} \text{solve,} \\ \left( \begin{array}{l} c_1 \\ c_2 \\ E \end{array} \right) \\ \text{float, 3} \end{array} \right. \rightarrow \left[ \begin{array}{l} \begin{pmatrix} -0.707 & -0.707 & (-3) \cdot \varepsilon - .125 \\ .707 & .707 & (-3) \cdot \varepsilon - .125 \\ .707 & -0.707 & 3 \cdot \varepsilon - .125 \\ -0.707 & .707 & 3 \cdot \varepsilon - .125 \end{pmatrix} \end{array} \right]$$

The wavefunctions of the perturbed 2s and 2p<sub>z</sub> orbitals are sp<sub>z</sub> hybrid states as shown below.

$$\frac{1}{\sqrt{2}} \cdot (2s + 2p_z) \quad E = (-.125 - 3 \cdot \varepsilon) \cdot E_h \qquad \frac{1}{\sqrt{2}} \cdot (2s - 2p_z) \quad E = (-.125 + 3 \cdot \varepsilon) \cdot E_h$$

Because the energy of the symmetric 1s state is unaffected by the electric field, the effect of this perturbation on the electronic spectrum of hydrogen is to split the n = 1 to n = 2 transition into three lines of relative intensity 1:2:1.

$$\langle 2s | H' | 2s \rangle = 0 \qquad \Psi_{1s}(r) := \frac{1}{\sqrt{\pi}} \cdot \exp(-r) \qquad \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{1s}(r) \cdot \varepsilon \cdot r \cdot \cos(\theta) \cdot \Psi_{1s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

