

Stark Effect

The Stark effect is the shift in atomic energy levels caused by an external electric field. There are various regimes to consider. The one treated here is the so-called strong field case, where the shift in energy levels due to the external electric field is large compared to fine structure (although still small compared to the spacings between the unperturbed atomic levels.) In the strong field limit, the Stark effect is independent of electron spin.

We start with the ordinary hydrogen Hamiltonian,

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$$

and add a term arising from a uniform electric field along the z axis.

$$H' = e\mathcal{E}z.$$

Note the $+$ sign on this term. It is easily checked by remembering that the force on the electron due to this term would be obtained by taking $-\partial_z$, which gives a force along the $-z$ axis, as it should for an electron. To understand the matrix elements that are non-zero, it is useful to temporarily give the external electric field an arbitrary direction,

$$H' = e\vec{\mathcal{E}} \cdot \vec{x}$$

The selection rules on the matrix elements of \vec{x} are

$$\langle n', l', m' | \vec{x} | n, l, m \rangle \neq 0, \quad l' = l \pm 1.$$

These follow from angular momentum conservation (\vec{x} has angular momentum 1), and parity (\vec{x} is odd under parity). Returning to the case of the electric field along the z axis, we have an additional selection rule on m ,

$$\langle n', l', m' | z | n, l, m \rangle \neq 0, \quad l' = l \pm 1, \quad m' = m$$

From these selection rules we see that non-zero matrix elements require different values of l . Now for $n = 1$ there is only $l = 0$, so

$$n = 1, l = 0 \rightarrow \text{no first order Stark Effect.}$$

However, for $n = 2$, we have two l values, so

$$n = 2, l = 0, 1, \rightarrow l = 0 \leftrightarrow l = 1$$

Listing the states for $n = 2$, we have

$$\Psi_{200}, \Psi_{211}, \Psi_{210}, \Psi_{21-1}$$

However, $l = 0$ has only $m = 0$, so the selection rule on m says we only have non-zero matrix elements

$$l = 0 \leftrightarrow l = 1 \rightarrow \Psi_{200} \leftrightarrow \Psi_{210}$$

Without the electric field these states have the same energy, so we have a 2×2 problem in degenerate perturbation theory. The matrix element we need is proportional to

$$\langle 210|z|200 \rangle = \langle 200|z|210 \rangle$$

We label the two degenerate states as follows:

$$200 \rightarrow 1 \quad 210 \rightarrow 2$$

Using this notation, we need to find new linear combinations of these degenerate states, and along the way we find values for the perturbed energy eigenvalues. The equations which accomplish both of these tasks are

$$\begin{pmatrix} E^{(1)} & 0 \\ 0 & E^{(1)} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$

By our selection rules, the diagonal matrix elements vanish,

$$H'_{11} = H'_{22} = 0$$

and

$$H'_{12} = H'_{21} = e\mathcal{E} \langle 200|z|210 \rangle.$$

The wave functions of our states are

$$\begin{aligned} \Psi_{200} &= N_{20} \left(1 - \frac{r}{2a_0}\right) \exp\left(-\frac{r}{2a}\right) \frac{1}{\sqrt{4\pi}}, \\ \Psi_{210} &= N_{21} r \exp\left(-\frac{r}{2a}\right) \sqrt{\frac{3}{4\pi}} \cos \theta, \end{aligned}$$

Where the N 's are normalization factors, given below. It is useful at this point to go over to atomic units,

$$z \rightarrow a_0 r' \cos \theta, \quad \mathcal{E} \rightarrow \frac{e}{a_0^2} \mathcal{E}',$$

and we subsequently drop the $'$ on atomic unit quantities. The matrix element we need is an exercise in elementary integrations. We have

$$\langle 200|r \cos \theta|210 \rangle = N_{20} N_{21} \int d\Omega \int r^2 dr \left(1 - \frac{r}{2}\right) \exp(-r/2) r (r \exp(-r/2)) \frac{\sqrt{3}}{4\pi} \cos^2 \theta = -3,$$

so

$$H'_{12} = H'_{21} = -3\mathcal{E}$$

Moving the matrix elements of H' to the left side of our equation, we have

$$\begin{pmatrix} E^{(1)} & 3\mathcal{E} \\ 3\mathcal{E} & E^{(1)} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0.$$

This only allows a non zero solution for c_1 and c_2 if the determinant of the coefficients vanishes, or

$$(E^{(1)})^2 - (3\mathcal{E})^2 = 0.$$

This gives the two eigenvalues

$$E^{(1)} = \pm 3\mathcal{E}.$$

These two values determine the amounts by which the $n = 2$ level is split by the external electric field. To determine the corresponding wave functions, we go back to the equations, with $E^{(1)}$ set equal to one of the eigenvalues. Taking first the lower eigenvalue, we have

$$E^{(1)} = -3\mathcal{E}, \quad \begin{pmatrix} -3\mathcal{E} & 3\mathcal{E} \\ 3\mathcal{E} & -3\mathcal{E} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0.$$

This gives

$$c_1 = c_2, \quad \Psi_- = \frac{1}{\sqrt{2}}[\Psi_{200} + \Psi_{210}],$$

where Ψ_- is now the correct unperturbed wave function corresponding to the lower eigenvalue. Said another way, the perturbing Hamiltonian has matrix element $-3\mathcal{E}$ in the state Ψ_- . Doing the same for the upper eigenvalue, we have

$$E^{(1)} = 3\mathcal{E}, \quad \begin{pmatrix} 3\mathcal{E} & 3\mathcal{E} \\ 3\mathcal{E} & 3\mathcal{E} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0,$$

which gives

$$c_1 = -c_2, \quad \Psi_+ = \frac{1}{\sqrt{2}}[\Psi_{200} - \Psi_{210}],$$

and Ψ_+ has $+3\mathcal{E}$ for the matrix element of the perturbed Hamiltonian. In writing Ψ_+ and Ψ_- , we have supplied the normalization factor $1/\sqrt{2}$. In atomic units, the states Ψ_{200} and Ψ_{210} with normalization factors supplied are

$$\Psi_{200} = R_{20}Y_0^0 = \frac{1}{\sqrt{2}}\left(1 - \frac{r}{2}\right)\exp\left(-\frac{r}{2}\right)\frac{1}{\sqrt{4\pi}},$$

and

$$\Psi_{210} = R_{21}Y_0^1 = \frac{1}{2\sqrt{6}}r\exp\left(-\frac{r}{2}\right)\sqrt{\frac{3}{4\pi}}\cos\theta$$

With these formulas the wave functions Ψ_+ and Ψ_- are easily constructed and their properties explored. This is done in more detail in Homework Set 2. The basic qualitative feature is that Ψ_- favors an increased electron density for $z < 0$ and a decreased electron density for $z > 0$ as expected for the effect of a force directed along the negative z axis.