11.7: Linear Stark Effect

Returning to the Stark effect, let us examine the effect of an external electric field on the energy levels of the $n=2$ states of a hydrogen atom. There are four such states: an $l=0$ state, usually referred to as $2S$, and three $l=1$ states (with $m=-1,0,1$), usually referred to as 2P. All of these states possess the same unperturbed energy, $E_{200}=-e^2/(32\pi\,\epsilon_0\,a_0)$. As before, the perturbing Hamiltonian is

$$H_1=e\,|\mathbf{E}|\,z. \tag{11.7.1}$$

According to the previously determined selection rules (i.e., $m'=m$, and $l'=l\pm 1$), this Hamiltonian couples ψ_{200} and ψ_{210}. Hence, non-degenerate perturbation theory breaks down when applied to these two states. On the other hand, non-degenerate perturbation theory works fine for the ψ_{211} and ψ_{21-1} states, because these are not coupled to any other $n=2$ states by the perturbing Hamiltonian.

In order to apply perturbation theory to the ψ_{200} and ψ_{210} states, we have to solve the matrix eigenvalue equation

$$\mathbf{U}\,\mathbf{x}=\lambda\,\mathbf{x}, \tag{11.7.2}$$

where $\mathbf{U}$ is the matrix of the matrix elements of H_1 between these states. Thus,

$$\mathbf{U}=e\,|\mathbf{E}|\begin{pmatrix} 0, & \langle 2,0,0|z|2,1,0\rangle \\ \langle 2,1,0|z|2,0,0\rangle, & 0\end{pmatrix}, \tag{11.7.3}$$

where the rows and columns correspond to ψ_{200} and ψ_{210}, respectively. Here, we have again made use of the selection rules, which tell us that the matrix element of z between two hydrogen atom states is zero unless the states possess l quantum numbers that differ by unity. It is easily demonstrated, from the exact forms of the 2S and 2P wavefunctions, that

$$\langle 2,0,0|z|2,1,0\rangle=\langle 2,1,0|z|2,0,0\rangle=3\,a_0. \tag{11.7.4}$$

It can be seen, by inspection, that the eigenvalues of $\mathbf{U}$ are $\lambda_1=3\,e\,a_0\,|\mathbf{E}|$ and $\lambda_2=-3\,e\,a_0\,|\mathbf{E}|$. The corresponding normalized eigenvectors are

$$\mathbf{x}_1=\begin{pmatrix}1/\sqrt{2}\\ 1/\sqrt{2}\end{pmatrix},$$
$$\mathbf{x}_2=\begin{pmatrix}1/\sqrt{2}\\ -1/\sqrt{2}\end{pmatrix}.$$

It follows that the simultaneous eigenstates of H_0 and H_1 take the form

$$\psi_1=\frac{\psi_{200}+\psi_{210}}{\sqrt{2}},$$
$$\psi_2=\frac{\psi_{200}-\psi_{210}}{\sqrt{2}}.$$

In the absence of an external electric field, both of these states possess the same energy, E_{200}. The first-order energy shifts induced by an external electric field are given by

$$\varDelta E_1=+3\,e\,a_0\,|\mathbf{E}|,$$
$$\varDelta E_2=-3\,e\,a_0\,|\mathbf{E}|.$$

Thus, in the presence of an electric field, the energies of states 1 and 2 are shifted upwards and downwards, respectively, by an amount $3\,e\,a_0\,|\mathbf{E}|$. These states are orthogonal linear combinations of the original ψ_{200} and ψ_{210} states. Note that the energy shifts are linear in the electric field-strength, so this effect—which is known as the *linear Stark effect*—is much larger than the quadratic effect described in Section 1.5. Note, also, that the energies of the ψ_{211} and ψ_{21-1} states are not affected by the electric field to first-order. Of course, to second-order the energies of these states are shifted by an amount which depends on the square of the electric field-strength. (See Section 1.5.)

Contributors and Attributions

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