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, \(\psi_{200}\) = \(-e^2/(32\pi\epsilon_0a_0)\). As before, the perturbing Hamiltonian is \(H_1 = e|\mathbf{E}|z\). According to the previously determined selection rules (i.e., \(m = m\'\)), this Hamiltonian couples \(\psi_{200}\) and \(\psi_{210}\). 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 \(\psi_{211}\) and \(\psi_{21-1}\) states, because these are not coupled to any other \(n=2\) states by the perturbing Hamiltonian.

In order to apply perturbation theory to the \(\psi_{200}\) and \(\psi_{210}\) states, we have to solve the matrix eigenvalue equation \(\mathbf{U}\mathbf{x} = \lambda\mathbf{x}\), where \(\mathbf{U}\) is the matrix of the matrix elements of \(H_1\) between these states. Thus, \(\mathbf{U} = e|\mathbf{E}|\left(\begin{array}{cc} 0, & \langle 2,0,0|z|2,1,0\rangle \\
\langle 2,1,0|z|2,0,0\rangle, & 0 \end{array}\right)\), where the rows and columns correspond to \(\psi_{200}\) and \(\psi_{210}\), 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 \(\langle 2,0,0|z|2,1,0\rangle = \langle 2,1,0|z|2,0,0\rangle = 3a_0\).

It can be seen, by inspection, that the eigenvalues of \(\mathbf{U}\) are \(\lambda_1 = 3e|\mathbf{E}|\) and \(\lambda_2 = -3e|\mathbf{E}|\). The corresponding normalized eigenvectors are \(\mathbf{x}_1 = \frac{1}{\sqrt{2}}\mathbf{a}_0\) and \(\mathbf{x}_2 = \frac{1}{\sqrt{2}}\mathbf{b}_0\). The simultaneous eigenstates of \(H_0\) and \(H_1\) take the form \(\psi_1 = \frac{\psi_{200} + \psi_{210}}{\sqrt{2}}\) and \(\psi_2 = \frac{\psi_{200} - \psi_{210}}{\sqrt{2}}\). 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
\[
\begin{aligned}
\Delta E_1 &= +3e a_0 |\mathbf{E}|, \\
\Delta E_2 &= -3e a_0 |\mathbf{E}|.
\end{aligned}
\]
Thus, in the presence of an electric field, the energies of states 1 and 2 are shifted upwards and downwards, respectively, by an amount \((3e a_0 |\mathbf{E}|)\). These states are orthogonal linear combinations of the original \((\psi_{200})\) and \((\psi_{210})\) 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 \((\psi_{211})\) and \((\psi_{21-1})\) 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.)

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**Contributors and Attributions**

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