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 \( \langle l=0 \rangle \) state, usually referred to as \( 2S \), and three \( \langle l=1 \rangle \) states (with \( m=-1,0,1 \)), usually referred to as 2P. All of these states possess the same unperturbed energy, \( \langle E \{ 200 \} \rangle = -e^2/(32 \pi \epsilon_0 a_0) \). As before, the perturbing Hamiltonian is \( \langle H_1 = e \langle \text{bf E} \rangle \cdot \text{z} \rangle \). According to the previously determined selection rules (i.e., \( m' = m \)), and \( \langle l'=l \pm 1 \rangle \), this Hamiltonian couples \( \langle \text{psi}_{\{ 200 \}} \rangle \) and \( \langle \text{psi}_{\{ 210 \}} \rangle \). 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 \( \langle \text{psi}_{\{ 211 \}} \rangle \) and \( \langle \text{psi}_{\{ 21-1 \}} \rangle \) states, because these are not coupled to any other \( \langle n=2 \rangle \) states by the perturbing Hamiltonian.

In order to apply perturbation theory to the \( \langle \text{psi}_{\{ 200 \}} \rangle \) and \( \langle \text{psi}_{\{ 210 \}} \rangle \) states, we have to solve the matrix eigenvalue equation \( \langle {\bf U} \rangle \langle {\bf x} \rangle = \lambda \langle {\bf x} \rangle \rangle \), where \( \langle {\bf U} \rangle \) is the matrix of the matrix elements of \( \langle H_1 \rangle \) between these states. Thus, \( \langle {\bf U} \rangle = e \langle {\bf E} \rangle \cdot \langle \text{left(begin \{array\} \{cc\} 0, & \langle l=0,0,0|2,1,0|2,0,0\rangle 0, & \langle l=1,0,0|2,0,0\rangle \end{array}\rangle \rangle \rangle \), where the rows and columns correspond to \( \langle \text{psi}_{\{ 200 \}} \rangle \) and \( \langle \text{psi}_{\{ 210 \}} \rangle \), respectively. Here, we have again made use of the selection rules, which tell us that the matrix element of \( \langle z \rangle \) between two hydrogen atom states is zero unless the states possess \( \langle l \rangle \) quantum numbers that differ by unity. It is easily demonstrated, from the exact forms of the 2S and 2P wavefunctions, that \( \langle \langle l=0,0,0|2,1,0|2,0,0\rangle \rangle \rangle = \langle \langle l=1,0,0|2,0,0\rangle \rangle = 3 a_0 \). It can be seen, by inspection, that the eigenvalues of \( \langle {\bf U} \rangle \) are \( \langle \text{lambda}_1 \rangle = 3 e a_0 \langle \text{bf E} \rangle \rangle \) and \( \text{lambda}_2 = -3 e a_0 \langle \text{bf E} \rangle \rangle \). The corresponding normalized eigenvectors are \( \langle \text{begin \{aligned\} \text{bf x}_1 & = \langle \text{left(begin \{array\} \{c\} 1/sqrt\{2\}\|0.5ex\} 1\langle l=0,0,0|2,1,0|2,0,0\rangle \end{array}\rangle \rangle \rangle \rangle \) and \( \langle \text{begin \{aligned\} \text{bf x}_2 & = \langle \text{left(begin \{array\} \{c\} 1/sqrt\{2\}\|0.5ex\} 1\langle l=0,0,0|2,0,0\rangle \end{array}\rangle \rangle \rangle \rangle \). It follows that the simultaneous eigenstates of \( \langle H_0 \rangle \) and \( \langle H_1 \rangle \) take the form \( \langle \text{begin \{aligned\} psi_1 & = \langle \text{frac\{psi\{200\}\} + psi\{210\}\{\sqrt\{2\}\}\rangle \rangle \rangle \rangle \rangle \) and \( \langle \text{begin \{aligned\} psi_2 & = \langle \text{frac\{psi\{200\}\} - psi\{210\}\{\sqrt\{2\}\}\rangle \rangle \rangle \rangle \rangle \rangle \). 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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