

6.2: The linear Stark Effect

As a more involved example of the level degeneracy lifting by a perturbation, let us discuss the Stark effect ⁶ - the atomic level splitting by an external electric field. Let us study this effect, in the linear approximation, for a hydrogen-like atom/ion. Taking the direction of the external electric field \mathcal{E} (which is practically always uniform on the atomic scale) for the z -axis, the perturbation may be represented by the following Hamiltonian:

$$\hat{H}^{(1)} = -F\hat{z} = -q\mathcal{E}\hat{z} = -q\mathcal{E}r\cos\theta. \quad (6.2.1)$$

(In the last form, the operator sign is dropped, because we will work in the coordinate representation.)

As you (should :-) remember, energy levels of a hydrogen-like atom/ion depend only on the principal quantum number n - see Eq. (3.201); hence all the states, besides the ground $1s$ state in which $n = 1$ and $l = m = 0$, have some orbital degeneracy, which grows rapidly with n . Let us consider the lowest degenerate level with $n = 2$. Since, according to Eq. (3.203), $0 \leq l \leq n - 1$, at this level the orbital quantum number l may equal either 0 (one $2s$ state, with $m = 0$) or 1 (three $2p$ states, with $m = 0, \pm 1$). Due to this 4-fold degeneracy, $\hat{H}^{(1)}$ is a 4×4 matrix with 16 elements:

$$\hat{H}^{(1)} = \begin{matrix} & \overbrace{m=0}^{l=0} & \overbrace{m=0, +1, -1}^{l=1} \\ \begin{matrix} m=0 \\ m=1 \end{matrix} & \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{pmatrix} & \begin{matrix} m=0, \\ m=0, \\ m=0, \end{matrix} \end{matrix} \quad (6.2.2)$$

However, there is no need to be scared. First, due to the Hermitian nature of the operator, only ten of these matrix elements (four diagonal and six off-diagonal ones) may be substantially different from each other. Moreover, due to a high symmetry of the problem, there are a lot of zeros even among these elements. Indeed, let us have a look at the angular components Y_l^m of the corresponding wavefunctions, with $l = 0$ and $l = 1$, described by Eqs. (3.174)-(3.175). For the states with $m = \pm 1$, the azimuthal parts of wavefunctions are proportional to $\exp\{\pm i\varphi\}$; hence the off-diagonal elements H_{34} and H_{43} of the matrix (30), relating these functions, are proportional to

$$\oint d\Omega Y_1^{\pm*} \hat{H}^{(1)} Y_1^{\mp} \propto \int_0^{2\pi} d\varphi (e^{\pm i\varphi})^* (e^{\mp i\varphi}) = 0. \quad (6.2.3)$$

The azimuthal-angle symmetry also kills the off-diagonal elements $H_{13}, H_{14}, H_{23}, H_{24}$ (and hence their complex conjugates $H_{31}, H_{41}, H_{32}, H_{42}$), because they relate states with $m = 0$ and $m = \pm 1$, and hence are proportional to

$$\oint d\Omega Y_1^{0*} \hat{H}^{(1)} Y_1^{\pm 1} \propto \int_0^{2\pi} d\varphi e^{\pm i\varphi} = 0 \quad (6.2.4)$$

For the diagonal matrix elements H_{33} and H_{44} , corresponding to $l = 1$ and $m = \pm 1$, the azimuthal-angle integrals do not vanish, but since the corresponding spherical functions depend on the polar angle as $\sin\theta$, these elements are proportional to

$$\oint d\Omega Y_1^{\pm 1*} \hat{H}^{(1)} Y_1^{\pm 1} \propto \int_0^\pi \sin\theta d\theta \sin\theta \cos\theta \sin\theta = \int_{-1}^{+1} \cos\theta (1 - \cos^2\theta) d(\cos\theta), \quad (6.2.5)$$

and hence are equal to zero - as any limit-symmetric integral of an odd function. Finally, for the states $2s$ and $2p$ with $m = 0$, the diagonal elements H_{11} and H_{22} are also killed by the polar-angle integration:

$$\begin{aligned} \oint d\Omega Y_0^{0*} \hat{H}^{(1)} Y_0^0 &\propto \int_0^\pi \sin\theta d\theta \cos\theta = \int_{-1}^1 \cos\theta d(\cos\theta) = 0, \\ \oint d\Omega Y_0^{1*} \hat{H}^{(1)} Y_0^1 &\propto \int_0^\pi \sin\theta d\theta \cos^3\theta = \int_{-1}^{+1} \cos^3\theta d(\cos\theta) = 0. \end{aligned}$$

Hence, the only non-zero elements of the matrix (30) are two off-diagonal elements H_{12} and H_{21} , which relate two states with the same $m = 0$, but different $l = \{0, 1\}$, because they are proportional to

$$\oint d\Omega Y_0^{0*} \cos \theta Y_1^0 = \frac{\sqrt{3}}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \cos^2 \theta = \frac{1}{\sqrt{3}} \neq 0. \quad (6.2.6)$$

What remains is to use Eqs. (3.209) for the radial parts of these functions to complete the calculation of those two matrix elements:

$$H_{12} = H_{21} = -\frac{q\mathcal{E}}{\sqrt{3}} \int_0^\infty r^2 dr R_{2,0}(r) r R_{2,1}(r). \quad (6.2.7)$$

Due to the additive structure of the function $R_{2,0}(r)$, the integral falls into a sum of two table integrals, both of the type MA Eq. (6.7d), finally giving

$$H_{12} = H_{21} = 3q\mathcal{E}r_0, \quad (6.2.8)$$

where r_0 is the spatial scale (3.192); for the hydrogen atom, it is just the Bohr radius r_B - see Eq. (1.10).

Thus, the perturbation matrix (30) is reduced to

$$\mathbf{H}^{(1)} = \begin{pmatrix} 0 & 3q\mathcal{E}r_0 & 0 & 0 \\ 3q\mathcal{E}r_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (6.2.9)$$

so that the condition (26) of self-consistency of the system (25),

$$\begin{vmatrix} -E_2^{(1)} & 3q\mathcal{E}r_0 & 0 & 0 \\ 3q\mathcal{E}r_0 & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = 0 \quad (6.2.10)$$

gives a very simple characteristic equation

$$\left(E_2^{(1)}\right)^2 \left[\left(E_2^{(1)}\right)^2 - (3q\mathcal{E}r_0)^2 \right] = 0. \quad (6.2.11)$$

with four roots:

$$\left(E_2^{(1)}\right)_{1,2} = 0, \quad \left(E_2^{(1)}\right)_{3,4} = \pm 3q\mathcal{E}r_0. \quad (6.2.12)$$

so that the degeneracy is only partly lifted - see the levels in Fig. 3. 7

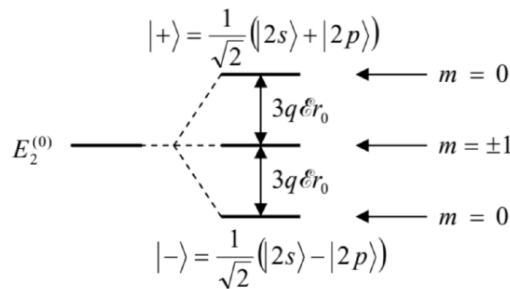


Fig. 6.3. The linear Stark effect for the level $n = 2$ of a hydrogen-like atom.

Generally, in order to understand the nature of states corresponding to these levels, we should return to Eq. (25) with each calculated value of $E_2^{(1)}$, and find the corresponding expansion coefficients $\langle n''^{(0)} | n' \rangle$ that describe the perturbed states. However, in our simple case, the outcome of this procedure is clear in advance. Indeed, since the states with $\{l = 1, m = \pm 1\}$ are not affected by the perturbation at all (in the linear approximation in the electric field), their degeneracy is not lifted, and energy is not affected - see the middle line in Fig. 3. On the other hand, the partial perturbation matrix connecting the states $2s$ and $2p$, i.e. the top left 2×2 part of the full matrix (39), is proportional to the Pauli matrix σ_x , and we already know the result of its diagonalization - see Eqs. (4.113)-(4.114). This means that the upper and lower split levels correspond to very simple linear combinations of the previously degenerate states with $m = 0$,

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|2s\rangle \pm |2p\rangle). \quad (6.2.13)$$

Finally, let us estimate the magnitude of the linear Stark effect for a hydrogen atom. For a very high electric field of $\mathcal{E} = 3 \times 10^6 \text{ V/m}$, ⁸ $|q| = e \approx 1.6 \times 10^{-19} \text{ C}$, and $r_0 = r_B \approx 0.5 \times 10^{-10} \text{ m}$, we get a level splitting of $3q\delta r_0 \approx 0.8 \times 10^{-22} \text{ J} \approx 0.5 \text{ meV}$. This number is much lower than the unperturbed energy of the level, $E_2 = -E_H / (2 \times 2^2) \approx -3.4 \text{ eV}$, so that the perturbative result is quite applicable. On the other hand, the calculated splitting is much larger than the resolution limit imposed by the line's natural width ($\sim 10^{-7} E_2$, see Chapter 9), so that the effect is quite observable even in substantially lower electric fields. Note, however, that our simple results are quantitatively correct only when the Stark splitting (42) is much larger than the fine-structure splitting of the same level in the absence of the field- see the next section.

⁶ This effect was discovered experimentally in 1913 by Johannes Stark and independently by Antonio Lo Surdo, so it is sometimes (and more fairly) called the "Stark - Lo Surdo effect". Sometimes this name is used with the qualifier "dc" to distinguish it from the *ac* Stark effect - the energy level shift under the effect of an ac field - see Sec. 5 below.

⁷ The proportionality of this splitting to the small field is responsible for the qualifier "linear" in the name of this effect. If observable effects grow only as ε^2 (see, e.g., Problem 9), the term quadratic Stark effect is used instead.

⁸ This value approximately corresponds to the threshold of electric breakdown in air at ambient conditions, due to the impact ionization. As a result, experiments with higher dc fields are rather difficult.

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