

11.5: Quadratic Stark Effect

Suppose that a hydrogen atom is subject to a uniform external electric field, of magnitude $|\mathbf{E}|$, directed along the z -axis. The Hamiltonian of the system can be split into two parts. Namely, the unperturbed Hamiltonian,

$$H_0 = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r}, \quad (11.5.1)$$

and the perturbing Hamiltonian

$$H_1 = e|\mathbf{E}|z. \quad (11.5.2)$$

Note that the electron spin is irrelevant to this problem (because the spin operators all commute with H_1), so we can ignore the spin degrees of freedom of the system. Hence, the energy eigenstates of the unperturbed Hamiltonian are characterized by three quantum numbers—the radial quantum number n , and the two angular quantum numbers l and m . (See Chapter [\[scent\]](#).) Let us denote these states as the ψ_{nlm} , and let their corresponding energy eigenvalues be the E_{nlm} . According to the analysis in the previous section, the change in energy of the eigenstate characterized by the quantum numbers n, l, m in the presence of a small electric field is given by

$$\begin{aligned} \Delta E_{nlm} = & e|\mathbf{E}| \langle n, l, m | z | n, l, m \rangle \\ & + e^2 |\mathbf{E}|^2 \sum_{n', l', m' \neq n, l, m} \frac{|\langle n, l, m | z | n', l', m' \rangle|^2}{E_{nlm} - E_{n'l'm'}}. \end{aligned}$$

This energy-shift is known as the *Stark effect*.

The sum on the right-hand side of the previous equation seems very complicated. However, it turns out that most of the terms in this sum are zero. This follows because the matrix elements $\langle n, l, m | z | n', l', m' \rangle$ are zero for virtually all choices of the two sets of quantum number, n, l, m and n', l', m' . Let us try to find a set of rules that determine when these matrix elements are non-zero. These rules are usually referred to as the *selection rules* for the problem in hand.

Now, because [see Equation ([\[e8.3\]](#))]

$$L_z = x p_y - y p_x, \quad (11.5.3)$$

it follows that [see Equations ([\[commxx\]](#))–([\[commxp\]](#))]

$$[L_z, z] = 0. \quad (11.5.4)$$

Thus,

$$\begin{aligned} \langle n, l, m | [L_z, z] | n', l', m' \rangle &= \langle n, l, m | L_z z - z L_z | n', l', m' \rangle \\ &= \hbar(m - m') \langle n, l, m | z | n', l', m' \rangle = 0, \end{aligned}$$

because ψ_{nlm} is, by definition, an eigenstate of L_z corresponding to the eigenvalue $m\hbar$. Hence, it is clear, from the previous equation, that one of the selection rules is that the matrix element $\langle n, l, m | z | n', l', m' \rangle$ is zero unless

$$m' = m. \quad (11.5.5)$$

Let us now determine the selection rule for l . We have

$$\begin{aligned} &= [L_x^2, z] + [L_y^2, z] \\ &= L_x [L_x, z] + [L_x, z] L_x + L_y [L_y, z] + [L_y, z] L_y \\ &= i\hbar(-L_x y - y L_x + L_y x + x L_y) \\ &= 2i\hbar(L_y x - L_x y + i\hbar z) \\ &= 2i\hbar(L_y x - y L_x) = 2i\hbar(x L_y - L_x y), \end{aligned}$$

where use has been made of Equations ([\[commxx\]](#))–([\[commxp\]](#)), ([\[e8.1\]](#))–([\[e8.3\]](#)), and ([\[e8.10\]](#)). Thus,

$$\begin{aligned}
] &= 2i\hbar (L^2, L_y x - L_x y + i\hbar z) \\
 &= 2i\hbar (L_y [L^2, x] - L_x [L^2, y] + i\hbar [L^2, z]) \\
 &= -4\hbar^2 L_y (y L_z - L_y z) + 4\hbar^2 L_x (L_x z - x L_z) \\
 &\quad - 2\hbar^2 (L^2 z - z L^2),
 \end{aligned}$$

which reduces to

$$\begin{aligned}
] &= -\hbar^2 \{4(L_x x + L_y y + L_z z) L_z - 4(L_x^2 + L_y^2 + L_z^2) z \\
 &\quad + 2(L^2 z - z L^2)\} \\
 &= -\hbar^2 \{4(L_x x + L_y y + L_z z) L_z - 2(L^2 z + z L^2)\}.
 \end{aligned}$$

However, it is clear from Equations ([e8.1])–([e8.3]) that

$$L_x x + L_y y + L_z z = 0. \quad (11.5.6)$$

Hence, we obtain

$$[L^2, [L^2, z]] = 2\hbar^2 (L^2 z + z L^2). \quad (11.5.7)$$

Finally, the previous expression expands to give

$$L^4 z - 2L^2 z L^2 + z L^4 - 2\hbar^2 (L^2 z + z L^2) = 0. \quad (11.5.8)$$

Equation ([e12.69]) implies that

$$\langle n, l, m | L^4 z - 2L^2 z L^2 + z L^4 - 2\hbar^2 (L^2 z + z L^2) | n', l', m \rangle = 0. \quad (11.5.9)$$

Because, by definition, ψ_{nlm} is an eigenstate of L^2 corresponding to the eigenvalue $l(l+1)\hbar^2$, this expression yields

$$\begin{aligned}
 \{l^2(l+1)^2 - 2l(l+1)l'(l'+1) + l'^2(l'+1)^2 \\
 - 2l(l+1) - 2l'(l'+1)\} \langle n, l, m | z | n', l', m \rangle = 0,
 \end{aligned}$$

which reduces to

$$(l+l'+2)(l+l')(l-l'+1)(l-l'-1) \langle n, l, m | z | n', l', m \rangle = 0. \quad (11.5.10)$$

According to the previous formula, the matrix element $\langle n, l, m | z | n', l', m \rangle$ vanishes unless $l = l' = 0$ or $l' = l \pm 1$. [Of course, the factor $l+l'+2$, in the previous equation, can never be zero, because l and l' can never be negative.] Recall, however, from Chapter [scent], that an $l = 0$ wavefunction is spherically symmetric. It, therefore, follows, from symmetry, that the matrix element $\langle n, l, m | z | n', l', m \rangle$ is zero when $l = l' = 0$. In conclusion, the selection rule for l is that the matrix element $\langle n, l, m | z | n', l', m \rangle$ is zero unless

$$l' = l \pm 1. \quad (11.5.11)$$

Application of the selection rules ([e12.63]) and ([e12.73]) to Equation ([e12.59]) yields

$$\Delta E_{nlm} = e^2 |\mathbf{E}|^2 \sum_{n', l' = l \pm 1} \frac{|\langle n, l, m | z | n', l', m \rangle|^2}{E_{nlm} - E_{n'l'm}}. \quad (11.5.12)$$

Note that, according to the selection rules, all of the terms in Equation ([e12.59]) that vary linearly with the electric field-strength vanish. Only those terms which vary quadratically with the field-strength survive. Hence, this type of energy-shift of an atomic state in the presence of a small electric field is known as the *quadratic Stark effect*. Now, the *electric polarizability* of an atom is defined in terms of the energy-shift of the atomic state as follows :

$$\Delta E = -\frac{1}{2} \alpha |\mathbf{E}|^2. \quad (11.5.13)$$

Hence, we can write

$$\alpha_{nlm} = 2e^2 \sum_{n', l' = l \pm 1} \frac{|\langle n, l, m | z | n', l', m \rangle|^2}{E_{n'l'm} - E_{nlm}}. \quad (11.5.14)$$

Unfortunately, there is one fairly obvious problem with Equation (11.5.14). Namely, it predicts an infinite energy-shift if there exists some non-zero matrix element $\langle n, l, m | z | n', l', m \rangle$ that couples two degenerate unperturbed energy eigenstates: that is, if $\langle n, l, m | z | n', l', m \rangle \neq 0$ and $E_{nlm} = E_{n'l'm}$. Clearly, our perturbation method breaks down completely in this situation. Hence, we conclude that Equations (11.5.14) and (11.5.16) are only applicable to cases where the coupled eigenstates are non-degenerate. For this reason, the type of perturbation theory employed here is known as *non-degenerate perturbation theory*. The unperturbed eigenstates of a hydrogen atom have energies that only depend on the radial quantum number n . (See Chapter 9.) It follows that we can only apply the previous results to the $n = 1$ eigenstate (because for $n > 1$ there will be coupling to degenerate eigenstates with the same value of n but different values of l).

Thus, according to non-degenerate perturbation theory, the polarizability of the ground-state (i.e., $n = 1$) of a hydrogen atom is given by

$$\alpha = 2e^2 \sum_{n>1} \frac{|\langle 1, 0, 0 | z | n, 1, 0 \rangle|^2}{E_{n00} - E_{100}}. \quad (11.5.15)$$

Here, we have made use of the fact that $E_{n10} = E_{n00}$. The sum in the previous expression can be evaluated approximately by noting that (see Section 10.4)

$$E_{n00} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}, \quad (11.5.16)$$

where

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \quad (11.5.17)$$

is the Bohr radius. Hence, we can write

$$E_{n00} - E_{100} \geq E_{200} - E_{100} = \frac{3}{4} \frac{e^2}{8\pi\epsilon_0 a_0}, \quad (11.5.18)$$

which implies that

$$\alpha < \frac{16}{3} 4\pi\epsilon_0 a_0 \sum_{n>1} |\langle 1, 0, 0 | z | n, 1, 0 \rangle|^2. \quad (11.5.19)$$

However, [see Equation (11.5.20)]

$$\begin{aligned} \sum_{n>1} |\langle 1, 0, 0 | z | n, 1, 0 \rangle|^2 &= \sum_{n>1} \langle 1, 0, 0 | z | n, 1, 0 \rangle \langle n, 1, 0 | z | 1, 0, 0 \rangle \\ &= \sum_{n', l', m'} \langle 1, 0, 0 | z | n', l', m' \rangle \langle n', l', m' | z | 1, 0, 0 \rangle \\ &= \langle 1, 0, 0 | z^2 | 1, 0, 0 \rangle = \frac{1}{3} \langle 1, 0, 0 | r^2 | 1, 0, 0 \rangle, \end{aligned}$$

where we have made use of the selection rules, the fact that the $\psi_{n', l', m'}$ form a complete set, and the fact the the ground-state of hydrogen is spherically symmetric. Finally, it follows from Equation (9.73) that

$$\langle 1, 0, 0 | r^2 | 1, 0, 0 \rangle = 3a_0^2. \quad (11.5.20)$$

Hence, we conclude that

$$\alpha < \frac{16}{3} 4\pi\epsilon_0 a_0^3 \simeq 5.3 \cdot 4\pi\epsilon_0 a_0^3. \quad (11.5.21)$$

The exact result (which can be obtained by solving Schrödinger's equation in parabolic coordinates) is

$$\alpha = \frac{9}{2} 4\pi \epsilon_0 a_0^3 = 4.5 \ 4\pi \epsilon_0 a_0^3. \quad (11.5.22)$$

Contributors and Attributions

- [Richard Fitzpatrick](#) (Professor of Physics, The University of Texas at Austin)

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