Reconciliation of experimental and theoretical electric tensor polarizabilities of the cesium ground state

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Abstract. – We present a new theoretical analysis of the strongly suppressed F- and M-dependent Stark shifts of the Cs ground-state hyperfine structure. Our treatment uses third-order perturbation theory including off-diagonal hyperfine interactions not considered in earlier treatments. A numerical evaluation of the perturbation sum using bound states up to $n = 200$ yields ground-state tensor polarizabilities $\alpha_2(6S_{1/2}, F)$ which are in good agreement with experimental values, thereby bridging the 40-year-old gap between experiments and theory. We have further found that the tensor polarizabilities of the two ground-state hyperfine manifolds have opposite signs, in disagreement with an earlier derivation. This sign error has a direct implication for the precise evaluation of the blackbody radiation shift in primary frequency standards.

Introduction. – Since its discovery, the Stark effect, *i.e.*, the interaction of an atom with an external electric field $\mathbb{E}$, has played an important role in the spectroscopic investigation of atomic structure. Because of parity conservation, the Stark effect arises only in second-order perturbation theory for atoms with non-degenerate orbital angular-momentum states. The energy shift $\Delta E(\gamma)$ of a magnetic sublevel $|\gamma\rangle = |nL_J, F, M\rangle$ of the hyperfine structure is conventionally parametrized in terms of a polarizability $\alpha(\gamma)$ as

$$\Delta E(\gamma) = -\frac{1}{2}\,\alpha(\gamma)\,\mathbb{E}^2\,. \tag{1}$$

In second-order perturbation theory the polarizability can be decomposed [1] into a scalar polarizability, $\alpha_0^{(2)}$, which leads to an F- and M-independent level shift, and a tensor polarizability, $\alpha_2^{(2)}$, which yields F- and M-dependent energy shifts. Because of rotational symmetry, the tensor polarizability vanishes for the spherical $nS_{1/2}$ and $nP_{1/2}$ states in the alkalis. As a consequence, the second-order Stark effect in the alkali ground state does not affect its hyperfine splitting, nor does it lift the Zeeman degeneracy of a given hyperfine level. However, Haun and Zacharias observed already in 1957 [2] that a static electric field does induce a quadratic Stark shift of the hyperfine transition frequency (F-dependent Stark effect), and in

1964, Lipworth and Sandars [3] demonstrated that a static electric field also lifts the Zeeman degeneracy within the $F = 4$ sublevel manifold of the cesium ground state (an $|M|$-dependent effect). Improved measurements were performed later by Carrico *et al.* [4] and Gould *et al.* [5], and were recently confirmed by our own measurements [6–8]. In 1967, Sandars [9] showed that the F- and $|M|$-dependence of the Stark effect can be explained when the perturbation theory is extended to third order after including the hyperfine interaction. His theoretical expressions for the third-order tensor polarizabilties $\alpha_2^{(3)}$ were evaluated numerically in [3] and [5] under simplifying assumptions. This yielded (absolute) values which were systematically larger than the experimental values for the five investigated alkali isotopes [5]. It is worth noting that in cesium the level shifts due to $\alpha_2^{(3)}$ are almost seven orders of magnitude smaller than the common shift of the ground-state levels due to the second-order scalar polarizability $\alpha_0^{(2)}$. While the scalar Stark shift is understood at a level of $(1–2) \cdot 10^{-3}$ [10–12], there has so far been no satisfactory theoretical description of the tensor polarizabilities, *i.e.*, of the $|M|$-dependent alterations of the scalar effect.

In this paper we extend the previous theoretical treatment of the third-order effects by including both diagonal and off-diagonal hyperfine interactions in the perturbation expansion. The numerical evaluation of the perturbation sum then yields a value of the Cs ground state tensor polarizability $\alpha_2(6S_{1/2}, F = 4)$ which is in very good agreement with the experimental results [4–8], thereby bridging the 40-year-old gap [8] between experiments and theory. We have also identified an error in Sandars' results [9] concerning the relative sign of the tensor polarizabilities of the two ground-state hyperfine levels. We discuss the relevance of this sign error for the determination of the blackbody radiation shift of primary frequency standards from measurements of the static Stark shift of the Cs clock frequency.

Theoretical model. – As shown by Sandars [9], the F- and M-dependent Stark shifts can be explained by a third-order perturbation treatment, in which the Stark interaction, $\mathrm{H_{St}} = -\vec{d}\cdot\vec{\mathbb{E}}$, and the dipole-dipole ($\mathrm{H_{hf}^d}$) and electric-quadrupole ($\mathrm{H_{hf}^q}$) hyperfine interactions, are treated on an equal footing. The contributions of $\mathrm{H_{St}}$ and $\mathrm{H_{hf}} = \mathrm{H_{hf}^d} + \mathrm{H_{hf}^q}$ can be expressed in terms of irreducible tensor operators

$$\mathrm{H_{St}} = |e|\, r\, \boldsymbol{C}^{(1)} \cdot \boldsymbol{E}^{(1)}, \tag{2}$$

$$\mathrm{H_{hf}^d} = \left(a_{l,j} \left\{ \boldsymbol{L}^{(1)} - \sqrt{10}\big[\boldsymbol{C}^{(2)} \times \boldsymbol{S}^{(1)}\big]^{(1)} \right\} + a_s \boldsymbol{S}^{(1)} \right) \cdot \boldsymbol{I}^{(1)}, \tag{3}$$

$$\mathrm{H_{hf}^q} = b_Q \boldsymbol{C}^{(2)} \cdot \big[\boldsymbol{I}^{(1)} \times \boldsymbol{I}^{(1)}\big]^{(2)}, \tag{4}$$

where $\boldsymbol{L}$, $\boldsymbol{S}$, and $\boldsymbol{I}$ are vector operators associated with the orbital angular momentum, the electronic spin, and the nuclear spin, respectively, and where the $\boldsymbol{C}^{(k)}$ are normalized spherical harmonics of rank k. The first and second terms of eq. (3) represent the magnetic interaction of the nuclear magnetic moment with the orbital and electron spin dipole moments, respectively (dipole-dipole interactions), while the third term represents the Fermi contact interaction and eq. (4) is the electric-quadrupole interaction. The corresponding coupling constants are $a_{l,j}$, a_s, and b_Q. The contact interaction term has non-zero matrix elements between S-states ($L = 0$) only, while the first two terms of eq. (3) apply to states with $L > 0$. The electric-quadrupole term of eq. (4) requires $L > 1$ and $J > 1$, and for Cs $nP_{3/2}$ states its matrix elements are two orders of magnitude smaller than all other contributions.

The third-order energy perturbation of the sublevel $|\alpha\rangle = |6S_{1/2}, F, M\rangle$ is given by

$$\Delta E^{(3)}(\alpha) = \sum_{\beta \neq \alpha, \gamma \neq \alpha} \frac{\langle\alpha|\, W\, |\beta\rangle\, \langle\beta|\, W\, |\gamma\rangle\, \langle\gamma|\, W\, |\alpha\rangle}{(E_\alpha - E_\beta)(E_\alpha - E_\gamma)} - \langle\alpha|\, W\, |\alpha\rangle \sum_{\beta \neq \alpha} \frac{|\langle\beta|\, W\, |\alpha\rangle|^2}{(E_\alpha - E_\beta)^2}, \tag{5}$$
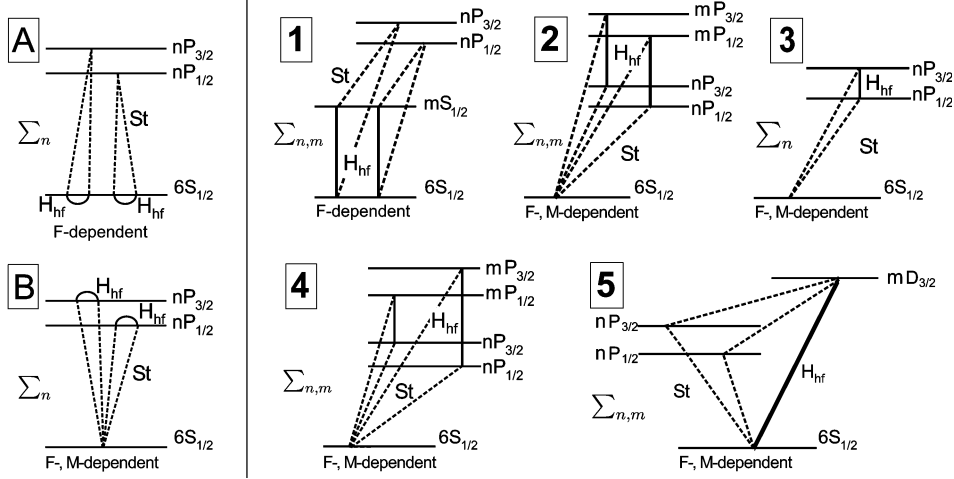
Fig. 1 – Contributions of diagonal (**A** and **B**) and off-diagonal (**1**–**5**) hyperfine matrix elements to the third-order Stark effect. Dotted/solid lines represent the Stark and hyperfine interactions, respectively. The relative contributions of the diagrams are given in the text.

where E_β and E_γ are the unperturbed state energies. Of all the terms obtained by substituting $W = \mathrm{H_{St}} + \mathrm{H_{hf}}$ into eq. (5) only those proportional to $\mathbb{E}^2$ give nonzero contributions to the Stark interaction, and the sums have to be carried out over all states according to the selection rules imposed by the operators.

We first address the second term of eq. (5), whose only non-vanishing contribution is

$$- \langle \alpha | \, \mathrm{H_{hf}} \, | \alpha \rangle \sum_{\beta \neq \alpha} \frac{|\langle \beta | \, \mathrm{H_{St}} \, | \alpha \rangle|^2}{(E_\alpha - E_\beta)^2} \equiv -E_{\mathrm{hf}}(\alpha) \sum_{\beta \neq \alpha} \frac{|\langle \beta | \, \mathrm{H_{St}} \, | \alpha \rangle|^2}{(E_\alpha - E_\beta)^2} \, , \qquad (6)$$

where $|\beta\rangle = |nP_j, f, m\rangle$. Diagram **A** of fig. 1 shows a graphical representation of this term in which the Fermi ground-state contact interaction appears as a multiplicative factor, making this contribution F-dependent. Comparing the sum in eq. (6) to the expression

$$\Delta E^{(2)}(\alpha) = \sum_{\beta \neq \alpha} \frac{|\langle \beta | \, \mathrm{H_{St}} \, | \alpha \rangle|^2}{E_\alpha - E_\beta} \, , \qquad (7)$$

for the second-order scalar Stark effect, one sees that the F-dependent third-order shift is suppressed by a factor on the order of $E_{\mathrm{hf}}(6S)/(E_{6P} - E_{6S}) \approx 10^{-5}$. Following the definition of eq. (1) the contribution of eq. (6) can be parametrized in terms of an F-dependent third-order scalar polarizability $\alpha_0^{(3)}(6S_{1/2}, F)$. This F-dependent term gives the main contribution to the Stark shift of the hyperfine transition frequency.

We next address the first term of eq. (5). The nonvanishing contributions involving *diagonal* matrix elements of $\mathrm{H_{hf}}$ are given by

$$\sum_{\beta \neq \alpha} \langle \beta | \, \mathrm{H_{hf}} \, | \beta \rangle \frac{|\langle \beta | \, \mathrm{H_{St}} \, | \alpha \rangle|^2}{(E_\alpha - E_\beta)^2} \equiv \sum_{\beta \neq \alpha} E_{\mathrm{hf}}(\beta) \frac{|\langle \beta | \, \mathrm{H_{St}} \, | \alpha \rangle|^2}{(E_\alpha - E_\beta)^2} \, , \qquad (8)$$

where $|\beta\rangle = |nP_j, f, m\rangle$. They are represented by diagram **B** of fig. 1 and are suppressed by a factor on the order of $E_{\mathrm{hf}}(6P)/(E_{6P} - E_{6S}) \approx 10^{-7}$ with respect to the second-order

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scalar shifts. The electric-field–dependent factor of eq. (8) has only a rank $k = 0$ (scalar) contribution, while the dipole-dipole (eq. (3)) and the electric-quadrupole (eq. (4)) parts of the H_{hf} factor in eq. (8) have the rotational symmetries of $k = 0, 2$ and $k = 2$ tensors, respectively. The contraction of the hyperfine and the Stark interactions in eq. (8) thus yields both scalar and second-rank tensor contributions. The scalar part of eq. (8) has the same F-dependence [8] as $\alpha_0^{(3)}(F)$, and gives a correction to the latter on the order of 1%, while the second-rank tensor part has an F- and M-dependence, which can be parametrized in terms of a third-order tensor polarizability $\alpha_2^{(3)}(6S_{1/2}, F)$.

The total third-order polarizability can thus be written as

$$\alpha^{(3)}(6S_{1/2}, F, M) = \alpha_0^{(3)}(6S_{1/2}, F) + \alpha_2^{(3)}(6S_{1/2}, F)\frac{3M^2 - F(F+1)}{2I(2I + 1)}f(\theta), \qquad (9)$$

where the dependence on the angle θ between the electric field and the quantization axis is given by $f(\theta) = 3\cos^2\theta - 1$. Equations (6), (8) can be reduced by applying the Wigner-Eckart theorem and angular-momentum decoupling rules. For cesium ($I = 7/2$) the explicit F- and M-dependences of the third-order polarizabilities for $\theta = 0$ are

$$\alpha^{(3)}(F = 4, M) = a_0 + (a_1 + a_2)\frac{3M^2 - 20}{28}, \qquad (10a)$$

$$\alpha^{(3)}(F = 3, M) = -\frac{9}{7}a_0 + \left(-a_1 + \frac{5}{3}a_2\right)\frac{3M^2 - 12}{28}. \qquad (10b)$$

The scalar part can be expressed in terms of radial integrals

$$a_0 = \frac{7}{54}\sum_n \left[\mathcal{C}_{nP_{1/2}}\left(3A_{6S_{1/2}} + A_{nP_{1/2}}\right) + 2\mathcal{C}_{nP_{3/2}}\left(3A_{6S_{1/2}} - 5A_{nP_{3/2}}\right)\right], \qquad (11)$$

where $A_{6S_{1/2}}$ and A_{nP_j} are the hyperfine coupling constants and where

$$\mathcal{C}_{nP_j} = \frac{e^2\left|R_{6S,nP_j}\right|^2}{\left(E_{6S_{1/2}} - E_{nP_j}\right)^2}. \qquad (12)$$

R_{6S,nP_j} is the radial integral between the ground state and the excited $|nP_j\rangle$ state. The Fermi-contact interaction (proportional to $A_{6S_{1/2}}$) provides the dominant contribution to a_0 which, as mentioned, also has a small contribution (proportional to A_{nP_j}) from the scalar part of the magnetic-dipole interactions. Equations (6) and (8) can be expressed in a similar way as

$$a_1 = -\frac{7}{54}\sum_n \left[\left(2A_{nP_{1/2}}\mathcal{C}_{nP_{1/2}} - 5A_{nP_{3/2}}\mathcal{C}_{nP_{3/2}}\right) + \left(2A_{nP_{1/2}}\mathcal{C}_{nP_{1/2}} + A_{nP_{3/2}}\mathcal{C}_{nP_{3/2}}\right)\right], \quad (13)$$

where we have explicitly separated the contribution of the orbital part of the interaction (first term) from that of the spin dipolar part (second term), and

$$a_2 = \frac{1}{9}\sum_n B_{nP_{3/2}}\mathcal{C}_{nP_{3/2}}, \qquad (14)$$

where $B_{nP_{3/2}}$ is the quadrupole hyperfine coupling constant.

Equations (10) closely resemble the expressions derived by Sandars [9], except for the negative sign of the a_1 term in eq. (10b) which is positive in Sandars' work. To our knowledge, this sign cannot be derived from any prior experiment. We have recently confirmed experimentally [7] that the tensor polarizabilities of the $F = 3$ and $F = 4$ states have indeed opposite signs as predicted by our calculation. This sign error has remained unnoticed in the literature for almost 40 years and we will come back to its relevance for atomic clocks below.
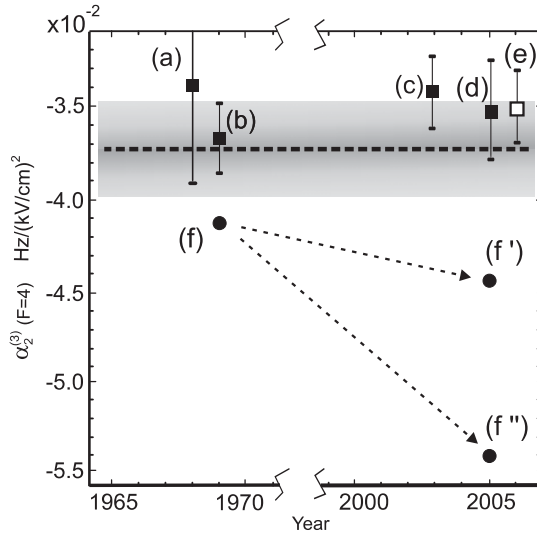
Fig. 2 – The third-order tensor polarizability of the $F = 4$ Cs ground state. The filled squares (■) represent experimental values of Carrico *et al.* [4] (a), Gould *et al.* [5] (b), Ospelkaus *et al.* [6] (c) and Ulzega *et al.* [7] (d). The empty square (□) (e) represents their weighted average. The dots (●) represent the theoretical value from [5] (f), and our re-evaluations (f′, f″) discussed in the text. The dashed horizontal line is the result of the present work with its uncertainty (shaded band).

Numerical evaluation of the tensor polarizability. – The tensor polarizability (a_1-term) of the $F = 4$ state of cesium was evaluated in [5] by considering only diagonal matrix elements of H_{hf} for the $6S_{1/2}$ and the $6P_J$ states. The contribution of the orbital magnetic-dipole hyperfine interaction (first term in eq. (13)) was neglected, as well as the spin-orbit splitting in the denominators of eq. (5). The authors assumed furthermore that $A_{6P_{1/2}}/A_{6P_{3/2}} = 5$, valid for one-electron atoms, while for Cs the corresponding ratio of experimental values is 5.8. Under the latter two approximations one can factor the second-order scalar polarizability $\alpha_0^{(2)}$ out of the expression for the tensor polarizability. Those simplifying assumptions yielded the $\alpha_2^{(3)}(F = 4)$ value represented as point (f) in fig. 2, in disagreement with the experimental results. We have re-evaluated the result by including the orbital part of the hyperfine interaction and then rescaling the value of [5] by using the most recent experimental value of $\alpha_0^{(2)}$ [10]. This yields the value (f′) in fig. 2, thus increasing the gap between theory and experiments. In a second, more precise, calculation we dropped all the simplifying assumptions mentioned above [8], still keeping diagonal matrix elements only, and numerically evaluated eqs. (13), (14) by using recent experimental values [13] of the reduced dipole matrix elements $\langle 6S_{1/2} \parallel d \parallel 6P_J \rangle$. As a result, the discrepancy with experiments becomes even larger (point (f″) in fig. 2), and does not change significantly when extending the perturbation sum to nP_J states with $n > 6$.

Off-diagonal hyperfine interaction. – All calculations described above considered only diagonal hyperfine matrix elements. However, the first term in eq. (5) allows also off-diagonal hyperfine terms. Figure 1 gives a schematic overview of all possible off-diagonal configurations compatible with the hyperfine and Stark operator selection rules. It is interesting to note that some off-diagonal hyperfine matrix elements (diagrams **1** and **2**, fig. 1) were already considered by Feichtner *et al.* [14] in their calculation of the clock transition Stark shift, but for unknown reasons such terms were never considered in the tensor polarizability calculation.

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The contact interaction selection rule $\Delta L = 0$ admits only off-diagonal matrix elements between the ground state and higher-lying $S_{1/2}$ states (diagram **1**, fig. 1). The orbital and spin dipolar magnetic interactions also obey $\Delta L = 0$ and have nonvanishing off-diagonal matrix elements of the form $\langle \beta_1 | H_{hf} | \beta_2 \rangle$, where $|\beta_i\rangle = |n_i P_{j_i}\rangle$ (diagrams **2**, **3** and **4**). Due to the second-rank tensor character of $\boldsymbol{C}^{(2)}$, the spin dipolar term also couples states with $\Delta L = \pm 2$ and can thus contribute to the third-order Stark effect with off-diagonal matrix elements between the ground state and $D_{3/2}$ states (diagram **5**). We have used the Schrödinger equation with a statistical Thomas-Fermi model potential to calculate the relevant wave functions of the free Cs atom. Corrections for the dipolar and quadrupolar core polarization as well as spin-orbit interaction with a relativistic correction factor following [15] were included. The electric-dipole and hyperfine matrix elements were calculated using the Schrödinger wave functions for all matrix elements for which no precise values could be found in the literature. In this way we evaluated all diagrams in fig. 1 by running the summation indices m and n up to 200.

Relative contributions and numerical results. – Diagrams **A** and **1** of fig. 1 yield only F-dependent energy shifts, and thus do not contribute to the tensor polarizability. All other diagrams produce F- and M-dependent effects. The relative importance with which diagrams **B** and **2**–**5** contribute to $\alpha_2^{(3)}$ is +145, +99, −40, −3, and −101%, respectively. A numerical evaluation of the perturbation sum with all diagonal and off-diagonal matrix elements mentioned above gives

$$\alpha_2^{(3)}(F = 4) = -3.72(25) \times 10^{-2} \text{ Hz/(kV/cm)}^2 , \tag{15}$$

for the tensor polarizability, in which the contribution of a_2 is 2×10^{-5} Hz/(kV/cm)^2. This result is shown as a dashed line in fig. 2 together with previous theoretical and experimental results. We estimate the uncertainty of our calculated value to be 7%, based on the precision (2–8%) with which our Schrödinger solutions can reproduce measured dipole matrix elements and hyperfine splittings, and considering that some (more precise) experimental values were included in the calculations, whenever they were available. We have also verified by explicit calculations using continuum wave functions that continuum states contribute only at a level of 10^{-4} to the diagrams relevant for $\alpha_2^{(3)}$ ($\sim a_1$), while it was recently shown [16,17] that the continuum contributes significantly ($\approx 10\%$) to diagram **1**, which dominates the BBR shift via the $\alpha_0^{(3)}$ ($\sim a_0$) term in eq. (16) [18].

The corrected sign of the a_1-terms has an important implication for frequency standards. From eqs. (10) the static Stark shift of the Cs clock frequency is given by

$$\Delta\nu_{00} = \Delta\nu\left(6S_{1/2}, 4, 0\right) - \Delta\nu\left(6S_{1/2}, 3, 0\right) = -\frac{1}{2}\left[\frac{16}{7}a_0 - \frac{4}{7}a_1 f\left(\theta\right)\right]\mathbb{E}^2 . \tag{16}$$

One of the leading systematic shifts of the clock transition frequency is due to the interaction of the atoms with the *dynamic* Stark interaction induced by the blackbody radiation (BBR) field. This shift can be calculated from eq. (16) by averaging $\mathbb{E}^2$ over the Planck spectrum [16,17,19]. Because of the isotropy of the blackbody radiation the θ-dependence in eq. (16) vanishes, so that the BBR shift is determined by the scalar part a_0 only. The BBR shift coefficient can be deduced from the measured shift of the clock transition frequency induced by a *static* electric field. For this one has to know the value of the a_1-term in eq. (16) which is affected by the sign error, the coefficient of a_1 being $-\frac{1}{7}$ when derived from Sandars' formula and $-\frac{4}{7}$ from our calculation. The most precise measurement of the static Stark shift was performed by Simon *et al.* [20] from which the authors extracted $-\frac{8}{7}a_0 = -2.273(4)$ kHz/(kV/cm)^2, while our evaluation with the correct sign yields $-\frac{8}{7}a_0 = -2.281(4)$ kHz/(kV/cm)^2. The correction

of the sign error thus changes the BBR shift rate by a value which is twice as large as the reported experimental uncertainty.

Conclusions. – We have extended a previous treatment of the Stark interaction by including off-diagonal hyperfine matrix elements in the third-order perturbation expansion. Our calculation of the tensor polarizability yields a good agreement with all experimental data, thereby removing a 40-year-old discrepancy. A sign error identified in Sandars' model leads to a new expression for the static Stark shift of the hyperfine transition frequency which requires Cs primary frequency standards to be corrected at a level of 6×10^{-17}, which is below their present accuracy.

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