Stark effect of the cesium ground state: electric tensor polarizability and shift of the clock transition frequency

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We present a theoretical analysis of the Stark effect in the hyperfine structure of the cesium ground state. We have used third order perturbation theory, including diagonal and off-diagonal hyperfine interactions, and have identified terms which were not considered in earlier treatments. A numerical evaluation using perturbing levels up to \( n = 18 \) yields new values for the tensor polarizability \( \alpha_2(6S_1/2) \) and for the Stark shift of the clock transition frequency in cesium. The polarizabilities are in good agreement with experimental values, thereby removing a 40-year-old discrepancy. The clock shift value is in excellent agreement with a recent measurement, but in contradiction with the commonly accepted value used to correct the black-body shift of primary frequency standards.

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Since its discovery, the Stark effect has been an important spectroscopic tool for elucidating atomic structure. The Zeeman degeneracy of the \( nS_1/2 \) ground state of alkali atoms cannot be lifted by a static electric field because of time reversal invariance. However, the joint effect of the hyperfine interaction and the Stark interaction leads to both \( F \) and \( |M| \) dependent energy shifts which in cesium are 5 and 7 orders of magnitude smaller than the shift due to the second order scalar polarizability. While the scalar Stark shift is understood at a level worth and Sandars \[6\] demonstrated that a static electric field also lifts the Zeeman degeneracy within the hyperfine structure. We have identified contributions which were not considered in earlier treatments. Of all the terms obtained by substituting \( W \) into Eq. (1) only those containing the product of two matrix elements of \( H_{hf} \) and one matrix element of \( H_{St} \) give nonzero contributions because of the selection rules \( \Delta L = \pm 1 \) for \( H_{hf} \) and \( \Delta L = 0, \pm 2 \) for \( H_{St} \).

We address first the second term of Eq. (1). The diagonal matrix element in front of the sum represents

\[
\Delta E^{(2)}(\alpha) = \sum_{\beta \neq \alpha, \gamma \neq \alpha} \frac{\langle \alpha | W | \beta \rangle \langle \beta | W | \gamma \rangle \langle \gamma | W | \alpha \rangle}{(E_{\alpha} - E_{\beta})(E_{\alpha} - E_{\gamma})}
- \langle \alpha | W | \alpha \rangle \sum_{\beta \neq \alpha} \frac{|\langle \beta | W | \alpha \rangle|^2}{(E_{\alpha} - E_{\beta})^2}, \tag{1}
\]

where \( E_{\beta} \) and \( E_{\gamma} \) are the energies of unperturbed states, and the perturbation \( W = H_{hf} + H_{St} \) describes the hyperfine and Stark interactions. Of all the terms obtained by substituting \( W \) into Eq. (1) only those containing the product of two matrix elements of \( H_{hf} \) and one matrix element of \( H_{St} \) give nonzero contributions because of the selection rules \( \Delta L = \pm 1 \) for \( H_{hf} \) and \( \Delta L = 0, \pm 2 \) for \( H_{St} \).

We address first the second term of Eq. (1). The diagonal matrix element in front of the sum represents
only the Fermi contact interaction in the ground state, while the sum is carried out over Stark interactions only. Diagram A of Fig. 1 represents this term in graphical form. The hyperfine matrix element $\langle \alpha | H_{hf} | \alpha \rangle$ is scalar, but $F$ dependent, and the sum is similar to the expression for the second order Stark effect, except for the squared energy denominator. As in the theory of the second order Stark effect [4], the sum can therefore be expressed as $\langle \alpha | H_{hf}^{(k=0)} + H_{hf}^{(k=2)} | \alpha \rangle$. The scalar contribution, $\langle \alpha | H_{hf}^{(0)} | \alpha \rangle$, depends only on the strength of the applied electric field, $E^2$, while the second rank tensor contribution $H_{hf}^{(2)}$ depends only on its orientation as $3E^2 - 2E^2$. The selection rules for tensor operators require that $\langle S_{1/2} | H_{hf}^{(2)} | S_{1/2} \rangle = 0$. As a consequence the second term of Eq. (1) gives a scalar contribution to the energy which depends on $F$, but not on $M$, and which can be parametrized by a third order scalar polarizability $\alpha^{(3)}_0 (6S_{1/2}, F)$ as

$$\Delta E^{(3)}_0 = -\frac{1}{2} \cdot \alpha^{(3)}_0 (F) \cdot E^2.$$

This term produces the major contribution to the Stark shift of the hyperfine transition frequency $\Delta \nu_{00} = \nu(F = 4, M = 0) - \nu(F = 3, M = 0)$. We next address the first term of Eq. (1) and consider only diagonal matrix elements of $H_{hf}$. As before, the Stark interaction part of the first term has only a rank $k = 0$ (scalar) contribution. The dipole-dipole and electric quadrupole parts of the hyperfine interaction have the rotational symmetry of $k = 0, 2$ and $k = 2$ tensors, respectively. Together with the scalar Stark interaction, the first term thus has scalar and tensor parts. The scalar part has the same $F$ dependence as $\alpha^{(3)}_0 (F)$, and corrects the latter by approximately 1%, while the second rank tensor parts have an $F$ and $M$ dependence, which can be parametrized in terms of a third order tensor polarization $\alpha^{(3)}_2 (6S_{1/2}, F)$ via

$$\Delta E^{(3)}_2 = -\frac{1}{2} \alpha^{(3)}_2 (F) \frac{3M^2 - F(F+1)}{2I(2I+1)} f(\theta)E^2,$$

where the dependence on the angle $\theta$ between the electric field and the quantization axis is given by $f(\theta) = 3 \cos^2 \theta - 1$. The $M$-dependence in Eq. (3) is responsible for lifting the Zeeman degeneracy in the ground state hyperfine levels, but gives also a correction to the shift of the clock transition frequency which itself is dominated by Eq. (2). The third order Stark effect of the two hyperfine levels can then be parametrized in terms of the third order polarizabilities by

$$\alpha^{(3)}(F, M) = \alpha^{(3)}_0 (F) + \alpha^{(3)}_a (F) \frac{3M^2 - F(F+1)}{2I(2I+1)} f(\theta).$$

In cesium the explicit $F$-dependence of Eq. (4) yields [12], for $\theta = 0$,

$$\alpha^{(3)}(4, M) = a_0 + (a_1 + a_2) \frac{3M^2 - 20}{28}, \quad \alpha^{(3)}(3, M) = -\frac{9}{7}a_0 + \left( -a_1 + \frac{5}{3}a_2 \right) \frac{3M^2 - 12}{28}.$$  

where $a_1$ is the contribution of the tensor part of the dipole-dipole hyperfine interaction, and $a_2$ the contribution of the electric quadrupole interaction. The Fermi-contact interaction provides the dominant contribution to $a_0$ which also has a small contribution from the scalar part of the dipole-dipole interaction. Equations (4) and (5) bear

FIG. 1: Contribution of diagonal hyperfine matrix elements to the third order Stark effect calculation. The dotted lines represent Stark interaction matrix elements while the solid lines represent hyperfine matrix elements.

FIG. 2: Contribution of off-diagonal hyperfine matrix elements to the third order calculation of the Stark effect.
a close resemblance to the expressions obtained by Sandars [9], except for the negative sign of the \( a_1 \) term in Eq. (5b), which is positive in Sandars work. We have confirmed the sign of our expression in a recent experiment [11]. That sign error, which seems to have remained unnoticed for almost 40 years, has no consequence for the tensor polarizability of the \( F = 4 \) state, which is the only one measured to date. It affects the static Stark shift of the clock transition at a level slightly below today's experimental sensitivity.

Sandars' equations were evaluated by [7] and [8], who considered only diagonal matrix elements of \( H_{\text{hf}} \) for the \( 6S_{1/2} \) and the \( 6P_3 \) states (Fig. 1). They further neglected the fine structure energy splitting in the denominators of Eq. (1) and assumed the relation \( A_{6S_{1/2}} = 5A_{6P_3} \) for the hyperfine constants, valid for one-electron atoms, while for Cs the corresponding ratio of experimental values is 5.8. Those assumptions yielded the value (f) in Fig. 4 which is in disagreement with the experimental results. We have reevaluated [12] their result by dropping the simplifying assumptions and by using recent experimental values of the reduced matrix elements \( \langle 6S_{1/2} \parallel d \parallel 6P_3 \rangle \) from [14]. As a result, the discrepancy becomes even larger [point (f')] in Fig. 4, and does not change significantly when the perturbation sum is extended to \( nP_3 \) states with \( n > 6 \).

The first term in Eq. (1) is not restricted to diagonal matrix elements of the hyperfine interaction. We have therefore extended the numerical evaluation of Eq. (1) by including off-diagonal terms. Figure 2 gives a schematic overview of all possible configurations which include off-diagonal hyperfine matrix elements and which are compatible with the hyperfine and Stark operator selection rules. It is interesting to note that the diagrams 1 and 2 were already considered by Feichtner et al. [17] in their calculation of the clock transition Stark shift. For unknown reasons, the off-diagonal terms were never included in the calculation of the tensor polarizability.

We have evaluated all the diagrams shown in Fig. 2 and in particular the diagrams 3, 4, and 5, which, to our knowledge, were never considered before. As noted in the figure, all diagrams lead to \( F \) and \( M \) dependent energy shifts, except for diagram 1, which gives an M independent shift. Thus all diagrams contribute, together with the diagonal contributions A and B of Fig. 1, to the Stark shift of the clock transition, while only the diagrams B and 2-5 contribute to the tensor polarizability. Moreover, the relative importance of the diagrams for the two effects of interest is quite different. In the case of the clock shift, we find that 90% (95%) of the total contribution (\( n=6-18 \)) comes from the diagrams A and 1 evaluated for \( n = 6, 7 (n = 6, 7, 8) \). In this case the contributing (electric dipole and hyperfine) matrix elements are directly or indirectly given by experimentally measured quantities. The diagonal hyperfine matrix elements are proportional to the measured hyperfine splittings, while the off-diagonal hyperfine matrix elements between \( S \) states of different principal quantum numbers \( n \) can be expressed in terms of the geometrical averages of the hyperfine splittings of the coupled states, a relation which holds at a level of \( 10^{-3} \) [20]. This gives us a high level of confidence in our value of the clock shift rate. The off-diagonal matrix elements of the diagrams 2-5 cannot be traced back to experimental quan-

FIG. 3: The third order tensor polarizability of the \( F=4 \) Cs ground state. The filled squares (●) represent experimental values of Carrico et al. [2](a), Gould et al. [3](b), Ospelkaus et al. [12](c) and Ulzega et al. [11](d). The empty square (□) (e) represents a weighted average of (a), (b), (c) and (d). The dots (●) represent the theoretical value from [5](f), and our re-evaluation of the latter value after dropping simplifying assumptions (f'). The dotted horizontal line is the result of the present work with its uncertainty (shaded band).

FIG. 4: The static Stark shift of the clock transition frequency. The squares (●) represent experimental values of Haun et al. [2](a), Mowat [15](c), Simon et al. [16](e), and Godone et al. [13](g). The dots (●) represent theoretical values of Feichtner et al. [17](b), Lee et al. [15](d), and Micalizio et al. [19](f). The circle (○) (b',f') represents the rescaled values of (b,f) as explained in the text. The error bar of point (e) is smaller than the symbol size. The dotted horizontal line shows our result with its uncertainty (shaded band).
We have calculated these matrix elements using wave functions obtained from the Schrödinger equation for a Thomas-Fermi potential, with corrections including dipolar and quadrupolar core polarization as well as spin-orbit interaction with a relativistic correction factor following [21]. We included \( nS_J, nP_J, \) and \( nD_J \) states up to \( n = 18 \) in the perturbation sum and obtained

\[
\Delta \nu_{00}/E^2 = -2.06(1) \text{ Hz/(kV/cm)}^2, \tag{6}
\]

for the shift of the clock transition frequency, and

\[
\alpha_2^{(3)} (F = I \pm J) = \mp 3.72(25) \times 10^{-2} \text{ Hz/(kV/cm)}^2, \tag{7}
\]

for the tensor polarizability. The results are shown as dotted lines in Figs. 8 and 11 together with previous theoretical and experimental results. The uncertainty of our calculated values is indicated by the shaded bands. The relative uncertainty of the clock shift is significantly smaller than that of the tensor polarizability due to the use of experimental values, with relatively small uncertainties. For the contributions which we calculated explicitly from the Schrödinger wave functions we use the accuracy (4%–8%) with which these wave functions reproduce experimental dipole matrix elements and hyperfine splittings to estimate the precision of our results. More details will be given in a forthcoming publication [11]. We can claim that the present calculation of \( \alpha_2^{(3)} \) yields a good agreement with all experimental data.

The situation with the Stark shift of the clock transition frequency is less clear as there are disagreeing experimental values. While the experimental results [5], [15], and [16] [(a), (c), and (e) in Fig. 4] are supported by the theoretical value of [18](d), our present result is in excellent agreement with the recent experimental value of Godone et al. [13] (g) and with the calculation of Micalizio et al. [19](f). The shift was also calculated by Feichtner et al. [17] in an approximation using hydrogenic wave functions, neglecting spin-orbit interactions, and considering only the diagrams A, B, 1, and 2 [point (b) in Fig. 4]. With these approximations the scalar polarizability \( \alpha_0 \) can be factored out of their final result.

We have rescaled point (b) in Fig. 4 using more precise (consistent) values of \( \alpha_0 \) given in [1, 2, 5], yielding point (b’) which is then consistent with the present result. We also rescaled point (f) in the same manner, yielding (f’) which cannot be distinguished from (b’).

We conclude by recalling the relevance of the latter result for primary frequency standards. One of the leading systematic shifts of the cesium clock frequency is due to the interaction of the atoms with the blackbody radiation (BBR) field. It was shown [22] that the dynamic BBR shift can be parametrized in terms of the static Stark shift investigated here. The correction factor for the BBR shift commonly used is based on the precise experimental value of Simon et al. [16] [point (e) in Fig. 4], whose difference with the present result is 21 (53) times the corresponding theoretical (experimental) uncertainty. In order to shine more light on this important issue we are preparing an alternative new experiment for measuring the static Stark shift of the clock transition frequency.

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