Hyperfine-mediated effects in a Lu$^+$ optical clock

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We consider hyperfine-mediated effects for clock transitions in $^{176}$Lu$^+$. Mixing of fine-structure levels due to the hyperfine interaction brings about modifications to the Landé $g$-factors and the quadrupole moment for a given state. Explicit expressions are derived for both the $g$-factor and quadrupole corrections, for which leading-order terms arise from the nuclear magnetic dipole coupling. High accuracy measurements of the $g$-factors for the $S_0$ and $D_1$ hyperfine levels are carried out, and they provide an experimental determination of the leading-order correction terms.

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I. INTRODUCTION

Singly ionized lutetium ($^{176}$Lu$^+$) is a unique optical clock candidate in that it provides three possible clock transitions. Of particular interest in this work is the $S_0 \leftrightarrow D_1$ transition at 848 nm, which has favorable clock properties relative to leading clock candidates [1]. At the Doppler cooling limit, the $D_1 \leftrightarrow S_0$ cooling transition provides a fractional second-order Doppler shift below $10^{-19}$. The large atomic mass and additional clock transitions allow micromotion shifts to be controlled to a similar level. The blackbody radiation (BBR) shift of the 848-nm transition is $-1.36(10) \times 10^{-18}$ at 300 K, which is the lowest of any optical clock system [1] and easily controllable to the low $10^{-19}$ with modest technical effort. More recently, experiments have demonstrated the potential for clock operation with multiple ions, which will ultimately provide improved stability [2,3]. Thus it can be anticipated that this transition will ultimately provide an error budget competitive with leading systems.

A crucial consideration for clock implementation with $^{176}$Lu$^+$ is the use of hyperfine averaging in which a reference frequency is defined by an average over all hyperfine states with a common magnetic quantum number, $m$ [4]. Provided $|m| < I - J$, where $I$ is the nuclear spin and $J$ is the electronic angular momentum, the averaging realizes an effective $J = 0$ level and practically eliminates dominant Zeeman shifts and shifts arising from rank 2 tensor interactions, such as the electric quadrupole moment [4]. The averaging principle holds even when there is a large amount of Zeeman mixing within a given fine-structure level, but it omits hyperfine-mediated mixing with other levels. Such mixing influences $g$-factors [5] and is the mechanism for the nonzero quadrupole moment of $^3P_0$ clock states in Al$^+$ and In$^+$ [6]. Consequently, it can be anticipated that similar effects will occur for $^{176}$Lu$^+$ and likely influence the effectiveness of hyperfine averaging.

In this paper, the influence of hyperfine-mediated mixing on the clock states of $^{176}$Lu$^+$ is investigated via high accuracy measurements of $g$-factors for the $S_0$ and $D_1$ hyperfine levels. Comparison with theoretical results provides an experimental determination of the leading-order correction terms, which arise from the nuclear magnetic dipole coupling. As similar corrections also apply to the quadrupole moments of $D_1$ states, the measurements also allow a reasonable estimate for the residual quadrupole moment arising from hyperfine averaging. Although the corresponding shift of the clock frequency will likely be well below $10^{-18}$, it will inevitably be an important consideration for upcoming clock assessments for this atom.

II. EXPERIMENT

A. Apparatus

The relevant level structure of $^{176}$Lu$^+$ and the laser systems required are shown in Figs. 1(a) and 1(b). Lasers at 350, 895, and 622 nm provide optical pumping to the $^2D_1$ state. A laser at 646 nm provides Doppler cooling and state detection for the $^2D_1$ state with fluorescence collected onto either a single photon counting module (SPCM) or an EMCCD camera. An additional $\pi$-polarized 646-nm laser addressing $F = 7$ to $F' = 7$ facilities state preparation into $^2D_1$, 7, 0). A clock laser at 848 nm drives the $S_0^\prime$-$D_1$ clock transition. Two microwave antennas are used to drive the $\Delta m = 0, \pm 1$ microwave transitions indicated in Fig. 1(b). On their respective microwave transitions, each antenna was positioned by hand to give approximately equal coupling to the $\Delta m = \pm 1$ transitions and reduced coupling for $\Delta m = 0$. 

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with axial end caps as described in previous work [7]. In the trap axis. The trap is a four-rod linear Paul trap is horizontal (vertical) with respect to the table top, and \( \hat{x} \) is along the trap axis. The trap drive frequency is 20.57 MHz, and the measured trap frequencies for a single \(^{138}\text{Ba}^+\) are \( \sim 2\pi \times (912, 795, 226) \) kHz, with the lowest trap frequency along the trap axis. As shown in Fig. 1(f), a dc magnetic field is applied in the \( xz \)-plane at an angle \( \phi = 33(2)^\circ \) with respect to \( \hat{x} \), which defines the quantization axis.

### B. Measurements

The \( g \)-factors of the \(^{176}\text{Lu}^+\) \( ^{1}\!S_{0} \) (\( F = 7 \)) and \( ^{3}\!D_{1} \) (\( F = 6, 7, 8 \)) levels are denoted \( g_{F} \) and \( g_{F} \), respectively, and they are measured via a comparison of Zeeman splittings. Comparisons between \(^{176}\text{Lu}^+\) and \(^{138}\text{Ba}^+\) enable determination of \( r_{6} \equiv g_{\text{Ba}}/g_{6} \) and \( r_{8} \equiv g_{\text{Ba}}/g_{8} \), where \( g_{\text{Ba}} \equiv \frac{1}{2}(g[D_{3}/2] - g[S_{1}/2]) \). The \( g \)-factors for \(^{138}\text{Ba}^+\) can then be inferred using the accurately known \( g \)-factors in \(^{138}\text{Ba}^+\) [7,8]. Ratios among \( g_{F} \) and \( g_{R} \) are measured using a single ion. Together the two sets of experiments provide a complete determination of \( g_{F} \) and \( g_{R} \) as well as consistency checks between the measurements.

The ratios \( r_{6} \) and \( r_{8} \) are measured at an applied magnetic field of \( \sim 1.573 \) mT. The experiment sequence consists of the following steps: 200 \( \mu \)s preparation of \(^{176}\text{Lu}^+\) in \(^{3}\!D_{1}\), Doppler cooling of \(^{138}\text{Ba}^+\) and \(^{176}\text{Lu}^+\) for 1 ms, 1 ms of optical pumping \(^{138}\text{Ba}^+\) to either \( |S_{1/2}, m = \pm \frac{1}{2} \rangle \) and \(^{176}\text{Lu}^+\) to \(|D_{1}, 7, 0 \rangle\), Rabi spectroscopy with a pulse duration of 1.5 ms being performed simultaneously on the \(^{138}\text{Ba}^+\) \(|D_{3/2}, m = \pm \frac{1}{2} \rangle\) transition and \(^{176}\text{Lu}^+\) \(|D_{1}, 7, 0 \rangle\) to \(|D_{1}, 6, \pm 1 \rangle\) (or \(|D_{1}, 8, \pm 1 \rangle\) transition, 8 ms shelving of the remaining \(^{176}\text{Lu}^+\) \(|D_{1}, 7, 0 \rangle\) population to \(|S_{0}, 7, \pm 1 \rangle\), sequential state detection of \(^{138}\text{Ba}^+\) and \(^{176}\text{Lu}^+\) for \( \lesssim 1 \) ms each, and finally preparation of \(^{176}\text{Lu}^+\) in the \( D_{1} \) state and detection for 20 ms. The last step detects the position of \(^{176}\text{Lu}^+\) in the two-ion crystal using the different photon collection efficiencies for the two possible crystal configurations. The sequence is repeated four times for Rabi interrogation at approximately the half maximum of either side of the respective pair of Zeeman transitions. Every 20 cycles, an integrating servo is updated to track the respective Zeeman splittings for both \(^{138}\text{Ba}^+\) and \(^{176}\text{Lu}^+\).

To account for possible spatial dependence on the magnetic field, an additional experiment is performed to calibrate the gradient along the crystal axis. This is done using correlation spectroscopy [9,10] on the \(|S_{1/2}, \pm \frac{1}{2} \rangle - |D_{3/2}, \pm \frac{1}{2} \rangle\) transition in a two-ion crystal of \(^{138}\text{Ba}^+\), similar to previous work [2]. Specifically, Ramsey spectroscopy is performed on both ions for a duration longer than the optical coherence time of the individuals ions, which is limited by the common mode magnetic field noise. The EMCCD camera is used for single shot detection of both ions. The parity, \( p_{12} = \langle \sigma_{e_{1}} | \sigma_{e_{2}} \rangle \), when averaged over all optical phases of the closing Ramsey pulse, is expected to yield \( p_{12} = \frac{\alpha}{\gamma} \cos[2\pi(f_{j} - f_{T})T] \), where \( \alpha_{c} \) characterizes the relative coherence between two oscillators, \( f_{j} \) is the resonant frequency of the \( j \)th ion, and \( T \) is the Ramsey time. Figure 2(a) shows the typical result as a function of Ramsey time. The difference frequency between the ions measured before and after the measurements of \( r_{6} \) and \( r_{8} \) was found to be stable at 20.92(8) Hz, which corresponds to a magnetic field gradient of 0.3917(15) mT/m.

The ratios of \( g_{F} \) are found by interleaved measurement of \(|D_{1}, F, \pm 1 \rangle\) Zeeman splittings via microwave spectroscopy.
HYPERFINE-MEDIATED EFFECTS IN A Lu⁺...

FIG. 2. (a) Correlation spectroscopy of the $|S_{1/2}, \frac{1}{2}\rangle - |D_{3/2}, \frac{3}{2}\rangle$ transition of two $^{138}$Ba⁺ ions. The oscillation frequency of 20.92(8) Hz corresponds to a differential field of 3.73(1) mT between the two ions. (b), (c) Allan deviation of $r_6$ and $r_8$ for Lu⁺ on either the left (orange) or right (blue) crystal position. The solid black is the quantum projection noise (QPN) limit. The dashed line is $\sqrt{2}$ above the QPN limit.

on a single Lu⁺ ion with an applied magnetic field of ~1.107 mT. The experimental sequence is similar to measurements of $r_6$ and $r_8$, but without the Ba⁺ lasers and a longer interrogation time of 16 ms. To probe the Zeeman splitting of the $F = 7$ hyperfine level, additional microwave pulses to transfer from $|D_1, 7, 0\rangle$ to $|D_1, 6, 0\rangle$ or $|D_1, 8, 0\rangle$ are inserted as required. A single cycle consists of sequential Rabi interrogation of four Zeeman pairs: $|D_1, 6, \pm 1\rangle$, $|D_1, 8, \pm 1\rangle$, and $|D_1, 7, \pm 1\rangle$ twice, starting from either $|D_1, 6, 0\rangle$ or $|D_1, 8, 0\rangle$ to check for consistency. Every 20 cycles, the four independent servos tracking the Zeeman splittings are updated.

An additional experiment measures the ratio $g_8/g_1$ by interleaved measurement of the $|D_1, 8, \pm 1\rangle$ splitting using a 16 ms interrogation time on the microwave transition and the $|S_{1/2}, \pm 1/2\rangle$ splitting using a 45 ms interrogation on the 848 nm optical transitions shown in Fig. 1(b). The 45 ms π-time allows for higher resolution of the much smaller ground-state Zeeman splitting and ensures negligible probe-induced shifts.

The $r_6$ and $r_8$ results are summarized in Table I with corrections given for the leading systematic effects. As the ions are observed to swap position every 18 min on average, which is much longer than the servo update period, data are sorted into the two possible crystal configurations. Figures 2(b) and 2(c) show the Allan deviations of $r_6$ and $r_8$ collected over the course of 5 h.

At the quantum projection noise (QPN) limit, the Allan deviation for the ratio of Zeeman splittings between two levels can be written as $\sigma_0/\sqrt{M}$, where $M$ is the number of servo updates and $\sigma_0$ fractional resolution from a single update. For Rabi spectroscopy used here, this can be written

$\sigma_0 = \frac{1.656\hbar}{2\mu_B B}\sqrt{\frac{1}{g_1^2 r_1^2} + \frac{1}{g_2^2 r_2^2}}^{1/2}$, \hspace{1cm} (1)

where $\mu_B$ is the Bohr magneton, $B$ is the applied magnetic field, $N$ is the number of interrogations per side of a given transition, $g_i$ are the $g$-factors for the levels involved, and $r_k$ are the respective interrogation times. The Allan deviations in Figs. 2(b) and 2(c) are observed to be slightly elevated above the QPN. We attribute this to the magnetic field noise, which is comparable to the QPN for the interrogation time used. To account for this, we take the statistical uncertainty in the resulting mean to be $\sqrt{2}$ above the QPN limit, as indicated by the dashed black lines in Figs. 2(b) and 2(c).

The leading systematic effects are: differential Zeeman shifts arising from the magnetic field gradient; ac Stark shifts from off-resonant microwave couplings in Lu⁺; and shifts in the Ba⁺ Zeeman splittings due to magnetic fields at the trap drive rf [11]. Assessment of the magnetic field gradient has already been discussed, leaving only the shifts from the microwave and trap-induced ac fields.

To evaluate the ac Stark shifts from the microwave probe fields, the polarization components at the ion from each antenna were assessed from the relative coupling strength on $\Delta m = (-1, 0, 1)$ transitions at fixed rf power. For the 1.5 ms π-time used during the measurements of $r_6$ and $r_8$, we estimate the ac Stark shift to be $\pm 0.21(2)$ Hz on the $|D_1, 7, 0\rangle - |D_1, 6, \pm 1\rangle$ transitions and $\mp 0.13(1)$ Hz for the $|D_1, 7, 0\rangle - |D_1, 8, \pm 1\rangle$ transitions.

Shifts from the trap-induced ac magnetic fields depend only on the component of the ac field perpendicular to the applied dc field [11]. This is measured from an Autler-Townes splitting exactly as described in previous work [7]. The inferred field amplitude of $B_\perp = 1.25(1)$ μT implies a $\mp 0.838(19)$ Hz shift on the $|S_{1/2}, \pm \frac{1}{2}\rangle - |D_{1/2}, \pm \frac{1}{2}\rangle$ transitions at the operating magnetic field of 1.573(1) mT.

Other systematic effects considered include shifts on $^{139}$Lu⁺ arising from the 1762-nm laser, the ac-magnetic field effect on Lu⁺, and shifts on $^{138}$Ba⁺ arising from microwave fields. These shifts are all well below the stated uncertainties and are omitted from the table. After accounting for systematic effects, the ratio results $r_6$ and $r_8$ are in statistical agreement for both crystal configurations as seen in Table I. For the final values, we take the weighted mean of results

| Description | Lu⁺left | Lu⁺right |
|-------------|---------|----------|
| $r_6$ raw   | 5.5965567(17) | 5.5965292(20) |
| magnetic gradient | $-1.3258(51)[−5]$ | $1.3258(51)[−5]$ |
| microwave ac Stark | $7.41(69)[−7]$ | $7.41(69)[−7]$ |
| ac magnetic field | $-5.31(12)[−7]$ | $-5.31(12)[−7]$ |
| $r_6$ corrected | 5.5965437(17) | 5.5965427(20) |
| $r_8$ raw | $-6.4770416(30)$ | $-6.4770088(22)$ |
| magnetic gradient | $1.5347(59)[−5]$ | $-1.5347(59)[−5]$ |
| microwave ac Stark | $6.24(43)[−7]$ | $6.24(43)[−7]$ |
| ac magnetic field | $6.15(14)[−7]$ | $6.15(14)[−7]$ |
| $r_8$ corrected | $-6.4770250(30)$ | $-6.4770229(22)$ |
for the two crystal configurations. As the measurements are not QPN limited, we use the larger uncertainty from the two configurations in each case, giving

$$r_6 = \frac{g_{Ba}}{g_6} = 5.5965433(20),$$

$$r_8 = \frac{g_{Ba}}{g_8} = -6.4770236(30).$$

Measurements on the single ion yield the following ratios:

$$r_{68} = \frac{g_6}{g_8} = -1.157326607(88),$$

$$r_{77} = \frac{g_6}{g_7} = -8.5026437(24),$$

$$r_{87} = \frac{g_8}{g_7} = 7.3467970(20),$$

$$r_{78} = \frac{g_7}{g_8} = 0.99999978(38),$$

$$r_{88} = \frac{g_8}{g_8} = -254.2897(17),$$

where $r_{77}$ is the ratio of the $|D_1, 7, \pm 1\rangle$ Zeeman splittings measured independently starting from either $|D_1, 6, 0\rangle$ or $|D_1, 8, 0\rangle$ and is statistically consistent with 1, as expected. The Allan deviations are shown in Figs. 3(a)–3(c). Again, the statistical uncertainties of $r_{68}$ and $r_{88}$ stated are given as $\sqrt{2}$ larger than the QPN limited uncertainty as indicated by Allan deviations in Figs. 3(a) and 3(c). With microwave and optical interrogation times of 16 and 45 ms, respectively, the systematic effects including shifts caused by the microwave fields and 848-nm light are negligible compared with stated statistical uncertainties.

To check the consistency of the results, $r_{68}$ can be independently evaluated from Eqs. (2a) and (2b) to give $r_{68} = g_{68}/g = -1.15732574(68)$, which differs from the measured value in Eq. (3a) by $8.7(6.9) \times 10^{-7}$. To determine $g_I$ and $g_F$, we take the weighted mean of the two values $r_{68} = -1.157326593(88)$, and

$$g_{Fa} = \frac{1}{2} \left[ 1.20036731(24) - 2.00249492(33) \right] = -0.40106232(12)$$

The Allan deviations are shown in Figs. 3(a)–3(c). Again, the weighted mean of the two values

$$g_{6} = \frac{g_{Ba}}{r_6} = -0.071662506(33),$$

$$g_{7} = \frac{g_{Ba}}{r_6 r_6 g_{6} g_{7}} = 0.0084282619(46),$$

$$g_{8} = \frac{g_{Ba}}{r_6 r_6 g_{8}} = 0.061920729(29),$$

$$g_{I} = \frac{g_{Ba}}{r_6 r_6 g_{8}} = -0.000243504(16).$$

III. DISCUSSION

From Appendix A2, the g-factors for $^{3}D_1$ may be written

$$g_{6} = -\frac{1}{2} g_{I} + 8 g_{F},$$

$$g_{7} = \frac{1}{2} g_{I} + \frac{5}{2} g_{F}$$

Neglecting $\delta g^{(2)}_I$ and using the measured values of $g_I$ and $g_F$, these equations can be solved for $g_I$, $\sum_J \beta_{1}^1$, and $\sum_J \beta_{1}^2$, which gives

$$g_{I} = 0.49823832(31),$$

$$\sum_J \beta_{1}^{1} = -8.65774(41) \times 10^{-4},$$

$$\sum_J \beta_{1}^{2} = 3.152(13) \times 10^{-5},$$

where uncertainties have been propagated from the measurements of $g_{Ba}$, $r_6$, $r_{68}$, $r_{87}$, and $r_{88}$.

To determine corrections from $\delta g^{(2)}_F$, we first note that they can be expressed in terms of $\beta_{1}^{1}$ and $\langle D_2 | \mathbf{m} \rangle | D_1 \rangle$, where $\mathbf{m}$ is the magnetic dipole moment operator as defined in Eq. (A5). Both $\sum_J \beta_{1}^{1}$ and $\sum_J \beta_{1}^{2}$ are largely determined by the $3D_2$ contribution such that they can be used to approximate $\beta_{1}^{1}$ to better than 2%. In addition, calculated matrix elements of $\mathbf{m}$ are typically accurate at the 1% level. Thus, we evaluate $\delta g^{(2)}_F$, as given in Appendix A2, using $\langle D_1 | \mathbf{m} \rangle | D_2 \rangle = -2.055 \mu_B$ from [12], and Eqs. (7b) and (7c) for $\beta_{1}^{1}$ and $\beta_{1}^{2}$, respectively. The resulting corrected values for the three quantities given in Eqs. (7) are then

$$g_{I} = 0.4982366(12).$$
As shown in the Appendix, \( \delta g_F^{(2)} \) can be written as a sum of two terms: one proportional to a difference in \( g \)-factors, and the other proportional to a difference in hyperfine level shifts. As there can be a significant cancellation of the corrections arising from these two contributions, it may well be that additional terms are needed to properly evaluate the corrections. Instead, for all cases, we have used the largest of the resulting two correction terms as the corresponding uncertainty when determining the overall uncertainties given in Eqs. (8). We note that the resulting values in Eqs. (8b) and (8c) are within 3\% and 17\%, respectively, of the theoretical estimates given in the Appendix, which is reasonable given the estimated uncertainties for calculated matrix elements given in [12].

Finally, the parameter \( \rho_{1,F}^0 \) from Eq. (A28) associated with hyperfine-mediated quadrupole corrections may be written

\[
\rho_{1,F}^0 = \beta_{1,F}^1 \frac{\mu g I (J' \| \Theta^{(2)} \| J)(J \| m \| 0)}{\langle J \| m \| 0 \rangle}.
\]

Using the same approximations as above for \( \beta_{1,2}^1 \) and matrix elements in Appendix A4, we obtain \( \rho_{1,2}^0 = -0.0133 \epsilon a_0^2 \). Thus

\[\langle \delta \Theta(J, F, m) \rangle_F \approx \frac{2}{105} \rho_{1,2}^0 \approx -2.54 \times 10^{-4} \epsilon a_0^2.\]  

As measured quadrupole moments are in agreement with theory to within 3\%, we would expect the above estimate to be accurate to the 5\% level. This represents the effective quadrupole moment for the hyperfine averaged reference frequency for the \( ^5S_0 - ^3D_1 \) clock transition. For a 2\( \pi \times 200 \text{ kHz} \) dc confinement, this would result in a maximum fractional frequency shift of \( 7 \times 10^{-19} \). In practice, this would be suppressed by the field orientation technique demonstrated in [2], which tunes the spatial dependence to zero leaving predominantly stray field contributions that may not be well aligned to the trap’s principal axes.

In summary, we have carried out precision measurements of \( g \)-factors for the \( ^5S_0 \) and \( ^3D_1 \) levels of \( ^{176}\text{Lu}^+ \). These measurements provide direct evidence of hyperfine-mediated mixing for clock states in \( ^{176}\text{Lu}^+ \), an accurate assessment of \( g_F(^3D_1) \), and an estimate of a hyperfine-mediated quadrupole moment that is not canceled by hyperfine-averaging. Although the corresponding shift of the clock frequency will likely be well below \( 10^{-18} \) for typical operating conditions, it will inevitably be an important consideration for upcoming clock assessments for this atom.

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APPENDIX A: THEORY

In this Appendix, relevant theoretical results for \( g \)-factor and quadrupole moments are given. Explicit expressions are given for the \( ^3D_1 \) states, but results can be readily applied to \( ^3D_2 \) and \( ^3D_2 \).

1. Hyperfine interaction theory

From the relativistic treatment in [13], the hyperfine Hamiltonian can be written as a sum of multipole interactions between electrons and nucleons,

\[H_{\text{hfs}} = \sum_{k=1}^{\infty} T_k^t \cdot T_k^n,\]  

where \( T_k^t \) and \( T_k^n \) are spherical tensor operators of rank \( k \) that operate on the space of electronic and nuclear coordinates, respectively. In the presence of the hyperfine interaction, the total angular momentum \( F = I + J \) is conserved, and basis states can be denoted \( |yIJm_f\rangle \), where \( y \) denotes all other quantum numbers. From the Wigner-Eckart theorem, a matrix element of \( H_{\text{hfs}} \) over the basis set is

\[
\langle y'I'J'F'm'|H_{\text{hfs}}|yIJm_f\rangle = \delta_{y'y} \delta_{I'I} \delta_{F'F} \sum_{k=1}^{\infty} \langle y'I'J'\| T_k^t \| yIJ \rangle \langle I\| T_k^n \| I_f \rangle.
\]

In particular, the nuclear magnetic dipole and electric quadrupole moments are defined as

\[
\mu_I = (T_k^1)^t_{11} \quad \text{and} \quad Q = 2(T_k^2)^t_{11}.
\]  

For a given interaction, \( H_I \), the first-order energy shift \( \langle JFm|H_I|JFm\rangle \) is modified by the hyperfine interaction. Following the treatment of the quadrupole moment in [6], the modification can be determined by treating \( H_I \) and \( H_{\text{hfs}} \) on an equal footing in perturbation theory. Explicitly, states are expanded to order \( n \) in the hyperfine interaction, and modification to the expectation value of \( H_I \) is then attributed to a state-dependent correction to the relevant property of the atom. In considering the importance of various terms, it should be noted that hyperfine interaction terms drop off significantly with \( k \) such that \( k = 2 \) terms at order \( n \) can be comparable to \( k = 1 \) terms at order \( n + 1 \).
With the Zeeman interaction
\[ H_z = -\mathbf{m} \cdot \mathbf{B} = \frac{\mu_B B}{h} (g_L L_z + g_S S_z + g_I I_z), \] (A5)
the term from first-order perturbation theory \( \langle J^F m | H_z | J^F m \rangle \) is the usual weak field Zeeman shift \( m g_F \mu_B B \). Corrections derived from \( n \)-th order perturbation theory in the hyperfine interaction also have a proportionality to \( m \mu_B B \) and thus represent a correction to \( g_F \), which we denote by \( \delta g_F^{(n)} \). Up to \( n = 1 \), we have
\[
\langle J^F m | H_z | J^F m \rangle = \left( \frac{m g_F \mu_B B (E_j - E_f)}{m \mu_B B (E_j - E_f)} \right),
\] (A6)
from which we obtain
\[
\delta g_F^{(1)} = 2 \sum_{j'} \frac{\langle J^F m | H_z | J^F m \rangle \langle J^F m | H^f_{\text{hs}} | J^F m \rangle}{m \mu_B B (E_j - E_f)}.
\] (A7)
Since \( H_z \) is a rank 1 tensor, only couplings to \( J' = J \pm 1 \) contribute. Using
\[
\langle J^F m | J^F m \rangle = \frac{m(-1)^I + I + F}{\sqrt{F(F+1)(2F+1)}} \left\{ \begin{array}{lll} F & F & 1 \\ J & J' & 1 \end{array} \right\} \langle J^F m | J^F m \rangle,
\] (A8)
and noting that \( I + J' + F \) must be integer, we have
\[
\delta g_F^{(1)} = 2 \sqrt{\frac{2F+1}{F(F+1)(2F+1)}} \sum_{j,k} \left\{ \begin{array}{lll} F & F & 1 \\ J & J' & 1 \end{array} \right\} \left\{ \begin{array}{lll} F & J' & I \\ \mu_B (E_j - E_f) \end{array} \right\},
\] (A9)
which may be written
\[
\delta g_F^{(1)} = \sum_{k,l} C_{F,F,J}^k \beta_{ij,l}^k,
\] (A10)
where
\[
\beta_{ij,l}^1 = \frac{\langle J^F m | J^F m \rangle \langle J^F m | J^F m \rangle}{E_j - E_f},
\] (A11)
\[
\beta_{ij,l}^2 = \frac{\langle J^F m | J^F m \rangle \langle J^F m | J^F m \rangle}{E_j - E_f}.
\] (A12)
and
\[
C_{F,F,J}^k = \frac{2F+1}{F(F+1)} \left\{ \begin{array}{lll} F & F & 1 \\ J & J' & 1 \end{array} \right\} \left\{ \begin{array}{lll} F & J' & I \\ \mu_B (E_j - E_f) \end{array} \right\}.
\] (A13)
For \( J = 1 \), this is dominated by coupling to \( \mathcal{D}_2 \) for which \( J' = J'' = 2 \). Hence
\[
\delta g_F^{(2)} \approx \left[ g_F(J') - g_F(J) \right] \frac{\langle J^F m | H^f_{\text{hs}} | J^F m \rangle}{(E_j - E_f)^2} + \left( W_{JF} - W_{JF} \right) \frac{2 \langle J^F m | J^F m \rangle | J^F m | H^f_{\text{hs}} | J^F m \rangle}{(E_j - E_f)^2},
\] (A16)
where \( W_{JF} = \langle J^F m | H^f_{\text{hs}} | J^F m \rangle \) are the diagonal matrix elements of the hyperfine interaction. Taking only the \( k = 1,2 \) contributions for the off-diagonal matrix elements and using the definitions of \( \beta_{ij,l} \), we have
\[
\delta g_F^{(2)} \approx \left[ g_F(J') - g_F(J) \right] \frac{2 \left\{ \begin{array}{lll} F & J' & I \\ k & J & I \end{array} \right\} (E_j - E_f)^{-1} \mu_B \beta_{ij,l}^k}{\langle J^F m | J^F m \rangle} - W_{JF} \frac{2 \langle J^F m | J^F m \rangle \langle J^F m | H^f_{\text{hs}} | J^F m \rangle}{(E_j - E_f)^2}.
\] (A17)
Following [14], $W_{IF}$ can be expressed in terms of the measured hyperfine splittings [14,15] and a smaller hyperfine-induced scalar shift common to all $F$ levels of a given $J$. Neglecting the scalar contributions, we obtain the estimates

$$\delta g^2_0 \approx -3.29 \times 10^{-7}, \quad (A18a)$$

$$\delta g^2_7 \approx 1.10 \times 10^{-8}, \quad (A18b)$$

$$\delta g^2_8 \approx 2.65 \times 10^{-7}, \quad (A18c)$$

where we have approximated $g_F$ using $g_I = 1/2$ and neglected $g_1$. Hence, $|\delta g^2_F| \lesssim 1 \times 10^{-3} g_I$.

3. Quadrupole moments

A similar treatment can be applied to determine hyperfine-mediated quadrupole moments. In this case, the resulting quadrupole correction does not average to zero and will thus be a limitation to hyperfine averaging. The analogous expression for the quadrupole correction is

$$\langle JFm|H_Q|JFm \rangle = \langle JFm|H_Q|JFm \rangle + 2 \sum_J \frac{\langle JFm|H_Q|JFm \rangle}{E_J - E_J}. \quad (A19)$$

The first term in this expression is exactly as derived by Itano [16] and can be written

$$\langle JFm|H_Q|JFm \rangle = C_{F,m} \Theta(J) f(\alpha, \beta), \quad (A20)$$

where

$$C_{F,m} = (-1)^{2F+m-J-m}(2F+1) \times \left( \begin{array}{ccc} F & 2 & F \\ -m & 0 & m \end{array} \right) \left( \begin{array}{ccc} J & J & 2 \\ -J & 0 & J \end{array} \right)^{-1} \quad (A21)$$

$\Theta(J)$ is the usual quadrupole moment for the fine-structure level defined by

$$\Theta(J) = \left( \begin{array}{ccc} J & 2 & J \\ -J & 0 & J \end{array} \right) \langle J||\Theta^{(2)}||J \rangle, \quad (A22)$$

and $f(\alpha, \beta)$ is determined by the orientation and strength of the applied external field. With the potential in the principal axis frame given by

$$\phi = A[x^2 + y^2 - 2z^2 + \epsilon(x^2 - y^2)], \quad (A23)$$

we have

$$f(\alpha, \beta) = -A[3 \cos^2 \beta - 1 - \epsilon \sin^2 \beta(\cos^2 \alpha - \sin^2 \alpha)], \quad (A24)$$

where $\alpha$ and $\beta$ are the Euler angles as defined in [16].

The matrix element $\langle JFm|H_Q|J'Fm \rangle$ can be found in the same way as Eq. (A20) giving

$$\langle JFm|H_Q|J'Fm \rangle = (-1)^{2F_1+F_2-J_1-m}(2F+1) \times \left( \begin{array}{ccc} F & 2 & F \\ -m & 0 & m \end{array} \right) \left( \begin{array}{ccc} J & J & 2 \\ -J & 0 & J \end{array} \right) \langle J||\Theta^{(2)}||J \rangle f(\alpha, \beta). \quad (A25)$$

As it has the same orientation dependence as Eq. (A20), the correction can be viewed as a change in the state-dependent quadrupole moment $\Theta(J, F, m) = C_{F,m} \Theta(J)$ by $\delta \Theta(J, F, m)$, which may be written

$$\delta \Theta(J, F, m) = 2(2F+1)\Theta(J) f(\alpha, \beta), \quad (A26)$$

where

$$\Theta(J, F, m) = (-1)^{2F_1+F_2-J_1-m}(2F+1) \times \left( \begin{array}{ccc} F & 2 & F \\ -m & 0 & m \end{array} \right) \left( \begin{array}{ccc} J & J & 2 \\ -J & 0 & J \end{array} \right) \langle J||\Theta^{(2)}||J \rangle f(\alpha, \beta). \quad (A27)$$

The average over $F$ is given by

$$\langle \delta \Theta(J, F, m) \rangle = \frac{2}{105} \sum_J \beta^Q_{J,F}. \quad (A28)$$

For $D_1$, the only contributions are from $D_2$ and $D_2$. For the $m = 0$ states of interest,

$$\delta \Theta(J, 6, 0) = -\frac{16}{75} \sum_J \beta^Q_{1,J,F}, \quad (A29a)$$

$$\delta \Theta(J, 7, 0) = \frac{1}{35} \sum_J \beta^Q_{1,J,F}, \quad (A29b)$$

$$\delta \Theta(J, 8, 0) = \frac{3}{35} \sum_J \beta^Q_{1,J,F}. \quad (A29c)$$

where

$$\beta^Q_{J,F} = (J||\Theta^{(2)}||J') \langle J' \rangle \langle J||T^Q_{J,J'}||\rangle E_J - E_J. \quad (A28)$$

For $D_2$, the only contributions are from $D_2$ and $D_2$. For the $m = 0$ states of interest,

$$\delta \Theta(J, 6, 0) = -\frac{16}{75} \sum_J \beta^Q_{1,J,F}, \quad (A29a)$$

$$\delta \Theta(J, 7, 0) = \frac{1}{35} \sum_J \beta^Q_{1,J,F}, \quad (A29b)$$

$$\delta \Theta(J, 8, 0) = \frac{3}{35} \sum_J \beta^Q_{1,J,F}. \quad (A29c)$$

which is independent of $m$ at this level of approximation. The dominant term is again the $D_2$ contribution for which $\beta^Q_{1,2} = -0.014$. Omitting the $D_2$ contribution, we get a theoretical estimate of $-2.63 \times 10^{-4} e a_0$ for the effective quadrupole moment of the hyperfine-averaged transition.

4. Matrix elements

Matrix elements used in this work are from results reported in Refs. [12,14]. However, signs of matrix elements are not
TABLE II. Reduced matrix elements used in this work. These are derived from the work in Ref. [12] and include the relative sign. Matrix elements of $T^e_1$ and $T^e_1$ are specified in MHz/$\mu_B$ and MHz/b, where $\mu_B$ is the nuclear magnetic moment and b is the barn unit of area. Matrix elements of $m$ and $\Theta^{(2)}_1$ are given in units of $\mu_B$ and $e\alpha_0^2$, respectively, where $\mu_B$ is the Bohr magneton, $e$ is the fundamental unit of charge, and $a_0$ is the Bohr radius.

| ME | Value | ME | Value |
|----|-------|----|-------|
| $\langle D_2 \| T^e_1 \| D_1 \rangle$ | $10\,618$ | $\langle D_2 \| T^e_2 \| D_1 \rangle$ | $70$ |
| $\langle D_2 \| T^e_1 \| D_1 \rangle$ | $686$ | $\langle D_2 \| T^e_2 \| D_1 \rangle$ | $-0.524$ |
| $\langle D_1 \| m \| D_2 \rangle$ | $-4.523$ | $\langle D_1 \| \Theta^{(2)} \| D_2 \rangle$ | $-1.018$ |

always specified, as the sign of a single matrix element can be set arbitrarily. As this work explicitly requires the relative sign between matrix elements, we give a list of the relevant matrix elements including the sign in Table II. Matrix elements of $T^e_2$ given in the table differ in sign from those given in [14]. This was due to a difference in the definition of $T^e_2$ relative to [13] that was discovered in the course of this work. This will result in minor changes to the calculated results in [12,14], but it will not significantly influence the results or conclusions in those reports.

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