Second-order effects on the hyperfine structure of $P$ states of alkali-metal atoms

K. Beloy and A. Derevianko

Physics Department, University of Nevada, Reno, Nevada 89557

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We analyze second-order $M_1$-$M_1$ and $M_1$-$E_2$ effects to the hyperfine structure (HFS) of the lowest energy $P$ states of alkali-metal atoms arising from the coupling of the two $(J = 1/2, 3/2)$ fine-structure levels through the hyperfine interaction. We find these effects to be especially sizable in Li, leading to a $\gamma_r$ correction to the most accurate reported experimental value of the $A(P_{1/2})$ HFS constant of $^7$Li [D. Das and V. Natarajan, J. Phys. B 41, 035001 (2008)]. For the remaining alkali-metal systems, the results tabulated within may be referenced as higher precision is sought in experimental determination of the HFS constants.

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I. INTRODUCTION

As experimental accuracy improves, the interpretation of measurements may require refined theoretical analysis. Measurements of the hyperfine structure (HFS) is one of such examples. The HFS of atomic systems arises from the coupling between the atomic electrons and the nuclear spin. Generally speaking, in the approximation that $J$, representing the electronic angular momentum, remains a “good” quantum number, the HFS can be accurately described by the conventional (first-order) HFS constants $A, B, C, \ldots$ [1]. Respectively, these constants describe the electronic interaction with the nuclear magnetic dipole ($M_1$), electric quadrupole ($E_2$), magnetic octupole ($M_3$), \ldots; these interactions are collectively referred to as the hyperfine interaction (HFI). Likewise, with $J$ being a “good” quantum number, experimental measurements of the HFS intervals, along with known values of the nuclear moments, can be used to definitively determine these HFS constants. However, for atomic states that are part of a fine-structure manifold, the nearby fine-structure levels may provide sizable contamination to the $J$-purity $^2S^3S_1^1$. In these situations, to make the connection between HFS interval measurements and HFS constants, it becomes necessary to consider the HFI coupling between fine-structure states [1].

In this paper, we provide results for calculations of the second-order corrections to the HFS for the lowest energy $P$ states of the naturally occurring alkali-metal isotopes. These isotopes, along with their respective nuclear properties, are displayed in Table I. The HFS constants $A(P_{1/2}), A(P_{3/2}),$ and $B(P_{3/2})$ have been experimentally measured for all of these isotopes (see Refs. [2, 3, 4] and references within). In a recent paper, Das and Natarajan [6] claim a significant improvement in experimental uncertainty over earlier works for most of these constants.

Due to its relatively small fine-structure splitting, the second-order effects of the HFI are most noticeable in Li, the lightest of the alkali-metal atoms. Over thirty years ago, in experimental determination of the HFS constants, Orth et al. [2, 3] recognized the need to consider the mixing of the fine-structure $P$ states of Li. However, more recent measurements of the $^6$Li $A(P_{1/2})$ constants [6, 9] have overlooked this important effect. Namely, we find that the second-order correction to the $^7$Li $A(P_{1/2})$ constant causes a shift which is a full order of magnitude more than claimed uncertainty of Das and Natarajan [6]. For the remaining alkali-metal isotopes, we find that the second-order effects are not significant at the current levels of experimental precision for the HFS constants. However as higher precision is sought, it may become necessary to include these effects. The compilation of second-order corrections provided herein may provide useful complementary data for future high-precision experiments on these isotopes.

In this paper, we present pertinent equations for the HFI and corresponding first- and second-order energies obtained from a standard perturbation theory analysis. In Section II we provide a reformulated tensorial analysis of the perturbation theory; this formalism provides more insight into the rotational symmetries of the various second-order contributions. We compile HFS expressions for the $P$ states of the alkali-metal atoms in Section III. In Section IV we tabulate our results, followed by concluding remarks in Section V. Furthermore, we include an Appendix.
containing notations and expressions for spherical tensor operators appearing in Sections II and III.

II. THE HYPERFINE INTERACTION

In this Section, we recapitulate the basic properties of the hyperfine interaction and the application of perturbation theory to analyze its effects on atomic structure. This Section is an abbreviated review of the presentation provided in Ref. [2]. We employ the notation \langle T_k \rangle_I to represent the expectation value of the zero-component operator of spherical tensor (of rank \( k \)) \( T_k \) in the “stretched” state \(| I, M_I = I \rangle \). This is related to the reduced matrix element through the expression

\[
\langle T_k \rangle_I = \left( \begin{array}{cc} I & k \\ -I & 0 \\ 1 \end{array} \right) \langle I | T_k | I \rangle.
\]

The hyperfine interaction can be expressed as a sum over scalar products of spherical tensors:

\[
H_{\text{HFI}} = \sum_k T_k^\alpha \cdot T_k^\epsilon,
\]

where \( T_k^\alpha \) and \( T_k^\epsilon \) are spherical tensors of rank \( k \) \((k > 0)\) acting in the nuclear and electronic spaces, respectively. As \( H_{\text{HFI}} \) is a scalar operator in the combined space, it is convenient to work in the conventional basis formed by coupling nuclear, \(|IM_I\rangle\), and electronic, \(|\gamma JM_J\rangle\), states,

\[
|\gamma IJF_MF\rangle = \sum_{M_{J1},M_{J2}} C^{F_M F}_{M_{J1};M_{J2}} |IM_I\rangle |\gamma JM_J\rangle,
\]

with \( \gamma \) encapsulating remaining electronic quantum numbers and the coupling coefficients being the Clebsch-Gordon coefficients. A matrix element of the HFI between these basis states is given by

\[
\langle \gamma'I'J'F'M'_F | H_{\text{HFI}} | \gamma IJF_MF \rangle = \delta_{F,F'}\delta_{M_F,M'_F} (-1)^{I+J'+F} \sum_k \left\{ \begin{array}{ccc} I & J & F \\ J' & I & k \end{array} \right\} T_k^\alpha \cdot T_k^\epsilon \langle I | T_k^\alpha | I \rangle \langle I | T_k^\epsilon | I \rangle \langle \gamma' J' | T_k^\epsilon | \gamma J \rangle.
\]

First-order and second-order energy corrections to the state described by electronic quantum numbers \( \gamma \) and \( J \) are

\[
\begin{align*}
W_F^{(1)} &= \langle \gamma IJF_MF | H_{\text{HFI}} | \gamma IJF_MF \rangle = (-1)^{I+J+F} \sum_k \left\{ \begin{array}{ccc} I & J & F \\ J' & I & k \end{array} \right\} \langle I | T_k^\alpha | I \rangle \langle I | T_k^\epsilon | I \rangle \langle \gamma J | T_k^\epsilon | \gamma J \rangle, \\
W_F^{(2)} &= \sum_{\gamma',J'} \frac{\langle \gamma IJF_MF | H_{\text{HFI}} | \gamma IJF_MF \rangle \langle \gamma' IJF_MF | H_{\text{HFI}} | \gamma IJF_MF \rangle}{E_{\gamma J} - E_{\gamma' J'}} \\
&= \sum_{\gamma',J'} \frac{(-1)^{J-J'} \sum_{k_1,k_2} \left\{ \begin{array}{ccc} I & J & F \\ J' & I & k_1 \\ \gamma' & J' & k_2 \end{array} \right\} \langle I | T_{k_1}^\alpha | I \rangle \langle I | T_{k_2}^\alpha | I \rangle \langle \gamma J | T_{k_1}^\epsilon | \gamma' J' \rangle \langle \gamma' J' | T_{k_2}^\epsilon | \gamma J \rangle}{E_{\gamma J} - E_{\gamma' J'}}.
\end{align*}
\]

Here the summations exclude the case \((\gamma' J') = (\gamma J)\); this will be implicit in similar summations to follow. We note here that, due to large energies associated with nuclear excitations, we treat the nuclear states as “good” quantum states. The reduced matrix elements \( \langle I | T_{k_1}^\alpha | I \rangle \langle I' | T_{k_2}^\alpha | I \rangle \langle \gamma J | T_{k_1}^\epsilon | \gamma' J' \rangle \langle \gamma' J' | T_{k_2}^\epsilon | \gamma J \rangle \) appearing here are associated with the nuclear moments. Specifically, the magnetic dipole \((k = 1)\), electric quadrupole \((k = 2)\), and magnetic octupole \((k = 3)\) are given by

\[
\mu = \langle T_1^\alpha \rangle_I, \\
Q = 2\langle T_2^\alpha \rangle_I, \\
\Omega = -\langle T_3^\alpha \rangle_I.
\]

Furthermore the product of reduced matrix elements \( \langle I | T_{k_1}^\alpha | I \rangle \langle I' | T_{k_2}^\alpha | I \rangle \langle \gamma J | T_{k_1}^\epsilon | \gamma' J' \rangle \langle \gamma' J' | T_{k_2}^\epsilon | \gamma J \rangle \) appearing in Eq. (5) correspond to the conventional first-order hyperfine constants. Specifically, through the \( C \) constant, these are given by

\[
\begin{align*}
A &= \frac{1}{12} \langle T_1^\alpha \rangle_I \langle T_1^\epsilon \rangle_I = \frac{1}{12} \mu \langle T_1^\epsilon \rangle_I, \\
B &= \frac{2}{9} \langle T_2^\alpha \rangle_I \langle T_2^\epsilon \rangle_I = \frac{2}{9} Q \langle T_2^\epsilon \rangle_I, \\
C &= \langle T_3^\alpha \rangle_I \langle T_3^\epsilon \rangle_I = -\Omega \langle T_3^\epsilon \rangle_I.
\end{align*}
\]

For electronic states within a fine-structure manifold, the leading second-order effects are due to mixing with the nearby states within the manifold (i.e., \( \gamma' = \gamma \)). Furthermore, these effects are dominated by the dipole-dipole (\( M1-M1 \)) and dipole-quadrupole (\( M1-E2 \)) terms. The constants \( \eta \) and \( \zeta \) have been used in Refs. [1, 3] to pa-
rameterize these effects and are given by
\[
\eta = \mp \frac{(I + 1)(2I + 1) \mu^2}{J} \frac{\langle \gamma | J | T^n_1 || \gamma | J + 1 \rangle^2}{E_{\gamma, J} - E_{\gamma, J + 1}}, \quad (6)
\]
\[
\zeta = \mp \frac{(I + 1)(2I + 1)}{J} \sqrt{\frac{2I + 3}{2I - 1}} \times \frac{\mu Q (\gamma | J | T^n_1 || \gamma | J + 1 \rangle \langle \gamma | J | T^n_2 || \gamma | J + 1 \rangle}{E_{\gamma, J} - E_{\gamma, J + 1}}, \quad (7)
\]
(If both \( J \pm 1 \) levels exist, it would be necessary to distinguish two independent \( \eta \)'s and \( \zeta \)'s.) Explicit formulas for matrix elements of the electronic tensors \( T^n_k \) are given in Ref. [4].

### III. TENSORIAL ANALYSIS OF SECOND-ORDER EFFECTS

In this section we reformulate the second-order contributions to the energy. We classify the second-order terms according to the underlying rotational symmetry in the nuclear and electronic spaces. As a result, specific second-order terms are connected to the first-order constants. However, if the second-order effects can- not affect experimental determination of the \( C \) constant, as proven by brute manner in Ref. [4]. However, the formalism here is also farther reaching, as it can easily be extended to other second-order terms past \( \eta \) and to higher orders.

We begin with an effective Hamiltonian, \( H_{\text{eff}} \), which produces the exact hyperfine energies when acting on the (unperturbed) coupled basis states, Eq. [2], i.e. \( H_{\text{eff}}^{(1)} | \gamma | J | I \rangle = W_F | \gamma | J | I \rangle M_F \). We decompose this effective Hamiltonian into contributions of increasing orders of the HFI, \( H_{\gamma , J} = H_{\gamma , J}^{(1)} + H_{\gamma , J}^{(2)} + \ldots \), with associated energy contributions given by \( W_F^{(m)} = \langle J | J | I \rangle M_F \rangle || \gamma | J | I \rangle M_F \). From Eq. [3], we may infer that the first-order Hamiltonian takes the form \( H_{\gamma , J}^{(1)} = H_{\text{HFI}} \). Furthermore, from Eq. [4], we infer the second-order Hamiltonian to be
\[
H_{\gamma , J}^{(2)} = H_{\text{HFI}} R_{\gamma , J} H_{\text{HFI}} = \sum_{k_1, k_2} (T^n_{k_1} \cdot T^n_{k_2}) R_{\gamma , J} (T^n_{k_1} \cdot T^n_{k_2}),
\]
where the latter expression is obtained by using Eq. [1] to represent \( H_{\text{HFI}} \). The operator \( R_{\gamma , J} \) here is the resolvent operator; it acts in the electronic space and is given by the expressions
\[
R_{\gamma , J} = \sum_{\gamma , J' M' J' \gamma'} \frac{|\gamma' J' M' J'|}{E_{\gamma , J} - E_{\gamma , J' \gamma'}},
\]
\[
= \sum_{\gamma , J' M' J' \gamma'} \frac{|\gamma' J' M' \gamma'|}{E_{\gamma , J} - E_{\gamma , J' \gamma'}} \times \sum_{\gamma , J' M' J' \gamma'} \frac{|\gamma' J' M' |}{E_{\gamma , J} - E_{\gamma , J' \gamma'}}.
\]
It is important to realize that the resolvent operator behaves as a scalar operator under rotations in the electronic space.

We may recouple the tensor operators of the second-order Hamiltonian, Eq. [5], to isolate parts acting in the nuclear and electronic spaces. The resulting expression is
\[
H_{\gamma , J}^{(2)} = \sum_{k_1, k_2, k} \left( -1 \right)^{k_1 + k_2 + k} \times \left\{ T^n_{k_1} \otimes T^n_{k_2} \right\}_k \cdot \left\{ T^n_{k_1} \otimes R_{\gamma , J} T^n_{k_2} \right\}_k.
\]
(See the Appendix for notational descriptions; see Ref. [10] for general relations involving spherical tensors.) The second-order correction to the energy is given by the diagonal matrix elements of \( H_{\gamma , J}^{(2)} \) in the coupled basis:
\[
W_F^{(2)} = \langle J | J | I \rangle M_F \rangle || \gamma | J | I \rangle M_F \rangle
\]
\[
= \left( -1 \right)^{J + F} \sum_{k_1, k_2, k} \left\{ -1 \right\}^{k_1 + k_2 + k} \times \left\{ T^n_{k_1} \otimes T^n_{k_2} \right\}_k \cdot \left\{ T^n_{k_1} \otimes R_{\gamma , J} T^n_{k_2} \right\}_k \langle \gamma | J \rangle \langle \gamma | J \rangle M_F \rangle || \gamma | J \rangle M_F \rangle.
\]
Comparing this to Eq. [3], we can see clearly that all \( k \)-dependent terms enter the first- and second-order energy expressions in an identical manner. However, because \( H_{\text{HFI}} \) does not contain a monopole contribution, the index \( k \) in Eq. [5] is limited by \( k > 0 \), whereas the summation here is inclusive of the case \( k = 0 \). Analyzing the \( F \)-dependent factors entering this expression, namely the phase factor and six-\( j \) symbol, under the condition of \( k = 0 \) gives
\[
\left( -1 \right)^{J + F} \left\{ I \right\} \left\{ J \right\} M_F \rangle || \gamma | J \rangle M_F \rangle = \frac{1}{\sqrt{(2I + 1)(2J + 1)}},
\]
and we see that \( F \)-dependence is lost. Thus, the second-order \( k = 0 \) terms here only cause an overall shift to the HFS energy levels, and do not affect the interval spacing between levels.

If all second- and higher-order effects are negligible, then the HFS intervals are determined completely by the terms \( \langle J | J | I \rangle M_F \rangle || \gamma | J \rangle M_F \rangle || \gamma | J \rangle M_F \rangle \) appearing in Eq. [3]; we mention again that these terms are related directly (see Eq. [5]) to the conventional hyperfine constants \( A (k = 1), B (k = 2), C (k = 3), \ldots \) As \( T^n_k \) and \( T^n_k \) are spherical tensors, the specific value of \( k \) represents the underlying rotational symmetry in the nuclear and electronic spaces, respectively. Experimental measurements of the HFS interval spacings may be used to determine these constants. However, if the second-order effects cannot be neglected, then the terms \( \langle J | J | I \rangle M_F \rangle || \gamma | J \rangle M_F \rangle || \gamma | J \rangle M_F \rangle \) can no longer be determined by the intervals. The “constants” which could be determined would also depend on second-order effects:
\[
\langle J | J | I \rangle M_F \rangle || \gamma | J \rangle M_F \rangle || \gamma | J \rangle M_F \rangle + \sum_{k_1, k_2} \left\{ -1 \right\}^{k_1 + k_2 + k} \times \left\{ T^n_{k_1} \otimes T^n_{k_2} \right\}_k || \gamma | J \rangle M_F \rangle || \gamma | J \rangle M_F \rangle.
\]
We note that second-order dipole-dipole \((k_1 = k_2 = 1)\) terms only affect determination of the \(A\) and \(B\) constants, as two rank-one tensors can only be coupled to form a tensor of rank \(k \leq 2\). This agrees with the proof given in Ref. [4], in which the \(C\) constant was shown not to be affected by the second-order constant \(\eta\). However, here we extend this conclusion to dipole-dipole terms which mix states outside of the fine-structure manifold as well. Similar conclusions can also be drawn here; for example, second-order dipole-octupole terms do not affect the determination of the \(A\) constant, as a rank-one and a rank-three tensor cannot be coupled to form a tensor of rank \(k = 1\).

The reduced matrix elements appearing here can be simplified, giving

\[
\langle I || \{T_{i_1}^k \otimes T_{j_1}^k \} || I \rangle = (-1)^{2I+k} \sqrt{2k+1} \times \sum \left\{ \begin{array}{ccc} k_1 & I & k_2 & I \\ k & I & k & I \end{array} \right\} \langle I || T_{i_1}^k || I \rangle \langle I || T_{j_1}^k || I \rangle,
\]

\[
\langle \gamma J || \{T_{k_1}^k \otimes R_{\gamma J} T_{k_1}^k \} || \gamma J \rangle = (-1)^{2J+k} \sqrt{2k+1} \times \sum \left\{ \begin{array}{ccc} k_1 & J & k_2 & J \\ k & J & k & J \end{array} \right\} \langle \gamma J || T_{i_1}^k || \gamma J \rangle \langle \gamma J || T_{j_1}^k || \gamma J \rangle.
\]

These expressions may be used in Eq. [9], at which point the summation over \(k\) may be carried out analytically by using a well-known six-\(j\) sum rule; the resulting expression is identical to Eq. [14].

The tensorial analysis of second-order HFI effects presented in this Section could be applied to higher-order effects as well, with similar insights following. For example, we could find that experimental determination of the \(D\) constant is not affected by third-order dipole-dipole-dipole terms, due to the fact that three rank-one tensors cannot be coupled to form a composite tensor with the rotational symmetry of a rank-four tensor.

**IV. EXPRESSIONS FOR \(P\)-STATES OF ALKALI METAL ATOMS**

In this Section we concern ourselves with the HFS equations of the lowest energy \(P\)-states of alkali-metal atoms, namely the isotopes of Table [I]. Specifically, we are considering the \(nP_{1/2}\) and \(nP_{3/2}\) states, with \(n = 2, 3, 4, 5, 6\) for isotopes of Li, Na, K, Rb, and Cs, respectively; the specific \(n\) will be implicit hereafter. As inferred from the arguments of the previous Section, to determine the (first-order) constants \(A, B, C, \ldots\) by measurement of HFS intervals, it is necessary to have a knowledge of the higher-order effects. Here we assume that these higher-order effects are sufficiently described by the second-order dipole-dipole and dipole-quadrupole constants \(\eta\) and \(\zeta\). These are defined in Eqs. [17]; one convenience of these definitions is that \(\eta\) and \(\zeta\) are identical for both the \(P_{1/2}\) and \(P_{3/2}\) states (i.e., \(\eta(P_{1/2}) = \eta(P_{3/2}) \equiv \eta\) and similar for \(\zeta\)). Below we compile specific expressions for the first-order constants in terms of the HFS intervals \(\delta W_{P(J)} = W_{P(J)} - W_{P(J-1)}\) and the constants \(\eta\) and \(\zeta\).

For \(^6\)Li \((I = 1)\) we have

\[
A(P_{1/2}) = \frac{2}{3} \delta W_{3/2}^{P(J)} + \frac{1}{36} \eta + \frac{1}{12 \sqrt{3}} \zeta,
\]

\[
A(P_{3/2}) = \frac{1}{6} \delta W_{3/2}^{P(J)} + \frac{3}{10} \delta W_{5/2}^{P(J)} + \frac{1}{72} \eta - \frac{1}{120 \sqrt{3}} \zeta,
\]

\[
B(P_{3/2}) = \frac{1}{3} \delta W_{3/2}^{P(J)} + \frac{1}{5} \delta W_{5/2}^{P(J)} + \frac{1}{36} \eta + \frac{1}{20 \sqrt{3}} \zeta.
\]

For the isotopes \(^7\)Li, \(^{23}\)Na, \(^{39}\)K, \(^{41}\)K, and \(^{87}\)Rb \((I = 3/2)\) we have

\[
A(P_{1/2}) = \frac{1}{2} \delta W_{2}^{P(J)} + \frac{1}{90} \eta + \frac{1}{15 \sqrt{3}} \zeta,
\]

\[
A(P_{3/2}) = \frac{1}{20} \delta W_{1}^{P(J)} + \frac{4}{25} \delta W_{2}^{P(J)} + \frac{21}{100} \delta W_{3}^{P(J)} + \frac{1}{180} \eta - \frac{1}{150 \sqrt{3}} \zeta,
\]

\[
B(P_{3/2}) = \frac{1}{4} \delta W_{1}^{P(J)} - \frac{7}{20} \delta W_{2}^{P(J)} + \frac{7}{20} \delta W_{3}^{P(J)} + \frac{1}{30} \eta + \frac{1}{20 \sqrt{3}} \zeta,
\]

\[
C(P_{3/2}) = -\frac{1}{80} \delta W_{1}^{P(J)} - \frac{1}{100} \delta W_{2}^{P(J)} + \frac{1}{400} \delta W_{3}^{P(J)} + \frac{1}{400 \sqrt{3}} \zeta.
\]

For \(^{85}\)Rb \((I = 5/2)\) we have

\[
A(P_{1/2}) = \frac{1}{3} \delta W_{3}^{P(J)} + \frac{1}{315} \eta + \frac{8}{105 \sqrt{30}} \zeta,
\]

\[
A(P_{3/2}) = \frac{3}{50} \delta W_{2}^{P(J)} + \frac{64}{525} \delta W_{3}^{P(J)} + \frac{9}{70} \delta W_{4}^{P(J)} + \frac{1}{630} \eta - \frac{4}{525 \sqrt{30}} \zeta,
\]

\[
B(P_{3/2}) = -\frac{1}{2} \delta W_{2}^{P(J)} - \frac{8}{21} \delta W_{3}^{P(J)} + \frac{15}{28} \delta W_{4}^{P(J)} + \frac{2}{63} \eta + \frac{1}{14 \sqrt{30}} \zeta,
\]

\[
C(P_{3/2}) = \frac{1}{40} \delta W_{2}^{P(J)} - \frac{1}{35} \delta W_{3}^{P(J)} + \frac{1}{112} \delta W_{4}^{P(J)} + \frac{3}{280 \sqrt{30}} \zeta.
\]
Finally, for $^{133}\text{Cs}$ ($I = 7/2$) we have

$$A(P_{1/2}) = \frac{1}{4} \delta W_4^{(P_{1/2})} + \frac{1}{756} \eta + \frac{1}{126} \zeta,$$

$$A(P_{3/2}) = \frac{3}{56} \delta W_3^{(P_{3/2})} + \frac{2}{21} \delta W_4^{(P_{3/2})} + \frac{11}{120} \delta W_5^{(P_{3/2})} + \frac{1}{1512} \eta - \frac{1}{120} \zeta,$$

$$B(P_{3/2}) = \frac{5}{8} \delta W_3^{(P_{3/2})} - \frac{1}{3} \delta W_4^{(P_{3/2})} + \frac{77}{120} \delta W_5^{(P_{3/2})} + \frac{1}{36} \eta + \frac{1}{120} \zeta,$$

$$C(P_{3/2}) = \frac{1}{32} \delta W_3^{(P_{3/2})} - \frac{1}{24} \delta W_4^{(P_{3/2})} + \frac{7}{480} \delta W_5^{(P_{3/2})} + \frac{1}{480} \zeta.$$

We note that in all of the above cases, the $\zeta$ contribution to $A(P_{3/2})$ is suppressed by a factor of $1/2$ $(-1/10)$ compared to its contribution to $A(P_{1/2})$.

V. RESULTS

In order to calculate the second-order constants $\eta$ and $\zeta$ from Eqs. (6,7), we must first generate the $P_{1/2}$ and $P_{3/2}$ electronic states. This involves solving the electron correlation problem. We employ an $ab$ initio relativistic-coupled-cluster method which includes single, double, and triple excitations from the lowest-order Dirac-Hartree-Fock state. While both core and valence single and double excitations are included, the triple excitations involve simultaneous excitation of the valence electron with two core electrons. In other words, the triple core excitations are not incorporated in the many-body wavefunction. We refer to this method as the CCSDvT method. The most sophisticated approximation within the CCSDvT method is described in our previous work [11] for three-electron Li. For heavier alkanes (beyond Li) the approximation of Ref. [11] becomes computationally expensive and we only keep the lowest-order terms on the right-hand-side of the valence triple excitations $T_3^{\text{exc}}$ and $T_5^{\text{exc}}$ terms in notation of Ref. [11]). For the electronic reduced matrix elements entering Eqs. (6,7), this method gives results with accuracies better than 0.1% for the lightest (Li) and better than a few percent for the heaviest (Cs) alkali-metal system.

Table II displays our computed values of the reduced matrix elements of the electronic tensors $T_1$ and $T_2$ between $P$ states, along with experimental values for the fine structure energy splitting. The variation in these values for different isotopes of the same atomic system is below the level of precision shown. Combining these values with the nuclear data for each isotope, Table II we obtain the second-order constants $\eta$ and $\zeta$. These are displayed in Table III. Also displayed in this Table are the “corrections” to the HFS constants $A(P_{1/2})$, $A(P_{3/2})$, $B(P_{3/2})$, and $C(P_{3/2})$ deduced from $\eta$ and $\zeta$. Here each correction is regarded as the difference between the actual constant and the measured constant based on the first-order equations. These can be inferred from the equations in Section IV, e.g., for $^{133}\text{Cs}$: $\Delta A(P_{1/2}) = (1/756)\eta + (1/126)\zeta$.

| Atom  | $\langle P_{3/2}||T_1||P_{1/2}\rangle$ (MHz/µK) | $\langle P_{1/2}||T_2||P_{3/2}\rangle$ (MHz/µK) | $\Delta E_0$ (cm$^{-1}$) |
|-------|------------------------------------------|------------------------------------------|-----------------|
| Li    | 19.0                                    | 11.9                                   | 0.3366          |
| Na    | 12.1                                    | 59.4                                   | 17.1963         |
| K     | −12.6                                   | −103                                   | 57.600          |
| Rb    | 20.1                                    | 213                                    | 237.598         |
| Cs    | 29.2                                    | 313                                    | 554.11          |

The most accurate reported value of the $^7\text{Li}$ $A(P_{1/2})$ constant based on experimental measurement of HFS intervals is that of Das and Natarajan, Ref. [6], wherein they give a value $A(P_{1/2}) = 46.024(3)$ MHz. However, this value is based on first-order HFS equations and is thus completely negligible of higher-order effects. From Table III we see that the second-order effects would cause a sizable shift of $\Delta A(P_{1/2}) = 27.0$ kHz to this value. This shift is a full order of magnitude larger than the claimed accuracy (3 kHz) of the constant itself. Das and Natarajan also claim accurate results for $A$ and $B$ constants for $P$ states of all isotopes in Table II with the exception of the $^{6,7}\text{Li}$ $P_{1/2}$ and $^{41}\text{K}$ $P_{1/2,3/2}$ states.

Figure II displays various reported values of the $^7\text{Li}$ $A(P_{1/2})$ constant and their associated error bars. Along with the value from Das and Natarajan, the Figure includes experimental values from Orth et al. [2] and Walls et al. [9]. The earlier value of Orth et al. accounted for second-order effects, whereas that of Walls et al. did not; both claim an accuracy of the same order as our computed $\Delta A(P_{1/2})$. Also included in this Figure are theoretical values recently reported by our group [11] and Derevianko et al. [12] and Yerokhin [13]. This Figure also displays “corrected” values using our computed $\Delta A(P_{1/2})$ for the applicable cases of Das and Natarajan [4] and Walls et al. [4]. We note that this correction causes these two values to shift farther away from the values of Orth et al. [2], Derevianko et al. [11], and Yerokhin [13]; we do not attempt to explain the resulting large discrepancy.

For the remaining HFS constants of Li, the second-order correction again proves to be sizable, though not as pronounced as in the $^7\text{Li}$ $A(P_{1/2})$ case. For the $^6\text{Li}$ $A(P_{1/2})$ constant, Das and Natarajan claim an accuracy of the same order of magnitude as our predicted second-order correction $\Delta A(P_{1/2}) = 4.01$ kHz.

Orth et al. [2, 3] performed HFS measurements of $^6,7\text{Li}$ in the presence of strong fields and used a complex fitting scheme to obtain the HFS constants. In addition
TABLE III: Second-order constants $\eta$ and $\zeta$ and corresponding second-order corrections to the HFS constants. All values are in kHz. $x[y]$ denotes $x \times 10^y$.

| Isotope | $\eta$ | $\zeta$ | $\Delta A(P_{1/2})$ | $\Delta A(P_{3/2})$ | $\Delta B(P_{3/2})$ | $\Delta C(P_{3/2})$ |
|---------|--------|--------|-----------------|-----------------|-----------------|-----------------|
| $^7$Li   | 1.45[+2] | -2.02[-1] | 4.01             | 2.01             | 4.02             |                  |
| $^7$Li   | 2.53[+2] | -3.41[+1] | 2.70[+1]        | 1.41[+1]        | 8.34[+1]        | -3.82[-2]       |
| $^{23}$Na| 9.25   | 3.72   | 2.14[-1]        | 4.03[-2]        | 3.92[-1]        | 4.16[-3]        |
| $^{39}$K | 9.33[-2] | 1.98[-1] | 6.94[-3]        | -7.20[-5]       | 7.54[-3]        | 2.21[-4]        |
| $^{41}$K | 2.81[-2] | 1.32[-1] | 4.25[-3]        | -2.38[-4]       | 3.89[-3]        | 1.48[-4]        |
| $^{85}$Rb| 8.76[-1] | 2.68    | 4.01[-2]        | -2.34[-3]       | 6.28[-2]        | 5.25[-3]        |
| $^{87}$Rb| 2.87    | 2.57    | 1.08[-1]        | 8.32[-3]        | 1.53[-1]        | 2.87[-3]        |
| $^{133}$Cs| 3.51    | -6.69[-2] | 4.11[-3]        | 2.38[-3]        | 9.70[-2]        | -1.39[-4]       |

Orth et al.\textsuperscript{a}  \rule{2cm}{0.4mm}
Walls et al.\textsuperscript{b}  \{
Das et al.\textsuperscript{c}  \{
Derevianko et al.\textsuperscript{d}
Yerokhin\textsuperscript{y}

FIG. 1: (Color online) Values of the HFS constant $A(P_{1/2})$ for $^7$Li. The heavy (hollow) squares denote experimental (theoretical) values reported in the respective reference, and the heavy diamonds denote the associated corrected values (of the immediately preceding value) using second-order correction $\Delta A(P_{1/2}) = 27.0$ kHz from Table III when applicable. The uncertainty of $\Delta A(P_{1/2})$ is negligible compared to the experimental uncertainties in these cases. No uncertainty is given for d. \textsuperscript{a}Ref. 12; \textsuperscript{b}Ref. 3; \textsuperscript{c}Ref. 4; \textsuperscript{d}Ref. 11; \textsuperscript{e}Ref. 16.

| Isotope | $\eta$ | $\zeta$ | $\Delta A(P_{3/2}, P_{1/2})$ |
|---------|--------|--------|-------------------------------|
| $^7$Li   | 11.9   | 11.87853 | 11.823(81)                   |

TABLE IV: Computed off-diagonal constant $A(P_{3/2}, P_{1/2})$ for $^7$Li compared to non-relativistic and experimental values. Units are MHz.

$\eta = 22.46$ kHz was used \textsuperscript{17}. In a following paper, Ref. \textsuperscript{18}, this effect was reevaluated using a more sophisticated third-order approach, resulting in a value of $\eta = 2.09$ kHz. Our present value ($\eta = 3.51$ kHz), based on the more complete CCSDvT method, is 68% larger than the latter value.

For the heavier alkali-metal atoms past Li, all of the predicted second-order corrections (Table III) are one to six orders of magnitude smaller than the uncertainty in the most precise reported experimental value of the respective HFS constant. Thus, at the current levels of precision, the neglect of second-order effects in these heavier systems is acceptable. However, as experimental techniques improve and higher precision is sought, it may become necessary to consider these higher-order effects.

VI. DISCUSSION

In this paper, we have demonstrated for the $P$ states of the alkali-metal atoms that the second-order effects cannot simply be neglected in deducing HFS constants from high-precision measurements of the HFS intervals. This is exemplified by the $^7$Li $A(P_{1/2})$ constant, where the second-order effects are shown to cause a $9\sigma$ shift to a recently reported value. Furthermore, we have compiled values for the leading second-order HFS effects caused by the dipole-dipole constants $\eta$ and the dipole-quadrupole constants $\zeta$ for all naturally occurring alkali-metal isotopes. These values can be used in conjunction with high-precision measurements of the HFS intervals of the alkali-metal atoms to determine the HFS constants.

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APPENDIX A: COUPLING OF SPHERICAL TENSORS: NOTATIONS AND DEFINITIONS

Here we provide a description for the notations used in Sections II and III along with basic definitions involving coupling of spherical tensors. For a more complete description of spherical tensors, including specific formulae for recoupling of spherical tensors and matrix elements of coupled tensor operators, see Ref. [10].

A spherical tensor of rank $k$, $P_k$, is a set of $2k+1$ operators. We denote the individual components (operators) as $P_{kq}$, with the index $q$ taking all integer values from $-k$ to $k$. Two spherical tensors, $P_{k_1}$ and $Q_{k_2}$, may be coupled together to form a composite spherical tensor of rank $k$. The rank of the composite tensor is limited by $|k_1 - k_2| \leq k \leq k_1 + k_2$. We denote the coupled tensor by $\{P_{k_1} \otimes Q_{k_2}\}k$; its components are given by

$$\{P_{k_1} \otimes Q_{k_2}\}k_q = \sum_{q_1, q_2} C^{kq}_{k_1 q_1; k_2 q_2} P_{k_1 q_1} Q_{k_2 q_2} , \quad (A1)$$

where $C^{kq}_{k_1 q_1; k_2 q_2}$ represents Clebsch-Gordon coefficients.

The scalar product of two tensors of equal rank is defined as

$$P_k \cdot Q_k = (-1)^k \sqrt{2k+1} \left\{P_k \otimes Q_k\right\}00 = \sum_q (-1)^q P_{kq} Q_{k-q} .$$

If one of the tensors in Eq. (A1) is a scalar, the components of the coupled operator are simply

$$\{P_{0} \otimes Q_{k}\}k_q = P_{00} Q_{kq} ;$$

$$\{P_{k} \otimes Q_{0}\}k_q = P_{kq} Q_{00} .$$

When $P$ ($Q$) here is understood to be a scalar, the composite tensor is then sufficiently represented by $P Q_k$ ($P_k Q$).

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