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Lithium hyperfine splitting

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We present an approach for the calculation of relativistic $m\alpha^6$ corrections to the lithium ground-state hyperfine splitting. It is based on the effective Hamiltonian derived from relativistic quantum electrodynamic theory. This approach with the help of appropriate nonrelativistic correlated basis sets has the potential to be more accurate than currently available relativistic computational methods such as the relativistic many-body perturbation theory, configuration interaction, or multiconfiguration Dirac-Fock method.

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I. INTRODUCTION

The calculation of relativistic and QED effects in few-electron systems is a long-standing problem. We will concentrate on lithium as the simplest alkali-metal atom, for which several precise spectroscopic measurements have been performed [1,2]. In the simplest approach one introduces some effective potential in which the one-electron Dirac equation is solved, which can be regarded as the zeroth-order approximation. The true electron-electron interaction is treated perturbatively order by order and this forms to so-called relativistic many-body perturbation theory [3]. If the perturbative terms are summed in all orders (in the sense of including all single, double, etc., excitations) then it forms the coupled cluster approach [4]; for a short review see Ref. [5]. So far nobody has included triple excitations in a complete way, which is a severe limitation of this approach. Within the relativistic configuration interaction (RCI) method [6] one expands the complete Hamiltonian in the basis of solutions of the one-electron Dirac equation in the effective potential, and afterwards solves numerically a large eigenvalue problem. Here the limitation is the size of basis sets, or in other words the number of included angular momenta. The most precise so far is multiconfiguration Dirac-Fock (MCDF) method, as calculated for lithium by Bieroń *et al.* in Ref. [7]. In this method the state of the atom is represented as a sum of various antisymmetrized electron configurations and the wave function is found by global minimization over all chosen configurations. Yan *et al.* in Ref. [8] have been able to calculate a relativistic correction to lithium hyperfine splitting (hfs) using nonrelativistic wave functions, however in a simplified approach by appropriate rescaling of the hydrogenic result.

Here we present in a pedagogical way an approach that has the potential to be more accurate than MCDF. If we consider lithium as a nonrelativistic system of three electrons, then correlated basis sets are the most adequate representation of the atomic wave function. In practice, one uses Gaussians, exponentials, or Hylleraas-type basis sets. So far, for lithium the most accurate results have been obtained in Ref. [9] with the help of the Hylleraas basis set. The nonrelativistic ground-state hyperfine splitting could be obtained by the calculation of the expectation value of the Fermi contact operator, which is proportional to a Dirac delta function at the origin [9]. We know, however, that there are higher-order relativistic and QED (quantum electrodynamics) corrections. In the approach presented below, these higher-order corrections are expressed in terms of some (more complicated) operators which act on the *nonrelativistic* wave function. As a result one can use the standard Rayleigh-Schrödinger perturbation theory to find higher-order corrections with a suitably optimized nonrelativistic wave function. This approach has already been applied in the simpler case of the helium atom. The Lamb shift of all low-lying states and the hfs of a 2^3S_1 state in ^{3}He [10] were calculated with high precision. We wish to extend this method to lithium, with the aim of calculating relative order $O(\alpha^2)$ relativistic corrections to the ground-state hyperfine splitting.

II. EFFECTIVE HAMILTONIAN

In the effective Hamiltonian approach relativistic and QED effects are expressed in terms of some effective interactions, for example, hyperfine splitting in the S state is given by the Fermi contact interaction. In general, the leading relativistic correction $H^{(4)}_{\rm hfs}$ of order $m\alpha^4$, which depends on nuclear spin I, is [11]

$$H^{(4)}_{\rm hfs}=\frac{m}{M}(1+k)(H^A_{\rm hfs}+H^B_{\rm hfs}+H^C_{\rm hfs}), \tag{1}$$

$$H^A_{\rm hfs}=\sum_{i=1}^{3}\frac{4Z\alpha}{3m^2}\boldsymbol{I}\cdot\boldsymbol{\sigma}_i\pi\delta^3(r_i)(1+a), \tag{2}$$

$$H^B_{\rm hfs}=\sum_{i=1}^{3}\frac{Z\alpha}{m^2}\frac{\boldsymbol{r}_i\times\boldsymbol{p}_i}{r_i^3}\cdot\boldsymbol{I}, \tag{3}$$

$$H^C_{\rm hfs}=\sum_{i=1}^{3}-\frac{Z\alpha}{2m^2}\frac{I^a\sigma_i^b}{r_i^3}\left(\delta^{ab}-3\frac{r_i^a r_i^b}{r_i^2}\right), \tag{4}$$

where a and k are the anomalous magnetic moments of the electron and the nucleus, respectively. The relation of k with the magnetic moment of the nucleus of charge Ze is $\boldsymbol{\mu}=2(1+k)Ze/(2M)\boldsymbol{I}$. m and M are the electron and nuclear

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*Email address: krp@fuw.edu.pl; URL: www.fuw.edu.pl/~krp mass, respectively. The expectation values of $H^B_{\rm hfs}$ and $H^C_{\rm hfs}$ vanish in any S state, but they will contribute in the second order of perturbation calculus, see below. Higher-order relativistic and QED corrections to hyperfine splitting can be written as

$$E_{\rm hfs}=\langle H^{(4)}_{\rm hfs}\rangle+\langle H^{(5)}_{\rm hfs}\rangle+\langle H^{(6)}_{\rm hfs}\rangle+2\left\langle H^{(4)}\frac{1}{(E-H)'}H^{(4)}_{\rm hfs}\right\rangle$$
$$+\langle H^{(6)}_{\rm rad}\rangle+E^{(7)}_{\rm hfs}+\cdots, \tag{5}$$

where $H^{(4)}$ is a Breit Hamiltonian in the nonrecoil limit [11]:

$$H^{(4)}=H^A+H^B+H^C, \tag{6}$$

$$H^A=\sum_{i=1}^{3}\left\{-\frac{p_i^4}{8m^3}+\frac{Z\alpha\pi}{2m^2}\delta^3(r_i)\right\}$$
$$-\sum_{i>j=1}^{3}\left\{\frac{\alpha}{2m^2}p_i^a\left(\frac{\delta^{ab}}{r}+\frac{r^a r^b}{r^3}\right)p_j^b+\frac{\pi\alpha}{m^2}\delta^3(r_{ij})\right.$$
$$\left.+\frac{2\pi\alpha}{3m^2}\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j\delta^3(r_{ij})\right\}, \tag{7}$$

$$H^B=\sum_{i=1}^{3}\left\{\frac{Z\alpha}{4m^2r_i^3}\boldsymbol{r}_i\times\boldsymbol{p}_i\cdot\boldsymbol{\sigma}_i\right\}$$
$$+\sum_{i,j=1,i\neq j}^{3}\left\{\frac{\alpha}{4m^2r_{ij}^3}\boldsymbol{r}_{ij}\times\boldsymbol{p}_j(2\boldsymbol{\sigma}_i+\boldsymbol{\sigma}_j)\right\}, \tag{8}$$

$$H^C=\sum_{i>j=1}^{3}\frac{\alpha}{4m^2}\frac{\sigma_i^a\sigma_j^b}{r_{ij}^3}\left(\delta^{ab}-\frac{3r_{ij}^ar_{ij}^b}{r_{ij}^2}\right), \tag{9}$$

and $\boldsymbol{r}_{ij}=\boldsymbol{r}_i-\boldsymbol{r}_j$, $r_{ij}=|\boldsymbol{r}_{ij}|$. $\langle H^{(5)}_{\rm hfs}\rangle$ is a correction of order $m\alpha^5$. It is a δ-function-like term with the coefficient obtained from the two-photon forward-scattering amplitude. It has the same form as in hydrogen and depends strongly on the nuclear structure. It also includes nuclear recoil effects and inelastic contribution. For the purpose of this work, we assume a heavy nucleus with magnetic moment μ. In this approximation $H^{(5)}_{\rm hfs}$ takes the form [12]

$$H^{(5)}_{\rm hfs}=\sum_{i=1}^{3}\frac{8(Z\alpha)^2}{3\pi M}\boldsymbol{I}\cdot\boldsymbol{\sigma}_i\delta^3(r_i)\int\frac{d^3p}{p^4}[G_E(-p^2)\,G_M(-p^2)$$
$$-(1+k)]. \tag{10}$$

$G_E(-p^2)$ and $G_M(-p^2)$ are electric charge and magnetic-moment distributions in the momentum space, so-called Sachs form factors, which are determined experimentally. The inelastic contribution, neglected here, tends sometimes to be important and depends significantly on the internal properties of nucleus. This correction usually limits the precision of theoretical predictions. The next term $H^{(6)}_{\rm hfs}$ includes nuclear-spin-dependent operators that contribute at order $m\alpha^6$. This term is not well known in the literature. However, in hydrogenic systems, it leads to the so-called Breit correction. For two-electron atoms it was presented in the work on ^{3}He hyperfine splitting [10], but without detailed derivation. We extend this result to lithium and present more details on its origin in the following section. $H^{(6)}_{\rm rad}$ is a QED radiative correction [12]

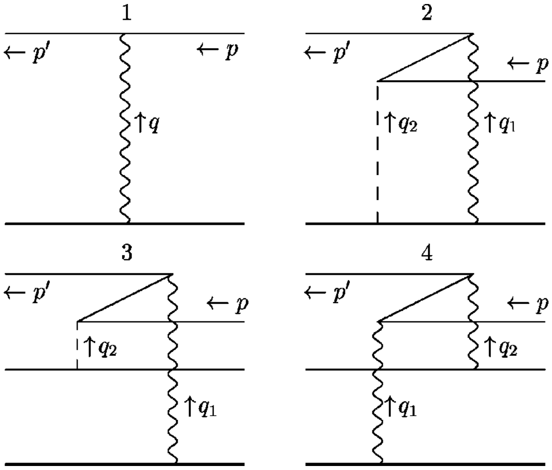

FIG. 1. Time-ordered diagrams contributing to hyperfine structure at order $m\alpha^6$. The dashed line is a Coulomb photon, the wavy line is a transverse photon, the thicker horizontal line denotes the nucleus, and the thiner horizontal line denotes electrons.

$$H^{(6)}_{\rm rad}=\alpha(Z\alpha)^2\frac{4}{3}\left(\ln 2-\frac{5}{2}\right)\frac{1}{mM}\sum_{i=1}^{3}\pi\delta^3(r_i)\boldsymbol{\sigma}_i\cdot\boldsymbol{I}(1+k), \tag{11}$$

which is similar to that in hydrogen. The last term $E^{(7)}_{\rm hfs}$ of order $m\alpha^7$ is discussed in the Summary.

III. DERIVATION OF HIGHER-ORDER CORRECTIONS

We use time-ordered perturbation theory which was previously used for the calculation of helium hfs [10], and the lithium case is not much different. There are four time-ordered diagrams which contribute to $H^{(6)}_{\rm hfs}$ and are presented in Fig. 1. The first two are the same as in hydrogen, the other two are three-body terms.

Let us start the derivation from the first diagram. We use the Coulomb gauge; the wavy line denotes a transverse photon, $1/(2q)(\delta^{ij}-q^iq^i/q^2)$, and the broken line is $1/q^2$. In general, ordering of the vertices of a transverse photon is important, and one diagram represents a whole class of diagrams with all possible ordering of vertices. In our case, however, retardation can be neglected, $1/(E-H-q)\to-1/q$, and two different orderings of vertices lead to $-1/q^2(\delta^{ij}-q^iq^i/q^2)$. The neglect of retardation is the reason for this wavy line to be vertical. The electron vertex is $(\boldsymbol{q}=\boldsymbol{p}'-\boldsymbol{p})$,

$$\begin{aligned}-eu^{+}(p')\alpha^{i}u(p)\approx -e\Bigg\{&\frac{1}{2m}(p^{i}+p'^{i})+\frac{i}{2m}(\boldsymbol{\sigma}\times\boldsymbol{q})^{i}\\&-\frac{1}{16m^{3}}[p^{i}(p'^{2}+3\,p^{2})+p'^{i}(p^{2}\\&+3p'^{2})]+\frac{i}{16m^{3}}[(\boldsymbol{p}'\times\boldsymbol{\sigma})^{i}(p^{2}+3p'^{2})\\&-(\boldsymbol{p}\times\boldsymbol{\sigma})^{i}(p'^{2}+3p^{2})]\Bigg\}.\end{aligned}\tag{12}$$

The corresponding vertex on the nucleus line is

$$Ze\frac{i}{M}[\boldsymbol{I}\times(-\boldsymbol{q})]^{j},\tag{13}$$

where we have neglected spin-independent terms. These terms can also be neglected in the electron vertex. We have omitted here the factor $(1+k)$, which will be included later, namely, in Eq. (20). The second term in Eq. (12) together with that in Eq. (13) lead to the Fermi contact interaction, which is omitted here because we are interested in higher-order corrections. Finally, we arrive at the following expression for the first diagram:

$$\begin{aligned}V_{1}=\int\frac{d^{3}q}{(2\pi)^{3}}e^{i\boldsymbol{q}\cdot\boldsymbol{r}}\frac{4\pi Z\alpha}{q^{2}}\frac{(\boldsymbol{I}\times\boldsymbol{q})^{j}}{M}\left(\delta^{ij}-\frac{q^{i}q^{j}}{q^{2}}\right)\frac{1}{16m^{3}}\\\times[(\boldsymbol{p}'\times\boldsymbol{\sigma})^{i}(p^{2}+3p'^{2})-(\boldsymbol{p}\times\boldsymbol{\sigma})^{i}(p'^{2}+3p^{2})].\end{aligned}\tag{14}$$

In the coordinate space it takes the form presented in Eq. (21), where we sum up over all electrons and assume that this operator acts on S states. This assumption is valid also for all other diagrams. For higher angular momenta, that expression would contain additional terms.

The second diagram contains the so-called one pair creation. The electron line between two vertices represents the projection operator $\Lambda_{-}=(E-H)/(2E)$ into the negative-energy solution of the free Dirac equation. The electron line is the sum of two terms:

$$\begin{aligned}u^{+}(p')\alpha^{j}\Lambda_{-}(p+q_{2})u(p)+u^{+}(p')\Lambda_{-}(p'-q_{2})\alpha^{i}u(p)\\\approx\frac{-i}{m}(\boldsymbol{q}_{2}\times\boldsymbol{\sigma})^{j},\end{aligned}\tag{15}$$

and the nucleus line is

$$\frac{2i}{M}(\boldsymbol{q}_{1}\times\boldsymbol{I})^{i}.\tag{16}$$

There is a factor -1 for each pair, and $1/(2m)$, which comes from the denominator. The complete diagram takes the form

$$\begin{aligned}V_{2}=-\int\frac{d^{3}q_{1}}{(2\pi)^{3}}\frac{d^{3}q_{2}}{(2\pi)^{3}}e^{i\boldsymbol{q}_{1}\cdot\boldsymbol{r}}e^{i\boldsymbol{q}_{2}\cdot\boldsymbol{r}}\frac{4\pi Z\alpha}{q_{2}^{2}}\frac{4\pi Z\alpha}{2q_{1}^{2}}\\\times\left(\delta^{ij}-\frac{q_{1}^{i}q_{1}^{j}}{q_{1}^{2}}\right)\times\frac{1}{m^{2}M}(\boldsymbol{q}_{2}\times\boldsymbol{\sigma})^{j}(\boldsymbol{q}_{1}\times\boldsymbol{I})^{i}.\end{aligned}\tag{17}$$

The sum over all electrons in coordinate space is presented in Eq. (22).

The third diagram is quite similar to the second one,

$$\begin{aligned}V_{3}=\int\frac{d^{3}q_{1}}{(2\pi)^{3}}\frac{d^{3}q_{2}}{(2\pi)^{3}}e^{i\boldsymbol{q}_{1}\cdot\boldsymbol{r}_{1}}e^{i\boldsymbol{q}_{2}\cdot\boldsymbol{r}_{12}}\frac{4\pi\alpha}{q_{2}^{2}}\frac{4\pi Z\alpha}{2q_{1}^{2}}\\\times\left(\delta^{ij}-\frac{q_{1}^{i}q_{1}^{j}}{q_{1}^{2}}\right)\times\frac{1}{m^{2}M}(\boldsymbol{q}_{2}\times\boldsymbol{\sigma}_{1})^{j}(\boldsymbol{q}_{1}\times\boldsymbol{I})^{i}.\end{aligned}\tag{18}$$

The sum over all pairs of electrons is presented in Eq. (23). In the fourth diagram this double vertex with the pair creation is described in the nonrelativistic limit by the term $A^{2}/(2m)$ from the nonrelativistic kinetic energy. It leads to the expression

$$\begin{aligned}V_{4}=\int\frac{d^{3}q_{1}}{(2\pi)^{3}}\frac{d^{3}q_{2}}{(2\pi)^{3}}e^{i\boldsymbol{q}_{1}\cdot\boldsymbol{r}_{1}}e^{i\boldsymbol{q}_{2}\cdot\boldsymbol{r}_{12}}\frac{4\pi Z\alpha}{q_{1}^{2}}\\\times\left(\delta^{ik}-\frac{q_{1}^{i}q_{1}^{k}}{q_{1}^{2}}\right)\frac{4\pi\alpha}{q_{2}^{2}}\left(\delta^{ik}-\frac{q_{2}^{i}q_{2}^{k}}{q_{2}^{2}}\right)\frac{1}{2m^{2}M}\\\times(\boldsymbol{q}_{1}\times\boldsymbol{I})^{i}(\boldsymbol{q}_{2}\times\boldsymbol{\sigma}_{1})^{j}.\end{aligned}\tag{19}$$

One derives the following operators in the coordinate space for all these diagrams [13]:

$$H_{\rm hfs}^{(6)}=(1+k)(V_{1}+V_{2}+V_{3}+V_{4}),\tag{20}$$

$$\begin{aligned}V_{1}=\sum_{i=1}^{3}-\frac{\boldsymbol{I}\cdot\boldsymbol{\sigma}_{i}}{24Mm^{3}}\Bigg\{&2p_{i}^{2}4\pi Z\alpha\delta^{3}(r_{i})+2\times4\pi Z\alpha\delta^{3}(r_{i})p_{i}^{2}\\&+\left[p_{i}^{2},\left[p_{i}^{2},\frac{Z\alpha}{r_{i}}\right]\right]\Bigg\},\end{aligned}\tag{21}$$

$$V_{2}=\sum_{i=1}^{3}\frac{(Z\alpha)^{2}}{r_{i}^{4}}\frac{\boldsymbol{I}\cdot\boldsymbol{\sigma}_{i}}{3Mm^{2}},\tag{22}$$

$$V_{3}=\sum_{i,j=1,i\neq j}^{3}-\frac{\boldsymbol{I}\cdot\boldsymbol{\sigma}_{i}}{3Mm^{2}}\frac{Z\alpha\boldsymbol{r}_{i}}{r_{i}^{3}}\cdot\frac{\alpha\boldsymbol{r}_{ij}}{r_{ij}^{3}},\tag{23}$$

$$V_{4}=\sum_{i,j=1,i\neq j}^{3}-\frac{\boldsymbol{I}\cdot\boldsymbol{\sigma}_{j}}{3Mm^{2}}\frac{Z\alpha\boldsymbol{r}_{i}}{r_{i}^{3}}\cdot\frac{\alpha\boldsymbol{r}_{ij}}{r_{ij}^{3}}.\tag{24}$$

The subtle point of this calculation is that the matrix element of $H_{\rm hfs}^{(6)}$ and the second-order term in Eq. (5) are separately divergent at small r_{1} or r_{2}. However these divergences cancel out in the sum. This is related to the fact that for hydrogen this sum is equal to the expectation value of γA on the

Dirac wave function and thus is finite. We introduce now the following regulator λ to the electron-nucleus Coulomb interaction

$$\frac{Z\alpha}{r_i}\rightarrow\frac{Z\alpha}{r_i}(1-e^{-\lambda m Z\alpha r_i}) \tag{25}$$

in all Hamiltonians in Eq. (5), as well as in the nonrelativistic one. This leads to the following further replacements in $H^{(6)}_{\rm hfs}$:

$$4\pi Z\alpha\,\delta^3(r_i)\equiv-\nabla^2\frac{Z\alpha}{r_i}\rightarrow-\nabla^2\frac{Z\alpha}{r_i}(1-e^{-\lambda m Z\alpha r_i}), \tag{26}$$

$$\frac{(Z\alpha)^2}{r_i^4}\equiv\left(\boldsymbol{\nabla}\frac{Z\alpha}{r_i}\right)^2\rightarrow\left(\boldsymbol{\nabla}\frac{Z\alpha}{r_i}(1-e^{-\lambda m Z\alpha r_i})\right)^2. \tag{27}$$

Once the interaction is regularized, one can calculate all matrix elements and take the limit λ→∞. As a first step, we rederived in Ref. [10] the known relativistic correction to hfs in hydrogen,

$$\delta E_{\rm hfs}=(1+k)\,\frac{\mu^3}{mM}\,\frac{(Z\alpha)^6}{n^3}\,\frac{\boldsymbol{I}\cdot\boldsymbol{\sigma}}{2}\left(\frac{44}{9}+\frac{4}{n}-\frac{44}{9n^2}\right), \tag{28}$$

where n is a principal quantum number. Since for lithium all matrix elements can be calculated only numerically, we will transform effective operators to the regular form, where λ can be taken to infinity before the numerical calculations. The initial expression for a complete set of relativistic corrections in atomic units is (with implicit λ regularization)

$$\delta E_{\rm hfs}=|1+k|\,\frac{\mu^3}{mM}\,\alpha^6\mathcal{E}, \tag{29}$$

$$\mathcal{E}=\mathcal{E}_A+\mathcal{E}_B+\mathcal{E}_C+\mathcal{E}_N+\mathcal{E}_R\,, \tag{30}$$

$$\mathcal{E}_A=2\left\langle H^A\,\frac{1}{(E-H)'}\,H^A_{\rm hfs}\right\rangle, \tag{31}$$

$$\mathcal{E}_B=2\left\langle H^B\,\frac{1}{(E-H)}\,H^B_{\rm hfs}\right\rangle, \tag{32}$$

$$\mathcal{E}_C=2\left\langle H^C\,\frac{1}{(E-H)}\,H^C_{\rm hfs}\right\rangle, \tag{33}$$

$$\mathcal{E}_N=\left\langle\sum_{i=1}^{3}\left(-\frac{2Z}{3}p_i^2\pi\delta^3(r_i)-\frac{1}{24}\left[p_i^2,\left[p_i^2,\frac{Z}{r_i}\right]\right]\right.\right.$$
$$\left.\left.+\frac{1}{3}\frac{Z^2}{r_i^4}\right)\boldsymbol{I}\cdot\boldsymbol{\sigma}_i-\sum_{i,j=1,i\neq j}^{3}\frac{1}{3}\,\frac{\boldsymbol{r}_{ij}}{r_{ij}^3}\cdot\frac{Z\boldsymbol{r}_i}{r_i^3}\boldsymbol{I}\cdot(\boldsymbol{\sigma}_i+\boldsymbol{\sigma}_j)\right\rangle, \tag{34}$$

$$\mathcal{E}_R=Z^2\,\frac{4}{3}\left(\ln 2-\frac{5}{2}\right)\left\langle\sum_{i=1}^{3}\ \pi\delta^3(r_i)\boldsymbol{I}\cdot\boldsymbol{\sigma}_i\right\rangle, \tag{35}$$

where all H_X are in atomic units: $m=1,\alpha=1$. This initial expression is rewritten to the regular form, where λ regularization is not necessary. The operators in the second-order term $\mathcal{E}_A$ are transformed with the use of

$$H'^A\equiv H^A-\frac{1}{4}\sum_{i=1}^{3}\left[\frac{Z}{r_i}(E-H)+(E-H)\frac{Z}{r_i}\right], \tag{36}$$

$$H'^A_{\rm hfs}\equiv H^A_{\rm hfs}+\frac{2}{3}\sum_{i=1}^{3}\left[\frac{Z}{r_i}\boldsymbol{I}\cdot\boldsymbol{\sigma}_i(E-H)+(E-H)\,\frac{Z}{r_i}\boldsymbol{I}\cdot\boldsymbol{\sigma}_i\right]. \tag{37}$$

This transformation leads to new forms for $\mathcal{E}'_A$ and $\mathcal{E}'_N$, such that

$$\mathcal{E}_A+\mathcal{E}_N=\mathcal{E}'_A+\mathcal{E}'_N\,, \tag{38}$$

$$\mathcal{E}'_A=2\left\langle H'^A\,\frac{1}{(E-H)'}\,H'^A_{\rm hfs}\right\rangle, \tag{39}$$

$$\mathcal{E}'_N=\mathcal{E}_N+\sum_{i=1}^{3}\left\{-\frac{1}{6}\left\langle\boldsymbol{I}\cdot\boldsymbol{\sigma}_i\frac{Z^2}{r_i^4}\right\rangle+\frac{1}{2}\left\langle\frac{Z}{r_i}H^A_{\rm hfs}\right\rangle\right.$$
$$\left.-\frac{4}{3}\left\langle\boldsymbol{I}\cdot\boldsymbol{\sigma}_i\frac{Z}{r_i}H^A\right\rangle-\frac{1}{2}\left\langle\frac{Z}{r_i}\right\rangle\langle H^A_{\rm hfs}\rangle+\frac{4}{3}\left\langle\boldsymbol{I}\cdot\boldsymbol{\sigma}_i\,\frac{Z}{r_i}\right\rangle\langle H^A\rangle\right\}, \tag{40}$$

both $\mathcal{E}'_A,\mathcal{E}'_N$ are separately finite.

IV. PROPOSAL FOR THE NUMERICAL CALCULATION OF MATRIX ELEMENTS

The main problem, as we see it, is the analytic calculation of matrix elements with the correlated basis set. Although all the integrals are manageable with Gaussians, these functions do not give precise values for the wave function at the coalescence points. On the other hand, the wave function expressed in the Hylleraas basis set fulfills well the cusp conditions. So far, this basis set, as applied both by Yan and by King [9], gives the most precise values for relativistic corrections. The disadvantage of this basis set is high complexity in the coding of relativistic matrix elements. Another basis set that we are considering at present is the following:

$$\phi=r_{12}^n r_{23}^m r_{31}^l e^{-\lambda_i r_1-\lambda_j r_2-\lambda_k r_3}, \tag{41}$$

with even tempered distribution of λ exponents. We have already derived analytic and simple formulas for matrix elements of the nonrelativistic Hamiltonian by expanding the general integration formula as obtained by Fromm and Hill in Ref. [14]. We mention also Ref. [15], where the authors were able to express matrix elements of the nonrelativistic Hamiltonian in terms of $\langle 1\rangle,\langle 1/r_i\rangle,\langle 1/r_{ij}\rangle$ only, which simplifies significantly the generation of the nonrelativistic wave function. However, the problem which we have not been able to solve so far is the efficient analytic calculation of matrix elements of the Breit Hamiltonian, particularly H_C. Some progress has been achieved in Ref. [16]. As in the case of helium [10], the calculation of second-order matrix elements requires a careful adjusting of exponents, and this is a computationally intensive process.

V. SUMMARY

We have derived here a complete expression for the relative order $O(\alpha^2)$ correction to lithium hyperfine splitting. It is written in terms of nonrelativistic although quite complicated operators. The advantage of this approach is a simple incorporation of electron correlation through the use of a correlated nonrelativistic basis set. Further advantages are the consistent inclusion of all relativistic and radiative effects at the order of $m\alpha^6$. We have not so far mentioned higher-order terms, denoted by $E^{(7)}_{\rm hfs}$. They are known in hydrogenic systems [17], and we think they could be derived as well for lithium. The most computationally difficult are the so-called Bethe log terms combined with the Fermi contact operator. Similar corrections have already been calculated for the helium fine structure [18], and the same approach will work for lithium as well. However, at present we do not have enough experience to pursue the numerical part of this project. We think that this work might stimulate progress in the numerically efficient calculation of matrix elements.

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