PHYSICAL REVIEW A **78**, 012513 (2008)

Hyperfine structure of Li and Be$^+$

V. A. Yerokhin

Center for Advanced Studies, St. Petersburg State Polytechnical University, Polytekhnicheskaya 29, St. Petersburg 195251, Russia

(Received 6 May 2008; published 29 July 2008)

A large-scale relativistic configuration-interaction (CI) calculation is performed for the magnetic-dipole and the electric-quadrupole hyperfine structure splitting in ^{7,6}Li and ^{9}Be$^+$. Numerical results for the $2\,^2S$, $3\,^2S$, $2\,^2P_{1/2}$, and $2\,^2P_{3/2}$ states are reported. The CI calculation based on the Dirac-Coulomb-Breit Hamiltonian is supplemented with separate treatments of the QED, nuclear-magnetization distribution, recoil, and negative-continuum effects.

DOI: 10.1103/PhysRevA.78.012513 PACS number(s): 31.15.aj, 31.15.am, 31.30.Gs, 32.10.Fn

I. INTRODUCTION

The hyperfine structure (hfs) of few-electron atoms has been an attractive subject of theoretical studies for decades, one of the reasons being a few ppm accuracy achieved in experiments on Li and Be$^+$ [1,2]. Despite the considerable attention received, a high-precision theoretical determination of hfs in few-electron atoms remains a difficult task. The main problem lies in the high singularity of the hfs interaction and, as a consequence, in the dependence of the calculated results on the quality of the many-electron wave function near the nucleus.

The hfs splitting of lithium has traditionally been one of the standard test cases for different theoretical methods [3]. Among various calculations reported in the literature, the nonrelativistic ones are the most numerous; their technique is well developed by now. The best numerical accuracy for the nonrelativistic hfs value is achieved in variational calculations that use multiple basis sets in Hylleraas coordinates [4–6]. Probably the most popular nonrelativistic approach is the multiconfigurational Hartree-Fock (MCHF) method [7,8], which is less computationally intensive but also produces less accurate results. The main drawback of the nonrelativistic methods is that the relativistic effects should be accounted for separately. There is a way to perform a direct evaluation of the leading relativistic correction [9], but such a calculation is difficult and has not yet been done. So far, the relativistic correction was estimated by comparing with less accurate calculations based on the Dirac-Coulomb-Breit Hamiltonian, or by rescaling the hydrogenic correction.

There were calculations performed for Li and Be$^+$ with the relativistic analog of the MCHF procedure, the multiconfigurational Dirac-Fock (MCDF) method [10–12]. The computational accuracy of these relativistic calculations turns out to be lower than that of the best nonrelativistic studies. This is to a large extent due to the fact that the electron correlation is more difficult to be accurately accounted for relativistically than nonrelativistically.

Methods that allow a straightforward generalization to the relativistic case are many-body perturbation theory [13] and its all-order extensions known as the coupled-cluster (CC) approach [14–18]. Calculations of the Li hfs performed with these methods so far did not account for most of the triple excitations (and, in most cases, for a part of the double excitations as well), which led to an incomplete treatment of the electron correlation and to a relatively low accuracy of the corresponding results. Significant progress in the CC calculations was reported in Ref. [19] for the case of Na. In that work, all valence triple excitations were included. Such an approach, when applied to the Li hfs, would significantly improve the accuracy of the CC results. The corresponding calculation is presently underway [20].

In the current investigation, a relativistic calculation of the hfs splitting in Li and Be$^+$ will be performed by employing the configuration-interaction (CI) method. Unlike the MCDF procedure, the CI method does not involve a variational minimization and thus is not handicapped by the danger of the variational collapse into the negative continuum (which manifests itself in a "sinking" of the ground-state energy due to the admixture of the negative energy states into the ground-state wave function). The CI method has a potential to be more accurate than the MCDF method. The only problem is that it requires the Dirac spectrum to be sufficiently well represented by the model space of one-electron wave functions, whereas the MCDF method can produce reasonable results with only a few configurations. While this might come as a limitation in the case of complicated many-electron atoms, the systems at hand, the Li-like atoms, are sufficiently simple to be very accurately described by the CI method.

The goal of the present investigation is to perform a calculation of the hfs in Li and Be$^+$ complete to the relative order α^2, where α is the fine-structure constant. Such a calculation requires, besides a high-precision determination of the dominant nonrelativistic contribution, a rigorous treatment of the leading relativistic correction $\sim\alpha^2$ and the inclusion of the QED effects $\sim\alpha$ and $\sim\alpha^2$. Nuclear effects (the recoil and the magnetization distribution) also contribute on this level. Because of their smallness, these effects can be treated nonrelativistically. Since we are concerned with the effects of order up to α^2 only, the Dirac-Coulomb-Breit Hamiltonian may be used as a convenient and sound starting point for our investigation.

The calculation complete to the relative order α^2 was reported for the hfs splitting of the $2\,^2S$ and $3\,^2S$ states of Li and Be$^+$ in our previous paper [21]. In this work, we extend our calculations to the $2\,^2P_J$ states and present a detailed analysis of various corrections. In particular, the recoil correction to the magnetic dipole hfs interaction is derived for the case of an arbitrary spin of the nucleus. This correction is shown to yield the dominant recoil contribution for the hfs splitting of the *P* and higher-*l* states in medium-*Z* H-like atoms. To the best of our knowledge, it has not previously been accounted for in systems other than hydrogen and deuterium.

The paper is organized as follows. In Sec. II, a brief summary of the CI method is given. In Sec. III, we present some basic formulas for the magnetic-dipole and the electric-quadrupole interaction and describe our CI calculation of the hfs splitting based on the Dirac-Coulomb-Breit Hamiltonian. Various corrections to the hfs are calculated in Sec. IV. The results obtained are discussed and compared with the experimental data in Sec. V.

Relativistic units $\hbar = c = 1$ and $\alpha = e^2/(4\pi)$ are used throughout this paper.

II. CONFIGURATION INTERACTION METHOD

The relativistic Hamiltonian of an *N*-electron atom can be written as

$$H_{DCB} = \sum_i h_D(i) + \sum_{i<j} [V_C(i,j) + V_B(i,j)], \tag{1}$$

where indices $i,j = 1,\ldots,N$ numerate the electrons, h_D is the one-particle Dirac Hamiltonian,

$$h_D(i) = \boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + (\beta - 1)m + V_{\text{nuc}}(r_i), \tag{2}$$

$\boldsymbol{\alpha}$ and β are the Dirac matrices, V_{nuc} is the binding potential of the nucleus, $V_C(i,j) = \alpha/r_{ij}$ is the Coulomb part of the electron-electron interaction, $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$, V_B is the Breit interaction,

$$V_B(i,j) = -\frac{\alpha}{2r_{ij}} [\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + (\boldsymbol{\alpha}_i \cdot \hat{\boldsymbol{r}}_{ij})(\boldsymbol{\alpha}_j \cdot \hat{\boldsymbol{r}}_{ij})], \tag{3}$$

and $\hat{\boldsymbol{r}} = \boldsymbol{r}/r$. It is assumed that H_{DCB} acts in the space of the positive-energy eigenfunctions of some one-particle Hamiltonian.

The *N*-electron wave function of the system with parity *P*, angular momentum quantum number *J*, and its projection *M* is represented as a linear combination of configuration-state functions (CSFs),

$$\Psi(PJM) = \sum_r c_r \Phi(\gamma_r PJM), \tag{4}$$

where γ_r denotes the set of additional quantum numbers that determine the CSF. The CSFs are constructed as antisymmetrized products of one-electron orbitals ψ_n of the form

$$\psi_n(\boldsymbol{r}) = \frac{1}{r} \begin{pmatrix} G_n(r)\chi_{\kappa_n m_n}(\hat{\boldsymbol{r}}) \\ iF_n(r)\chi_{-\kappa_n m_n}(\hat{\boldsymbol{r}}) \end{pmatrix}, \tag{5}$$

where $\chi_{\kappa m}$ is the spin-angular spinor [22], $\kappa = (-1)^{j+l+1/2}(j+1/2)$ is the relativistic angular parameter, and *m* is the angular momentum projection. In the present work, we chose the one-electron orbitals ψ_n to be the (positive-energy) eigenfunctions of the one-electron Dirac Hamiltonian with the frozen-core Dirac-Fock (DF) potential,

$$h_{\text{DF}} = \boldsymbol{\alpha} \cdot \boldsymbol{p} + (\beta - 1)m + V_{\text{nuc}}(r) + V_{\text{DF}}^{N-1}(\boldsymbol{r}). \tag{6}$$

The (nonlocal) potential V_{DF}^{N-1} is defined by its action on a wave function,

$$V_{\text{DF}}^{N-1}(\boldsymbol{r}_1)\psi(\boldsymbol{r}_1) = \sum_c \int d\boldsymbol{r}_2 \psi_c^{+}(\boldsymbol{r}_2) \frac{\alpha}{r_{12}} \times [\psi_c(\boldsymbol{r}_2)\psi(\boldsymbol{r}_1) - \psi_c(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)], \tag{7}$$

where the index *c* runs over the core orbitals. The eigenfunctions of the Hamiltonian h_{DF} form a complete and orthogonal basis of one-electron orbitals.

In the CI method, the energy of the system and the mixing coefficients c_r in Eq. (4) are obtained by solving the secular equation

$$\det\{\langle \gamma_r PJM | H_{DCB} | \gamma_s PJM \rangle - E_r \delta_{rs}\} = 0. \tag{8}$$

The matrix elements of the Hamiltonian between the CSFs can be represented as linear combinations of the one- and two-particle radial integrals,

$$\begin{aligned} \langle \gamma_r PJM | H_{DCB} | \gamma_s PJM \rangle &= \sum_{ab} d_{rs}(ab) I(ab) \\ &\quad + \alpha \sum_k \sum_{abcd} v_{rs}^{(k)}(abcd)[R_k^C(abcd) + R_k^B(abcd)]. \end{aligned} \tag{9}$$

Here, *a*, *b*, *c*, and *d* specify the one-electron orbitals, d_{rs} and $v_{rs}^{(k)}$ are the angular coefficients, $I(ab)$ are the one-electron radial integrals, and R_k^C $(abcd)$ and R_k^B $(abcd)$ are the Coulomb and Breit two-electron radial integrals. The radial integrals are defined by

$$\langle a | h_D | b \rangle = \delta_{\kappa_a,\kappa_b} \delta_{m_a,m_b} I(ab), \tag{10}$$

$$\langle ab | V_{C,B} | cd \rangle = \alpha \sum_{km_k} \frac{(-1)^{k-m_k+j_c-m_c+j_d-m_d}}{2k+1} \times C^{km_k}_{j_a m_a, j_c -m_c} C^{km_k}_{j_d m_d, j_b -m_b} R_k^{C,B}(abcd), \tag{11}$$

where $C^{jm}_{j_1 m_1, j_2 m_2}$ are the Clebsch-Gordan coefficients. After integrating over angular variables, the expression for the one-particle integral reads

$$I(ab) = \int_0^\infty dr \left[F_a \left(\frac{d}{dr} + \frac{\kappa}{r} \right) G_b - G_a \left(\frac{d}{dr} - \frac{\kappa}{r} \right) F_b + (G_a G_b + F_a F_b) V_{\text{nuc}} - 2m F_a F_b \right]. \tag{12}$$

The Coulomb integral is given by

$$R_k^C(abcd) = (-1)^k \langle \kappa_a \| \boldsymbol{C}^{(k)} \| \kappa_c \rangle \langle \kappa_b \| \boldsymbol{C}^{(k)} \| \kappa_d \rangle \times \int_0^\infty dr_1 dr_2 \frac{r_<^k}{r_>^{k+1}} W_{ac}(r_1) W_{bd}(r_2), \tag{13}$$

where $W_{ab} = G_a G_b + F_a F_b$ and $\boldsymbol{C}^{(J)}$ is the spherical tensor with components $C_M^{(J)}(\hat{\boldsymbol{r}}) = \sqrt{4\pi/(2J+1)} Y_{JM}(\hat{\boldsymbol{r}})$. The expression for the Breit integral is more complex; it can be found in Ref.

[23]. The angular coefficients d_{rs} and $v_{rs}^{(k)}$ can be evaluated analytically [24,25]. In the general case, formulas for them are rather cumbersome. A number of packages are available in the literature for the numerical evaluation of the angular coefficients [24,26–29].

III. HYPERFINE SPLITTING

A. Magnetic dipole hyperfine splitting

The relativistic Fermi-Breit operator of the magnetic dipole hyperfine interaction is given by

$$H_{M1} = \frac{|e|}{4\pi}\boldsymbol{\mu}\cdot\boldsymbol{T}^{(1)}, \tag{14}$$

where $\boldsymbol{\mu}$ is the operator of the nuclear magnetic moment, acting in the nuclear subspace. The operator $\boldsymbol{T}^{(1)}$ acts in the electronic subspace; it is given by the sum of the one-electron operators $\boldsymbol{t}^{(1)}(i)$,

$$\boldsymbol{T}^{(1)} = \sum_i \boldsymbol{t}^{(1)}(i) = \sum_i \frac{\boldsymbol{r}_i\times\boldsymbol{\alpha}_i}{r_i^3}. \tag{15}$$

In the nonrelativistic limit, the operator $\boldsymbol{t}^{(1)}$ turns into $\boldsymbol{t}_{NR}^{(1)}$,

$$\boldsymbol{t}_{NR}^{(1)} = \frac{1}{m}\left[\frac{\boldsymbol{l}}{r^3} + \frac{3\hat{\boldsymbol{r}}(\boldsymbol{s}\cdot\hat{\boldsymbol{r}})-\boldsymbol{s}}{r^3} + \frac{8\pi}{3}\delta(\boldsymbol{r})\boldsymbol{s}\right], \tag{16}$$

where $\boldsymbol{l}$ and $\boldsymbol{s}$ are the one-electron operators of orbital angular momentum and spin, respectively. The three terms in the brackets are often referred to as the orbital, the spin dipole, and the Fermi contact term, respectively,

$$\boldsymbol{t}_{NR}^{(1)} = \boldsymbol{t}_l^{(1)} + \boldsymbol{t}_{sd}^{(1)} + \boldsymbol{t}_c^{(1)}. \tag{17}$$

The relativistic value of the energy shift due to the magnetic dipole hyperfine interaction is obtained as the expectation value of the Fermi-Breit operator on the wave function of the system with atomic angular momentum F and its projection M_F. Employing the Wigner-Eckart theorem, the nuclear variables are separated and integrated out and the energy shift is represented in terms of the reduced matrix element of the operator $\boldsymbol{T}^{(1)}$,

$$\begin{aligned}\Delta E_{M1} &= \langle FM_F|H_{M1}|FM_F\rangle \\ &= \frac{|e|}{4\pi}\frac{\mu}{2I}[F(F+1)-I(I+1)-J(J+1)] \\ &\quad\times\frac{\langle J\|\boldsymbol{T}^{(1)}\|J\rangle}{\sqrt{J(J+1)(2J+1)}},\end{aligned} \tag{18}$$

where μ is the magnetic moment of the nucleus, $\mu = \langle II|\boldsymbol{\mu}_0|II\rangle$, I is the nuclear spin, and J is the total angular momentum of the electron. Experimental data for the magnetic dipole hfs splitting are usually expressed in terms of the hyperfine interaction constant A_J, which does not depend on F,

$$A_J = \frac{\Delta E_{M1}}{\langle FM_F|\boldsymbol{I}\cdot\boldsymbol{J}|FM_F\rangle} = \frac{|e|}{4\pi}\frac{\mu}{I}\frac{\langle J\|\boldsymbol{T}^{(1)}\|J\rangle}{\sqrt{J(J+1)(2J+1)}}. \tag{19}$$

The reduced matrix element of the operator $\boldsymbol{T}^{(1)}$ should be evaluated with the CI many-electron wave functions (4), obtained by solving the secular equation (8). Matrix elements of the operator $\boldsymbol{T}^{(1)}$ between individual CSFs can be expressed as linear combinations of matrix elements of the one-electron operator $\boldsymbol{t}^{(1)}$ between the single-particle orbitals,

$$\langle\gamma_r PJ\|\boldsymbol{T}^{(1)}\|\gamma_s PJ\rangle = \sum_{a\le b} d_{rs}^{(1)}(ab)\langle a\|\boldsymbol{t}^{(1)}\|b\rangle, \tag{20}$$

where a and b numerate the one-electron orbitals and $d_{rs}^{(1)}$ are the angular recoupling coefficients. Packages for the numerical evaluation of the coefficients $d_{rs}^{(1)}$ are available in the literature [26,29]. The reduced matrix element of the one-electron operator $\boldsymbol{t}^{(1)}$ is given by

$$\begin{aligned}\langle a\|\boldsymbol{t}^{(1)}\|b\rangle &= -(\kappa_a+\kappa_b)\langle-\kappa_a\|\boldsymbol{C}^{(1)}\|\kappa_b\rangle \\ &\quad\times\int_0^\infty dr\, r^{-2}(G_aF_b+F_aG_b).\end{aligned} \tag{21}$$

The energy shift due to the hfs splitting can easily be calculated for the hydrogenlike ion. In this case, the sum (20) consists of a single term and the radial integral in Eq. (21) is calculated analytically (in the point-nucleus limit). In the present work, we will need the nonrelativistic limit of Eq. (21) for the hydrogenlike ion, which reads

$$\langle njl\|\boldsymbol{t}^{(1)}\|njl\rangle_{NR} = \frac{2(Z\alpha)^3m^2}{n^3}\frac{1}{2l+1}\sqrt{\frac{2j+1}{j(j+1)}}. \tag{22}$$

Using this result, it is convenient to introduce the following parametrization of the magnetic hyperfine constant A_J:

$$A_J = \frac{\alpha(Z\alpha)^3}{n^3}\frac{m^2}{m_p}\frac{\mu}{\mu_N}\frac{1}{IJ(J+1)(2L+1)}G_{M1}(Z), \tag{23}$$

where n is the principal quantum number of the valence electron, m_p is the proton mass, and $\mu_N = |e|/(2m_p)$ is the nuclear magneton. The function $G_{M1}(Z)$ is dimensionless; its numerical value is unity for a hydrogenlike nonrelativistic atom in the point-nucleus and nonrecoil limit. G_{M1} is a slowly varying function of the nuclear charge number Z and the quantum numbers J and L, which is convenient for the representation of numerical results. This definition of the function G_{M1} differs slightly from the one used in our previous work [21] by the fact that it does not include the nonrelativistic mass scaling factor $(1+m/M)^{-3}$. We presently choose to treat this part of the recoil effect (also referred to as the normal mass shift) on an equal footing with the other recoil corrections. A parametrization similar to that in Eq. (23) was previously used in Refs. [30,31].

Numerical results of nonrelativistic calculations are often presented in terms of the orbital (a_l), the spin-dipole (a_{sd}), and the Fermi contact (a_c) hyperfine parameters, induced by the three terms in Eq. (17) and defined as [3]

$$a_l = \langle LSM_LM_S|\sum_{i=1}^N \frac{l_0^{(1)}(i)}{r_i^3}|LSM_LM_S\rangle, \tag{24}$$

$$a_{sd} = \langle LSM_LM_S|\sum_{i=1}^N \frac{2C_0^{(2)}(i)s_0^{(1)}(i)}{r_i^3}|LSM_LM_S\rangle, \tag{25}$$

$$a_c = \langle LSM_LM_S|\sum_{i=1}^{N}\frac{2s_0^{(1)}(i)\,\delta(r_i)}{r_i^2}|LSM_LM_S\rangle, \tag{26}$$

with $M_L=L$ and $M_S=S$. The connection of the (nonrelativistic limit of the) function G_{M1} with the hyperfine parameters expressed in atomic units is given by

$$G_{M1}(Z) = \frac{n^3J(J+1)(2L+1)}{2Z^3}(c_la_l + c_{sd}a_{sd} + c_ca_c). \tag{27}$$

The coefficients c_i are [3]

$$c_l = \frac{\langle \boldsymbol{L}\cdot\boldsymbol{J}\rangle}{LJ(J+1)}, \tag{28}$$

$$c_{sd} = \frac{3\langle \boldsymbol{S}\cdot\boldsymbol{L}\rangle\langle \boldsymbol{L}\cdot\boldsymbol{J}\rangle - L(L+1)\langle \boldsymbol{S}\cdot\boldsymbol{J}\rangle}{SL(2L-1)J(J+1)}, \tag{29}$$

$$c_c = \frac{\langle \boldsymbol{S}\cdot\boldsymbol{J}\rangle}{3SJ(J+1)}, \tag{30}$$

where

$$\langle \boldsymbol{L}\cdot\boldsymbol{J}\rangle = [J(J+1) + L(L+1) - S(S+1)]/2, \tag{31}$$

$$\langle \boldsymbol{S}\cdot\boldsymbol{J}\rangle = [J(J+1) - L(L+1) + S(S+1)]/2, \tag{32}$$

$$\langle \boldsymbol{S}\cdot\boldsymbol{L}\rangle = [J(J+1) - L(L+1) - S(S+1)]/2. \tag{33}$$

B. Electric quadrupole hyperfine splitting

The scalar part of the interaction between an electron and the nucleus is given by

$$V(\boldsymbol{r},\boldsymbol{r}_{p_1},\ldots,\boldsymbol{r}_{p_Z}) = -\alpha\sum_{j=1}^{Z}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}_{p_j}|}, \tag{34}$$

where $\mathbf{r}$ and $\boldsymbol{r}_{p_j}$ are the coordinates of the electron and the jth proton, respectively. Averaging this interaction over the internal nuclear coordinates and using the standard multipole expansion of $|\mathbf{r}-\boldsymbol{r}_{p_j}|^{-1}$, one obtains (see Ref. [32] for the details)

$$\begin{aligned}V_{\rm av}(\boldsymbol{r},\Theta,\Phi) \equiv \langle V\rangle_{\rm intern} = {}& -\alpha\sum_{l=0}^{\infty}\int_0^{\infty}dr'\,r'^2\rho_l(r')\\ &\times\left[\frac{r^l}{r'^{l+1}}\theta(r'-r) + \frac{r'^l}{r^{l+1}}\theta(r-r')\right]\\ &\times\boldsymbol{C}^{(l)}(\hat{\boldsymbol{r}})\cdot\boldsymbol{C}^{(l)}(\Theta,\Phi),\end{aligned} \tag{35}$$

where $\langle\cdots\rangle$ denotes the averaging, Θ and Φ are the angles that fix the orientation of the intrinsic nuclear system with respect to the laboratory frame, and the nuclear charge density component ρ_l is defined as

$$\rho_l(r) = \int d\hat{\boldsymbol{r}}\,\rho(\boldsymbol{r})C_0^{(l)}(\hat{\boldsymbol{r}}). \tag{36}$$

The first term in Eq. (35) ($l=0$) yields the standard Coulomb interaction between the electron and the nucleus with an extended charge distribution. The term with $l=1$ vanishes after averaging with the electron wave function of a definite parity. The term with $l=2$ gives rise to a splitting of the energy level (of an electronic state with $J>1/2$), known as the electric quadrupole one. The corresponding interaction is conveniently written in the form

$$H_{E2} = \alpha\boldsymbol{T}^{(2)}\cdot\boldsymbol{Q}_{\rm av}^{(2)}. \tag{37}$$

Here, $\mathbf{Q}_{\rm av}^{(2)}$ is the operator of the nuclear quadrupole moment averaged over the internal (radial) nuclear coordinates,

$$\boldsymbol{Q}_{\rm av}^{(2)} = \langle\boldsymbol{Q}^{(2)}\rangle_{\rm intern} = N\boldsymbol{C}^{(2)}(\Theta,\Phi). \tag{38}$$

The normalization constant N is

$$N = \int_0^R dr\,r^4\rho_2(r), \tag{39}$$

where R is the nuclear radius. The operator $\mathbf{T}^{(2)}$ acts on the electronic variables. It is given by

$$\boldsymbol{T}^{(2)} = \sum_i \boldsymbol{t}^{(2)}(i) = -\sum_i f(r_i)\boldsymbol{C}^{(2)}(\hat{\boldsymbol{r}}_i), \tag{40}$$

where the radial distribution function $f(r)$ is

$$f(r) = \begin{cases}\dfrac{1}{r^3}, & r>R,\\[2ex] \dfrac{1}{N}\displaystyle\int_0^R dr'\,r'^2\rho_2(r')\frac{r_<^2}{r_>^3}, & r\leqslant R.\end{cases} \tag{41}$$

The distribution function $f(r)$ can easily be calculated analytically for several simple models of the nuclear-charge distribution. So, if ρ_2 does not depend on r within the nucleus, $\rho_2(r)\propto\theta(R-r)$,

$$f(r) = \frac{r^2}{R^5}\left(1 + 5\ln\frac{R}{r}\right), \quad r\leqslant R. \tag{42}$$

If $\rho_2(r)\propto\delta(R-r)$, then

$$f(r) = \frac{r^2}{R^5}, \quad r\leqslant R. \tag{43}$$

In the point-quadrupole limit, the function $f(r)$ takes the standard form, $f(r)=r^{-3}$.

The finite nuclear size effect is very small for the electric quadrupole splitting and its inclusion in calculations is not necessary at present. However, we observed that the usage of the extended charge distribution considerably improves the stability and the convergence of numerical calculations. The reason for this is that the extended distribution removes the r^{-3} singularity of the point-quadrupole interaction.

Using the standard technique of the angular-momentum algebra (see, e.g., Ref. [3]), the energy shift due to the electric quadrupole interaction can be expressed in terms of the reduced matrix elements of the electronic operator $\mathbf{T}^{(2)}$. The correction to the energy is usually expressed in terms of the hyperfine structure constant B_J, which does not depend on the total angular momentum of the system F,

$$\Delta E_{E2} = \frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(J+1)} B_J, \tag{44}$$

where $C=F(F+1)-I(I+1)-J(J+1)$ and

$$B_J = 2Q\sqrt{\frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)}}\langle J\|\boldsymbol{T}^{(2)}\|J\rangle. \tag{45}$$

Here, Q is the nuclear quadrupole moment, defined as

$$Q = \langle IM|\sum_{j=1}^{Z}(3z_{p_j}^2 - r_{p_j}^2)|IM\rangle_{M=I} = 2\langle II|\boldsymbol{Q}_0^{(2)}|II\rangle. \tag{46}$$

The reduced matrix element of the operator $\mathbf{T}^{(2)}$ should be evaluated with the many-electron wave functions (4), obtained by the solution of the secular equation (8). Matrix elements of the operator $\mathbf{T}^{(2)}$ between individual CSFs can be expressed as linear combinations of matrix elements of the one-electron operator $\mathbf{t}^{(2)}$ between the single-particle orbitals,

$$\langle \gamma_r PJ\|\boldsymbol{T}^{(2)}\|\gamma_s PJ\rangle = \sum_{a\leqslant b} d_{rs}^{(2)}(ab)\langle a\|\boldsymbol{t}^{(2)}\|b\rangle, \tag{47}$$

where a and b numerate the one-electron orbitals and $d_{rs}^{(2)}$ are the angular recoupling coefficients [26]. The reduced matrix element of the one-electron operator $\mathbf{t}^{(2)}$ is given by

$$\langle a\|\boldsymbol{t}^{(2)}\|b\rangle = -\langle \kappa_a\|\boldsymbol{C}^{(2)}\|\kappa_b\rangle\int_0^\infty dr f(r)(G_aG_b + F_aF_b). \tag{48}$$

Similarly to the magnetic dipole hyperfine constant A_J, the electric quadrupole hyperfine constant B_J can be conveniently parametrized by introducing the dimensionless function G_{E2}, which turns into unity for a nonrelativistic hydrogenlike ion in the point-nucleus and nonrecoil limit,

$$B_J = Q\frac{\alpha(Z\alpha)^3 m^3}{n^3}\frac{2J-1}{J+1}\frac{1}{\kappa(\kappa+1)(2L+1)}G_{E2}(Z), \tag{49}$$

where $\kappa=(-1)^{J+L+1/2}(J+1/2)$.

Results of nonrelativistic calculations are often expressed in terms of the quadrupole parameter b_q, defined as

$$b_q = \langle LSM_LM_S|\sum_{i=1}^{N}\frac{2C_0^{(2)}(\hat{\boldsymbol{r}}_i)}{r_i^3}|LSM_LM_S\rangle_{M_L=L,M_S=S}. \tag{50}$$

The connection between the (nonrelativistic limit of the) function G_{E2} and the parameter b_q expressed in atomic units is given by

$$G_{E2}(Z) = \frac{n^3(J+1)\kappa(\kappa+1)(2L+1)}{Z^3(2J-1)}(-c_qb_q), \tag{51}$$

where the coefficient c_q is [3]

$$c_q = \frac{6\langle \boldsymbol{L}\cdot\boldsymbol{J}\rangle^2 - 3\langle \boldsymbol{L}\cdot\boldsymbol{J}\rangle - 2L(L+1)J(J+1)}{L(2L-1)(2J+3)(J+1)}. \tag{52}$$

C. Details of the CI calculation

To perform a CI calculation, we devised a code, incorporating and adapting a number of existing packages [24,26–28,33] for setting up the CSFs, calculating angular-momentum coefficients, and diagonalizing the Hamiltonian matrix. The largest number of CSFs simultaneously handled was about a half a million. A careful optimization of the code was necessary to keep the time and memory consumption of the calculation within reasonable limits. Care was taken to prevent recalculating the angular-momentum coefficients for the pairs of CSFs that differ by the principal quantum number of a single electron only. An optimized ordering of CSFs allows one to drastically reduce the number of angular-momentum coefficients to be evaluated. A similar optimization was introduced in the calculation of the Coulomb and Breit radial integrals. The radial integrals with the same pair of electron states in the innermost radial integration were grouped together and evaluated simultaneously.

The dominant part of the hfs splitting is delivered by the Dirac-Coulomb Hamiltonian. This is the most demanding part of the calculation, since a high relative precision is required. One of the factors defining the accuracy of the calculation is the quality and the size of the space of one-electron orbitals from which the CSFs are constructed. We take this space to be a part of the finite basis set of eigenvectors of the Dirac equation, obtained by the dual-kinetic-balance method [34] and constructed with B-splines [35].

For a given number of B-splines n_a, all eigenstates were taken with the energy $0<\varepsilon\leqslant mc^2(1+Z\alpha E_{\max})$ and the orbital quantum number $l\leqslant l_{\max}$, where the value of $E_{\max}$ was varied between 0.5 and 6, and $l_{\max}$ between 1 and 7. Three main sets of one-electron orbitals were employed in the present work: (A) 20s 20p 19d 19f 18g 18h with $n_a=44$ and $E_{\max}=3.0$, (B) 14s 14p 14d 13f 13g 13h 12i 12k with $n_a=34$ and $E_{\max}=0.5$, and (C) 25s 25p 25d with $n_a=54$ and $E_{\max}=6.0$. Here, e.g., 20p means 20$p_{1/2}$ 20$p_{3/2}$. Calculational results were first obtained with the set (A) and then corrected for contributions of the higher partial waves with the set (B) and for a more complete representation of the Dirac spectrum with the set (C). The computation became rather intensive for the P states, so the basis set (A) was reduced to include the states with $l\leqslant 3$ only in this case. Usage of several sets of one-electron orbitals allowed us to efficiently control the completeness of the representation of the Dirac spectrum in our calculations.

The analysis of the convergence of the partial-wave expansion was performed by identifying increments of the results induced by the increasing cutoff parameter $l_{\max}$. The omitted tail of the expansion was estimated by a polynomial least-squares fitting of the increments in $1/l$. In most cases, the error due to the termination of the expansion was found to yield the largest uncertainty to the Dirac-Coulomb hfs value.

The set of the CSFs employed in the calculation was obtained by taking all single, double, and triple excitations of the reference configuration with at least one electron orbital with $l\leqslant 1$ present. The contribution of the remaining triple excitations was found to be negligible for the S states. For the P states, it was estimated by repeating the calculation with a smaller basis but with the above restriction replaced by $l \leqslant 2$.

Inclusion of the Breit interaction into the Dirac-Coulomb Hamiltonian yields only a small correction in the case of Li and Be^{+}. Because of this, it is sufficient to use much smaller basis sets for its evaluation, which simplifies the computation greatly. The Breit-interaction correction was obtained as the difference of the CI results with and without the Breit interaction included into the Hamiltonian, evaluated with the same set of CSFs.

Results of our CI calculations of the magnetic dipole and the electric quadrupole hfs splitting are presented in Tables I and II, respectively. The CI values obtained with the Dirac-Coulomb Hamiltonian are listed under the entry "Coulomb;" the entry "Breit" contains the correction due to the inclusion of the Breit interaction. The comparison presented in the tables demonstrates significant deviations of our CI values from the MCDF results by Bieroń *et al.* [10,11] and from the CC results of Johnson *et al.* [18]. In the case of Be^{+}, Ref. [11] reports estimations of the calculational errors, considered by the authors to be the conservative ones, but our CI results are well out of these error bars for all the states studied.

The deviation from the MCDF calculations is the strongest for the quadrupole splitting in Be^{+}. In this case, our CI value differs from the MCDF one already in the second digit, while the claimed accuracy of the MCDF result is about 10^{-5}. A similar deviation is observed also for the quadrupole splitting in Li. At the same time, agreement of our calculations with the nonrelativistic studies [8,36] is much better, on the level of 10^{-3}. This observation leads us to a conclusion that the MCDF results for the quadrupole splitting are, most probably, in error. A possible explanation for this is that the highly singular point-quadrupole interaction might lead to considerable numerical errors when evaluated on approximate relativistic wave functions. In our calculations, we detected such problems; they were solved by using the extended charge distribution for the quadrupole interaction.

In order to make possible a detailed comparison with high-precision nonrelativistic results available in the literature, we have to identify the nonrelativistic part of our CI values. This was achieved by repeating the full set of the CI calculations for different values of the fine-structure constant α (namely, three values with ratios $\alpha'/\alpha = 0.9$, 1, and 1.1 were used). For each value of α, the finite nuclear-charge distribution correction was evaluated (as described in the next section) and subtracted from the CI values. The point-nucleus results thus obtained were fitted to a polynomial in α, assuming the absence of the linear term. In this way, the CI results with the physical value of α were separated into three parts: the nonrelativistic point-nucleus contribution, the relativistic correction, and the finite nuclear-charge correction.

For the P states and the magnetic dipole hfs, the nonrelativistic limit of the CI results needs to be separated into three parts, corresponding to the three terms of the nonrelativistic decomposition of the hfs operator (17). To this end, we carried out identical calculations both for the relativistic magnetic dipole hfs operator (15) and for the spin-dipole and the orbital parts of its nonrelativistic decomposition. Applying the fitting procedure described above, we identify the nonrelativistic limit of the CI values as well as the spin-dipole and orbital hfs parameters a_l and a_{sd}. The remaining contact parameter a_c is then unambiguously deduced. (We prefer not to perform a direct calculation for the contact term since the corresponding operator contains a δ function and needs a regularization when evaluated on relativistic wave functions.)

The nonrelativistic hfs parameters obtained in this way are listed in Table III. The nonrelativistic results for the $2\,^2P$ state were obtained from the relativistic calculations for the $2\,^2P_{1/2}$ state. Since in the present work the hfs parameters are needed for the purpose of comparison only, we do not assign the uncertainty to them (which is difficult to do reliably since they are obtained by a fit). The comparison with the previous nonrelativistic calculations [5,8,36] presented in the table exhibits a remarkably good agreement of our values with the high-precision results obtained in a Hylleraas-type calculation by Yan *et al.* [5].

In Tables I and II, the entry "NR(point)" labels the nonrelativistic, point-nucleus limits of the functions G_{M1} and G_{E2} obtained by the fitting procedure described above. Because of the fitting, the uncertainties are not ascribed to them; we expect that they are somewhat less accurate than the corresponding relativistic values. The comparison is drawn with the most accurate previous nonrelativistic calculations. A much better agreement is observed with the previous nonrelativistic results than with the relativistic ones.

IV. CORRECTIONS TO THE HYPERFINE SPLITTING

While the evaluation of the relativistic hfs value is the most computationally intensive part of the calculation, a high-precision theoretical determination of the hfs splitting requires inclusion of a number of important corrections. In this section, we present a detailed description of each of them in turn.

A. QED effects

For the magnetic dipole hfs splitting, the leading (in $Z\alpha$) QED contribution originates from the anomalous magnetic moment of the electron g_e. The effect is accounted for by multiplying the spin-dependent terms in Eq. (16) by $g_e/2 \approx \alpha/(2\pi)$; see, e.g., Ref. [3]. So, the leading QED correction to the function G_{M1} is given by

$$\delta G_{M1}^{\mathrm{QED},0}(Z) = \frac{\alpha}{2\pi}[G_{M1,sd}(Z) + G_{M1,c}(Z)], \tag{53}$$

where $G_{M1,sd}$ and $G_{M1,c}$ are the contributions to the function G_{M1} induced by the spin-dipole and the contact term in Eq. (16), respectively.

The higher-order terms of the $Z\alpha$ expansion (the *binding* QED corrections) induce important contributions and should be taken into account alongside the leading effect. The binding corrections to the contact term can be written in a form analogous to that for the hydrogen hfs [5,9,44],

TABLE I. Individual contributions to the magnetic dipole hfs splitting in ^{6,7}Li and ^{9}Be$^+$, in terms of the function G_{M1} if not specified otherwise. For ^{6}Li, only the contributions different from those for ^{7}Li are listed. The values of the nuclear magnetic moments are taken from Ref. [37]. The entries are labeled as follows: "NR(point)" denotes the point-nucleus nonrelativistic result; "Relativistic" is the total relativistic correction; "Coulomb" is the relativistic hfs value obtained with the Dirac-Coulomb Hamiltonian; "Breit" is the Breit-interaction correction; "BW" is the nuclear magnetization distribution correction; "NMS" is the normal mass shift; "SMS" is the specific mass shift; "SO" is the sum of the normal and specific spin-orbital recoil corrections induced by Eqs. (61) and (62); and "Negative-energy" is the contribution of the negative-energy part of the Dirac spectrum.

		$2\,^2S$	$3\,^2S$	$2\,^2P_{1/2}$	$2\,^2P_{3/2}$	Ref.
			^{7}Li			
NR(point)		0.215251	0.168340	0.073905	−0.024348	
		0.215254(4)	0.168351(13)			Hylleraas [5]
		0.21519	0.16828	0.07389	−0.02451	MCHF [8]
Relativistic		0.000205	0.000159	0.000018	−0.000036	
Coulomb		0.215385(5)	0.168440(9)	0.073923(1)	−0.024364(10)	
		0.21527		0.07396	−0.02476	MCDF [10]
		0.21565	0.16861	0.07389	−0.02425	CCSD [18]
Breit		0.000016	0.000016	−0.000003	0.000000	
QED		0.000182(4)	0.000143(3)	0.000048(1)	−0.000085(2)	
BW		−0.000024(5)	−0.000019(4)	−0.000002	0.000009(2)	
Recoil	NMS	−0.000050	−0.000039	−0.000017	0.000006	
	SMS	0.000002	0.000002	0.000027	−0.000055	
	SO	0.000000	0.000000	−0.000001(1)	−0.000002(1)	
Negative-energy		0.000002(1)	0.000002(1)	−0.000003(1)	−0.000003(2)	
Total		0.215512(8)	0.168544(11)	0.073972(2)	−0.024493(10)	
Total[a] (MHz)		401.755(15)	93.095(6)	45.966(1)	−3.044(1)	
Experiment (MHz)		401.7520433(5)[b]	93.106(11)[c]	45.914(25)[d]	−3.055(14)[d]	
				46.010(25)[e]		
				46.024(3)[f]		
			^{6}Li			
Coulomb		0.215382(5)	0.168438(9)	0.073922(1)	−0.024363(10)	
BW		−0.000022(13)	−0.000017(10)	−0.000002(1)	0.000008(5)	
Recoil	NMS	−0.000059	−0.000046	−0.000020	0.000007	
	SMS	0.000002	0.000002	0.000031	−0.000064	
Total		0.215504(14)	0.168538(14)	0.073974(2)	−0.024502(11)	
Total[g] (MHz)		152.122(10)	35.250(3)	17.4058(5)	−1.1530(5)	
Experiment (MHz)		152.136839(2)[b]	35.263(15)[c]	17.375(18)[h]	−1.155(8)[h]	
				17.386(31)[e]		
				17.394(4)[f]		
			^{9}Be$^+$			
NR(point)		0.390544	0.335066	0.221132	0.00989	
		0.390549(9)				Hylleraas [5]
		0.39050	0.33504	0.22113	0.00967	MCHF [8]
Relativistic		0.000664	0.000563	0.000162	−0.00015	
Coulomb		0.391030(6)	0.335468(9)	0.221302(2)	0.009800(25)	
		0.39094(4)		0.22140(1)	0.0091(4)	MCDF [11]
Breit		0.000039	0.000042	−0.000021	−0.000001	
QED		0.000289(12)	0.000248(10)	0.000137(5)	−0.000181(7)	
BW		−0.000062(6)	−0.000053(5)	−0.000005(1)	0.000027(3)	
Recoil	NMS	−0.000071	−0.000061	−0.000040	−0.000002	
	SMS	0.000002	0.000002	0.000057	−0.000080	

TABLE I. (*Continued.*)

	$2\,^2S$	$3\,^2S$	$2\,^2P_{1/2}$	$2\,^2P_{3/2}$	Ref.
SO	0.000000	0.000000	−0.000007(2)	−0.000018(5)	
Negative-energy	0.000005(3)	0.000005(2)	−0.000009(4)	−0.000011(6)	
Total	0.391233(15)	0.335651(15)	0.221413(7)	0.009533(27)	
Total[i] (MHz)	−625.08(2)	−158.897(7)	−117.919(4)	−1.015(3)	
Total[j] (MHz)	−625.11(3)	−158.905(7)	−117.925(4)	−1.016(3)	
Experiment (MHz)	−625.00883705(1)[k]		−118.6(36)[l]		

[a] $\mu(^7\text{Li})=3.2564268(17)$.
[b] Beckmann *et al.*, 1974 [1].
[c] Bushaw *et al.*, 2003 [38].
[d] Orth *et al.*, 1975 [39].
[e] Walls *et al.*, 2003 [40].
[f] Das and Natarajan, 2008 [41].
[g] $\mu(^6\text{Li})=0.8220473(6)$.
[h] Orth *et al.*, 1974 [42].
[i] $\mu(^9\text{Be})=-1.177432(3)$.
[j] $\mu(^9\text{Be})=-1.177492(17)$.
[k] Wineland *et al.*, 1983 [2].
[l] Bollinger *et al.*, 1985 [43].

$$\delta G_{M1}^{\text{QED,bind}}(Z)=\frac{\alpha}{\pi}G_{M1,c}(Z)\left\{Z\alpha\pi\left(\ln 2-\frac{5}{2}\right)+(Z\alpha)^2\left[-\frac{8}{3}\ln^2(Z\alpha)+a_{21}\ln(Z\alpha)+a_{20}\right]\right\}. \tag{54}$$

The coefficients a_{21} and a_{20} are different from the hydrogenic case and not known at present. One can, however, use their hydrogenic values as crude estimates. In our calculations, we will use the results for the hydrogenic $2s$ state, $a_{21}=-1.1675$, $a_{20}=11.3522$ [44,45], and assume a 100% uncertainty for them. This treatment of the QED effects coincides with those of Refs. [5,6] but is different from other previous investigations, where the binding effects were continually neglected. Such neglect can hardly be justified since the higher-order terms change the total QED contribution by 40% for lithium and by 60% for beryllium.

The binding corrections to the spin-dipole and orbital parts of hfs are relevant for the states with $l>0$ only. They enter in the relative order $\alpha(Z\alpha)^2$ and are presently unknown. Numerical calculations for the hydrogenic case [46] show that their nominal order can be enhanced by the second power of logarithm. We thus estimate the uncertainty due to their neglect by

$$|G_{M1,sd}+G_{M1,l}|\frac{\alpha}{\pi}(Z\alpha)^2\ln^2(Z\alpha). \tag{55}$$

For the electric quadrupole splitting, the QED correction has not been calculated so far. Its relative nominal order is $\alpha(Z\alpha)^2$. According to our analysis, this correction diverges in the point-quadrupole limit $R\to 0$, which means that the nominal order is enhanced by $\ln R\approx 6$. We therefore estimate the error in G_{E2} due to the neglect of the QED effects by multiplying it by the factor of

$$10\alpha(Z\alpha)^2.$$

TABLE II. Individual contributions to the electric quadrupole hfs splitting of the $2\,^2P_{3/2}$ state, in terms of the function G_{E2} if not specified otherwise. The notations are the same as in Table I. The values of the nuclear quadrupole moments are taken from Ref. [37].

	^{7}Li	^{6}Li	^{9}Br$^+$	Ref.
NR(point)	0.050260	0.050260	0.172140	
	0.0498		0.1717	MCHF [8]
	0.0498		0.1727	FCPC [36]
Relativistic	−0.000004	−0.000004	−0.000013	
Coulomb	0.050260(3)	0.050260(3)	0.172150(7)	
	0.051085		0.18356(3)	MCDF [10,11]
Breit	−0.000004	−0.000004	−0.000024	
QED	0.000000(2)	0.000000(2)	0.000000(11)	
NMS	−0.000012	−0.000014	−0.000031	
SMS	0.000012	0.000014	0.000030	
Total	0.050256(4)	0.050256(4)	0.172125(13)	
Total (MHz)	−0.216(4)[a]	−0.0044(1)[b]	2.281(16)[c]	
Experiment (MHz)	−0.221(29)	−0.010(14)		[39,42]

[a] $Q(^7\text{Li})=-40.55(80)$ mb.
[b] $Q(^6\text{Li})=-0.82(2)$ mb.
[c] $Q(^9\text{Be})=-52.88(38)$ mb.

TABLE III. Nonrelativistic hfs parameters, in a.u.

	$2\,^2S$	$3\,^2S$	$2\,^2P$				
Ion	a_c	a_c	a_c	a_{sd}	a_l	b_q	Ref.
Li	2.90589	0.67336	−0.21467	−0.013477	0.063125	−0.022617	This work
	2.90592(5)	0.67341(5)	−0.21478(5)				Hylleraas [5]
	2.9051	0.6731	−0.2151	−0.01346	0.06311	−0.02239	MCHF [8]
	2.903	0.6745	−0.2136	−0.01341	0.06309	−0.02242	FCPC [36]
Be$^+$	12.4974	3.1769	−1.0842	−0.10269	0.48520	−0.18362	This work
	12.4976(3)						Hylleraas [5]
	12.496	3.1767	−1.0856	−0.10265	0.48516	−0.18310	MCHF [8]
	12.493	3.181	−1.070	−0.1020	0.4851	−0.1842	FCPC [36]

B. Nuclear recoil

Within the nonrelativistic approach, the nuclear recoil effect on the energy levels and on the wave functions of the system is accounted for by introducing two additional terms in the Hamiltonian, traditionally referred to as the normal mass shift (NMS) and the specific mass shift (SMS). They are given by

$$H_{\mathrm{NMS}} = \sum_i \frac{\boldsymbol{p}_i^2}{2M}, \tag{56}$$

$$H_{\mathrm{SMS}} = \sum_{i<j} \frac{\boldsymbol{p}_i \cdot \boldsymbol{p}_j}{M}, \tag{57}$$

respectively, where M is the mass of the nucleus. Alterations of the wave function due to the additions to the Hamiltonian give rise to the corresponding corrections to the hfs. The NMS part of the recoil can be factorized out and expressed in terms of the reduced mass. It is accounted for by multiplying the nonrelativistic hfs value by a factor of $(1+m/M)^{-3}$ [47]. The inclusion of H_{NMS} into the CI Hamiltonian leads to the same effect but adds some relativistic corrections. The SMS part of the recoil effect is to be evaluated numerically, by incorporating H_{SMS} into the CI Hamiltonian and by identifying the corresponding alteration of the hfs splitting.

It should be stressed that, despite the fact that our original CI Hamiltonian is the relativistic one, the inclusion of the operators H_{NMS} and H_{SMS} in it does not fully account for the relativistic recoil effects, since the operators themselves are obtained within the nonrelativistic approximation only. This fact was often disregarded in the past, e.g., in Ref. [48]. The complete treatment of the leading $[\sim(Z\alpha)^2]$ relativistic recoil correction to energy levels of the system is achieved by employing the operator [49]

$$H_{\mathrm{rec}} = \frac{1}{2M} \sum_{ij} \left\{ \boldsymbol{p}_i \cdot \boldsymbol{p}_j - \frac{Z\alpha}{r_i} [\boldsymbol{\alpha}_i + (\boldsymbol{\alpha}_i \cdot \hat{\boldsymbol{r}}_i)\hat{\boldsymbol{r}}_i] \cdot \boldsymbol{p}_j \right\}. \tag{58}$$

Numerical calculations with this operator were performed, e.g., in Ref. [50]. In our present investigation, the relativistic recoil effects are negligible as compared to other sources of the theoretical uncertainty. We thus use the nonrelativistic operators for the description of the recoil effects.

Matrix elements of H_{SMS} between the individual CSFs can be expressed in terms of the angular coefficients $v_{rs}^{(k)}$ introduced in Eq. (9), with the multipolarity $k=1$,

$$\langle \gamma_r PJM | H_{\mathrm{SMS}} | \gamma_s PJM \rangle = -\frac{1}{M} \sum_{abcd} v_{rs}^{(1)}(abcd) V(ac) V(bd), \tag{59}$$

where the radial integrals are (see, e.g., Ref. [48])

$$V(ac) = \langle \kappa_a \| \boldsymbol{C}^{(1)} \| \kappa_c \rangle \int_0^\infty dr \times \left\{ G_a \left[\frac{d}{dr} - \frac{\kappa_a(\kappa_a+1) - \kappa_c(\kappa_c+1)}{2r} \right] G_c + F_a \left[\frac{d}{dr} - \frac{\kappa_a(\kappa_a-1) - \kappa_c(\kappa_c-1)}{2r} \right] F_c \right\}. \tag{60}$$

So far, we discussed the recoil corrections to hfs that are induced by the wave functions. There are, however, also recoil corrections to the hyperfine interaction itself. The recoil correction to the magnetic dipole hfs interaction arises through the spin-orbit coupling in the scalar component of the nuclear current. This correction depends on the spin of the nucleus I. In the case of hydrogen $(I=1/2)$, it was derived many years ago in Ref. [51], whereas in Ref. [52] it was reported for the case of deuterium $(I=1)$. To the best of our knowledge, this correction was previously unknown for the arbitrary spin of the nucleus and was not accounted for in calculations of the hfs of systems other than hydrogen and deuterium.

The spin-orbital (SO) recoil correction to the magnetic dipole hfs interaction is obtained in the Appendix by using the expression for the current of a particle with an arbitrary spin derived in Ref. [53]. The result is represented by Eq. (A7). It can be conveniently split into the normal (SON) and specific (SOS) parts, analogously to the normal and the specific mass shift of energy levels, $H_{\mathrm{SO}}=H_{\mathrm{SON}}+H_{\mathrm{SOS}}$, with

$$H_{\mathrm{SON}} = \frac{Z\alpha}{2M^2}(g-1)\boldsymbol{I} \cdot \sum_i \frac{\boldsymbol{l}_i}{r_i^3}, \tag{61}$$

$$H_{\mathrm{SOS}} = \frac{Z\alpha}{2M^2}(g-1)\boldsymbol{I} \cdot \sum_{i<j} \boldsymbol{t}_{\mathrm{SOS}}(i,j), \tag{62}$$

$$\boldsymbol{t}_{\mathrm{SOS}}(i,j)=\frac{\boldsymbol{r}_i\times\boldsymbol{p}_j}{r_i^3}+\frac{\boldsymbol{r}_j\times\boldsymbol{p}_i}{r_j^3}. \tag{63}$$

Here, $\boldsymbol{I}$ is the operator of the nuclear spin, $\boldsymbol{l}_i$ is the operator of the orbital angular momentum of the ith electron, and g is the g factor of the nucleus,

$$g=\frac{\mu}{\mu_N}\frac{M}{m_p}\frac{1}{I}. \tag{64}$$

The SON interaction is proportional to the orbital part of the nonrelativistic decomposition of the magnetic dipole hfs operator. It is easy to see that this part of the SO recoil effect can be accounted for by modifying the orbital hyperfine parameter a_l by

$$a_l\to a_l\left[1+\frac{m}{M}Z\frac{g-1}{g}\right]. \tag{65}$$

It is interesting to note that, comparing to the NMS effect, the SON correction is enhanced by a factor of Z, which makes it a dominant recoil effect in the hfs splitting of medium-Z H-like ions (for electronic states with $l>0$). For Li^{2+}, the ratio of the SON and the NMS effects is -0.5 for the $2p_{1/2}$ state and -1.2 for the $2p_{3/2}$ state. For the lithiumlike systems, however, the SON and the SOS corrections tend to cancel each other, the net effect being rather small numerically.

In the present work, we calculate the SOS correction by using perturbation theory to the lowest order. For the electronic configuration with a single valence electron beyond the closed core shell, the contribution to the function G_{M1} due to the SOS effect can be expressed as

$$\delta G_{M1}^{\mathrm{SOS}}=\left[\frac{(Z\alpha)^3m^3}{n^3J(J+1)(2L+1)}\right]^{-1}\frac{Zm}{M}\frac{g-1}{g}\sum_{\mu_c}(-1)\times\langle cv|t_{\mathrm{SOS}_0}|vc\rangle, \tag{66}$$

where v denotes the valence electron state with the angular momentum projection $\mu_v=1/2$, c is the core electron state with the angular momentum projection μ_c, and t_{SOS_0} is the zeroth spherical component of the operator $\boldsymbol{t}_{\mathrm{SOS}}$. The radial integral is evaluated to yield

$$\langle cv|t_{\mathrm{SOS}_0}|vc\rangle=\sqrt{\frac{6}{j_v(j_v+1)(2j_v+1)}}\times\begin{Bmatrix}1 & 1 & 1\\ j_v & j_v & j_c\end{Bmatrix}U(cv)V(vc), \tag{67}$$

where

$$U(cv)=\langle\kappa_c\|\boldsymbol{C}^{(1)}\|\kappa_v\rangle\int_0^\infty dr r^{-2}(G_cG_v+F_cF_v), \tag{68}$$

and $V(vc)$ is defined by Eq. (60). It is easy to see that the radial integral (67) vanishes for the S states.

The calculational results for the individual recoil contributions to the magnetic dipole hfs splitting are listed in Table I under entries "NMS," "SMS," and "SO." The results obtained for the NMS and SMS parts are in good agreement with the previous evaluations of these corrections. The entry "SO" represents the sum of the SON and the SOS corrections. Because of a large cancellation between these two parts, we calculate both of them by perturbation theory. The uncertainty specified in the table was evaluated by comparing results obtained with different potentials in the zeroth-order Hamiltonian.

The scalar component of the nuclear current yields also a correction to the electric quadrupole interaction [52,53]. This correction is induced by the nuclear spin and can be interpreted as a shift of the nuclear quadrupole moment (see the Appendix for details). The induced contribution is included into the observable value of the nuclear quadrupole moment and thus is not needed to be taken into account in the theoretical description of the electric quadrupole hfs.

C. Nuclear size and magnetization distribution

Due to a high singularity of the hfs interaction at the origin, the nuclear structure effects (particularly, the distribution of the nuclear magnetic moment) have a significant influence on the magnetic dipole hfs and should be taken into account in atomic calculations. An accurate theoretical description of these effects is a demanding problem. A way for its rigorous solution was paved in recent studies [54–56]. Practical realizations of this approach, however, are so far restricted to two- and three-nucleon systems [54,55] and their extension to more complex nuclei like ^{7}Li and ^{9}Be looks problematic.

The most widely used approach up to now is to account for the extended nuclear magnetization distribution [the Bohr-Weisskopf (BW) effect] by means of the Zemach formula [57]. According to the original formulation, the nuclear correction to the magnetic dipole hfs of an S state of an H-like atom is represented by a simple multiplicative factor,

$$\delta G_{M1}^{\mathrm{nuc}}(Z)=-2Z\alpha\langle r\rangle_{em}G_{M1}(Z), \tag{69}$$

where $\langle r\rangle_{em}$ is the Zemach moment obtained by folding together the electric charge $\rho_e(r)$ and magnetization $\rho_m(r)$ densities

$$\langle r\rangle_{em}=\int d\boldsymbol{r}d\boldsymbol{r}'\,\rho_e(r)\rho_m(r')|\boldsymbol{r}-\boldsymbol{r}'|. \tag{70}$$

Formula (69) accounts for both the charge and the magnetization distribution. Since the charge-distribution effect is usually taken into account in a more complete way by modifying the Coulomb nuclear potential in the Hamiltonian (2), it should be subtracted from the total Zemach correction. The finite nuclear charge (FNC) correction is obtained from Eq. (69) by setting $\langle r\rangle_{em}=\langle r\rangle_e$, where $\langle r\rangle_e$ is the electric charge radius defined as

$$\langle r\rangle_e=\int d\boldsymbol{r}\rho_e(r)|\boldsymbol{r}|. \tag{71}$$

More detailed studies of the FNC correction in H-like atoms with including the relativistic effects were reported in Refs. [30,58]. For lithium and beryllium, the relativistic effects are small and enter mainly through the alteration of the exponent

TABLE IV. Nuclear parameters (in fm) and the relative values of the nuclear corrections (in ppm) to the magnetic dipole hfs. The abbreviations are as follows: "FNS" denotes the nuclear charge distribution correction, "Zemach" labels the BW correction obtained with the Zemach formula, "SP" labels the BW correction evaluated within the SP approach, and "const" indicates that the odd-nucleon wave function is taken to be a constant within the nucleus.

					Bohr-Weisskopf effect				
Isotope	$\langle r^2\rangle_e^{1/2}$ (fm)	$\langle r^2\rangle_m^{1/2}$ (fm)	$\langle r\rangle_{em}-\langle r\rangle_e$ (fm)	FNS	Zemach	SP	SP(const)	Total	Total nuclear correction
^{6}Li	2.54(3)	3.12(22)	1.38(19)	−268(3)	−160(20)	−50	−89	−100(60)	−368(60)
^{7}Li	2.43(3)	2.80(8)	1.19(8)	−257(3)	−135(9)	−112	−99	−112(23)	−369(23)
^{9}Be	2.52(1)	2.67(6)	1.06(5)	−356(4)	−160(8)	−158	−161	−158(16)	−514(16)

in the $Z\alpha$ and $\langle r\rangle_e$ dependence by terms $\sim(Z\alpha)^2$.

Using the hydrogenic result [30] for the exponent of the $Z\alpha$ and $\langle r\rangle_e$ dependence, we write the generalization of the nonrelativistic FNC correction in the form valid for an arbitrary state of few-electron atoms,

$$\delta G_{M1}^{\mathrm{FNC}}(Z) = -2(Z\alpha\langle r\rangle_e)^{2\gamma-1} G_{M1,c}(Z), \tag{72}$$

where $\gamma=\sqrt{1-(Z\alpha)^2}$ and $G_{M1,c}$ is the contact part of G_{M1}. Using Eq. (72), one should keep in mind that the charge radius $\langle r\rangle_e$ is different from the charge root-mean-square (rms) radius $\langle r^2\rangle_e^{1/2}$, which is usually listed in tables. The conversion factor depends somewhat on the model of the nuclear charge distribution. For the Gaussian model, the connection is $\langle r\rangle_e=\sqrt{8/(3\pi)}\langle r^2\rangle_e^{1/2}$. The values of the rms radii of the nuclei ^{6,7}Li and ^{9}Be were taken from Ref. [59]. The rms radii and the numerical results for the FNS correction obtained by Eq. (72) are presented in Table IV (the relative values of the correction, $\delta G_{M1}^{\mathrm{FNC}}/G_{M1,c}$, are listed). An independent evaluation of the FNS correction was performed, by repeating the CI calculations for different values of the nuclear radius and by fitting the increments to the analytical form (72). The FNS correction obtained in this way agreed very well with the analytical results presented in the table.

In the present investigation, separate values of the FNS correction are not necessary since this effect is already included in the CI part of the calculation. However, we use the values of the FNS correction in order to identify the point-nucleus limit of our results (particularly, for the comparison with the point-nucleus results of Ref. [5]) and for improving the stability of the fit in extracting the nonrelativistic limit of our calculations (the FNC correction is the only part of the CI values that is linear in α).

There is no need to specify explicitly to which electronic states the results for the nuclear corrections in Table IV correspond, because the relative values of the corrections are listed. Our numerical calculations show that, with a good accuracy, the relative values of the nuclear corrections do not depend on the particular state. (Of course, for the P states, the relative value should be evaluated with respect to the contact part of the correction.)

The Zemach correction induced by the magnetization distribution (the BW effect) can be written in a form valid for an arbitrary state as

$$\delta G_{M1}^{\mathrm{BW}}(Z) = -2Z\alpha[\langle r\rangle_{em}-\langle r\rangle_e] G_{M1,c}(Z). \tag{73}$$

The Zemach radius is usually not tabulated and should be derived from data available for the charge and magnetization rms radii according to Eq. (70), with an additional input of the distribution models. For the Gaussian model

$$\rho(r) = \rho_0 \exp(-\Lambda r^2) \tag{74}$$

employed for the charge and magnetization distributions, the Zemach radius is readily obtained analytically,

$$\langle r\rangle_{em} = \sqrt{\frac{8}{3\pi}}(\langle r^2\rangle_e + \langle r^2\rangle_m)^{1/2}. \tag{75}$$

For more sophisticated distribution models, one has to evaluate radial integrations in Eq. (70) numerically. In order to test the model dependence of the Zemach radius (with fixed values of the charge and magnetization rms radii), we performed its numerical evaluation with the two-parameter Fermi model. The same results as for the Gaussian model are obtained, which leads us to conclude that the model dependence is negligible.

The values listed in Table IV for the magnetic rms radius are the average of data tabulated in Ref. [60] and the errors are their mean-square deviation. Under the entry "Zemach," we tabulate the numerical results for the BW correction obtained by Eq. (73); the error ascribed to them originates from the uncertainties of the magnetization and charge radii.

The second approach to the description of the BW effect considered in the present work is based on the single-particle (SP) model of the nuclear magnetic moment and will be referred to as the SP approach in the following. Within the SP model, the nuclear magnetic moment is assumed to be induced by the odd nucleon (proton when Z and A are odd, and neutron when Z is even and A is odd). The odd nucleon is assumed to have an effective g factor, which is fixed so that it yields the experimental value of the nuclear magnetic moment. The treatment of the magnetization distribution effect on hfs within the SP model was originally developed in Refs. [61,62] and later in Ref. [30]. The spin-orbit interaction of the odd nucleon was introduced into this approach in Ref. [31]. Our present treatment closely follows the procedure described in Refs. [31,63].

The wave function of the odd nucleon is assumed to satisfy the Schrödinger equation with the central potential of the Woods-Saxon form and the spin-orbital term included (see, e.g., Ref. [64]),

$$V(\boldsymbol{r}) = -V_0\mathcal{F}(r) + \frac{1}{m_p}\phi_{\rm so}(r)\boldsymbol{l}\cdot\boldsymbol{\sigma} + V_C(r), \tag{76}$$

where

$$\phi_{\rm so}(r) = \frac{V_{\rm so}}{4m_p r}\frac{d\mathcal{F}(r)}{dr}, \tag{77}$$

$$\mathcal{F}(r) = \left[1+\exp\left(\frac{r-R}{a}\right)\right]^{-1}, \tag{78}$$

and V_C is the Coulomb part of the interaction (absent for neutron), with the uniform distribution of the charge $(Z-1)$ over the nuclear sphere. The parameters V_0, $V_{\rm so}$, R, and a were taken from Ref. [64], where they were obtained by fitting electron scattering data. The fitting was not evaluated for ^{9}Be, so we use the parameters for its closest odd-neutron neighbor, ^{12}C. For ^{6}Li, the nuclear spin is integer $(I=1)$, and so one needs to make an additional assumption about the value of the orbital angular momentum of the nucleus. We used the value $L=0$ [65] in our calculations.

The nuclear magnetic moment can be evaluated within the SP model to yield [31]

$$\frac{\mu}{\mu_N} = \begin{cases} \frac{1}{2}g_S + \left[I-\frac{1}{2}+\frac{2I+1}{4(I+1)}\langle\phi_{\rm so}r^2\rangle\right]g_L & \text{for } I=L+\frac{1}{2}, \\ -\frac{I}{2(I+1)}g_S + \left[\frac{I(2I+3)}{2(I+1)}-\frac{2I+1}{4(I+1)}\langle\phi_{\rm so}r^2\rangle\right]g_L & \text{for } I=L-\frac{1}{2}, \end{cases} \tag{79}$$

where I and L are the total and the orbital angular momentum of the nucleus, respectively, g_L is the g factor associated with the orbital motion of the nucleon ($g_L=1$ for proton and $g_L=0$ for neutron), and g_S is the effective nucleon g factor, determined by the condition that Eq. (79) yields the experimental value of the magnetic moment.

It was demonstrated in Ref. [31] that, within the SP model, the BW effect can be accounted for by adding a multiplicative magnetization-distribution function $F(r)$ to the standard point-dipole hfs interaction (15). The distribution function is given by [63]

$$\begin{aligned} F(r) = {} & \frac{\mu_N}{\mu}\int_0^r dr' r'^2|u(r')|^2\left[\frac{1}{2}g_S + \left(I-\frac{1}{2}\right.\right. \\ & \left.\left. + \frac{2I+1}{4(I+1)}r^2\phi_{\rm so}(r)\right)g_L\right] + \frac{\mu_N}{\mu}\int_r^\infty dr' r'^2|u(r')|^2\frac{r^3}{r'^3} \\ & \times\left[-\frac{2I-1}{8(I+1)}g_S + \left(I-\frac{1}{2}+\frac{2I+1}{4(I+1)}r^2\phi_{\rm so}(r)\right)g_L\right] \end{aligned} \tag{80}$$

for $I=L+1/2$ and

$$\begin{aligned} F(r) = {} & \frac{\mu_N}{\mu}\int_0^r dr' r'^2|u(r')|^2\left[-\frac{I}{2(I+1)}g_S + \left(\frac{I(2I+3)}{2(I+1)}\right.\right. \\ & \left.\left. - \frac{2I+1}{4(I+1)}r^2\phi_{\rm so}(r)\right)g_L\right] + \frac{\mu_N}{\mu}\int_r^\infty dr' r'^2|u(r')|^2\frac{r^3}{r'^3} \\ & \times\left[\frac{2I+3}{8(I+1)}g_S + \left(\frac{I(2I+3)}{2(I+1)}-\frac{2I+1}{4(I+1)}r^2\phi_{\rm so}(r)\right)g_L\right] \end{aligned} \tag{81}$$

for $I=L-1/2$. In the above formulas, $u(r)$ is the wave function of the odd nucleon. It can easily be seen that $F(r)=1$ outside the nucleus.

In the present work, we evaluated the BW correction within the SP approach as described above. In addition, we considered a simplified version of this approach obtained by assuming the wave function of the odd nucleon to be just a constant within the nucleus. By comparing the two corresponding results, we can conservatively estimate the dependence of the SP values on the parameters employed in the Woods-Saxon potential. Calculational results for the BW correction obtained within the SP approach are listed in Table IV under the labels "SP" (the full SP approach) and "SP-(const)" (the SP approach with the constant wave function of the odd nucleon).

The total results for the BW correction listed in the table were obtained as follows. For ^{7}Li and ^{9}Be, we employ the results of the SP model as the final values. The uncertainty for ^{7}Li was taken to be the largest deviation from the final result. For ^{9}Be, all three values fall very close to each other, so we assign the 10% uncertainty to the final result. The nucleus ^{6}Li has an odd neutron and an odd proton; one thus can hardly expect it to be described well by the SP model. In this case, we use the plain average of the three values; the error was chosen so that it covers all three results.

We would like to stress that there are nontrivial nuclear structure effects, which are ignored both within the SP model and within the Zemach approach. Since these effects cannot be reasonably estimated at present, our uncertainties of the BW correction yield the order of the expected error only.

The final values of the BW correction and their uncertainties are listed in Table I under the entry "BW." Our results for ^{7}Li and ^{9}Be are reasonably close to the Zemach-formula values of Ref. [5]. The result of Ref. [11] for ^{9}Be is larger than ours by a factor of 4. This is because the authors of Ref. [11] used $\langle r \rangle_m$ instead of $\langle r \rangle_{em} - \langle r \rangle_e$ in Eq. (73). In Ref. [6], the BW correction was evaluated within the SP approach with the constant odd-nucleon wave function. The corresponding results for ^{6,7}Li nearly coincide with our values obtained within the same approach. In Refs. [12,66], the BW correction was calculated by using the Fermi [12] or the uniform [66] distribution of the magnetization density over the nucleus. Their results fall between our values obtained with different models. In most of the other previous studies, the BW effect was not accounted for.

D. Negative continuum

The negative-continuum (NC) contribution might be of some importance in calculations involving the operators that mix the upper and the lower components of the Dirac wave function. The magnetic dipole hfs operator is of this kind, so we have to obtain an estimation for this correction. In the present investigation, we calculate the NC contribution by employing perturbation theory to the first order.

For the electronic configuration with a single valence electron beyond the closed core shell and to first order in the electron-electron interaction, the NC correction can be written as

$$\delta G_{M1}^{\mathrm{NC}} = \left[\frac{(Z\alpha)^3 m^2}{n^3 J(J+1)(2L+1)} \right]^{-1} \times 2 \sum_{n}^{\varepsilon_n<0} \Biggl\{ \sum_{\mu_c} \frac{[\langle vc|V_{CB}|nc\rangle - \langle cv|V_{CB}|nc\rangle]\langle n|t_0^{(1)}|v\rangle}{\varepsilon_v - \varepsilon_n} + \sum_{\mu_c} \frac{[\langle vc|V_{CB}|vn\rangle - \langle cv|V_{CB}|vn\rangle]\langle n|t_0^{(1)}|c\rangle}{\varepsilon_c - \varepsilon_n} - \frac{\langle v|U|n\rangle\langle n|\boldsymbol{t}_0^{(1)}|v\rangle}{\varepsilon_v - \varepsilon_n} \Biggr\}, \qquad (82)$$

where v denotes the valence electron state with the angular momentum projection $\mu_v = \frac{1}{2}$, c is the core electron state with the angular momentum projection μ_c, $t_0^{(1)}$ is the spherical component of the magnetic dipole hfs operator $\boldsymbol{t}^{(1)}$ defined by Eq. (15), $V_{CB} = V_C + V_B$ is the sum of the Coulomb and Breit parts of the electron-electron interaction, and the summation over n is performed over the negative-energy part of the Dirac spectrum. The states v, c, and n are assumed to be eigenvectors of a single-particle Dirac Hamiltonian h with the screening potential U, $h = \boldsymbol{\alpha} \cdot \boldsymbol{p} + (\beta - 1)m + V_{\mathrm{nuc}}(r) + U(\boldsymbol{r})$.

We mention that the NC correction may depend strongly on the choice of the Hamiltonian h. It is therefore important to use the same single-particle Hamiltonian for the evaluation of the NC correction as in the CI part of the calculation. So, in the present investigation the screening potential U in Eq. (82) was fixed as $U = V_{\mathrm{DF}}^{N-1}$.

It should be also noted that, evaluating Eq. (82), one cannot neglect the Breit part of the electron-electron interaction as compared to the Coulomb one. For the negative-energy part of the Dirac spectrum, both of these interactions induce contributions of the same order of magnitude.

Formula (82) for the NC correction ignores contributions of the second and higher orders in the electron-electron interaction. Their unambiguous description is possible within QED only. For lithium and beryllium, the electron correlation is strong and the perturbation expansion converges slowly. We thus assign the uncertainty of 50% to the NC contribution obtained by Eq. (82).

V. DISCUSSION

The calculational results for the magnetic-dipole hfs splitting of the $2\,^2S$, $3\,^2S$, $2\,^2P_{1/2}$, and $2\,^2P_{3/2}$ states of ^{6,7}Li and ^{9}Be$^+$ are listed in Table I, expressed in terms of the dimensionless function G_{M1} defined by Eq. (23). The values presented for the S states differ from those in our previous work [21] in two ways. First, we now treat the normal mass shift as a correction, rather than by including it into the definition of the function G_{M1}. (Of course, this difference has no effect on the total theoretical prediction for the hfs or the hyperfine constant A_J.) Second, we perform a more detailed analysis of the BW effect, and so the uncertainty of this correction is changed.

In order to convert the function G_{M1} into the hyperfine constant A_J, an additional experimental input in the form of the magnetic moment of the nucleus is needed. This issue might contain some ambiguities since the tabulated values of the nuclear magnetic moments [37] are often inconsistent. In the case of ^{6}Li and ^{7}Li, we assume the values originally obtained by Beckmann *et al.* [1] to be the most reliable ones. For ^{9}Be, the choice is less obvious, and we present the theoretical results for the hyperfine constant A_J for two different experimental values of the magnetic moment.

For ^{7}Li, we observe good agreement of our theoretical predictions with all the experimental results listed, except the recent measurement of the $2\,^2P_{1/2}$ state by Das and Natarajan [41], which claims to be accurate to better than 0.01%. The theoretical prediction is away from this measurement by about 18σ and we presently see no way to explain this deviation theoretically.

Our theoretical prediction for the ground-state hfs splitting of ^{6}Li is in slight disagreement with the high-precision experimental result. For the ground state of beryllium, the deviation is larger and amounts to 3 or 4σ, depending on the value of the nuclear magnetic moment used. There are two possible explanations of these discrepancies: underestimated systematic effects in the experimental values of the nuclear magnetic moments and nontrivial nuclear-structure effects in the theoretical predictions. On the basis of the experimental data available, we cannot unambiguously distinguish between these two explanations. It would have been possible if the hfs splitting of two different states were accurately measured for the same isotope. The existing measurements of the hfs of excited states, however, are not yet sensitive to the inconsistencies in values of the nuclear magnetic moment.

The comparison presented for the hfs of excited states of lithium and beryllium indicates that our theoretical predictions are more accurate than the experimental results. The general agreement with the experimental data for the excited states is good, the only exception being the results of Ref. [41].

Our calculational results for the electric quadrupole hfs splitting of the $2\,^2P_{3/2}$ state in ^{6,7}Li and ^{9}Be$^+$ are listed in Table II, expressed in terms of the dimensionless function G_{E2} defined by Eq. (49). It is remarkable that all theoretical contributions to the electric quadrupole splitting seem to be well under control, so that the resulting theoretical predictions for the function G_{E2} are obtained with very good accuracy. If accurate experimental investigations of the quadrupole splitting were possible for Li-like ions, they would lead to a high-precision determination of the nuclear quadrupole moments, which are difficult to measure directly. In the absence of such investigations, the theoretical predictions for the hyperfine constant B_J are obtained by using the tabulated values of the nuclear quadrupole moments [37]. Our results are in agreement with the scarce experimental data available.

ACKNOWLEDGMENTS

I wish to thank V. M. Shabaev for valuable advice and, particularly, for pointing out the presence of the two-electron part in the spin-orbital recoil correction. Helpful discussions with K. Pachucki and A. Derevianko are gratefully acknowledged. The work presented in this paper was supported by the “Dynasty” foundation and by RFBR (Grant No. 06-02-04007).

APPENDIX: CORRECTIONS TO THE HYPERFINE SPLITTING DUE TO THE SCALAR COMPONENT OF THE NUCLEAR CURRENT

Let us first consider the simplest case of the electron and the nucleus being the spin-$\frac{1}{2}$ Dirac particles. The electron-nucleus interaction is then given by the standard scattering amplitude [67]

$$M = -e^2 Z D_{\mu\nu}(q) j_e^{\mu} j_{\text{nuc}}^{\nu}, \tag{A1}$$

where $D^{\mu\nu}$ is the photon propagator and j_e and j_{nuc} are the electromagnetic current of the electron and the nucleus, respectively,

$$j^{\mu} = \bar{u}(p')\gamma^{\mu}u(p) = \frac{1}{2m}\bar{u}(p')[(p'+p)^{\mu} + i\sigma^{\mu\nu}q_{\nu}]u(p). \tag{A2}$$

Here, u is the free Dirac spinor, m is the mass of the particle, $q=p'-p$, and $\sigma^{\mu\nu}=(i/2)[\gamma_{\mu},\gamma_{\nu}]$. Expressing the time component of the nuclear current in terms of the free spinors w in the rest frame, one arrives at [67]

$$j_{\text{nuc}}^{0} = w^{*}\left(1 - \frac{q^2}{8M^2} + \frac{i\boldsymbol{\sigma}\cdot\boldsymbol{q}\times\boldsymbol{p}}{4M^2}\right)w, \tag{A3}$$

where M is the nuclear mass. The first term in the brackets in the above expression corresponds to the standard Coulomb interaction between electron and the nucleus. The third term represents the spin-orbital coupling and induces a recoil correction to the hfs we are interested in here.

The generalization of the expression (A2) for the case of the nucleus with an arbitrary spin was obtained in Ref. [53]. The time component of the current reads

$$j_{\text{nuc}}^{0} = \frac{1}{2M}\bar{\psi}(p')[F_e(E+E') + G_m\gamma^0\boldsymbol{\Gamma}\cdot\boldsymbol{q}]\psi(p), \tag{A4}$$

where F_e and G_m are the electric and magnetic form factors of the nucleus, respectively,

$$\boldsymbol{\Gamma} = \begin{pmatrix} 0 & \boldsymbol{\Sigma} \\ -\boldsymbol{\Sigma} & 0 \end{pmatrix}, \tag{A5}$$

and the vector $\boldsymbol{\Sigma}$ is constructed from components Σ_i, which are generalizations of the Pauli matrices. After expressing the current in terms of the spinors ξ_0 in the rest frame, one gets the generalization of Eq. (A3) to the case of an arbitrary-spin nucleus [53],

$$j_{\text{nuc}}^{0} = \xi_0'^{*}\left[F_e - (2G_m - F_e)\frac{(\boldsymbol{\Sigma}\cdot\boldsymbol{q})^2}{8M^2} + (2G_m - F_e)i\frac{\boldsymbol{I}\cdot(\boldsymbol{q}\times\boldsymbol{p})}{2M^2}\right]\xi_0, \tag{A6}$$

where I is the operator of the spin of the nucleus. The form factors are identified as [53] $F_e(0)=1$ and $G_m(0)=g/2$, where g is the g factor of the nucleus.

The third term in the brackets of Eq. (A6) induces a first-order (in the electron-nucleus mass ratio) recoil correction to the magnetic dipole hfs splitting. Taking into account that, in the center-of-mass system, the total momentum of the atom is zero and transforming this term into the coordinate space (see Ref. [67]), we obtain the interaction of the form

$$H_{\text{SO}} = \frac{Z\alpha}{2M^2}(g-1)\boldsymbol{I}\cdot\sum_i\left(\frac{\boldsymbol{r}_i\times\boldsymbol{p}_i}{r_i^3} + \sum_{j\neq i}\frac{\boldsymbol{r}_i\times\boldsymbol{p}_j}{r_i^3}\right), \tag{A7}$$

where indices i and j numerate the electrons in the atom. For the hydrogen atom, $\boldsymbol{I}=(1/2)\boldsymbol{\sigma}$, Eq. (A7) reproduces the well-known result of Ref. [51]. A similar recoil correction to the Zeeman splitting of multielectron atoms was reported in Ref. [68].

The second term in the brackets of Eq. (A6) can be split into the contact and the quadrupole part, which induce corrections to the Lamb shift and to the quadrupole hfs splitting, respectively. Both of these corrections were evaluated in Ref. [53]. The result for the quadrupole interaction due to the second term in Eq. (A6) is (with the additional factor of 2, corrected in Ref. [69])

$$\delta H_{E2} = \frac{Z\alpha(g-1)}{2M^2}\Lambda\nabla_i\nabla_j\frac{1}{r}\left(I_iI_j - \frac{1}{3}\delta_{ij}I^2\right), \tag{A8}$$

where

$$\Lambda = \begin{cases} 1/(2I-1), & I \text{ is integer}, \\ 1/(2I), & I \text{ is half-integer}. \end{cases} \tag{A9}$$

Using the standard angular-momentum algebra, we transform Eq. (A8) into the form analogous to Eq. (37),

$$\delta H_{E2} = \alpha\boldsymbol{T}^{(2)}\cdot\delta\boldsymbol{Q}^{(2)}, \tag{A10}$$

where $\delta\mathbf{Q}^{(2)}$ is the correction to the operator of the quadrupole moment,

$$\delta Q^{(2)} = -\frac{Z(g-1)\Lambda}{2M^2}\sqrt{6}(I \otimes I)^{(2)}. \tag{A11}$$

Taking into account Eq. (46), the correction to the nuclear quadrupole moment is identified, which is

$$\delta Q_{\mathrm{ind}} = \begin{cases} -\dfrac{Z(g-1)I}{M^2}, & I \text{ is integer}, \\ -\dfrac{Z(g-1)(I-1/2)}{M^2}, & I \text{ is half-integer}. \end{cases} \tag{A12}$$

The numerical values of the induced quadrupole moment for the isotopes considered in this work are $\delta Q_{\mathrm{ind}}(^7\mathrm{Li}) = -0.39$ mb, $\delta Q_{\mathrm{ind}}(^6\mathrm{Li}) = -0.15$ mb, and $\delta Q_{\mathrm{ind}}(^9\mathrm{Be}) = -0.18$ mb, to be compared with the total values of the nuclear quadrupole moments [37]: $Q(^7\mathrm{Li}) = -40.55(80)$ mb, $Q(^6\mathrm{Li}) = -0.82(2)$ mb, and $Q(^9\mathrm{Be}) = 52.88(38)$ mb.

It should be mentioned that the correction (A12) does not have immediate experimental consequences. It vanishes for the nuclear spin $I=0$ and $\frac{1}{2}$. Nuclei with the spin $I > \frac{1}{2}$ have a quadrupole moment, and so the correction (A12) appears only together with the "pure" nuclear quadrupole moment. If the values of the nuclear quadrupole moments are derived from experimental observations, the induced correction is included in them and thus does not have to be accounted for in theoretical descriptions of the quadrupole splitting. It should be included, however, when the nuclear quadrupole moments are calculated basing on microscopic nuclear models, as, e.g., in Ref. [70].

[1] A. Beckmann, K. D. Böklen, and D. Elke, Z. Phys. **270**, 173 (1974).

[2] D. J. Wineland, J. J. Bollinger, and W. M. Itano, Phys. Rev. Lett. **50**, 628 (1983).

[3] A. Hibbert, Rep. Prog. Phys. **38**, 1217 (1975).

[4] F. W. King, Phys. Rev. A **40**, 1735 (1989).

[5] Z.-C. Yan, D. K. McKenzie, and G. W. F. Drake, Phys. Rev. A **54**, 1322 (1996).

[6] F. W. King, Phys. Rev. A **76**, 042512 (2007).

[7] J. Carlsson, P. Jönsson, and C. Froese Fischer, Phys. Rev. A **46**, 2420 (1992).

[8] M. Godefroid, C. Froese Fischer, and P. Jönsson, J. Phys. B **34**, 1079 (2001).

[9] K. Pachucki, Phys. Rev. A **66**, 062501 (2002).

[10] J. Bieroń, P. Jönsson, and C. Froese Fischer, Phys. Rev. A **53**, 2181 (1996).

[11] J. Bieroń, P. Jönsson, and C. F. Fischer, Phys. Rev. A **60**, 3547 (1999).

[12] S. Boucard and P. Indelicato, Eur. Phys. J. D **8**, 59 (2000).

[13] I. Lindgren, Rep. Prog. Phys. **47**, 345 (1984).

[14] I. Lindgren, Phys. Rev. A **31**, 1273 (1985).

[15] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **40**, 2233 (1989).

[16] A.-M. Mårtensson-Pendrill and A. Ynnerman, Phys. Scr. **41**, 329 (1990).

[17] R. Pal, M. S. Safronova, W. R. Johnson, A. Derevianko, and S. G. Porsev, Phys. Rev. A **75**, 042515 (2007).

[18] W. R. Johnson, U. I. Safronova, A. Derevianko, and M. S. Safronova, Phys. Rev. A **77**, 022510 (2008).

[19] S. G. Porsev and A. Derevianko, Phys. Rev. A **73**, 012501 (2006).

[20] A. Derevianko (private communication).

[21] V. A. Yerokhin, Phys. Rev. A **77**, 020501(R) (2008).

[22] M. E. Rose, *Relativistic Electron Theory* (Wiley, New York, 1961).

[23] W. R. Johnson, S. A. Blundell, and J. Sapirstein, Phys. Rev. A **37**, 2764 (1988).

[24] I. Grant, Comput. Phys. Commun. **5**, 263 (1973).

[25] I. Grant and N. C. Pyper, J. Phys. B **9**, 761 (1976).

[26] N. Pyper, I. Grant, and N. Beatham, Comput. Phys. Commun. **15**, 387 (1978).

[27] I. Grant, B. McKenzie, P. Norrington, D. Mayers, and N. Pyper, Comput. Phys. Commun. **21**, 207 (1980).

[28] G. Gaigalas, S. Fritzsche, and I. P. Grant, Comput. Phys. Commun. **139**, 263 (2001).

[29] G. Gaigalas and S. Fritzsche, Comput. Phys. Commun. **148**, 349 (2002).

[30] V. M. Shabaev, J. Phys. B **27**, 5825 (1994).

[31] V. M. Shabaev, M. Tomaselli, T. Kühl, A. N. Artemyev, and V. A. Yerokhin, Phys. Rev. A **56**, 252 (1997).

[32] Y. S. Kozhedub, O. V. Andreev, V. M. Shabaev, I. I. Tupitsyn, C. Brandau, C. Kozhuharov, G. Plunien, and T. Stöhlker, Phys. Rev. A **77**, 032501 (2008).

[33] A. Stathopoulos and C. Froese Fischer, Comput. Phys. Commun. **79**, 268 (1994).

[34] V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. Lett. **93**, 130405 (2004).

[35] C. de Boor, *A Practical Guide to Splines* (Springer, New York, 1978).

[36] X.-X. Guan and Z.-W. Wang, Eur. Phys. J. D **2**, 21 (1998).

[37] N. J. Stone, At. Data Nucl. Data Tables **75**, 75 (2005).

[38] B. A. Bushaw, W. Nörtershäuser, G. Ewald, A. Dax, and G. W. F. Drake, Phys. Rev. Lett. **91**, 043004 (2003).

[39] H. Orth, H. Ackermann, and E. W. Otten, Z. Phys. A **273**, 221 (1975).

[40] J. Walls, R. Ashby, J. Clarke, B. Lu, and W. van Wijngaarden, Eur. Phys. J. D **22**, 159 (2003).

[41] D. Das and V. Natarajan, J. Phys. B **40**, 035001 (2008).

[42] H. Orth, R. Veit, H. Ackermann, and E. W. Otten (1974), as cited in E. Arimondo, M. Inguscio, and P. Violino, Rev. Mod. Phys. **49**, 31 (1977).

[43] J. J. Bollinger, J. S. Wells, D. J. Wineland, and W. M. Itano, Phys. Rev. A **31**, 2711 (1985).

[44] J. R. Sapirstein and D. R. Yennie, in *Quantum Electrodynamics*, edited by T. Kinoshita (World Scientific, Singapore, 1990), p. 560.

[45] S. G. Karshenboim and V. G. Ivanov, Eur. Phys. J. D **19**, 13 (2002).

[46] J. Sapirstein and K. T. Cheng, Phys. Rev. A **74**, 042513 (2006).
[47] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).
[48] F. A. Parpia, M. Tong, and C. F. Fischer, Phys. Rev. A **46**, 3717 (1992).
[49] V. M. Shabaev, Phys. Rev. A **57**, 59 (1998).
[50] I. I. Tupitsyn, V. M. Shabaev, J. R. Crespo López-Urrutia, I. Draganić, R. S. Orts, and J. Ullrich, Phys. Rev. A **68**, 022511 (2003).
[51] W. A. Barker and F. N. Glover, Phys. Rev. **99**, 317 (1955).
[52] S. J. Brodsky and R. G. Parsons, Phys. Rev. **163**, 134 (1967).
[53] I. B. Khriplovich, A. I. Milstein, and R. A. Sen'kov, Phys. Lett. A **221**, 370 (1996).
[54] J. L. Friar and G. L. Payne, Phys. Rev. C **72**, 014002 (2005).
[55] J. L. Friar and G. L. Payne, Phys. Lett. B **618**, 68 (2005).
[56] K. Pachucki, Phys. Rev. A **76**, 022508 (2007).
[57] A. C. Zemach, Phys. Rev. **104**, 1771 (1956).
[58] A. V. Volotka, V. M. Shabaev, G. Plunien, and G. Soff, Eur. Phys. J. D **23**, 51 (2003).
[59] I. Angeli, At. Data Nucl. Data Tables **87**, 185 (2004).
[60] C. W. de Jager, H. de Vries, and C. de Vries, At. Data Nucl. Data Tables **14**, 479 (1974).
[61] A. Bohr and V. F. Weisskopf, Phys. Rev. **77**, 94 (1950).
[62] A. Bohr, Phys. Rev. **81**, 331 (1951).
[63] O. M. Zherebtsov and V. M. Shabaev, Can. J. Phys. **78**, 701 (2000).
[64] L. Elton and A. Swift, Nucl. Phys. A **94**, 52 (1967).
[65] P. E. Nemirovsky, *Modern Models of Atomic Nuclei* (Atomizdat, Moscow, 1960) (in Russian).
[66] J. Sapirstein and K. T. Cheng, Phys. Rev. A **67**, 022512 (2003).
[67] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Quantum Electrodynamics* (Pergamon, Oxford, 1971).
[68] M. Phillips, Phys. Rev. **76**, 1803 (1949).
[69] A. A. Pomeranskiĭ and I. B. Khriplovich, Zh. Eksp. Teor. Fiz. **113**, 1537 (1998) [JETP **86**, 839 (1998)].
[70] T. Mertelmeier and H. M. Hofmann, Nucl. Phys. A **459**, 387 (1986).