



Ground-state hyperfine splitting in the Be⁺ ion

Mariusz Puchalski^{1,2} and Krzysztof Pachucki¹

¹*Faculty of Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland*

²*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*

(Received 18 February 2014; published 13 March 2014)

Relativistic and QED corrections are calculated for the hyperfine splitting (hfs) in the $2S_{1/2}$ ground state of ${}^9\text{Be}^+$ ions with an exact account for electronic correlations. The achieved accuracy is sufficient to determine the finite nuclear size effects from the comparison to the experimental hfs value. The obtained results establish the ground to determine the neutron halo in ${}^{11}\text{Be}$.

DOI: [10.1103/PhysRevA.89.032510](https://doi.org/10.1103/PhysRevA.89.032510)

PACS number(s): 31.30.J-, 31.15.ac, 21.10.Ft

I. INTRODUCTION

High-precision atomic spectroscopy makes possible the accurate determination of the electromagnetic properties of nuclei, including short-lived exotic isotopes. The best known example is the mean-square nuclear charge radius, which can be obtained from the isotope shift of atomic transition energies [1]. Here, we develop a computational technique for the determination of magnetic properties of nuclei, which can be obtained from hyperfine splitting. Apart from the magnetic moment, they are very much unknown. The atomic hyperfine splitting is sensitive to the distribution of the magnetic moment and, to some extent, to combined polarizabilities. Altogether it can be expressed in terms of the effective Zemach radius \tilde{r}_Z [2]. The results recently obtained for ${}^6,7\text{Li}$ indicate that $\tilde{r}_Z({}^6\text{Li})$ is more than 40% smaller than $\tilde{r}_Z({}^7\text{Li})$, which is not necessarily easy to understand. This significant difference can probably be resolved only by detailed nuclear structure calculations.

In this work we perform analogous, accurate calculations of hyperfine splitting in the $2S_{1/2}$ ground-state Be⁺ ions, in order to determine \tilde{r}_Z for ${}^7,9,11\text{Be}$ isotopes. Since the magnetic moment is known for ${}^9\text{Be}$, we can compare $\tilde{r}_Z({}^9\text{Be})$ with theoretical predictions here. For other ${}^7,11\text{Be}$ isotopes our calculations lay the foundation for the determination of \tilde{r}_Z , once the magnetic moment is experimentally known. It would be very interesting to confirm the large neutron halo in ${}^{11}\text{Be}$ using atomic spectroscopy measurements, and to study the dependence of Bohr-Weisskopf effects on the isotope.

Our computational approach is based on explicitly correlated basis functions. This allows us to accurately solve the Schrödinger equation, while relativistic and QED effects are calculated perturbatively in terms of expectation values with the nonrelativistic wave function.

II. EFFECTIVE HAMILTONIAN

Hyperfine splitting is a result of the interaction between the nuclear magnetic moments of atomic nuclei and electrons. In the nonrelativistic QED approach, relativistic and QED corrections are expressed in terms of an effective Hamiltonian, so the expansion in the fine-structure constant α is of the form

$$E_{\text{hfs}} = \langle H_{\text{hfs}}^{(4)} \rangle + \langle H_{\text{hfs}}^{(5)} \rangle + 2 \left\langle H^{(4)} \frac{1}{(E - H)} H_{\text{hfs}}^{(4)} \right\rangle + \langle H_{\text{hfs}}^{(6)} \rangle + \langle H_{\text{rad}}^{(6)} \rangle + \langle H_{\text{hfs}}^{(7)} \rangle + \dots, \quad (1)$$

where $H^{(n)} \sim m\alpha^n$, and the nonrelativistic Hamiltonian in the clamped nucleus limit and the nonrelativistic energy of the ground state are H and E , respectively. Higher-order terms, denoted by dots, are neglected as the highest-order term $H_{\text{hfs}}^{(7)}$ will be calculated in an approximate way.

A. Leading-order hfs

The leading interaction $H_{\text{hfs}}^{(4)}$ of order $m\alpha^4$ between the nuclear spin \vec{I} and electron spins $\vec{\sigma}_a$ is obtained from the nonrelativistic coupling of electrons to the electromagnetic field

$$H_{\text{hfs}}^{(4)} = - \sum_a \frac{e}{m} \vec{p}_a \cdot \vec{A}(\vec{r}_a) - \frac{e}{2m} \frac{g}{2} \vec{\sigma}_a \cdot \vec{B}(\vec{r}_a), \quad (2)$$

with \vec{A} and \vec{B} fields derived from the nuclear magnetic moment $\vec{\mu}$,

$$e\vec{A}(\vec{r}) = \frac{e}{4\pi} \vec{\mu} \times \frac{\vec{r}}{r^3} = -Z\alpha \frac{g_N}{2M} \vec{I} \times \frac{\vec{r}}{r^3}, \quad (3)$$

$$eB^i(\vec{r}) = (\nabla \times \vec{A})^i = -Z\alpha \frac{g_N}{2M} \frac{8\pi}{3} \delta^3(r) I^i + Z\alpha \frac{g_N}{2M} \frac{1}{r^3} \left(\delta^{ij} - 3 \frac{r^i r^j}{r^2} \right) I^j. \quad (4)$$

After some simplifications, Eq. (2) becomes

$$H_{\text{hfs}}^{(4)} = \varepsilon \left(\frac{g}{2} H_{\text{hfs}}^A + H_{\text{hfs}}^B + H_{\text{hfs}}^C \right), \quad (5)$$

$$H_{\text{hfs}}^A \equiv \sum_a \vec{I} \cdot \vec{\sigma}_a H_{a,\text{hfs}}^A = \sum_a \frac{4Z\alpha}{3m^3} \vec{I} \cdot \vec{\sigma}_a \pi \delta^3(r_a), \quad (6)$$

$$H_{\text{hfs}}^B \equiv \vec{I} \cdot \vec{H}_{\text{hfs}}^B = \sum_a \frac{Z\alpha}{m^3} \vec{I} \cdot \frac{\vec{r}_a \times \vec{p}_a}{r_a^3}, \quad (7)$$

$$H_{\text{hfs}}^C \equiv I^i \sigma_a^j H_{a,\text{hfs}}^{Cij} = \sum_a - \frac{Z\alpha}{2m^3} \frac{I^i \sigma_a^j}{r_a^3} \left(\delta^{ij} - 3 \frac{r_a^i r_a^j}{r_a^2} \right), \quad (8)$$

where

$$\varepsilon = \frac{m^2}{M} \frac{g_N}{2}, \quad (9)$$

M (m) are masses, and g_N (g) are g factors of the nucleus (electron). The relation of g_N to the magnetic moment μ of the nucleus with charge Z is

$$g_N = \frac{M}{Zm_p} \frac{\mu}{\mu_N} \frac{1}{I}, \quad (10)$$

where μ_N is the nuclear magneton and I is the nuclear spin. The only nonvanishing term in the ground state H_{hfs}^A is well known as the Fermi contact interaction. Expectation values of H_{hfs}^B and H_{hfs}^C contribute in the second order of perturbation calculus. In principle these terms also involve the electron g factor, but here we set $g = 2$.

B. Correction of order $m\alpha^5$

Correction $\langle H_{\text{hfs}}^{(5)} \rangle$ of order $m\alpha^5$ is a Dirac- δ interaction with the coefficient obtained from the two-photon forward-scattering amplitude. It has the same form as in hydrogen and depends on the nuclear structure. At the limit of a point spin-1/2 nucleus, it is

$$H_{\text{hfs}}^{(5)} = -H_{\text{hfs}}^A \frac{3Z\alpha}{\pi} \frac{m}{m_N} \ln\left(\frac{m_N}{m}\right) \equiv H_{\text{rec}}^{(5)}, \quad (11)$$

a small nuclear recoil correction. For a finite-size nucleus $H_{\text{hfs}}^{(5)}$ does not vanish at the nonrecoil limit. When assuming a heavy and rigid nucleus, $H_{\text{hfs}}^{(5)}$ takes the form

$$H_{\text{hfs}}^{(5)} = \varepsilon H_{\text{hfs}}^A (-2Z\alpha m r_Z), \quad (12)$$

where

$$r_Z = \int d^3r d^3r' \rho_E(r) \rho_M(r') |\vec{r} - \vec{r}'| \quad (13)$$

and ρ_E and ρ_M are electric charge and magnetic-moment density. The inelastic contribution, usually neglected, is sometimes important. Since it depends on nuclear excitations, this correction is very difficult to estimate and usually limits the precision of theoretical predictions. For this reason, we will interpret our calculation using experimental values as a determination of the effective Zemach radius according to Eq. (12), where r_Z is replaced by \tilde{r}_Z .

C. Relativistic correction of order $m\alpha^6$

The first term for the relativistic correction of order $m\alpha^6$ in Eq. (1) comes from a perturbation of the wave function by the Breit-Pauli Hamiltonian $H^{(4)}$ in the nonrecoil limit:

$$H^{(4)} = H^A + H^B + H^C, \quad (14)$$

$$H^A \equiv \sum_a H_a^A = \sum_a \left[-\frac{p_a^4}{8m^3} + \frac{Z\alpha\pi}{2m^2} \delta^3(r_a) \right] + \sum_{a>b} \left[\frac{\pi\alpha}{m^2} \delta^3(r_{ab}) - \frac{\alpha}{2m^2} p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3} \right) p_b^j \right], \quad (15)$$

$$H^B \equiv \sum_a \vec{\sigma}_a \cdot \vec{H}_a^B = \sum_a \frac{Z\alpha}{4m^2} \frac{\vec{r}_a}{r_a^3} \times \vec{p}_a \cdot \vec{\sigma}_a + \sum_{a \neq b} \frac{\alpha}{4m^2} \frac{\vec{r}_{ab}}{r_{ab}^3} \times (2\vec{p}_b - \vec{p}_a) \cdot \vec{\sigma}_a, \quad (16)$$

$$H^C \equiv \sum_{a>b} \sigma_a^i \sigma_b^j H_{ab}^{Cij} = \sum_{a>b} \frac{\alpha}{4m^2} \frac{\sigma_a^i \sigma_b^j}{r_{ab}^3} \left(\delta^{ij} - \frac{3r_{ab}^i r_{ab}^j}{r_{ab}^2} \right). \quad (17)$$

The next term, $H_{\text{hfs}}^{(6)}$, includes nuclear spin-dependent operators that contribute at order $m\alpha^6$. In hydrogenic systems it leads to the so-called Breit correction. For three-electron atoms this term was first derived in Ref. [3] and recently rederived and simplified in [2]. The result is

$$H_{\text{hfs}}^{(6)} = \varepsilon \sum_a \vec{\sigma}_a \cdot \vec{I} \left[\frac{(Z\alpha)^2}{6m^4} \frac{1}{r_a^4} - \frac{Z\alpha}{12m^5} \{p_a^2, 4\pi\delta^3(r_a)\} + \sum_{b \neq a} \frac{Z\alpha^2}{6m^4} \frac{\vec{r}_{ab}}{r_{ab}^3} \cdot \left(2\frac{\vec{r}_b}{r_b^3} - \frac{\vec{r}_a}{r_a^3} \right) \right], \quad (18)$$

where braces denote an anticommutator. The resulting operators are divergent, and in the next section we describe the cancellation of singularities with those in second-order matrix elements.

D. Radiative corrections of order $m\alpha^{6,7}$

$H_{\text{rad}}^{(6)}$ in Eq. (1) is a QED radiative correction [4,5]

$$H_{\text{rad}}^{(6)} = H_{\text{hfs}}^A \alpha(Z\alpha) \left(\ln 2 - \frac{5}{2} \right), \quad (19)$$

which is similar to that in hydrogen. There are no further corrections of this order, so all terms at $m\alpha^6$ are known exactly.

The last term $E_{\text{hfs}}^{(7)}$ of order $m\alpha^7$ is calculated approximately using the hydrogenic value for the one-loop correction from [6] and the two-loop correction from [5],

$$H_{\text{hfs}}^{(7)} = H_{\text{hfs}}^A \left[\frac{\alpha}{\pi} (Z\alpha)^2 \left(-\frac{8}{3} \ln^2(Z\alpha) + a_{21} \ln(Z\alpha) + a_{20} \right) + \frac{\alpha^2}{\pi} (Z\alpha) b_{10} \right], \quad (20)$$

where $a_{21}(2S) = -1.1675$, $a_{20}(2S) = 11.3522$, and $b_{10} = 0.771652$.

E. Hyperfine structure constant

The hyperfine splitting can be expressed in terms of the hyperfine constant A

$$E_{\text{hfs}} = \vec{I} \cdot \vec{J} A, \quad (21)$$

where \vec{J} is the total electronic angular momentum. If we use the notation that $H_{\text{hfs}} = \vec{I} \cdot \vec{H}_{\text{hfs}}$, then

$$A = \frac{1}{J(J+1)} \langle \vec{J} \cdot \vec{H}_{\text{hfs}} \rangle. \quad (22)$$

The expansion of A in α takes the form

$$A = \varepsilon \left(\frac{g}{2} \alpha^4 A^{(4)} + \sum_{n=5}^{\infty} \alpha^n A^{(n)} \right). \quad (23)$$

All the results of numerical calculations will be presented here in terms of dimensionless coefficients $A^{(n)}$. The leading-order term $A^{(4)}$ obtained from Eq. (6) is in turn expanded in the reduced electron mass μ to the nuclear mass M ratio

$$A^{(4)} = \frac{1}{J(J+1)} \frac{4\pi Z}{3} \left\langle \vec{J} \cdot \vec{\sigma}_a \left[\delta^3(r_a) - \frac{\mu}{M} (3\delta^3(r_a) + 2[\delta^3(r_a)]_{\text{mp}}) \right] \right\rangle \quad (24)$$

$$= A^{(4,0)} - \frac{\mu}{M} A^{(4,1)}. \quad (25)$$

The finite mass correction due to mass scaling of the $\delta^3(r_a)$ operator is included into $A^{(4,1)}$, as well as the second-order element with the mass polarization correction to the wave function

$$[\delta^3(r_a)]_{\text{mp}} = \delta^3(r_a) \frac{1}{(H - E_Y)} \sum_{b>c} \vec{p}_b \cdot \vec{p}_c. \quad (26)$$

The next to leading correction $A^{(5)}$ and all others are obtained in the leading order in the mass ratio, so that

$$A_{\text{rec}}^{(5)} = -A^{(4)} \frac{3Z}{\pi} \frac{m}{m_N} \ln \left(\frac{m_N}{m} \right), \quad (27)$$

$$A^{(5)} = A^{(4)} (-2Zm\tilde{r}_Z). \quad (28)$$

The most demanding part of the calculation is the correction of order $m\alpha^6$ given by $A^{(6)}$. Due to the symmetry of intermediate states in the second-order matrix element of Eq. (1), the A , B , and C parts of the hfs Hamiltonian give the nonvanishing contributions with the corresponding A , B , and C parts of Eq. (14). Of note, the matrix element of the first-order term in Eq. (18) and the second-order A terms are divergent separately at small r_a . However, these divergences can be eliminated in the sum of both terms denoted by $A_{AN}^{(6)}$. So the complete $A^{(6)}$ is of the form

$$A^{(6)} = A_{AN}^{(6)} + A_B^{(6)} + A_C^{(6)} + A_R^{(6)}, \quad (29)$$

$$A_{AN}^{(6)} = \frac{2}{J(J+1)} \left\langle \sum_a \vec{J} \cdot \vec{\sigma}_a H_{a,\text{hfs}}^A \frac{1}{(E - H_Y)} H^A \right\rangle + \frac{1}{J(J+1)} \left\langle \vec{J} \cdot \vec{\sigma}_a \left[\frac{Z^2}{6} \frac{1}{r_a^4} - \frac{2Z}{3} p_a^2 \pi \delta^3(r_a) + \sum_{b \neq a} \frac{Z}{6} \frac{\vec{r}_{ab}}{r_{ab}^3} \cdot \left(2 \frac{\vec{r}_b}{r_b^3} - \frac{\vec{r}_a}{r_a^3} \right) \right] \right\rangle, \quad (30)$$

$$A_B^{(6)} = \frac{2}{J(J+1)} \left\langle \vec{J} \cdot \vec{H}_{\text{hfs}}^B \frac{1}{(E - H_Y)} H^B \right\rangle, \quad (31)$$

$$A_C^{(6)} = \frac{2}{J(J+1)} \left\langle \sum_a J^i \sigma_a^j H_a^{Cij} \frac{1}{(E - H_Y)} H^C \right\rangle, \quad (32)$$

$$A_R^{(6)} = A^{(4)} \left(\ln 2 - \frac{5}{2} \right), \quad (33)$$

and the higher-order term is

$$A^{(7)} = A^{(4)} \left[\frac{Z^2}{\pi} \left(-\frac{8}{3} \ln^2(Z\alpha) + a_{21} \ln(Z\alpha) + a_{20} \right) + \frac{Z}{\pi} b_{10} \right]. \quad (34)$$

III. CALCULATIONS

A. Cancellation of singularities in $A_{AN}^{(6)}$

The operators in Eq. (30) are transformed with the use of

$$4\pi \delta^3(r_a) \equiv 4\pi [\delta^3(r_a)]_r - \sum_a \left\{ \frac{2}{r_a}, E - H \right\}, \quad (35)$$

$$H^A \equiv [H^A]_r + \frac{1}{4} \sum_a \left\{ \frac{Z}{r_a}, E - H \right\}. \quad (36)$$

Regularized operators $[H^A]_r$ and $[\delta^3(r_a)]_r$ have exactly the same expectation value as the operator inside the square brackets if the exact wave function is used. From Eq. (35) and Eq. (36) we can obtain the following formulas:

$$4\pi [\delta(r_a)]_r = 4(E - V) \frac{1}{r_a} - 2 \sum_b \vec{p}_b \frac{1}{r_a} \vec{p}_b, \quad (37)$$

$$[H^A]_r = \sum_a \left[-\frac{1}{8} [p_a^4]_r + \frac{1}{2} p_a^i \left(V + \frac{Z}{2} \sum_b \frac{1}{r_b} \right) p_a^i \right] - \left(V + \frac{Z}{2} \sum_b \frac{1}{r_b} \right) (E - V) + \sum_{a>b} \left[3\pi \delta^3(r_{ab}) - \frac{1}{2} p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3} \right) p_b^j \right], \quad (38)$$

$$\sum_a [p_a^4]_r = 4(E - V)^2 - 2 \sum_{a>b} \vec{p}_a^2 \vec{p}_b^2. \quad (39)$$

After this transformation both the first- and second-order matrix elements in $A_{AN}^{(6)}$ become separately finite:

$$A_{AN}^{(6)} = A_A^{(6)} + A_N^{(6)}, \quad (40)$$

$$A_A^{(6)} = \frac{2}{J(J+1)} \left\langle \sum_a \vec{J} \cdot \vec{\sigma}_a [H_{a,\text{hfs}}^A]_r \frac{1}{(E - H_Y)} [H^A]_r \right\rangle,$$

$$A_N^{(6)} = \frac{1}{J(J+1)} \left\langle \vec{J} \cdot \vec{\sigma}_a \frac{Z}{6} \left[\frac{1}{r_a} \sum_b p_b^4 - 4\pi \delta^3(r_a) p_a^2 + \sum_{b \neq a} \frac{\vec{r}_{ab}}{r_{ab}^3} \cdot \left(2 \frac{\vec{r}_b}{r_b^3} - \frac{\vec{r}_a}{r_a^3} \right) + 4\pi Z \sum_{b \neq a} \left(\frac{\delta^3(r_a)}{r_b} - \frac{\delta^3(r_b)}{r_a} \right) \right] \right\rangle$$

$$\begin{aligned}
 & -\frac{2}{r_a} \sum_{b>c} 4\pi\delta^3(r_{bc}) + 4 \sum_{b>c} p_b^i \frac{1}{r_a} \left(\frac{\delta^{ij}}{r_{bc}} + \frac{r_{bc}^i r_{bc}^j}{r_{bc}^3} \right) p_c^j \\
 & - 4\pi Z\delta^3(r_a) \left[\sum_b \frac{1}{r_b} \right] + \frac{8}{r_a} \langle H^A \rangle \Big]. \quad (41)
 \end{aligned}$$

It is still necessary, however, to remove apparent singularities in some of the first-order operators by repeated use of the Schrödinger equation, namely

$$\begin{aligned}
 & \left\langle \frac{1}{r_a} \sum_b p_b^4 - 4\pi\delta^3(r_a) p_a^2 \right\rangle \\
 & = \left\langle -2 \sum_{b;b \neq a} \frac{\vec{r}_{ab}}{r_{ab}^3} \cdot \frac{\vec{r}_a}{r_a^3} + \frac{4}{r_a} \left[(E - V)^2 - \frac{Z^2}{r_a^2} \right] \right. \\
 & \quad - 2 \sum_{b,c;b>c} p_b^2 \frac{1}{r_a} p_c^2 + 2Z\vec{p}_a \frac{1}{r_a^2} \vec{p}_a \\
 & \quad \left. + \left[8\pi\delta^3(r_a) + \frac{4Z}{r_a^2} \right] \left(\sum_{b;b \neq a} \frac{p_b^2}{2} + V + \frac{Z}{r_a} - E \right) \right\rangle. \quad (42)
 \end{aligned}$$

In this form, all matrix elements with the nonrelativistic wave function can safely be calculated.

B. Wave function and first-order operators

The wave function for a lithiumlike system in the ground state is represented as a linear combination of ψ terms, the antisymmetrized product of S -symmetry spatial ϕ , and doublet spin functions [7],

$$\psi = \frac{1}{\sqrt{6}} \mathcal{A}[\phi(\vec{r}_1, \vec{r}_2, \vec{r}_3)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\alpha(3)], \quad (43)$$

where \mathcal{A} denotes antisymmetrization with respect to electron variables, and the spin functions are defined by $\sigma_z \alpha(\cdot) = \alpha(\cdot)$ and $\sigma_z \beta(\cdot) = -\beta(\cdot)$.

Until now, the most accurate nonrelativistic wave functions for lithiumlike systems were obtained using the Hylleraas-type basis functions [7–11] with elements of the form

$$\phi_H(\vec{r}_1, \vec{r}_2, \vec{r}_3) = r_{23}^{n_1} r_{31}^{n_2} r_{12}^{n_3} r_1^{n_4} r_2^{n_5} r_3^{n_6} e^{-\alpha_1 r_1 - \alpha_2 r_2 - \alpha_3 r_3}, \quad (44)$$

with non-negative integers n_k . We use the wave function obtained variationally [11] to evaluate most of the first-order matrix elements of the hyperfine structure operators, including the Fermi contact term in Eq. (24). Such matrix elements can be expressed as a linear combination of Hylleraas integrals, defined as

$$\begin{aligned}
 f(n_1, n_2, n_3, n_4, n_5, n_6) & = \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \int \frac{d^3 r_3}{4\pi} \\
 & \times r_{23}^{n_1-1} r_{31}^{n_2-1} r_{12}^{n_3-1} r_1^{n_4-1} r_2^{n_5-1} r_3^{n_6-1} \\
 & \times e^{-w_1 r_1 - w_2 r_2 - w_3 r_3}. \quad (45)
 \end{aligned}$$

In a series of papers, we have formulated an analytic method for calculations of Hylleraas integrals with recursion relations [7,12,13], which is sufficient for the evaluation of energy levels including corrections up to $m\alpha^5$ order [14,15]. At higher orders, additional classes of Hylleraas integrals are necessary, e.g., $f(-1, -1, n_3, n_4, n_5, n_6)$. These difficult

TABLE I. Symmetrization coefficients in matrix elements.

(k, l, m)	c_{klm}	c_{klm}^A	c_{klm}^{F1}	c_{klm}^{F2}	c_{klm}^{F3}
(1, 2, 3)	2	1	0	0	2
(1, 3, 2)	-1	-1	1	-1	-1
(2, 1, 3)	2	1	0	0	2
(2, 3, 1)	-1	-1	-1	1	-1
(3, 1, 2)	-1	1	1	-1	-1
(3, 2, 1)	-1	-1	-1	1	-1

integrals have been solved with the use of Neumann-type expansions [16], but this approach is not effective enough in large-scale calculations. There is also an exceptional group of operators of $A_N^{(6)}$ with accompanying Dirac- δ operators. We are not able to regularize them by rewriting in a form analogous to Eq. (37). However, the direct treatment of Dirac- δ is applicable in the Hylleraas basis set, where the matrix elements are expressed in terms of well-known two-electron integrals [17–19].

It has been demonstrated recently [2] that matrix elements of some complicated operators, which are intractable in the Hylleraas basis, can be calculated with exponentially correlated Gaussian (ECG) functions [20],

$$\phi_G(\vec{r}_1, \vec{r}_2, \vec{r}_3) = e^{-\alpha_1 r_1^2 - \alpha_2 r_2^2 - \alpha_3 r_3^2 - \beta_1 r_{23}^2 - \beta_2 r_{13}^2 - \beta_3 r_{12}^2}. \quad (46)$$

Even if the wave function in the ECG basis decays too fast at long interparticle distances and fails to correctly satisfy the Kato cusp condition, it can be sufficiently accurate to obtain matrix elements of these complicated hfs operators with at least 4–5-digit precision (see numerical results in Table II). This has been verified by more accurate calculations using correlated Slater functions [11,21] for the lithium case [2]. Hopefully, the numerically dominating operators in $A_N^{(6)}$ are those obtained with Hylleraas functions. This is especially important due to the cancellation of about 2–3 digits in this sum. Calculations of mean values with the ECG basis for operators like $\frac{\vec{r}_{ab} \cdot \vec{r}_a}{r_{ab}^3 r_a^3}$, $p_b^2 \frac{1}{r_a} p_c^2$, or $p_b^i \frac{1}{r_a} \left(\frac{\delta^{ij}}{r_{bc}} + \frac{r_{bc}^i r_{bc}^j}{r_{bc}^3} \right) p_c^j$ involve nonstandard classes of integrals that nevertheless have been considered in the Gaussian basis set with linear terms [22].

C. Spin variables reduction

Matrix elements of each spin-independent operator Q , after eliminating spin variables, takes the standard form

$$\langle \psi' | Q | \psi \rangle \equiv \langle \phi'(r_1, r_2, r_3) | Q | \mathcal{P}[c_{123} \phi(r_1, r_2, r_3)] \rangle, \quad (47)$$

with c_{klm} coefficients defined in Table I, and \mathcal{P} is the sum of all permutations of 1, 2, and 3. This reduction is applicable in an evaluation of the overlap matrix and the Hamiltonian. Another useful form is obtained for the Fermi contact matrix element. If we denote

$$\langle \psi' | Q_a | \psi \rangle_F \equiv \left\langle \phi'(r_1, r_2, r_3) | \mathcal{P} \left[\sum_a c_{123}^{F_a} Q_a \phi(r_1, r_2, r_3) \right] \right\rangle, \quad (48)$$

then for the ground state of Be^+ with $J = 1/2$ and $\vec{J} = \sum_a \vec{\sigma}_a/2$, we get

$$\frac{1}{J(J+1)} \langle \psi' | \vec{J} \cdot \sum_a \vec{\sigma}_a Q_a | \psi \rangle = 2 \langle \psi' | Q_a | \psi \rangle_F. \quad (49)$$

Second-order terms involve spatially antisymmetric states,

$$\psi_A = \frac{1}{\sqrt{6}} \mathcal{A}[\phi(\vec{r}_1, \vec{r}_2, \vec{r}_3) \alpha(1)\alpha(2)\alpha(3)], \quad (50)$$

for which reduced matrix elements are of the form

$$\langle \psi'_A | Q_a | \psi \rangle_A \equiv \langle \phi'(r_1, r_2, r_3) | \times \mathcal{P}[c_{123}^A(Q_1 - Q_2)\phi(r_1, r_2, r_3)], \quad (51)$$

$$\langle \psi'_A | Q_{ab} | \psi \rangle_A \equiv \langle \phi'(r_1, r_2, r_3) | \times \mathcal{P}[c_{123}^A(Q_{12} - Q_{23})\phi(r_1, r_2, r_3)]. \quad (52)$$

D. Second-order matrix elements

Calculations of the second-order terms in Eqs. (31), (32), and (41) are also highly nontrivial. The approach using Hylleraas functions encounters severe numerical problems. Namely, the optimization of the nonlinear parameters for the pseudostate in the second-order matrix elements leads to differences of many orders of magnitude between variational parameters, and it destroys the numerical stability of the recursion method for extended Hylleraas integrals [13]. Also, the complexity of such calculations makes an optimization

process very time consuming. An alternative solution is the use of a well-optimized ECG basis. With this, function representations of pseudostates can be determined sufficiently accurately and very efficiently.

At the first step, we reduce spin variables with the help of a computer algebra program. Next, the second-order elements for the ground state of the lithiumlike atom involve spatial coordinates only and are of the following form:

$$A_A^{(6)} = 4 \sum_{n \neq 0} \frac{\langle \psi | [H_{a,\text{hfs}}^A]_r | \psi_n \rangle_F \langle \psi_n | [H^A]_r | \psi \rangle}{E - E_n}, \quad (53)$$

$$A_B^{(6)} = \frac{4}{3} \sum_n \frac{\langle \psi | H_{\text{hfs}}^{Bi} | \psi_n^i \rangle \langle \psi_n^j | H_b^{Bj} | \psi \rangle_F}{E - E_n}, \quad (54)$$

$$A_C^{(6)} = \frac{8}{3} \sum_n \frac{\langle \psi | H_{a,\text{hfs}}^{Cij} | \psi_{nA}^{ij} \rangle \langle \psi_{nA}^{kl} | H_{ab}^{Ckl} | \psi \rangle_A}{E - E_n}. \quad (55)$$

The symmetry of internal pseudostates in the above is determined as follows. Since, $[H^A]_r$ is a scalar operator, the symmetry of the pseudostate in $A_A^{(6)}$ has to be exactly the same as that of the wave function in Eq. (43). For $A_B^{(6)}$ and $A_C^{(6)}$, the spatial part can be represented with elements of P -even and D symmetry,

$$\phi_{ab}^i(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \epsilon_{ijk} r_a^j r_b^k \phi(\vec{r}_1, \vec{r}_2, \vec{r}_3), \quad (56)$$

$$\phi_{ab}^{ij}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \left(\frac{r_a^i r_b^j}{2} + \frac{r_b^i r_a^j}{2} - \frac{\delta^{ij}}{3} \vec{r}_a \cdot \vec{r}_b \right) \phi(\vec{r}_1, \vec{r}_2, \vec{r}_3), \quad (57)$$

respectively. The normalization of the corresponding wave functions is set by Eq. (47) with an implicit sum over

TABLE II. Numerical values of first-order operators in the ground state of Li (Ref. [2]) and Be^+ ; H: Hylleraas basis; G: Gaussian basis.

Operator	Basis	Li	Be^+
$E = \langle H \rangle$	H	-7.478 060 323 910 10(32) ^a	-14.324 763 176 790 43(22) ^a
$\langle H_A \rangle$	H	-12.049 907 85(6)	-43.688 013 68(8)
$\langle \delta^3(r_a) \rangle_F$	H	0.231 249 661(2)	0.994 525 337(5)
$\langle [\delta^3(r_a)]_{\text{mp}} \rangle_F$	H	-0.027 726 521(11)	-0.087 880 92(4)
$\langle r_a^{-1} \rangle$	H	5.718 110 882 476 5(4)	7.973 888 857 015 4(5)
$\langle r_a^{-1} \rangle_F$	H	0.360 344 320 41(8)	0.628 135 118 56(2)
$\langle \delta^3(r_a) \sum_{b \neq a} r_b^{-1} \rangle_F$	H	0.419 203 4(10)	2.620 526 3(15)
$\langle r_a^{-1} \sum_{b \neq a} \delta^3(r_b) \rangle_F$	H	4.095 692 0(4)	16.792 994(4)
$\langle r_a^{-1} \sum_{b > c} \delta^3(r_{bc}) \rangle_F$	H	0.173 834 1(2)	0.846 757 5(3)
$\langle \delta^3(r_a) (\sum_{b \neq a} p_b^2/2 + V + Zr_a^{-1} - E) \rangle_F$	H	0.733 477(4)	4.857 754(5)
$\langle r_a^{-2} (\sum_{b \neq a} \frac{p_b^2}{2} + V + Zr_a^{-1} - E) \rangle_F$	H	1.506 463(3)	7.372 057 2(8)
$\langle r_a^{-1} [(E - V)^2 - Z^2 r_a^{-2}] \rangle_F$	H	43.824 14(2)	232.429 630(7)
$\langle \vec{p}_a r_a^{-2} \vec{p}_a \rangle_F$	H	4.863 37(4)	28.631 62(3)
$E = \langle H \rangle$	G	-7.478 060 322 96	-14.324 763 175 15
$\langle \sum_{b \neq a} \frac{\vec{r}_{ab}}{r_{ab}^3} \cdot \frac{\vec{r}_a}{r_a^3} \rangle_F$	G	0.017 363 5(7)	0.081 258 7(9)
$\langle \sum_{b \neq a} \frac{\vec{r}_{ab}}{r_{ab}^3} \cdot \frac{\vec{r}_b}{r_b^3} \rangle_F$	G	-0.065 937 5(6)	-0.438 358 5(6)
$\langle \sum_{b > c} p_b^2 r_a^{-1} p_c^2 \rangle_F$	G	12.663 6(8)	74.893(4)
$\langle \sum_{b > c} p_b^i r_a^{-1} (\frac{\delta^{ij}}{r_{bc}} + \frac{r_{bc}^i r_{bc}^j}{r_{bc}^3}) p_c^j \rangle_F$	G	0.266 794(3)	0.922 84(3)

^aReference [11].

TABLE III. Numerical values of dimensionless relativistic and QED corrections to the hyperfine splitting in Be^+ ion; results from [23] in terms of G_{M1} are multiplied by 256/3.

Contribution	Value
$A^{(4,0)}$	33.326 863 92(18)
Ref. [24]	33.326 8(8)
$A^{(4,1)}$	97.035 673 8(13)
Ref. [24]	102(18)
$A_A^{(6)}$	1 196.97(4)
$A_N^{(6)}$	-133.631(16)
$A_B^{(6)}$	0.134 6(2)
$A_C^{(6)}$	0.814 2(6)
$A_R^{(6)}$	-240.866 95
$A^{(6)}$	823.42(4)
Ref. [23]	823
Ref. [24]	756(42)
$A^{(7)}$	-2 992(481)

Cartesian indices. In the calculations of the second-order matrix elements, we generated the ground-state wave function with ECG basis functions of progressively doubling size from 256 to 2048 terms. Next, for the given external wave function of a given size N , the nonlinear parameters for pseudostates were optimized using a symmetric second-order element with the corresponding hyperfine operator. Such a matrix element can be minimized using the adopted variational principle. In our approach, the basis set for the pseudostate in $A_A^{(6)}$ is divided into two sectors. The first sector is built of the basis functions with the nonlinear parameters of size $N/2$ determined in the optimization of the external wave function. The nonlinear parameters here are fixed during the optimization in order to enable accurate representation of the states orthogonal to the ground state. The second sector, of size N , consists of basis functions that undergo optimization. For $A_B^{(6)}$ and $A_C^{(6)}$ an orthogonality to the ground state is realized by a different symmetry of the basis functions in Eqs. (56) and (57). Then, only a single sector is needed with all parameters to be optimized for the basis sizes N and $2N$, respectively. The size of the pseudostate is chosen to achieve convergence for a fixed external wave function. We noted that the symmetric second-order element with H^{Cij} is divergent. Therefore, in the optimization of the pseudostate for the $A_C^{(6)}$ term we use a lower singular operator by decreasing the power of r_a by one. Due to the more complicated structure of the second-order matrix elements, both the convergence and the cost of the optimization are less favorable in comparison to the wave-function optimization.

IV. RESULTS

The final results of the numerical calculations are presented in Tables II and III. The values and their uncertainties have been obtained by extrapolation of the results obtained for several sizes of basis sets. Most of the first-order matrix elements in Table II were obtained in Hylleraas basis sets because of the much higher accuracy that can be obtained in comparison to using the ECG functions. However, some

TABLE IV. Contributions in MHz to the hyperfine splitting constant A in ${}^9\text{Be}^+$; physical constants are $g = 2.002\,319\,304\,361\,53(53)$ and $\alpha^{-1} = 137.035\,999\,074(44)$. The second uncertainty of A_{theor} comes from the nuclear magnetic moment.

	${}^9\text{Be}^+$
$\mu[\mu_N]$ (Ref. [25])	-1.177 432(3)
Atomic mass [u] (Ref. [26])	9.012 182 20(43)
g_N	-1.755 335 5(25)
$\varepsilon \times 10^{-9}$	-6.602 679(17)
$\varepsilon\alpha^4 g/2A^{(4)}$	-624.600 44
$\varepsilon\alpha^5 A_{\text{rec}}^{(5)}$	0.006 85
$\varepsilon\alpha^6 A^{(6)}$	-0.820 96
$\varepsilon\alpha^7 A^{(7)}$	0.021 8(36)
A_{theor} (point nucleus)	-625.392 7(36)(16)
Ref. [23]	-625.401(22)
A_{expt} (Ref. [27])	-625.008 837 048(10)
$(A_{\text{expt}} - A_{\text{theor}})/A_{\text{expt}}$	-614(6)(3) ppm
Ref. [23] (theory)	-514(16) ppm
\tilde{r}_Z	4.07(5)(2) fm
r_E (Ref. [28])	2.519(12) fm

of the matrix elements have been calculated only with Gaussians. These are the most complicated ones, but they are numerically less significant than the other terms in $A_N^{(6)}$. The achieved numerical accuracy is sufficiently high that the main uncertainty comes from estimation of higher-order terms, such as those in Table IV. All the second-order matrix elements have been calculated only with Gaussian functions by global optimization of nonlinear parameters in about 1000 functions, which are used to represent the sum over intermediate states. In spite of the fact that Gaussian functions do not satisfy the cusp condition at the coalescent points, they are flexible enough to achieve much greater accuracy than with Hylleraas functions for second-order matrix elements.

Results of the expansion of (dimensionless) hyperfine constant \mathcal{A} in powers of α and the mass ratio for the Be^+ ion are presented in Table III. Leading-order terms, the Fermi contact interaction, and the mass polarization correction are compared with previous results by Yan *et al.* [24]. Our result for $A^{(6)}$ are in excellent agreement with the relativistic CI calculations of Yerokhin [23]. It gives us confidence in the theoretical approach and in the numerical results obtained in this work. Table IV summarizes the results for the ${}^9\text{Be}^+$ ion. From the measured hyperfine constant and the magnetic moment, we determined finite nuclear size effects, which are expressed in terms of the effective Zemach radius \tilde{r}_Z . We observed that the experimentally determined $\tilde{r}_Z({}^9\text{Be})$ does not agree well with the approximate nuclear structure calculations in Ref. [23]. Bearing in mind the significant differences in \tilde{r}_Z in Li isotopes, considerable theoretical work is needed to correctly describe the finite nuclear size and polarizability effects in the atomic hyperfine splitting.

V. SUMMARY

We have developed a nonrelativistic QED approach to the hyperfine splitting in light atomic systems and have demonstrated that from the comparison to experimental values

one can obtain valuable information about the finite nuclear distribution. We observed in Ref. [2] that the Zemach radius for ${}^6\text{Li}$ is about 40% smaller than that of ${}^7\text{Li}$. Here we demonstrate that by means of atomic spectroscopy one can obtain the Zemach radius for Be isotopes, and give example for ${}^9\text{Be}$, for which the magnetic moment is well known. For other Be isotopes, although hyperfine splitting is known [29,30], the magnetic moment has not yet been measured with sufficient accuracy. We do not attempt here to accurately relate \tilde{r}_Z to the distribution of the magnetic moment, as our knowledge

of nuclear theory is not sufficient. We point out, however, that this model is an independent and very accurate (as accurate as the magnetic moment) method to approach nuclear magnetic-moment distribution.

ACKNOWLEDGMENTS

The authors acknowledge support from NCN Grants No. 2012/04/A/ST2/00105 and No. 2011/01/B/ST4/00733.

-
- [1] W. Nörtershäuser *et al.*, *Phys. Rev. A* **83**, 012516 (2011).
 [2] M. Puchalski and K. Pachucki, *Phys. Rev. Lett.* **111**, 243001 (2013).
 [3] K. Pachucki, *Phys. Rev. A* **66**, 062501 (2002).
 [4] P. J. Mohr, B. N. Taylor, and D. B. Newell, *Rev. Mod. Phys.* **84**, 1527 (2012).
 [5] M. I. Eides, H. Grotch, and V. A. Shelyuto, *Phys. Rep.* **342**, 63 (2001).
 [6] B. J. Wundt and U. D. Jentschura, *Phys. Rev. A* **83**, 052501 (2011).
 [7] M. Puchalski and K. Pachucki, *Phys. Rev. A* **73**, 022503 (2006).
 [8] F. W. King, *J. Mol. Struct.: THEOCHEM* **400**, 7 (1997).
 [9] Z.-C. Yan and G. W. F. Drake, *Phys. Rev. A* **52**, 3711 (1995); Z.-C. Yan, M. Tambasco, and G. W. F. Drake, *ibid.* **57**, 1652 (1998); Z.-C. Yan, W. Nörtershäuser, and G. W. F. Drake, *Phys. Rev. Lett.* **100**, 243002 (2008); **102**, 249903(E) (2009).
 [10] L. M. Wang, Z.-C. Yan, H. X. Qiao, and G. W. F. Drake, *Phys. Rev. A* **85**, 052513 (2012).
 [11] M. Puchalski, D. Kedziera, and K. Pachucki, *Phys. Rev. A* **80**, 032521 (2009).
 [12] K. Pachucki, M. Puchalski, and E. Remiddi, *Phys. Rev. A* **70**, 032502 (2004).
 [13] K. Pachucki and M. Puchalski, *Phys. Rev. A* **71**, 032514 (2005); **77**, 032511 (2008).
 [14] M. Puchalski and K. Pachucki, *Phys. Rev. A* **78**, 052511 (2008).
 [15] M. Puchalski, D. Kędziera, and K. Pachucki, *Phys. Rev. A* **87**, 032503 (2013).
 [16] P. J. Pelzl, G. J. Smethells, and F. W. King, *Phys. Rev. E* **65**, 036707 (2002); D. M. Feldmann, P. J. Pelzl, and F. W. King, *J. Math. Phys.* **39**, 6262 (1998).
 [17] R. A. Sack, C. C. J. Roothaan, and W. Kołos, *J. Math. Phys.* **8**, 1093 (1967).
 [18] V. I. Korobov, *J. Phys. B* **35**, 1959 (2002).
 [19] F. E. Harris, A. M. Frolov, and V. H. Smith, Jr., *J. Chem. Phys.* **121**, 6323 (2004).
 [20] J. Mitroy, S. Bubin, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, *Rev. Mod. Phys.* **85**, 693 (2013).
 [21] M. Puchalski and K. Pachucki, *Phys. Rev. A* **81**, 052505 (2010).
 [22] K. Pachucki and J. Komasa, *Chem. Phys. Lett.* **389**, 209 (2004); *Phys. Rev. A* **70**, 022513 (2004).
 [23] V. A. Yerokhin, *Phys. Rev. A* **78**, 012513 (2008).
 [24] Z.-C. Yan, D. K. McKenzie, and G. W. F. Drake, *Phys. Rev. A* **54**, 1322 (1996).
 [25] W. M. Itano, *Phys. Rev. B* **27**, 1906 (1983).
 [26] G. Audi, A. H. Wapstra, and C. Thibault, *Nucl. Phys. A* **729**, 337 (2003).
 [27] D. J. Wineland, J. J. Bollinger, and W. M. Itano, *Phys. Rev. Lett.* **50**, 628 (1983).
 [28] J. A. Jansen, R. Th. Peerdeman, and C. deVries, *Nucl. Phys. A* **188**, 337 (1972).
 [29] K. Okada *et al.*, *Phys. Rev. Lett.* **101**, 212502 (2008).
 [30] A. Takamine *et al.* (unpublished).