Fine and hyperfine splitting of the 2P state in Li and Be$^+$

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(Received 17 January 2009; published 17 March 2009)

Accurate calculations of the fine and hyperfine splitting of the 2P state in Li and Be$^+$ isotopes using the explicitly correlated Hylleraas basis set are presented. Theoretical predictions including the mixing of $P_{1/2}$ and $P_{3/2}$ states, relativistic and quantum electrodynamic effects on hyperfine interactions, are compared with experimental values. It is concluded that precise spectroscopic determination of the nuclear magnetic moments requires elimination of nuclear structure effects by combining measurements for two different states.

DOI: 10.1103/PhysRevA.79.032510 PACS number(s): 31.30.Gs, 31.15.aj, 21.10.Ky

I. INTRODUCTION

The calculation of relativistic effects in the atomic structure is most often performed with the explicit use of the Dirac equation, as in relativistic configuration interaction [1], many-body perturbation theory [2], relativistic coupled-cluster [3], or multiconfiguration Dirac-Fock [4] methods. For light atomic systems the more accurate approach is based on the expansion of the energy in the fine-structure constant α. This method allows for a systematical inclusion of relativistic and quantum electrodynamics (QED) contributions, as each correction can be expressed in terms of the expectation value of some operator with the nonrelativistic wave function. With the use of explicitly correlated basis functions, the nonrelativistic Schrödinger equations for few electron systems can be solved very accurately. The high precision is achieved also for relativistic and QED corrections, provided more complicated integrals with inverse powers of interelectronic distances can be performed. Such calculations, which rely on expansion in α, have been performed for hydrogen and hydrogenlike ions up to the very high order of $m\alpha^8$ [5]. Slightly lower precision was achieved for the helium fine structure and for other helium energy levels, all terms up to $m\alpha^6$ order have been obtained with approximate inclusion of dominant $m\alpha^7$ corrections [6]. For three- and four-electron atoms calculations have reached the order $m\alpha^5$ with partial inclusion of $m\alpha^6$ terms, which come from the electron self-energy. The complete calculation of the $m\alpha^6$ contribution for three-electron systems has not been performed so far.

In this work we present accurate calculation of the fine and hyperfine splittings in Li and Be$^+$ ions through $m\alpha^4$ and $m\alpha^5$ orders including the finite nuclear mass corrections. Lithium fine structure have already been calculated in Hylleraas functions by Yan and Drake in [7], but in a relatively small basis and with the neglect of $P_{1/2}$ and $P_{3/2}$ mixing, which we find to play a significant role in the isotope shift. The hyperfine splitting of P states was calculated in many works using explicitly relativistic methods [1–4] and with the nonrelativistic multiconfiguration Hartree-Fock method in [8,9]. We find by a comparison with our results that the most accurate previous calculation was that performed by Yerokhin in [1]. For the comparison with experimental values we include $O(\alpha^2)$ relativistic corrections from [1], known $O(\alpha^2)$ QED corrections, and draw a conclusion that a largest uncertainty comes from the not well-known nuclear structure effects.

II. FINE AND HYPERFINE OPERATORS

Let us briefly start with the description of the fine and hyperfine splitting in an arbitrary few electron atom. The fine structure, neglecting relativistic $O(\alpha^2)$ corrections, can be expressed as the expectation value with the nonrelativistic wave function of the following operator:

$$H_{\rm fs} = \sum_a \frac{Z\alpha}{2r_a^3}\vec{s}_a\left[\frac{(g-1)}{m^2}\vec{r}_a\times\vec{p}_a - \frac{g}{mm_N}\vec{r}_a\times\vec{p}_N\right] + \sum_{a\neq b}\frac{\alpha}{2m^2r_{ab}^3}\vec{s}_a[g\vec{r}_{ab}\times\vec{p}_b-(g-1)\vec{r}_{ab}\times\vec{p}_a], \quad (1)$$

where g is the free-electron g factor, which includes here all QED corrections, Z is the nuclear charge in units of the elementary charge e, m and m_N are the electron and nuclear masses, respectively, and finally $\vec{s}_a$ is the electron-spin operator. For convenience of further calculations we express $H_{\rm fs}$ in terms of F_a^i and four elementary operators f_a^i in atomic units, namely,

$$H_{\rm fs} = -i\sum_a \vec{s}_a\cdot\vec{F}_a,$$

$$F_a^i = \varepsilon\left[\frac{Z(g-1)}{2}f_{1a}^i + \frac{Zg}{2}\frac{m}{m_N}f_{2a}^i + \frac{g}{2}f_{3a}^i - \frac{(g-1)}{2}f_{4a}^i\right], \quad (2)$$

where $\varepsilon = m\alpha^4$ and

$$\vec{f}_{1a} = \frac{\vec{r}_a}{r_a^3}\times\vec{\nabla}_a, \quad (3)$$

$$\vec{f}_{2a} = \frac{\vec{r}_a}{r_a^3}\times\sum_b\vec{\nabla}_b, \quad (4)$$

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TABLE I. Data. for lithium and beryllium isotopes. Atomic binding energy of $E_{\rm Li}=-7.281$ a.u., $E_{\rm Be}=-14.669$ a.u. The value for the quadrupole moment of ^{7}Be is a theoretical estimate [16].

	Atomic mass (amu)	Ref.	I^π	μ (units of μ_N)	Ref.	Q (fm^2)	Ref.	r_E (a.u.)	Ref.
^{6}Li	6.015122794(16)	[19]	1^+	0.822 047 3(6)	[20,21]	−0.0806(6)	[22]	2.540(28)	[35]
^{7}Li	7.0160034256(45)	[23]	$3/2^-$	3.256 426 8(17)	[20,21]	−4.00(3)	[24]	2.390(30)	[36]
^{8}Li	8.02248624(12)	[19]	2^+	1.653560(18)	[20,21]	+3.14(2)	[25]	2.281(32)	[35]
^{9}Li	9.02679020(21)	[19]	$3/2^-$	3.43678(6)	[25]	−3.06(2)	[25]	2.185(33)	[35]
^{11}Li	11.04372361(69)	[19]	$3/2^-$	3.6712(3)	[26]	−3.33(5)	[26]	2.426(34)	[35]
^{7}Be	7.016 929 83(11)	[27]	$3/2^-$	−1.39928(2)	[29]	−6.11	[17]	2.646(14)	[33]
^{9}Be	9.012 182 20(43)	[27]	$3/2^-$	−1.177 432(3)	[30,31]	−5.288(38)	[32]	2.519(12)	[37]
^{10}Be	10.013 533 82(43)	[27]	0^+					2.358(16)	[33]
^{11}Be	11.021 661 55(63)	[28]	$1/2^+$	−1.681 3(5)	[33,34]			2.463(16)	[33]
^{12}Be	12.026 921(16)	[27]	0^+						
^{14}Be	14.042 890(140)	[27]	0^+						

$$\vec{f}_{3a}=\sum_{b\neq a}\frac{\vec{r}_{ab}}{r_{ab}^3}\times\vec{\nabla}_b, \tag{5}$$

$$\vec{f}_{4a}=\sum_{b\neq a}\frac{\vec{r}_{ab}}{r_{ab}^3}\times\vec{\nabla}_a. \tag{6}$$

The hyperfine structure, neglecting relativistic $O(\alpha^2)$ corrections, is given by $H_{\rm hfs}$ operator in Eq. (8). We will treat the nucleus as any other particle with mass m_N and with the g factor g_N which is related to the magnetic moment μ by the formula

$$g_N=\frac{m_N}{Zm_p}\frac{\mu}{\mu_N}\frac{1}{I}, \tag{7}$$

where μ_N is the nuclear magneton and I is the nuclear spin. Nuclear masses, spins, magnetic-dipole, and electric-quadrupole moments of Li and Be isotopes are taken from literature and are all presented in Table I. With the help of g_N $H_{\rm hfs}$ can be written as

$$\begin{aligned}H_{\rm hfs}=\sum_a\Bigg[&\frac{2}{3}\frac{Z\alpha g g_N}{m m_N}\vec{s}_a\cdot\vec{I}\pi\delta^3(r_a)-\frac{Z\alpha g g_N}{4m m_N}\frac{s_a^i I^j}{r_a^3}\left(\delta^{ij}-3\frac{r_a^i r_a^j}{r_a^2}\right)\\&+\frac{Z\alpha g_N}{2m m_N}\vec{I}\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_a-\frac{Z\alpha(g_N-1)}{2m_N^2}\vec{I}\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_N\\&+\frac{Q}{6}\frac{\alpha}{r_a^3}\left(\delta^{ij}-3\frac{r_a^i r_a^j}{r_a^2}\right)\frac{3I^iI^j}{I(2I-1)}\Bigg],\end{aligned} \tag{8}$$

$$\equiv\vec{I}\cdot\vec{G}+\frac{H^{ij}}{6}\frac{3I^iI^j}{I(2I-1)}, \tag{9}$$

where Q is the electric-quadrupole moment. For convenience of further calculations we express $H_{\rm hfs}$ in terms of H_a, H_a^{ij}, H^i, and H^{ij} operators, namely,

$$G^i=\sum_a s_a^i H_a+\sum_a s_a^j H_a^{ij}-iH^i, \tag{10}$$

$$H_a=\varepsilon Z g_N\frac{m}{m_N}\frac{g}{6}h_a, \tag{11}$$

$$H_a^{ij}=-\varepsilon Z g_N\frac{m}{m_N}\frac{g}{4}h_a^{ij}, \tag{12}$$

$$H^i=\varepsilon\left[\frac{Z}{2}g_N\frac{m}{m_N}h_1^i-\frac{Z}{2}(g_N-1)\frac{m^2}{m_N^2}h_2^i\right], \tag{13}$$

$$H^{ij}=\varepsilon m^2 Q h^{ij}, \tag{14}$$

where h operators (in atomic units) are

$$\vec{h}_1=\sum_a\frac{\vec{r}_a}{r_a^3}\times\vec{\nabla}_a, \tag{15}$$

$$\vec{h}_2=\sum_a\frac{\vec{r}_a}{r_a^3}\times\sum_b\vec{\nabla}_b, \tag{16}$$

$$h_a=4\pi\delta^3(r_a), \tag{17}$$

$$h_a^{ij}=\frac{1}{r_a^3}\left(\delta^{ij}-3\frac{r_a^ir_a^j}{r_a^2}\right), \tag{18}$$

$$h^{ij}=\sum_a\frac{1}{r_a^3}\left(\delta^{ij}-3\frac{r_a^ir_a^j}{r_a^2}\right). \tag{19}$$

III. MATRIX ELEMENTS

Matrix elements of the fine and hyperfine operators are evaluated with the nonrelativistic wave function. This function is obtained by solving the Schrödinger equation in the three-electron Hylleraas basis set. Finite nuclear mass corrections are included by reduced mass scaling and perturbative treatment of the mass polarization correction. All matrix el-

TABLE II. Matrix elements in atomic units of operators involved in the fine and hyperfine splitting of P states, infinite mass, and the mass polarization correction with the coefficient $-m/(m+m_N)$. $\langle k|h_a|k\rangle_F$ corresponds to a_c from Ref. [1], $\langle i|h_a^{ij}|j\rangle_F$ to $10a_{sd}$, $\epsilon^{ijk}\langle i|h_1^j|k\rangle_S$ to $2a_l$, and $\langle i|h^{ij}|j\rangle_S$ to $b_q/2$. Numerical uncertainties are due to extrapolation to the infinite basis set and reflect the numerical convergence.

Operator	Li$(2P)_\infty$	Mass pol. corr.	Be$^+(2P)_\infty$	Mass pol. corr.	Ref.
$\epsilon^{ijk}\langle i\vert f_{1a}^j\vert k\rangle_F$	−0.125 946 353 2(18)	0.376 388(3)	−0.969 131 4(8)	3.043 395 (9)	
$\epsilon^{ijk}\langle i\vert f_{2a}^j\vert k\rangle_F$	0.022 524 89(15)		0.339 008 2(2)		
$\epsilon^{ijk}\langle i\vert f_{3a}^j\vert k\rangle_F$	0.038 473 58(12)	−0.213 52(3)	0.360 851 6(2)	−1.549 82(12)	
$\epsilon^{ijk}\langle i\vert f_{4a}^j\vert k\rangle_F$	−0.224 640 68(6)	0.570 582(6)	−1.659 492 5(2)	4.53262(13)	
$\langle k\vert h_a\vert k\rangle_F$	−0.214 620 4(19)	2.376 4(5)	−1.083 916 1(8)	12.232(12)	
	−0.214 67		−1.084 2		[1]
	−0.214 78(5)				[38]
$\langle i\vert h_a^{ij}\vert j\rangle_F$	−0.134 775 3(5)	0.357 1(17)	−1.026 978(3)	2.775 0 (8)	
	−0.134 77		−1.026 9		[1]
$\epsilon^{ijk}\langle i\vert h_1^j\vert k\rangle_S$	−0.126 256 153(17)	0.400 67(5)	−0.970 443 9(3)	3.116 48 (5)	
	−0.126 250		−0.970 32		[1]
$\epsilon^{ijk}\langle i\vert h_2^j\vert k\rangle_S$	0.044 419 16 (19)		0.398 663 5 (7)		
$\langle i\vert h^{ij}\vert j\rangle_S$	−0.113 097(2)	0.334 9(9)	−0.918 134(3)	2.628(3)	
	−0.113 085		−0.918 10		[1]

ements are expressed in terms of Hylleraas integrals, which are obtained with the help of recursion relations [10–13]. The high accuracy is achieved by the use of a large number of about 15 000 Hylleraas functions, and we have already demonstrated the advantages of this approach by the calculation of the isotope shift in Li [14] and Be$^+$ ions [15].

The nonrelativistic wave function is the antisymmetrized product of spatial and spin functions of the form

$$\psi_a^j = \mathcal{A}[\phi_a^i(\vec{r}_1,\vec{r}_2,\vec{r}_3)\chi], \tag{20}$$

$$\phi_a^i(\vec{r}_1,\vec{r}_2,\vec{r}_3) = r_a^i e^{-w_1r_1-w_2r_2-w_3r_3} r_{23}^{n_1} r_{31}^{n_2} r_{12}^{n_3} r_1^{n_4} r_2^{n_5} r_3^{n_6}, \tag{21}$$

$$\chi = [\alpha(1)\beta(2) - \beta(1)\alpha(2)]\alpha(3), \tag{22}$$

where $\sigma_z\alpha(.)=\alpha(.)$ and $\sigma_z\beta(.)=-\beta(.)$. Matrix elements of each operator, after eliminating spin variables, can take the standard form

$$\begin{aligned}\langle i|H|j\rangle_S \equiv \langle \phi'^i(r_1,r_2,r_3)|H|2\phi^j(r_1,r_2,r_3) + 2\phi^j(r_2,r_1,r_3)\\ - \phi^j(r_2,r_3,r_1) - \phi^j(r_3,r_2,r_1) - \phi^j(r_3,r_1,r_2)\\ - \phi^j(r_1,r_3,r_2)\rangle\end{aligned} \tag{23}$$

and what we call the Fermi form

$$\begin{aligned}\langle i|H_a|j\rangle_F \equiv \langle \phi'^i(r_1,r_2,r_3)|2H_3[\phi^j(r_1,r_2,r_3) + \phi^j(r_2,r_1,r_3)]\\ - (H_1 - H_2 + H_3)[\phi^j(r_2,r_3,r_1) + \phi^j(r_3,r_2,r_1)]\\ - (H_2 - H_1 + H_3)[\phi^j(r_1,r_3,r_2) + \phi^j(r_3,r_2,r_1)]\rangle,\end{aligned} \tag{24}$$

with the assumption that the norm is $\Sigma_{i=1}^3\langle i|i\rangle_S=1$. The matrix element of the fine-structure Hamiltonian becomes

$$\langle H_{\rm fs}\rangle_J = \left\langle -i\sum_a \vec{s}_a\cdot\vec{F}_a\right\rangle_J = \epsilon^{ijk}\langle i|F_a^j|k\rangle_F \begin{cases}\frac{1}{2}, & J=1/2\\ -\frac{1}{4}, & J=3/2\end{cases} \tag{25}$$

and the fine splitting is

$$E_{\rm fs} = \langle H_{\rm fs}\rangle_{3/2} - \langle H_{\rm fs}\rangle_{1/2} = -\tfrac{3}{4}\epsilon^{ijk}\langle i|F_a^j|k\rangle_F. \tag{26}$$

The matrix elements of the hyperfine-structure Hamiltonian takes the form

$$\begin{aligned}\langle H_{\rm hfs}\rangle_J = \left\langle \vec{I}\cdot\vec{G} + \frac{3I^iI^j}{I(2I-1)}\frac{H^{ij}}{6}\right\rangle = A_J\vec{I}\cdot\vec{J}\\ + \frac{B_J}{6}\frac{3(I^iI^j)^{(2)}}{I(2I-1)}\frac{3(J^iJ^j)^{(2)}}{J(2J-1)},\end{aligned} \tag{27}$$

where A_J and B_J are magnetic-dipole and electric-quadrupole hyperfine constants. They are all expressed in terms of standard and Fermi matrix elements, namely,

$$A_J = \frac{1}{J(J+1)}\langle \vec{J}\cdot\vec{G}\rangle_J, \tag{28}$$

$$A_{1/2} = -\tfrac{1}{3}\langle k|H_a|k\rangle_F - \tfrac{2}{3}\epsilon^{ijk}\langle i|H^j|k\rangle_S + \tfrac{2}{3}\langle i|H_a^{ij}|j\rangle_F,$$

$$A_{3/2} = \tfrac{1}{3}\langle k|H_a|k\rangle_F - \tfrac{1}{3}\epsilon^{ijk}\langle i|H^j|k\rangle_S - \tfrac{1}{15}\langle i|H_a^{ij}|j\rangle_F,$$

$$B_J = \frac{2}{(2J+3)(J+1)}\langle J^iJ^jH^{ij}\rangle_J, \tag{29}$$

$$B_{1/2} = 0,$$

TABLE III. Finestructure splitting of $2P$ states in Li and Be^+ isotopes in MHz with $\varepsilon=2Rc\alpha^2=6\,579\,683\,921$ MHz. ΔE_{fs} is the isotope shift with respect to ^{7}Li and ^{9}Be. It is not clear whether the experimental value of Orth *et al.* [42] for the ^{7}Li fine structure includes δE_{fs} due to their diagonal and off-diagonal parametrization of hyperfine matrix elements.

	^{6}Li	^{7}Li	^{8}Li	^{9}Li	^{11}Li	Ref.
$E_{fs}^{(0)}$	10 053.7072(83)	10 053.707 2(83)	10 053.707 2(83)	10 053.707 2(83)	10 053.707 2(83)	
$E_{fs}^{(1)}$	−2.786 8(6)	−2.389 1(5)	−2.089 3(4)	−1.856 8(4)	−1.517 7(3)	
δE_{fs}	0.012 17	0.159 16	0.036 93	0.177 23	0.202 21	
ΔE_{fs}	−0.544 7(1)	10 051.477(8)	0.177 6(1)	0.550 4(1)	0.91 5(2)	
	−0.396	10 051.235(12)	0.298	0.529	0.851	[7,43]
Expt.	0.863(79)	10 053.184(58)				[42,44]
Expt.	−0.155(77)	10 053.39(21)				[45,46]
	^{7}Be$^+$	^{9}Be$^+$	^{10}Be$^+$	^{11}Be$^+$	^{14}Be$^+$	
$E_{fs}^{(0)}$	197 039.150(81)	197 039.150(81)	197 039.150(81)	197 039.150(81)	197 039.150(81)	
$E_{fs}^{(1)}$	−27.320(3)	−21.270(2)	−19.141(2)	−17.391(2)	−13.6492(15)	
δE_{fs}	0.045 56	0.032 25	0.000	0.118 34	0.000	
ΔE_{fs}	−6.037(1)	197017.727(21)	2.097(1)	3.965(1)	7.589(1)	
	−6.049		2.13	3.878		[43]

$$B_{3/2} = -\tfrac{1}{5}\langle i|H^{ij}|j\rangle_S.$$

Numerical values for all matrix elements involved in these calculations are presented in Table II. They have been obtained by extrapolation to infinite basis set and uncertainties reflect the numerical convergence. Matrix elements of the fine-structure operators have been derived previously by Yan and Drake in [7] and later by us in [15]. Small differences with results of [7] come from the not very large number of basis functions used in that work. The hyperfine operators have been previously obtained in several works, i.e., [1,9,39] and we compare our result with the most accurate one from [1] with which we agree well.

IV. SECOND-ORDER CONTRIBUTION

The hyperfine Hamiltonian H_{hfs} mixes $2^2P_{1/2}$ with $2^2P_{3/2}$ which leads to additional contributions to fine and hyperfine splittings [40]. Since this mixing is not very large one can use the second-order perturbative formula which involves off-diagonal matrix elements

$$\delta E(P_{1/2})_{m_1m_2} = \sum_m \frac{\langle P_{1/2},m_1|H_{hfs}|P_{3/2},m\rangle\langle P_{3/2},m|H_{hfs}|P_{1/2},m_2\rangle}{E(P_{1/2})-E(P_{3/2})},$$

$$\delta E(P_{3/2})_{m_1m_2} = \sum_m \frac{\langle P_{3/2},m_1|H_{hfs}|P_{1/2},m\rangle\langle P_{1/2},m|H_{hfs}|P_{3/2},m_2\rangle}{E(P_{3/2})-E(P_{1/2})}. \tag{30}$$

To calculate them one can use Clebsch-Gordan coefficients and Racah algebra [41]. In the simpler approach presented here, we introduce the operator K, such that $\langle J,m|\vec{K}|J,m'\rangle =0$ for $J=1/2,3/2$, but does not change L nor S, namely,

$$\vec{K} = \vec{S} - \vec{J}\left(\frac{1}{2} - \frac{5}{8J(J+1)}\right) = \begin{cases} \vec{S} + \frac{1}{3}\vec{J}, & J=1/2 \\ \vec{S} - \frac{1}{3}\vec{J}, & J=3/2. \end{cases} \tag{31}$$

Then the off-diagonal matrix elements can be transformed to the form

$$\begin{aligned}\langle P_J,m|H_{hfs}|P_{J'},m'\rangle &= I^i\langle P_J,m|G^i|P_{J'},m'\rangle + \frac{3I^iI^j}{I(2I-1)}\frac{\langle P_J,m|H^{ij}|P_{J'},m'\rangle}{6} \\ &= I^iX\langle J,m|K^i|J',m'\rangle + \frac{3I^iI^j}{I(2I-1)}\frac{Y}{6} \\ &\quad\times\langle J,m|(L^iL^j)^{(2)}|J',m'\rangle \end{aligned} \tag{32}$$

with X and Y coefficients being

$$X = \langle k|H_a|k\rangle_F + \frac{\epsilon^{ijk}}{2}\langle i|H^j|k\rangle_S + \frac{1}{4}\langle i|H_a^{ij}|j\rangle_F, \tag{33}$$

$$Y = -\tfrac{3}{5}\langle i|H^{ij}|j\rangle_S. \tag{34}$$

The second-order correction to energy due to H_{hfs} in Eq. (30) neglecting the small Y^2 term becomes

$$\begin{aligned}\delta E(P_{1/2}) &= -\frac{X^2}{E_{fs}}I^iI^j\langle K^iK^j\rangle_{J=1/2} - \frac{XY}{E_{fs}} \\ &\quad\times\frac{I^kI^iI^j}{I(2I-1)}\langle K^k(L^iL^j)^{(2)}\rangle_{J=1/2} \\ &= -\frac{X^2}{E_{fs}}\frac{2}{9}(\vec{I}^2+\vec{I}\cdot\vec{J}) + \frac{XY}{E_{fs}}\frac{2I+3}{9I}\vec{I}\cdot\vec{J},\end{aligned} \tag{35}$$

TABLE IV. Hyperfine splitting of the 2*P* states in Li isotopes in MHz. Results of Yerokhin [1] are corrected by inclusion of δA and δB, and by the use of more accurate electric-quadrupole moments for ^{6}Li and ^{7}Li. Results of Orth *et al.* [42,47] for *A* and *B* constants in ^{7}Li are shifted by δA and δB, as these authors parametrized results of their measurement by diagonal and off-diagonal parts separately. Uncertainties of final theoretical predictions are due to higher-order corrections and the approximate treatment of the nuclear structure contribution. Not shown are uncertainties due to inaccuracies of magnetic-dipole and electric-quadrupole moments.

	^{6}Li	^{7}Li	^{8}Li	^{9}Li	^{11}Li	Ref.
$A_{1/2}^{\mathrm{nrel}}$	17.404 70(4)	45.96337(11)	17.504 24(4)	48.50752(11)	51.815 18(12)	
$\delta A_{1/2}$	−0.004 05	−0.027 29	−0.004 37	−0.030 69	−0.035 00	
	−0.004 01	−0.027 0				[40]
$A_{1/2}^{\mathrm{rel}}$	0.003 53	0.009 32	0.003 55	0.009 84	0.010 51	[1]
$A_{1/2}^{\mathrm{qed}}$	−0.001 08	−0.002 86	−0.001 09	−0.003 01	−0.003 22	
$A_{1/2}^{\mathrm{fns}}$	−0.001 36	−0.003 39	−0.001 23	−0.003 27	−0.003 88	
$A_{1/2}$	17.401 7(4)	45.939 2(11)	17.501 1(4)	48.480 4(11)	51.783 6(13)	
	17.401 8(5)	45.939(1)				[1]
Expt.	17.371(18)	45.887 (25)				[42,47]
Expt.	17.386(31)	46.010(25)				[48]
Expt.	17.394(4)	46.024(3)				[49]
$A_{3/2}^{\mathrm{nrel}}$	−1.152 35(2)	−3.042 14(4)	−1.158 31(2)	−3.209 24(4)	−3.427 19(4)	
$\delta A_{3/2}$	−0.002 03	−0.014 25	−0.002 03	−0.015 84	−0.018 07	
	−0.002 01	−0.014 1				[40]
$A_{3/2}^{\mathrm{rel}}$	−0.001 84	−0.004 85	−0.001 85	−0.005 12	−0.005 46	[1]
$A_{3/2}^{\mathrm{qed}}$	0.001 08	0.00 86	0.001 09	0.003 01	0.003 22	
$A_{3/2}^{\mathrm{fns}}$	0.001 36	0.00 39	0.00 23	0.00 27	0.003 88	
$A_{3/2}$	−1.153 7(4)	−3.055 0(11)	−1.159 8(4)	−3.223 8(11)	−3.443 6(13)	
	−1.155 0(5)	−3.058(1)				[1]
Expt.	−1.157(8)	−3.069(14)				[42,47]
$B_{3/2}^{\mathrm{nrel}}$	−0.004 28	−0.212 59	0.166 88	−0.162 63	−0.176 98	
$\delta B_{3/2}$	−0.004 05	−0.084 14	−0.024 85	−0.093 91	−0.107 13	
	−0.004 02	−0.083 4				[40]
$B_{3/2}^{\mathrm{rel}}$	0.000 00	0.000 02	−0.00001	0.000 01	0.000 01	[1]
$B_{3/2}$	−0.008 33	−0.296 71(8)	0.142 02(2)	−0.256 53(9)	−0.284 10(11)	
	−0.008 33	−0.296 69(2)				[1]
Expt.	−0.014(14)	−0.305(29)				[42,47]

$$\begin{aligned}\delta E(P_{3/2}) &= \frac{X^2}{E_{\mathrm{fs}}} I^i I^j \langle K^i K^j \rangle_{J=3/2} + \frac{XY}{E_{\mathrm{fs}}} \frac{I^k I^i I^j}{I(2I-1)} \\ &\quad \times \langle K^k (L^i L^j)^{(2)} \rangle_{J=3/2} \\ &= \frac{X^2}{E_{\mathrm{fs}}} \frac{1}{9} [\vec{I}^2 - \vec{I}\cdot\vec{J} - (I^i I^j)^{(2)} (J^i J^j)^{(2)}] + \frac{XY}{E_{\mathrm{fs}}} \\ &\quad \times \left[-\frac{(2I+3)}{90I} \vec{I}\cdot\vec{J} + \frac{1}{18} \frac{3(I^i I^j)^{(2)}}{I(2I-1)} \times (J^i J^j)^{(2)} \right],\end{aligned} \tag{36}$$

where we omitted the magnetic octupole coupling, the so-called C_J coefficient. Resulting corrections to the fine and hyperfine splittings are

$$\delta E_{\mathrm{fs}} = \frac{X^2}{E_{\mathrm{fs}}} \frac{I(I+1)}{3}, \tag{37}$$

$$\delta A_{1/2} = -\frac{2}{9} \frac{X^2}{E_{\mathrm{fs}}} + \frac{2I+3}{9I} \frac{XY}{E_{\mathrm{fs}}}, \tag{38}$$

$$\delta A_{3/2} = -\frac{1}{9} \frac{X^2}{E_{\mathrm{fs}}} - \frac{2I+3}{90I} \frac{XY}{E_{\mathrm{fs}}}, \tag{39}$$

$$\delta B_{3/2} = -\frac{2I(2I-1)}{9} \frac{X^2}{E_{\mathrm{fs}}} + \frac{1}{3} \frac{XY}{E_{\mathrm{fs}}}. \tag{40}$$

V. RESULTS

Numerical results for the fine splitting in Li and Be$^+$ isotopes are shown in Table II. $E_{\mathrm{fs}}^{(0)}$ is the leading contribution with the exact electron *g* factor, but in the infinite nuclear mass limit, $E_{\mathrm{fs}}^{(1)}$ is the finite nuclear mass correction and δE_{fs} is the $P_{1/2}-P_{3/2}$ mixing term. The higher-order relativistic

TABLE V. Hyperfine splitting of $2P$ states in Be^+ isotopes in MHz. Results of Yerokhin [1] are corrected by inclusion of δA and δB. Uncertainties of final theoretical predictions are due to higher-order corrections and the approximate treatment of the nuclear structure contribution. Not shown are uncertainties due to inaccuracies of magnetic-dipole and electric-quadrupole moments.

	$^7Be^+$	$^9Be^+$	$^{11}Be^+$	Ref.
$A_{1/2}^{\rm nrel}$	−140.069 6(3)	−117.859 2(3)	−504.874 5(8)	
$\delta A_{1/2}$	−0.009 61	−0.006 83	−0.105 20	
$A_{1/2}^{\rm rel}$	−0.096 8	−0.081 5	−0.349	[1]
$A_{1/2}^{\rm qed}$	0.008 26	0.006 95	0.029 75	
$A_{1/2}^{\rm fns}$	0.010 85	0.008 69	0.055 50	
$A_{1/2}$	−140.157(3)	−117.932(3)	−505.245(16)	
		−117.926(4)		[1]
Expt.	−140.17(18)	−118.00(4)	−505.41(5)	[33]
Expt.		118.6(36)		[50]
$A_{3/2}^{\rm nrel}$	−1.215 33(2)	−1.024 81(2)	−4.395 48(8)	
$\delta A_{3/2}$	−0.003 90	−0.002 76	−0.052 60	
$A_{3/2}^{\rm rel}$	0.02 3	0.01 1	0.073 5	[1]
$A_{3/2}^{\rm qed}$	−0.008 26	−0.006 95	−0.029 75	
$A_{3/2}^{\rm fns}$	−0.010 85	−0.008 69	−0.055 50	
$A_{3/2}$	−1.218(3)	−1.026(3)	−4.460(16)	
		−1.018(3)		[1]
$B_{3/2}^{\rm nrel}$	−2.636 19(1)	−2.281 54(1)		
$\delta B_{3/2}$	−0.025 43	−0.018 03		
$B_{3/2}^{\rm rel}$	0.000 20	0.000 17		[1]
$B_{3/2}$	−2.661 42(3)	−2.299 40(3)		
		−2.299 25(17)		[1]

and QED corrections are not known as they have not yet been evaluated. Finally $\Delta E_{\rm fs}$ is the isotope shift with respect to ^{7}Li and $^9Be^+$. Our result for this isotope shift in the fine structure $\Delta E_{\rm fs}$ of Li differs significantly from the previous calculations in [7] due to the inclusion of the important second-order contribution $\delta E_{\rm fs}$. However, it differs also from all the experimental values (see Table III).

Numerical values of all significant contributions to the hyperfine constants of the $2^2P_{1/2}$ and $2^2P_{3/2}$ states in Li and Be^+ isotopes are shown in Tables IV and V. $A_{1/2}^{\rm nrel}$ according to Eq. (8) involves the exact electron g factor, and thus includes the leading QED corrections. The relativistic corrections $A^{\rm rel}$ and $B^{\rm rel}$ have been calculated by Yerokhin in [1] in terms of G_{M1} and G_{E2} functions. G_{M1} is defined by

$$A_J = \varepsilon \frac{Z^3}{8} \frac{m}{m_p} \frac{\mu}{\mu_N I} \frac{1}{3J(J+1)} G_{M1}, \tag{41}$$

where relativistic corrections to G_{M1} are equal to 0.000 015 for $2^2P_{1/2}$, −0.000 039 for $2^2P_{3/2}$ states of Li, and 0.000 00153 for $2^2P_{1/2}$, −0.000161 for $2^2P_{3/2}$ states of Be^+. These number include also the so-called negative-energy contributions. G_{E2} is related to B_J coefficient by

$$B_{3/2} = \varepsilon m^2 Q \frac{Z^3}{60} G_{E2}, \tag{42}$$

where relativistic corrections to G_{E2} for $2^2P_{3/2}$ are equal to −0.000004 in Li and −0.000013 in Be^+. These relativistic corrections can in principle be evaluated within nonrelativistic QED (NRQED) approach [51] but so far we have not been able to obtain analytic formula for all Hylleraas integrals involved in matrix elements. The next to leading radiative (QED) correction $A_{1/2}^{\rm qed}$ (beyond the anomalous magnetic moment) is proportional to the Fermi contact interaction and is known from hydrogenic atoms. In terms of the H_a operator it is

$$H_a^{\rm qed} = H_a \frac{2}{g} Z\alpha^2 \left(\ln 2 - \frac{5}{2}\right). \tag{43}$$

The last significant contribution is the finite-nuclear-size correction, the extended electric and magnetic distribution within nucleus. It is given by the formula

$$H_a^{\rm fns} = H_a(-2Z\alpha m r_Z), \tag{44}$$

where

$$r_Z = \int d^3r d^3r' \rho_E(r)\rho_M(r')|\vec{r} - \vec{r}'|. \tag{45}$$

Using exponential parametrization of electric and magnetic form factors

$$\rho_E(r) = \frac{3\sqrt{3}}{\pi r_E^3} e^{-2\sqrt{3}r/r_E}, \tag{46}$$

$$\rho_M(r) = \frac{3\sqrt{3}}{\pi r_M^3} e^{-2\sqrt{3}r/r_M}, \tag{47}$$

the Zemach radius r_Z is

$$r_Z = \frac{35(r_E + r_M)^4 + 14(r_E^2 - r_M^2)^2 - (r_E - r_M)^4}{32\sqrt{3}(r_E + r_M)^3}. \tag{48}$$

For all but ^{11}Be nuclei we assume $r_E = r_M$, thus

$$r_Z = \frac{35 r_E}{16\sqrt{3}} = 1.263 r_E, \tag{49}$$

and take charge radii from the recent isotope shift measurements in Li [35] and Be^+ [33] supplemented with isotope shift calculations in [15]. For the Gaussian distribution one obtains [1] $r_Z = 1.30 r_E$ which demonstrates a weak dependence of r_Z on an arbitrarily assumed shape of the charge distribution, with one exception. The ^{11}Be nucleus has a single neutron halo, which means that r_M is much larger than r_E and the nuclear finite size becomes much larger. We employ here the result of direct calculations from [52], which is

$$H_a^{\rm fns} = H_a(-0.000717). \tag{50}$$

At the same time the nuclear polarizability correction is also much larger and of the opposite sign to the finite-size effect. Since it is very difficult to estimate, it will be neglected here. The final results for $A_{1/2}$, $A_{3/2}$, and $B_{3/2}$ include the uncertainty coming from the higher order corrections, which we estimate to be 25% of $A^{\rm qed}$ and the uncertainty due to the approximate treatment of the nuclear structure which we estimate to be 25% of $A^{\rm fns}$ for all A coefficients, while for the B coefficients we assume the final uncertainty to be the sum of 10% of $B^{\rm rel}$ and 0.1% of δB.

VI. CONCLUSIONS

In comparison to experimental values we observe significant discrepancies for the isotope shift in the fine structure (see Table III). Although the theoretical fine structure of ^{7}Li is consistent with experimental values, the differences can be associated to $O(\alpha^2)$ relativistic corrections, the isotope shift, as it has already been noted in [7,43], differs significantly between different experiments and theoretical predictions. In view of the recent determination of the nuclear charge radii from the isotope shift of $2S_{1/2}-2P_{1/2}$ transition in Be$^+$ ions, it is important to resolve these discrepancies. In this respect, we note the recent critical examinations [53] of all experimental values of the fine structure and isotope shift measurements in ^{6}Li and ^{7}Li. Considering hyperfine splittings we observe good agreement with the previous calculations of Yerokhin in [1], particularly for the $A_{1/2}$ coefficients. Slight discrepancies with experiments for the A coefficients of the $2P$ state indicate that the magnetic moment obtained from the hyperfine structure (hfs) measurement for the $2S$ state may not be as accurate as claimed. This is because the treatment of the nuclear structure corrections by the elastic charge and magnetic form factors is very approximate, and the accuracy of this approximation is not known. We think that the more accurate approach shall employ the effective nuclear Hamiltonian using the so-called chiral perturbation theory. Then the nuclear structure correction to the atomic hfs consists of the leading Low correction, Zemach corrections from individual nucleons, and the nuclear vector polarizability [54]. Unfortunately, the explicit calculations for nuclei with more than three nucleons is difficult and has not been performed so far. Certainly the nuclear vector polarizability correction is significant for halo nuclei, and it would be worth to calculate it. At present, without detailed knowledge of nuclear structure, the determination of magnetic moments from atomic spectroscopy measurements can be uncertain. Therefore, better accuracy can be achieved when two measurements are combined in such a way, that this nuclear structure correction, proportional to the Fermi interaction cancels out, for example in $A_{1/2}+A_{3/2}$ of the P state of Li and Be$^+$. Theoretical accuracy for this combination is limited only by higher-order QED corrections and knowing both A constants, we shall be able to derive magnetic moments with relative precision of about 1×10^{-5} without referencing to magnetic moments of stable isotopes, or with precision of the magnetic moment of the reference nucleus.

ACKNOWLEDGMENTS

Authors wish to acknowledge fruitful discussions with Vladimir Yerokhin. This work was support by NIST through Precision Measurement Grant through Grant No. PMG 60NANB7D6153.

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