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

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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 electrodynamics 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.

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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 multi-configuration 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 inter-electronic distances can be performed. Such calculations, which rely on expansion in α, have been performed for hydrogen and hydrogen-like 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 3- and 4-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 3-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 multi-configuration 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

$$\begin{aligned} H_{\rm fs} &= \sum_a \frac{Z\,\alpha}{2\,r_a^3}\,\vec s_a \left[\frac{(g-1)}{m^2}\,\vec r_a\times\vec p_a - \frac{g}{m\,m_{\rm N}}\,\vec r_a\times\vec p_{\rm N}\right] \\ &\quad + \sum_{a\neq b}\frac{\alpha}{2\,m^2\,r_{ab}^3}\,\vec s_a\big[g\,\vec r_{ab}\times\vec p_b-(g-1)\,\vec r_{ab}\times\vec p_a\big] \end{aligned} \tag{1}$$

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, $m_{\rm N}$ are the electron and nuclear masses respectively, 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 4 elementary operators f_a^i in atomic units, namely

$$\begin{aligned} H_{\rm fs} &= -i\sum_a \vec s_a\cdot\vec F_a, \\ F_a^i &= \varepsilon\left[\frac{Z\,(g-1)}{2}\,f_{1a}^i + \frac{Z\,g}{2}\,\frac{m}{m_{\rm N}}\,f_{2a}^i + \frac{g}{2}\,f_{3a}^i \right. \\ &\quad \left. -\frac{(g-1)}{2}\,f_{4a}^i\right], \end{aligned} \tag{2}$$

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

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

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

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

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

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 $m_{\rm N}$ and with the g-factor $g_{\rm N}$ which is related to the magnetic moment μ by the formula

$$g_{\rm N} = \frac{m_{\rm N}}{Z\,m_{\rm p}}\,\frac{\mu}{\mu_{\rm N}}\,\frac{1}{I}, \tag{7}$$

where $\mu_{\rm N}$ 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 $g_{\rm N}$ $H_{\rm hfs}$ can be written as

$$\begin{aligned} H_{\rm hfs} &= \sum_a \biggl[\frac{2}{3}\,\frac{Z\,\alpha\,g\,g_{\rm N}}{m\,m_{\rm N}}\,\vec{s}_a\cdot\vec{I}\,\pi\,\delta^3(r_a) \\ &\quad -\frac{Z\,\alpha\,g\,g_N}{4\,m\,m_N}\,\frac{s_a^i\,I^j}{r_a^3}\left(\delta^{ij}-3\frac{r_a^i\,r_a^j}{r_a^2}\right) \\ &\quad +\frac{Z\,\alpha\,g_N}{2\,m\,m_N}\,\vec{I}\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_a - \frac{Z\,\alpha\,(g_N-1)}{2\,m_N^2}\,\vec{I}\cdot\frac{\vec{r}_a}{r_a^3}\times\vec{p}_N \\ &\quad +\frac{Q}{6}\,\frac{\alpha}{r_a^3}\left(\delta^{ij}-3\frac{r_a^i\,r_a^j}{r_a^2}\right)\frac{3\,I^i\,I^j}{I\,(2\,I-1)}\biggr] \qquad (8) \\ &\equiv \vec{I}\cdot\vec{G} + \frac{H^{ij}}{6}\,\frac{3\,I^i\,I^j}{I\,(2\,I-1)}, \qquad (9) \end{aligned}$$

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

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

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

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

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

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

where h operators (in atomic units) are

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

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

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

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

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

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 3-electron Hylleraas basis set. Finite nuclear mass corrections are included by reduced mass scaling and perturbative treatment of the mass polarization correction. All matrix elements 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 15000 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 spacial and spin functions of the form

$$\begin{aligned} \psi_a^i &= \mathcal{A}[\phi_a^i(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,\chi], \qquad (20) \\ \phi_a^i(\vec{r}_1,\vec{r}_2,\vec{r}_3) &= r_a^i\,e^{-w_1\,r_1-w_2\,r_2-w_3\,r_3} \\ &\quad r_{23}^{n_1}\,r_{31}^{n_2}\,r_{12}^{n_3}\,r_1^{n_4}\,r_2^{n_5}\,r_3^{n_6}, \qquad (21) \\ \chi &= [\alpha(1)\,\beta(2)-\beta(1)\,\alpha(2)]\,\alpha(3), \qquad (22) \end{aligned}$$

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

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

and, what we call, the Fermi form

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

with the assumption that the norm is $\sum_{i=1}^3 \langle i|i\rangle_S = 1$. The

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

	atomic mass [u]	Ref.	I^π	$\mu[\mu_N]$	Ref.	$Q[\mathrm{fm}^2]$	Ref.	r_E	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^+						

matrix element of the fine structure Hamiltonian becomes

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

and the fine splitting is

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

The matrix elements of the hyperfine structure Hamiltonian takes the form

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

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

$$\begin{aligned}A_J &= \frac{1}{J\,(J+1)}\,\langle\vec{J}\cdot\vec{G}\rangle_J, \qquad (28)\\ A_{1/2} &= -\frac{1}{3}\,\langle k|H_a|k\rangle_F - \frac{2}{3}\,\epsilon^{ijk}\,\langle i|H^j|k\rangle_S + \frac{2}{3}\,\langle i|H_a^{ij}|j\rangle_F\\ A_{3/2} &= \frac{1}{3}\,\langle k|H_a|k\rangle_F - \frac{1}{3}\,\epsilon^{ijk}\,\langle i|H^j|k\rangle_S - \frac{1}{15}\,\langle i|H_a^{ij}|j\rangle_F\end{aligned}$$

$$\begin{aligned}B_J &= \frac{2}{(2\,J+3)\,(J+1)}\,\langle J^i J^j\,H^{ij}\rangle_J, \qquad (29)\\ B_{1/2} &= 0,\\ B_{3/2} &= -\frac{1}{5}\,\langle i|H^{ij}|j\rangle_S.\end{aligned}$$

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. THE SECOND ORDER CONTRIBUTION

The hyperfine Hamiltonian $H_{\rm hfs}$ mixes $2^2P_{1/2}$ with $2^2P_{3/2}$ what 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

$$\begin{aligned}&\delta E(P_{1/2})_{m_1 m_2} = \qquad (30)\\ &\sum_m \frac{\langle P_{1/2},m_1|H_{\rm hfs}|P_{3/2},m\rangle\,\langle P_{3/2},m|H_{\rm hfs}|P_{1/2},m_2\rangle}{E(P_{1/2})-E(P_{3/2})}\\ &\delta E(P_{3/2})_{m_1 m_2} =\\ &\sum_m \frac{\langle P_{3/2},m_1|H_{\rm hfs}|P_{1/2},m\rangle\,\langle P_{1/2},m|H_{\rm hfs}|P_{3/2},m_2\rangle}{E(P_{3/2})-E(P_{1/2})}\end{aligned}$$

To calculate them one can use Clebsch-Jordan 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

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

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

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

with X and Y coefficients being

$$\begin{aligned}X &= \langle k|H_a|k\rangle_F + \frac{\epsilon^{ijk}}{2}\,\langle i|H^j|k\rangle_S + \frac{1}{4}\langle i|H_a^{ij}|j\rangle_F \qquad (33)\\ Y &= -\frac{3}{5}\,\langle i|H^{ij}|j\rangle_S. \qquad (34)\end{aligned}$$

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 $-m/(m+m_{\rm N})$. $\langle k|h_a|k\rangle_F$ corresponds to a_c from Ref. [1], $\langle i|h_a^{ij}|j\rangle_F$ to $10\,a_{sd}$, $\epsilon^{ijk}\,\langle i|h_1^j|k\rangle_S$ to $2\,a_l$, 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	$\mathrm{Li}(2P)_\infty$	mass pol. corr.	$\mathrm{Be}^+(2P)_\infty$	mass pol. corr.	Ref.
$\epsilon^{ijk}\,\langle i\vert f_{1a}^j\vert k\rangle_F$	$-0.125\,946\,353\,2(18)$	$0.376\,388(3)$	$-0.969\,131\,4(8)$	$3.043\,395(9)$	
$\epsilon^{ijk}\,\langle i\vert f_{2a}^j\vert k\rangle_F$	$0.022\,524\,89(15)$		$0.339\,008\,2(2)$		
$\epsilon^{ijk}\,\langle i\vert f_{3a}^j\vert k\rangle_F$	$0.038\,473\,58(12)$	$-0.213\,52(3)$	$0.360\,851\,6(2)$	$-1.549\,82(12)$	
$\epsilon^{ijk}\,\langle i\vert f_{4a}^j\vert k\rangle_F$	$-0.224\,640\,68(6)$	$0.570\,582(6)$	$-1.659\,492\,5(2)$	$4.532\,62(13)$	
$\langle k\vert h_a\vert k\rangle_F$	$-0.214\,620\,4(19)$	$2.376\,4(5)$	$-1.083\,916\,1(8)$	$12.232(12)$	
	$-0.214\,67$		$-1.084\,2$		[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]

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

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

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

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

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

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

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

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

V. RESULTS

Numerical results for the fine splitting in Li and Be^+ isotopes are shown in Table III. $E_{\rm fs}^{(0)}$ is the leading contribution with the exact electron g-factor, but in the infinite nuclear mass limit, $E_{\rm fs}^{(1)}$ is the finite nuclear mass correction, and $\delta E_{\rm fs}$ is the $P_{1/2}-P_{3/2}$ mixing term. The higher order relativistic 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 $^9\mathrm{Be}^+$. 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

$$A_J = \varepsilon\,\frac{Z^3}{8}\,\frac{m}{m_{\rm p}}\,\frac{\mu}{\mu_{\rm N} I}\,\frac{1}{3\,J\,(J+1)}\,G_{M1}, \tag{41}$$

where relativistic corrections to G_{M1} are equal to 0.000015 for $2^2P_{1/2}$, -0.000039 for $2^2P_{3/2}$ states of Li, and 0.000153 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 $-0.000\,004$ in Li and $-0.000\,013$ in Be^+. These relativistic corrections can in principle be evaluated within 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

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

TABLE III: Fine splitting of 2P-states in Li and Be^{+} isotopes in MHz with $\varepsilon = 2\,R\,c\,\alpha^2 = 6\ 579\ 683\ 921$ MHz. $\Delta E_{\rm fs}$ 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 $\delta E_{\rm fs}$ due to their diagonal and of-diagonal parametrization of hyperfine matrix elements.

	^{6}Li	^{7}Li	^{8}Li	^{9}Li	^{11}Li	Ref.
$E_{\rm fs}^{(0)}$	$10\,053.707\,2(83)$	$10\,053.707\,2(83)$	$10\,053.707\,2(83)$	$10\,053.707\,2(83)$	$10\,053.707\,2(83)$	
$E_{\rm fs}^{(1)}$	$-2.786\,8(6)$	$-2.389\,1(5)$	$-2.089\,3(4)$	$-1.856\,8(4)$	$-1.517\,7(3)$	
$\delta E_{\rm fs}$	$0.012\,17$	$0.159\,16$	$0.036\,93$	$0.177\,23$	$0.202\,21$	
$\Delta E_{\rm fs}$	$-0.544\,7(1)$	$10\,051.477(8)$	$0.177\,6(1)$	$0.550\,4(1)$	$0.914\,5(2)$	
	-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$^+$	
$E_{\rm fs}^{(0)}$	$197\,039.150(81)$	$197\,039.150(81)$	$197\,039.150(81)$	$197\,039.150(81)$	$197\,039.150(81)$	
$E_{\rm fs}^{(1)}$	$-27.320(3)$	$-21.270(2)$	$-19.141(2)$	$-17.391(2)$	$-13.649\,2(15)$	
$\delta E_{\rm fs}$	$0.045\,56$	$0.032\,25$	0.000	$0.118\,34$	0.000	
$\Delta E_{\rm fs}$	$-6.037(1)$	$197017.727(21)$	$2.097(1)$	$3.965(1)$	$7.589(1)$	
	-6.049		2.13	3.878		[43]

TABLE IV: Hyperfine splitting of the $2P$-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 of-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.
$A_{1/2}^{\rm nrel}$	$17.404\,70(4)$	$45.963\,37(11)$	$17.504\,24(4)$	$48.507\,52(11)$	$51.815\,18(12)$	
$\delta A_{1/2}$	$-0.004\,05$	$-0.027\,29$	$-0.004\,37$	$-0.030\,69$	$-0.035\,00$	
	$-0.004\,01$	$-0.027\,0$				[40]
$A_{1/2}^{\rm rel}$	$0.003\,53$	$0.009\,32$	$0.003\,55$	$0.009\,84$	$0.010\,51$	[1]
$A_{1/2}^{\rm qed}$	$-0.001\,08$	$-0.002\,86$	$-0.001\,09$	$-0.003\,01$	$-0.003\,22$	
$A_{1/2}^{\rm fns}$	$-0.001\,36$	$-0.003\,39$	$-0.001\,23$	$-0.003\,27$	$-0.003\,88$	
$A_{1/2}$	$17.401\,7(4)$	$45.939\,2(11)$	$17.501\,1(4)$	$48.480\,4(11)$	$51.783\,6(13)$	
	$17.401\,8(5)$	$45.939(1)$				[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]
$A_{3/2}^{\rm nrel}$	$-1.152\,35(2)$	$-3.042\,14(4)$	$-1.158\,31(2)$	$-3.209\,24(4)$	$-3.427\,19(4)$	
$\delta A_{3/2}$	$-0.002\,03$	$-0.014\,25$	$-0.002\,03$	$-0.015\,84$	$-0.018\,07$	
	$-0.002\,01$	$-0.014\,1$				[40]
$A_{3/2}^{\rm rel}$	$-0.001\,84$	$-0.004\,85$	$-0.001\,85$	$-0.005\,12$	$-0.005\,46$	[1]
$A_{3/2}^{\rm qed}$	$0.001\,08$	$0.002\,86$	$0.001\,09$	$0.003\,01$	$0.003\,22$	
$A_{3/2}^{\rm fns}$	$0.001\,36$	$0.003\,39$	$0.001\,23$	$0.003\,27$	$0.003\,88$	
$A_{3/2}$	$-1.153\,7(4)$	$-3.055\,0(11)$	$-1.159\,8(4)$	$-3.223\,8(11)$	$-3.443\,6(13)$	
	$-1.155\,0(5)$	$-3.058(1)$				[1]
expt.	$-1.157(8)$	$-3.069(14)$				[42, 47]
$B_{3/2}^{\rm nrel}$	$-0.004\,28$	$-0.212\,59$	$0.166\,88$	$-0.162\,63$	$-0.176\,98$	
$\delta B_{3/2}$	$-0.004\,05$	$-0.084\,14$	$-0.024\,85$	$-0.093\,91$	$-0.107\,13$	
	$-0.004\,02$	$-0.083\,4$				[40]
$B_{3/2}^{\rm rel}$	$0.000\,00$	$0.000\,02$	$-0.000\,01$	$0.000\,01$	$0.000\,01$	[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]

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

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

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 formfactors

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

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

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]
$A_{3/2}^{\rm nrel}$	$-1.215\,33(2)$	$-1.024\,81(2)$	$-4.395\,48(8)$	
$\delta A_{3/2}$	$-0.003\,90$	$-0.002\,76$	$-0.052\,60$	
$A_{3/2}^{\rm rel}$	$0.020\,3$	$0.017\,1$	$0.073\,5$	[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]

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] $r_Z = 1.30\,r_E$ what 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, what 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

$$H_a^{\rm fns} = H_a\,(-0.000\,717). \tag{50}$$

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 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 formfactors 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 3 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 10^{-5} without referencing to magnetic moments of stable isotopes, or with precision of the magnetic moment of the reference nucleus.

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