Hyperfine structure of hydrogenlike and lithiumlike atoms

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The hyperfine splitting values of the ground state of hydrogenlike atoms $^{13}C^{5+}$, $^{14}N^{6+}$, and $^{17}O^{7+}$, the lithiumlike atoms $^{7}Li^{0}$, $^{14}N^{4+}$, $^{19}F^{6+}$, $^{23}Na^{8+}$, $^{25}Mg^{9+}$, $^{27}Al^{10+}$, $^{29}Si^{11+}$, $^{35}Cl^{14+}$, and $^{57}Fe^{23+}$ are calculated. The calculations of the lithiumlike ions ($Z \geq 7$) are based on a combination of the $\frac{1}{Z}$ perturbation theory and the configuration interaction Hartree-Fock method. The relativistic corrections are calculated in the zeroth and first orders in $\frac{1}{Z}$. The nuclear charge and magnetization distribution corrections and the radiative corrections are taken into account. The uncertainty of the calculations is estimated to be $\sim 0.02\%$ for the hydrogenlike ions and $\sim 0.06\%$ for the lithiumlike ions, except $^{57}Fe^{23+}$, for which the uncertainty is about 0.15%. The hyperfine structure constant of the ground state of Li is calculated to be $A = 401.5(4)$ MHz. The results of the calculations are compared with the theoretical values obtained with other methods and with experiment.

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I. INTRODUCTION

Astronomical search of the radio lines in the millimeter region, corresponding to the transitions between the hyperfine structure components of multicharged ions, requires the prediction of the wavelengths with accuracy $\sim 0.1\%$. Candidates for such a search planned in IRAM (France) [1] are $^{13}C^{5+}$, $^{14}N^{6+}$, $^{14}N^{4+}$, $^{17}O^{7+}$, $^{23}Na^{8+}$, $^{25}Mg^{9+}$, $^{27}Al^{10+}$, $^{29}Si^{11+}$, $^{35}Cl^{14+}$, and $^{57}Fe^{23+}$. In this paper we present calculations of the hyperfine structure of the ground state of these ions with the required precision. In addition, to compare our results with calculations carried out by other methods and with experiment the hyperfine structure of $^{7}Li^{0}$ and $^{19}F^{6+}$ is also calculated.

II. HYDROGENLIKE ATOMS

The hyperfine splitting of the ground state of hydrogenlike atoms is conveniently written in the form

$$\Delta E_\mu = \frac{4}{3}\alpha(\alpha Z)^3 \frac{\mu}{\mu_N}\frac{m}{m_p}\frac{2I+1}{2I}\frac{1}{(1+\frac{m}{M})^3}mc^2 \times\{A(\alpha Z)(1-\delta)(1-\varepsilon)+x_{\rm rad}\}\,. \quad (1)$$

Here α is the fine structure constant, Z is the nuclear charge, m is the electron mass, m_p is the proton mass, μ is the nuclear magnetic moment, μ_N is the nuclear magneton, I is the nuclear spin, and M is the nuclear mass. $A(\alpha Z)$ denotes the relativistic factor [2]

$$A(\alpha Z) = \frac{1}{\gamma(2\gamma-1)} = 1+\frac{3}{2}(\alpha Z)^2+\frac{17}{8}(\alpha Z)^4+\cdots\,, \quad (2)$$

where $\gamma = \sqrt{1-(\alpha Z)^2}$. δ is the nuclear charge distribution correction, ε is the nuclear magnetization distribution correction (the Bohr-Weisskopf correction) [3–5]. $x_{\rm rad}$ denotes the radiative correction which in the lowest orders in α and αZ is [6–8]

$$\begin{aligned} x_{\rm rad} = {} & \frac{\alpha}{2\pi} - 0.328\frac{\alpha^2}{\pi^2} + \left(\ln 2 - \frac{5}{2}\right)\alpha(\alpha Z) \\ & -\frac{8}{3\pi}\ln^2\left(\frac{1}{\alpha Z}\right)\alpha(\alpha Z)^2 \\ & +\frac{2}{\pi}\left(\frac{37}{72}+\frac{4}{15}-\frac{8}{3}\ln 2\right)\ln\left(\frac{1}{\alpha Z}\right)\alpha(\alpha Z)^2 \\ & +(4.90\pm 0.09)\alpha(\alpha Z)^2\,. \end{aligned} \quad (3)$$

The correction δ is found from Table I of [9] by interpolation. For the ions with the half-integer nuclear spin the correction ε, considered within the single-particle model

TABLE I. The wavelengths λ (cm) of the transition between the hyperfine structure components of the ground state of the hydrogenlike ions.

Ion	I^π	$\frac{\mu}{\mu_N}$	$A(\alpha Z)$	δ	ε	$x_{\rm rad}$	λ (cm)
$^{13}C^{5+}$	$\frac{1}{2}-$	0.702 412(1)	1.002 88	0.000 55	0.000 36	0.000 50	0.387 40(8)
$^{14}N^{6+}$	$1+$	0.403 761	1.003 93	0.000 67	-0.000 04	0.000 40	0.565 19(11)
$^{17}O^{7+}$	$\frac{5}{2}+$	-1.8938(1)	1.005 14	0.000 82	0.000 33	0.000 29	0.100 85(2)

TABLE II. The wavelengths λ (cm) of the transition between the hyperfine structure components of the ground state of the lithiumlike ions.

Ion	I^π	$\frac{\mu}{\mu_N}$	$A(\alpha Z)$	$\frac{B(\alpha Z)}{Z}$	$\frac{R(Z,0)}{Z^2}$	δ	ε	$\Delta_{\rm rad}$	λ (cm)
$^{14}N^{4+}$	1+	0.403 76	1.005 57	-0.381 71	0.018 00	0.000 67	-0.000 04	0.000 42	7.072(4)
$^{19}F^{6+}$	$\frac{1}{2}$+	2.628 9	1.009 23	-0.298 08	0.010 90	0.000 99	0.000 36	0.000 22	0.341 02(20)
$^{23}Na^{8+}$	$\frac{3}{2}$+	2.217 6(1)[a]	1.013 84	-0.245 11	0.007 11	0.001 25	0.000 35	0.000 02	0.309 24(19)
$^{25}Mg^{9+}$	$\frac{5}{2}$+	-0.855 45(8)	1.016 50	-0.225 33	0.006 18	0.001 42	0.000 58	-0.000 07	0.667 9(4)
$^{27}Al^{10+}$	$\frac{5}{2}$+	3.641 5	1.019 41	-0.208 65	0.005 24	0.001 55	0.000 48	-0.000 16	0.120 60(7)
$^{29}Si^{11+}$	$\frac{1}{2}$+	-0.555 29(3)	1.022 57	-0.194 41	0.004 44	0.001 72	0.000 63	-0.000 25	0.372 50(22)
$^{35}Cl^{14+}$	$\frac{3}{2}$+	0.821 87	1.033 55	-0.162 00	0.002 98	0.002 32	-0.000 26	-0.000 49	0.200 73(12)
$^{57}Fe^{23+}$	$\frac{1}{2}$−	0.090 623	1.081 30	-0.111 33	0.001 28	0.004 52	0.002 8	-0.001 06	0.307 2(5)
		0.090 764							0.306 8(5)
		0.090 44(7)							0.307 9(5)

[a]An average of the values given in [10] is used.

of the nucleus with taking account of the angular asymmetry of the spin distribution, is also calculated by using the analytical formulas and the related table from [9].

In the case of $^{14}N^{6+}$, where $I = 1$, we assume that the total nuclear moment is possessed by the odd neutron and proton. Using the formulas from [5] we find in this case

$$\varepsilon = \varepsilon_n + \varepsilon_p\,, \tag{4}$$

$$\varepsilon_n = \frac{1}{g_I}\left[-\frac{1}{6}g_s^{(n)}\langle K_S\rangle_n + \frac{1}{3}g_s^{(n)}(\langle K_L\rangle_n - \langle K_S\rangle_n)\right], \tag{5}$$

$$\varepsilon_p = \frac{1}{g_I}\left[-\frac{1}{6}g_s^{(p)}\langle K_S\rangle_p + \frac{2}{3}g_l^{(p)}\langle K_L\rangle_p + \frac{1}{3}g_s^{(p)}(\langle K_L\rangle_p - \langle K_S\rangle_p)\right], \tag{6}$$

where $g_I = \frac{\mu}{\mu_N I}$ is the nuclear gyromagnetic ratio, $g^{(n)}$ and $g^{(p)}$ are the neutron and proton gyromagnetic ratios ($g_l^{(n)} = 0$, $g_l^{(p)} = 1$). The values $\langle K_S\rangle_{n(p)}$ and $\langle K_L\rangle_{n(p)}$ are defined by

$$\langle K_S\rangle_{n(p)} = \int_0^\infty K_S(R)|u_{n(p)}(R)|^2R^2\,dR\,, \tag{7}$$

$$\langle K_L\rangle_{n(p)} = \int_0^\infty K_L(R)|u_{n(p)}(R)|^2R^2\,dR\,, \tag{8}$$

$$K_S(R) = \frac{\int_0^R fg\,dr}{\int_0^\infty fg\,dr}\,, \tag{9}$$

$$K_L(R) = \frac{\int_0^R\left(1-\frac{r^3}{R^3}\right)fg\,dr}{\int_0^\infty fg\,dr}\,, \tag{10}$$

where g and f are the radial parts of the Dirac wave function of the electron; $u_n(R)$ and $u_p(R)$ are the radial parts of the wave functions of the odd neutron and proton, respectively. The value $g_s^{(n)}$ is evaluated from the equation

$$g = \frac{\langle \mathbf{S}\cdot\mathbf{I}\rangle}{I(I+1)}g_s + \frac{\langle \mathbf{L}\cdot\mathbf{I}\rangle}{I(I+1)}g_l \tag{11}$$

using the experimental value of g for ^{13}C [10]. Thereby we assume that the addition of the odd proton does not affect on the state of the odd neutron. We obtain $g_s^{(n)} = -4.2145$. The value $g_s^{(p)}$ is obtained from the experimental value of g for ^{14}N by using the equation

$$g = \frac{\langle \mathbf{I}_n\cdot\mathbf{I}\rangle}{I(I+1)}g^{(n)} + \frac{\langle \mathbf{I}_p\cdot\mathbf{I}\rangle}{I(I+1)}g^{(p)}\,. \tag{12}$$

We find $g_s^{(p)} = 5.7919$. Using these values and the analytical formulas for $K_S(R)$ and $K_L(R)$ from [9] and assuming, for simplicity, that the radial part of the probability density of the odd nucleons is homogeneously distributed over the nucleus, we obtain $\varepsilon = -0.35\times10^{-4}$.

The wavelengths of the transition between the hyperfine structure components of the hydrogenlike ions are presented in Table I. The nuclear magnetic moments are taken from [10]. Because the single-particle model of the

TABLE III. The hyperfine structure constant A (MHz) divided by g of the ground state of $^{19}F^{6+}$ for the excited nuclear level ($I = \frac{5}{2}$+, $g = 1.44$).

Method	$\frac{A}{g}$ (MHz)
This work	167 22(10)
MBPT [14]	167 50(100)
MBPT [15][a]	168 85
Rel. MBPT [16]	166 45
Hylleraas [17][a]	167 71
Experiment [18]	169 00(350)

[a]The relativistic correction (0.9%) from Ref. [14] has been added.

TABLE IV. The Fermi contact term a_c of the ground state of lithiumlike atoms.

Atom	a_c (HF)	a_c (UHF)	a_c (CI-HF)
Li	2.0932	2.8235	2.9034
N^{4+}	99.429	109.097	109.522
Ft^{6+}	243.075	260.358	260.917
Na^{8+}	482.008	509.000	509.564
Mg^{9+}	644.705	677.339	678.131
Al^{10+}	840.222	879.023	879.851
Si^{11+}	1071.56	1117.05	1117.84
Cl^{14+}	2010.49	2079.20	2080.07
Fe^{23+}	7733.53	7900.26	7901.64

nucleus is too rough for the ions with $A < 20$ (A is the number of the nucleons) [11], we assume that the uncertainty of the wavelengths is about 0.02% for all the ions listed in the table.

III. LITHIUMLIKE IONS

The hyperfine splitting of the ground state of lithiumlike ions in the range Z =7–26 is conveniently represented in the form

$$\Delta E_\mu = \frac{1}{6}\alpha(\alpha Z)^3 \frac{m}{m_p}\frac{\mu}{\mu_N}\frac{2I+1}{2I}\frac{1}{(1+\frac{m}{M})^3}mc^2 \times\Big\{A(\alpha Z)+\frac{1}{Z}B(\alpha Z)+\frac{1}{Z^2}R(Z,\alpha Z)\Big\} \times(1-\delta)(1-\varepsilon)(1+\Delta_{\rm rad})\,. \quad (13)$$

Here $A(\alpha Z)$ is the one-electron relativistic factor [2]

$$A(\alpha Z) = \frac{2[2(1+\gamma)+\sqrt{2(1+\gamma)}]}{(1+\gamma)^2\gamma(4\gamma^2-1)} = 1+\frac{17}{8}(\alpha Z)^2+\frac{449}{128}(\alpha Z)^4+\cdots\,. \quad (14)$$

The term $\frac{1}{Z}B(\alpha Z)$ denotes the $\frac{1}{Z}$ interelectronic interaction contribution calculated in [12, 13]. In the lowest orders in αZ the function $B(\alpha Z)$ is given by

$$B(\alpha Z) = -2.6557 - 6.2138(\alpha Z)^2. \quad (15)$$

In αZ the exact values of $B(\alpha Z)$ are listed in [13]. The term $\frac{1}{Z^2}R(Z,\alpha Z)$ is the interelectronic interaction contribution with the $\frac{1}{Z}$ term subtracted. We evaluate this term in the nonrelativistic approximation by subtracting the nonrelativistic limit of the first two terms in the curly brackets of (13) from the total nonrelativistic contribution calculated by the configuration interaction Hartree-Fock (CI-HF) method:

$$\frac{1}{Z^2}R(Z,0) = \Big\{\cdots\Big\}_{\rm nr} - \Big(1-\frac{2.6557}{Z}\Big). \quad (16)$$

The CI-HF calculation is discussed in detail in the next section of the paper. The nuclear corrections δ and ε are calculated with relative error $\sim \frac{1}{Z}$ by the same formulas as for hydrogenlike atoms (see [9] and the preceding section of the present paper). The radiative correction, with relative error $\sim \alpha$, is determined by the one-electron contribution which in the lowest orders in αZ is equal to [6–8]

$$\Delta_{\rm rad} = \frac{\alpha}{2\pi}+\Big(\ln 2-\frac{5}{2}\Big)\alpha(\alpha Z)-\frac{8}{3\pi}\ln^2\Big(\frac{1}{\alpha Z}\Big)\alpha(\alpha Z)^2 +\frac{2}{\pi}\Big(-\frac{16}{3}\ln 2+\frac{37}{72}+\frac{4}{15}+\frac{7}{2}\Big)\ln\Big(\frac{1}{\alpha Z}\Big)\alpha(\alpha Z)^2 +(3.12\pm 0.09)\alpha(\alpha Z)^2-\frac{1}{2\pi}\frac{17}{8}\alpha(\alpha Z)^2\,. \quad (17)$$

Here we add the last term to cancel the contribution arising from the relativistic correction $\frac{17}{8}(\alpha Z)^2$ multiplied by $\frac{\alpha}{2\pi}$.

The wavelengths of the transition between the hyperfine structure components, calculated by the formula (13), are presented in Table II. For the ions in the range $Z = 7-17$ the uncertainty of the hyperfine splitting values, due to errors in the calculations of ε, δ, $\frac{1}{Z^2}R(Z,0)$, and an uncertainty of the uncalculated terms ($\sim \alpha^2$), is about 0.06%. In the case of $^{57}Fe^{23+}$ we suppose that the uncertainty of λ, caused mainly by an error in the calculation of ε, is about 0.15%. In Table III we compare our value of the ground-state hyperfine structure constant $[A = \Delta E_\mu/(I+\frac{1}{2})]$ divided by g for the excited nuclear level of $^{19}F^{6+}$ ($I = \frac{5}{2}+$, $g = 1.44$, $\varepsilon = 0.000\,30$) with the values obtained with other methods [14–17] and with experiment [18].

IV. CI-HF CALCULATIONS AND THE HYPERFINE STRUCTURE OF Li

We consider now the procedure of calculating the total nonrelativistic contribution to the hyperfine structure. As is known, the hyperfine splitting of the ground state of the lithiumlike atom in the nonrelativistic approximation is defined as the expectation value of the Fermi contact operator

$$H_\mu = \frac{16\pi}{3}\mu_B\boldsymbol{\mu}\cdot\sum_{i=1}^{3}\mathbf{s}_i\delta(\mathbf{r}_i)\,, \quad (18)$$

where μ_B is the Bohr magneton, μ is the nuclear magnetic moment, $\mathbf{s}$ is the spin operator. The hyperfine splitting value is often characterized by the Fermi contact term a_c which is related with the hyperfine structure constant A by

$$A = \frac{4}{3}(\mu_B\mu_N g/a_0^3)a_c\,, \quad (19)$$

where a_0 is the Bohr radius. In order to calculate the Fermi contact term we used the configuration interaction (CI) Hartree-Fock method. The wave function for the ground state of lithiumlike atoms, la-

TABLE V. The Fermi contact term a_c of the ground state of lithiumlike atoms for equivalent CI-HF and CI-HFD calculations. In the CI-HFD calculations the homogeneously charged sphere model of the nucleus and the pointlike nuclear moment have been used.

Atom	a_c (CI-HF)	a_c (CI-HFD–point nuc.)	a_c (CI-HFD–fin.nuc.)	a_c (CI-HFD–fin.nuc.)/a_c (CI-HF)
Li	2.891 265	2.893 803	2.893 039	1.000 614
Mg^{9+}	678.1351	688.9414	687.9594	1.014 487
Fe^{23+}	7902.174	8533.119	8494.340	1.074 937

beled as γLS, is expanded in terms of Slater determinants $\Psi(\gamma LS) = \sum_j C_j S_j^{\rm det}$. The Slater determinants were constructed from the basis of one-electron orbitals $\varphi_a(r) = R_a(r)Y_{l_a m_a}(\theta,\varphi)\chi_{m_s}$. For the occupied one-electron $1s$ and $2s$ states we used the convenient HF functions. In order to generate the virtual orbitals for the excited states we used the following procedure. We constructed Sturm-like basis radial functions R_a by multiplying the nodeless R_{1s} function on the simple function $r^{n-1}\exp(-\alpha_{nl}r)$ and then orthogonalized them to each other by means of the Shmidt orthogonalization method. The parameters α_{nl} were fitted to minimize the energy of the lithium ($Z = 3$) ground state and then were extrapolated to another values of Z. The virtual functions $R_a(r)$ give the expectation values of r ($\langle r\rangle_a$) close to the value $\langle r\rangle_{1s}$, while the $\langle r\rangle_a$ for the standard Hartree-Fock orbitals for the excited states strongly increases with the enlarging of quantum number n. This fact leads to the poor convergence when one uses standard Hartree-Fock orbitals. Moreover it is well known that the complete basis set of the Fock operator has to contain the continuous spectrum functions. So, the discrete Sturm-like basis set is more convenient in our case. After the generation of the basis set the standard CI procedure was used. In the active set all the orbitals ns ($n \le 19$), np ($n \le 12$), nd ($n \le 8$), nf ($n \le 6$), and ng ($n \le 5$) were included. All possible configuration states of a proper parity were generated from the active basis set. In Table IV we present the results of CI calculations for the Fermi contact term a_c. In order to estimate the spin polarization and correlation effects we calculated a_c by one-configuration Hartree-Fock (HF) and unrestricted-Hartree-Fock (UHF) methods too. The results are given in the same table. The relativistic and finite nuclear size effects have to be taken into account when we want to receive the data with high accuracy. To this end we calculated the constant a_c by the CI-Hartree-Fock-Dirac (CI-HFD) method with finite nuclear charge size using the relativistic Fermi-Breit expression for the hyperfine interaction [2]. For the small active basis set ns ($n \le 13$), np ($n \le 7$), nd ($n \le 6$) we calculated the value a_c for Li, Mg^{9+}, and Fe^{23+} and compared the obtained data with the results of the nonrelativistic CI-HF calculations with the same basis set (see Table V). In the case of Li the relativistic and finite-nuclear-charge-size correction,

$$\frac{\Delta E_\mu(\text{CI-HFD–fin.nuc.})}{\Delta E_\mu(\text{CI-HF})} = 1.000\,61\,,$$

is to be compared with the related correction, 1.000 53, found in [19] by using a smaller active basis set. For Mg^{9+} and Fe^{23+} these corrections are in good agreement with the corresponding corrections calculated by the $1/Z$ perturbation theory. So, for Mg^{9+} the value

$$\frac{\Delta E_\mu(\text{CI-HFD-fin.nuc.})}{\Delta E_\mu(\text{CI-HF})} = 1.014\,49$$

can be compared with

$$\frac{A(\alpha Z) + \frac{B(\alpha Z)}{Z}}{1+\frac{b_0}{Z}}(1-\delta) = 1.014\,58$$

found from Table II.

TABLE VI. The hyperfine structure constant A (MHz) for the ground state of Li [$\mu = 3.256\,426\,8(17)\mu_N$ [10]].

Method	A (MHz)
CI-HF (this work)	401.5(4)
MCHF [19]	401.71
Finite-element MCHF [20][a]	401.60
MBPT [21][a]	403.53
MBPT [22]	400.90
Rel. MBPT [23]	402.47
Hylleraas [17][a]	401.94
CI-spin-density convergence [24][a]	402.24
Experiment [25]	401.75

[a]Calculated in [19] from published values of the hyperfine structure parameters.

Let us find the hyperfine structure constant for Li taking into account the relativistic, radiative, and nuclear corrections. Using the QED corrected magnetic moment of electron $\frac{\mu_e}{\mu_B} = 1.011\,596\,6$ gives a main (exact in the lowest order in α) part of the radiative correction. The relativistic and nuclear charge distribution corrections are defined from Table V. The "reduced electron mass" correction is found by multiplying the hyperfine structure constant with the factor $(1+m/M)^{-3}$. In such a calculation the radiative (except the anomal magnetic moment correction) and nuclear magnetization distribution corrections as well as the mass-polarization correction are omitted. We estimate that the total uncertainty, including the uncertainty of the omitted terms, is about 0.1% of the hyperfine splitting value. In Table VI we compare our value of the hyperfine structure constant A (MHz) for the ground state of Li with calculations of other authors and with experiment. We find that our result, $A = 401.5(4)$ MHz, is in good agreement with the most precise theoretical values obtained with other methods and with experiment.

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