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Effects of electron correlation, relativity, and nuclear structure on hyperfine constants of Be$^+$ and F^{6+}

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The hyperfine constants for the ground states of Be$^+$ and F^{6+}, and for the two lowest excited states of Be$^+$, are calculated in a multiconfiguration Dirac-Fock model. Convergence of the calculated magnetic dipole constants is studied as the active set of orbitals is systematically increased. The final results are compared with experimental data and theoretical values obtained from other methods. [S1050-2947(99)03910-4]

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I. INTRODUCTION

The lithiumlike systems are the simplest species in which the Pauli exclusion principle forces the electronic wave function to form two (or more) space-separated electronic shells. This feature makes lithium and its isoelectronic ions a natural testbed for atomic many-body theories, since in very accurate calculations the electron correlation effects have to be evaluated both for the outer (valence) electron as well as within the inner (core) shell itself. Recently, the hyperfine constants of several states of neutral lithium and singly ionized beryllium have been calculated very accurately both variationally [1–4], as well as perturbatively [5]. There is also a growing interest in studying hyperfine structures of heavy lithiumlike ions, which is partially fueled by the development of atomic traps [6] and storage rings [7], where even the heaviest elements can be stripped down to virtually any ionization stage [8]. The principal aims of the study of the hyperfine structures of highly ionized heavy elements are to probe QED effects in strong magnetic fields [9] and to investigate the charge and magnetization distribution inside the nucleus [10–13]. The insight into the structure of nuclei is also important in the search for the nuclear anapole moment [14] and for the permanent electric dipole moment [13,15].

Calculations involving high-Z species must account properly for the direct and indirect effects of relativity [16] and a four-component description becomes necessary, particularly for calculations of those atomic properties, which depend strongly on the behavior of the wave function in the proximity of the nucleus. If inner-shell electrons are involved directly in the atomic process, the nuclear structure effects become important, and eventually, with the increase of the atomic number Z, self-energy, vacuum polarization, and higher-order QED effects [12] come into play [17].

The objective of the present paper is to extend the tests of the new version [18–20] of the multiconfiguration Dirac-Fock (MCDF) package GRASP [21–23] to all experimentally known hyperfine constants of low-Z lithiumlike species, as well as to complement Dirac-Fock calculations of hyperfine structures in the vicinity of the neutral end of the lithium isoelectronic sequence, where electron correlation effects dominate the corrections to the single-particle model.

The hyperfine constant A for the $2s\ ^2S_{1/2}$ state of $^9_4\mathrm{Be}^+$ has been measured very accurately with the use of laser-fluorescence spectroscopy by Wineland, Bolinger, and Itano [24] with the relative accuracy of better than 3 ppm. The experimental value for the diagonal hyperfine coupling constant A for the $2p\ ^2P_{1/2}$ state of $^9_4\mathrm{Be}^+$ has been measured [25] much less accurately, to about 3%, while for the $2p\ ^2P_{3/2}$ state there exists [26] only an upper limit.

II. THEORY

The theoretical approach employed is sketched briefly below. Details can be found elsewhere [27–30] in the literature. Except where noted, atomic units are used throughout this paper.

A. MCDF

In the MCDF method [28], the relativistic atomic state function Ψ for a state labeled ΓPJM is represented as a sum of symmetry-adapted configuration state functions (CSF)

$$\Psi(\Gamma PJM)=\sum_r c_r \Phi(\gamma_r PJM). \tag{1}$$

Configuration mixing coefficients c_r are obtained through diagonalization of the Dirac Coulomb Hamiltonian

$$H_{DC}=\sum_i c\boldsymbol{\alpha}_i\cdot\boldsymbol{p}_i+(\beta_i-1)c^2-Z/r_i+\sum_{i>j}1/r_{ij}. \tag{2}$$

Configuration state functions Φ, which are eigenfunctions of J^2, J_z, and parity P, are constructed as linear combinations of Slater determinants. In the restricted Dirac-Fock model a Slater determinant is a product of one-electron Dirac orbitals

$$|n\kappa m\rangle = \frac{1}{r}\begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\hat{r}) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\hat{r}) \end{pmatrix}, \tag{3}$$

where n is the principal quantum number, and κ and m are the relativistic angular quantum number and its z component, respectively; $\kappa = \pm(j+1/2)$ for $l = j \pm 1/2$, with l and j being the orbital and total angular momenta of the electron. $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small component one-electron radial wave functions, and $\chi_{\kappa m}(\hat{r})$ is the spinor spherical harmonic in the lsj coupling scheme

$$\chi_{\kappa m}(\hat{r}) = \chi_{\kappa m}(\theta,\varphi,\sigma)$$
$$= \sum_{m_s} \langle l m - m_s \tfrac{1}{2} m_s | l \tfrac{1}{2} j m \rangle Y_{l m - m_s}(\theta,\varphi)\xi_{m_s}(\sigma). \tag{4}$$

The radial functions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are obtained as a self-consistent-field solution of the one-electron Dirac-Fock equation [28].

B. Hyperfine interaction

The hyperfine structure of atomic energy levels (hereafter abbreviated as hfs) is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus. In accurate calculations of hyperfine structures it is necessary to take relativistic effects into account even for relatively light elements [33,34]. The effects of relativity scale as the square of the atomic number Z and can usually be treated as perturbations for light elements. These effects become important with increasing atomic number, and, at some point, it becomes necessary to employ a fully relativistic approach if accurate results are to be expected [35]. This necessity is more pronounced in calculations of hyperfine structures than other atomic properties, because the hyperfine interaction is sensitive to the form of the calculated electronic wave functions close to the nucleus, where direct and indirect effects of relativity [16] are difficult to account for by quasirelativistic methods.

The hyperfine contribution to the Hamiltonian can be represented by a multipole expansion

$$H_{\mathrm{hfs}} = \sum_{k \geq 1} \mathbf{T}^{(k)} \cdot \mathbf{M}^{(k)}, \tag{5}$$

where $\mathbf{T}^{(k)}$ and $\mathbf{M}^{(k)}$ are spherical tensor operators of rank k in the electronic and nuclear space, respectively [36]. The $k=1$ term represents the magnetic dipole interaction and the $k=2$ term the electric quadrupole interaction.

The electronic tensor operators are sums of one-particle tensor operators

$$\mathbf{T}^{(k)} = \sum_{j=1}^{N} \mathbf{t}^{(k)}(j), \quad k=1,2. \tag{6}$$

The magnetic dipole operator $\mathbf{t}^{(1)}$ in the nonrelativistic framework takes the form [36]

$$\mathbf{t}^{(1)} = \frac{\alpha^2}{2}\sum_{i=1}^{N} \{2\mathbf{l}^{(1)}(i) r_i^{-3} + g_s \tfrac{8}{3}\pi\delta(\mathbf{r}_i)\mathbf{s}^{(1)}(i)$$
$$- g_s\sqrt{10}[\mathbf{C}^{(2)}(i)\times\mathbf{s}^{(1)}(i)]^{(1)} r_i^{-3}\}. \tag{7}$$

The three terms in Eq. (7) are usually called *orbital*, *Fermi-contact*, and *spin-dipole* terms, respectively. The magnetic dipole operator $\mathbf{t}^{(1)}$ in the relativistic framework takes the form [36]

$$\mathbf{t}^{(1)} = -i\alpha\sum_{i=1}^{N} \boldsymbol{\alpha}(i)\cdot\mathbf{l}(i) \;\; \mathbf{C}^{(1)}(i) r^{-2}(i), \tag{8}$$

while the electric quadrupole term has the form

$$\mathbf{t}^{(2)} = -\sum_{i=1}^{N} \mathbf{C}^{(2)}(i) r^{-3}(i). \tag{9}$$

In the formulas above α is the fine-structure constant, $\boldsymbol{\alpha}$ is the vector of the three Dirac matrices, and $\mathbf{C}^{(k)}$ is a spherical tensor with the components related to the spherical harmonics as

$$C_q^{(k)} = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_{kq}. \tag{10}$$

The reader is referred to our previous papers [30,23] for the evaluation of the matrix elements of the hyperfine interaction in the framework of symmetry-adapted configuration state functions.

C. Method of calculation

The configuration expansions were obtained with the active space method in which configuration state functions of a particular parity and symmetry are generated by substitutions from a reference configuration to an active set of orbitals. The active set is then increased systematically until the convergence of the hyperfine constant is obtained. The generation of the wave functions followed essentially the scheme described in our previous papers [31,32]. First, the spectroscopic orbitals required to form a reference wave function were obtained in a single configuration calculation, with full relaxation. All virtual orbitals were generated in several consecutive steps. At each step the virtual space has been extended by one layer of virtual orbitals, corresponding to one line in Tables I, III, V, and VIII, with all previous configuration expansions included, with all previously generated orbitals included, and all new orbitals made orthogonal to others of the same symmetry. The starting shapes of all radial orbitals have been obtained in the Thomas-Fermi potential, and then optimized to the accuracy of the order of 10^{-8}, with full relaxation. The optimal level form of the variational expression [22] has been applied in all variational calculations. For smaller orbital sets employed in this study, the complete active space method was employed, in which all electrons are subject to substitutions within a particular active set. For larger orbital sets the complete active space becomes prohibitively expensive and certain limitations were needed to keep the number of configuration state functions below the limit acceptable by the computer memory constraints. This

TABLE I. Diagonal magnetic dipole hyperfine structure parameter A (in MHz) for the $1s^22s\ ^2S_{1/2}$ state of $^9_4\mathrm{Be}^+$, as the function of orbital set. SDT means single, double, and triple substitutions from the reference $1s^22s$ configuration. Column 2 gives the number of configurations. Notation $3s2p1d$ in the third column means expansions formed by substitutions from reference configurations to virtual space constructed from three orbitals of the s symmetry, two orbitals of the p symmetry, and one orbital of the d symmetry.

Type	NCF	Orbital set	A
(DF)	1	$2s$	-507.782
SDT	8	$2s1p$	-505.293
SDT	79	$3s2p1d$	-623.215
SDT	410	$4s3p2d1f$	-615.034
SDT	1463	$5s4p3d2f1g$	-626.173
SDT	3710	$6s5p4d3f2g$	-622.044
SD	3975	$7s6p5d4f3g$	-625.159
SD	3227	$8s7p6d5f3g$	-624.038
SD	3588	$9s8p7d6f3g$	-624.805
SD	4585	$12s11p9d6f3g$	-624.487
SD	4288	$13s12p9d6f3g$	-624.605
SD	4488	$14s12p9d6f3g$	-624.496
SD	4716	$15s12p9d6f3g$	-624.757
SD	4974	$16s12p9d6f3g$	-624.569
SD	5264	$17s12p9d6f3g$	-624.603
SD	5588	$18s12p9d6f3g$	-624.600
CI	7017	$18s12p9d6f3g$	0.032(32)
Bohr-Weisskopf			0.252(76)
Nuclear recoil			0.114
Breit			-0.069(7)
$g_s/2$			-0.7243
Neglected high-l orbitals			-0.045(6)
Total			-625.04(8)
MBPT[a]			-625.63(9)
Hylleraas[b]			-625.022(60)
FCPC[c]			-624.51[d]
Experiment[e]			-625.008837048(10)

[a] Reference [5].

[b] Reference [4].

[c] Reference [53].

[d] Not corrected for nuclear size and relativistic effects.

[e] Reference [24].

was accomplished by (1) restricting the electron substitutions to single and double for the orbitals with high values of principal quantum number and by (2) excluding CSF's with weights smaller than a certain threshold value. The effects of these restrictions were later evaluated by separate configuration interaction calculations. The actual sets employed are presented in Tables I, III, V, and VIII. All single, double, and triple substitutions have been allowed to all orbitals with principal quantum numbers $n=2,3,4,5$. For $n=6$ only s,p,d,f,g symmetries have been permitted; the h and higher symmetries have been excluded. Starting with $n=7$ only single and double substitutions have been permitted and the set of orbital symmetries has been systematically decreased until there were only s orbitals $(14s,15s, \ldots)$ added to the list. The single, double, and triple (SDT) substitutions to $6s5p4d3f2g$ orbital sets were carried over to all subsequent larger orbital sets.

III. RESULTS

The value of the nuclear magnetic dipole moment of $^9_4\mathrm{Be}$ has been adopted from the paper by Itano [37] and that of $^{19}_{9}\mathrm{F}$ from the tables of Raghavan [38]. The nuclear electric quadrupole moment of $^9_4\mathrm{Be}$ has been taken from the paper by Sundholm and Olsen [39]. Conversion from atomic units to MHz used the factor of 1 a.u.=6 579 683 900 MHz.

A. $2s\ ^2S_{1/2}$ state of Be^+

Table I presents the magnetic dipole constant A for the ground state of Be^+ as a function of configuration space expansion. It shows that 18 energy-optimized layers of orbitals were required to converge the A value. As discussed in Sec. II C, the computational resources at our disposal did not allow us to include all configuration state functions arising from the orbital sets and substitutions presented in Table I.

TABLE II. The effect of the Breit interaction on the calculated diagonal magnetic dipole hyperfine structure parameter A (in MHz) for the $1s^2 2s\ ^2S_{1/2}$ state of $^9_4\mathrm{Be}^+$. Column 2 gives the number of configurations which survived the condensing procedure for five different values of threshold.

Threshold	NCF	MCDF	MCDF+Breit	Correction	Factor
0.01	1	-371.903	-371.903	0.0	1.0
0.001	32	-604.560	-604.758	-0.20	1.000 33
0.0001	197	-593.932	-594.134	-0.20	1.000 34
0.000 01	793	-624.324	-624.411	-0.09	1.000 14
0.000 001	1887	-624.579	-624.653	-0.07	1.000 12
		extrapolated			1.000 11

To overcome this limitation, we have employed a condensing procedure, similar to that described in our previous paper [3]. It eliminates those configuration state functions, whose contribution to the wave function was less than a specified threshold value. As the next step, the configuration-interaction (CI) calculation has been performed, to evaluate the effect of the configurations, which had been excluded from the CSF lists due to condensing or restrictions imposed on the allowed substitutions. The CI entry in Table I has been obtained by a configuration interaction calculation, where (1) all single, double, and triple substitutions to the set $1s,2s,2p,\ldots,6s,6p,6d,7s,8s,\ldots,17s,18s$ were allowed and (2) all single and double substitutions to the full active set were allowed (no condensing). A reliable assessment of the uncertainty of the calculated A value arising from all limitations imposed on the configuration lists within the virtual orbital set employed in this study, would constitute a very expensive task. An attempt in this direction has been made in the case of neutral lithium [3]. For the purpose of the present study we employed the conservative estimate taken as the difference between the CI value and the value of A calculated with the largest configuration state list (the line above CI entry in Table I). By comparison with the calculations for neutral lithium [3], it can be argued that this estimate certainly exceeds the errors arising from the above-mentioned limitations, as well as from the numerical precision of the Dirac-Fock code, convergence criteria, and other numerical properties associated with the self-consistent-field procedure. The contributions from the orbitals beyond this set can be estimated by an extrapolation procedure, which will be discussed in Sec. III A 4. After the above two corrections have been included, we arrive at the level of approximation, which might be called MCDF limit, bearing in mind, that this concept is somewhat more fuzzy than its nonrelativistic counterpart, and perhaps a ‘‘no-pair’’ MCDF limit would be a better description. There are several small effects beyond the so defined MCDF model, which have to be accounted for before a comparison with experiment can be made. These effects include finite nuclear size, finite nuclear mass, Breit interaction, and QED corrections.

1. Bohr-Weisskopf correction

The magnetization distribution inside the nucleus due to nuclear structure (Bohr-Weisskopf correction [10]) is the dominant source of uncertainty in the present calculations. Bohr and Weisskopf estimated that this effect would lower the A value of the hfs of the $2s\ ^2S_{1/2}$ state by about 0.01% in the extreme situation where spin and orbital nuclear magnetic moments are aligned [10]. The effect increases with Z approximately as $Z^{4/3}$ and certainly would have to be considered for heavy nuclei [9,10,40].

We employed the modified approach of Zemach [41], who evaluated the multiplicative correction factor arising from the magnetization distribution. The correction depends on the model chosen for a particular nucleus, particularly for heavy nuclei. For one-electron systems the correction reads

$$C_{BW}=1-2Z\langle r\rangle_m/a_0, \tag{11}$$

where $\langle r\rangle_m$ is the effective radius of the magnetization distribution within the nucleus. The value $\langle r\rangle_m=2.67$ fm has been taken as an average of several results quoted in the tables of de Jager, de Vries, and de Vries [42]. Shabaev [11] argues, that for the single-particle model of the nucleus, the above formula can change as much as 30%, depending on the shape of the radial part of the probability density of the odd nucleon. If the asymmetry of the nucleus is taken into account, the change of C_{BW} can be considerably larger, by a factor of 3 [11]; but it is normally a property of heavy nuclei, so the above-mentioned 30% deviation should constitute a reasonable estimate of the uncertainty associated with the Bohr-Weisskopf correction. Several other approaches to this problem have been proposed [11–13,17,40,43–45], but all of them require the knowledge of the magnetization distribution within the nucleus, which not only is generally unknown, but can differ from the electric charge distribution [13], which renders all calculations based on phenomenological models prone to large uncertainties.

2. Breit interaction correction

The Breit contribution is very difficult to evaluate in the direct calculation, even as a perturbation, due to the extremely high CPU cost. The effect of the Breit interaction on the calculated hfs constants has been estimated from a series of CI calculations performed with the full orbital set but condensed down to a small number of CSF’s. The Breit interaction has been treated as a perturbation to the Coulomb Hamiltonian. The effect on the calculated hfs value is presented in Table II as a function of the size of the CI expansion. It has to be mentioned here that the condensing procedure is based on Coulomb-only Hamiltonian matrix. Since angular properties of the Breit operator are different than those of the Coulomb energy operator, it is important that the CI expansion arising from the condensing described above is sufficiently large to include all important contributions. As can be seen in Table II the MCDF hfs value is almost fully

TABLE III. Diagonal magnetic dipole hyperfine structure parameter A (in MHz) for the $1s^22p\ {}^2P_{1/2}$ state of ${}^{9}_{4}\mathrm{B}^{+}$, as the function of the orbital set. SDT means single, double, and triple substitutions from the reference $1s^22p$ configuration. Column 2 gives the number of configurations. Notation $3s2p1d$ in the third column means expansions formed by substitutions from reference configurations to virtual space constructed from three orbitals of the s symmetry, two orbitals of the p symmetry, and one orbital of the d symmetry.

Type	NCF	Orbital set	A
(DF)	1	$1s1p$	-93.582
SDT	6	$2s1p$	-113.125
SDT	76	$3s2p1d$	-115.852
SDT	403	$4s3p2d1f$	-118.831
SDT	1454	$5s4p3d2f1g$	-117.932
SDT	3697	$6s5p4d3f2g$	-118.064
SD	4171	$7s6p5d4f3g$	-117.862
SD	4662	$8s7p6d5f3g$	-117.825
SD	5237	$9s8p7d6f3g$	-117.918
SD	5716	$10s9p8d6f3g$	-117.846
SD	6223	$11s10p9d6f3g$	-117.888
SD	6549	$12s11p9d6f3g$	-117.935
SD	4196	$13s12p9d6f3g$	-117.906
SD	4305	$14s12p9d6f3g$	-117.911
SD	4417	$15s12p9d6f3g$	-117.906
CI	7148	$15s12p9d6f3g$	-0.006(6)
Bohr-Weisskopf			0.048(30)
Nuclear recoil			0.022
Breit			0.008(4)
$g_s/2$			-0.080
Total			-117.91(3)
MBPT[a]			-117.94(1)
FCPC[b]			-117.25[c]
Experiment[d]			-118.6(36)

[a] Reference [5].

[b] Reference [53].

[c] Not corrected for nuclear size and relativistic effects.

[d] Reference [25].

recovered in the largest CI calculation and the Breit contribution has saturated. The resulting Breit correction has been obtained by employing the factor extrapolated from Table II.

3. Nuclear recoil correction

The nuclear motion correction can be determined by adding the normal mass shift and specific mass shift operators [46] to the Hamiltonian (2), evaluating the wave function in a a configuration-interaction calculation, and computing the hyperfine constants again, in a manner similar to that used for the Breit correction. The effect can also be evaluated by employing the mass scaling correction [47,48], i.e., by multiplying the A value by a factor

$$(1+m_e/M_{\mathrm{Be}})^{-3}=0.9\,998\,174. \tag{12}$$

Within the precision of the calculated value of A, even for a system as light as beryllium, both above-mentioned approaches yield identical results.

TABLE IV. The effect of the Breit interaction on the calculated diagonal magnetic dipole hyperfine structure parameter A (in MHz) for the $1s^22p\ {}^2P_{1/2}$ state of ${}^{9}_{4}\mathrm{Be}^{+}$. Column 2 gives the number of configurations which survived the condensing procedure for five different values of threshold.

Threshold	NCF	MCDF	MCDF+Breit	Correction	Factor
0.01	5	-94.579	-94.579	0.0	1.0
0.001	62	-125.468	-125.463	0.0059	0.999 953
0.000 1	416	-116.718	-116.714	0.0039	0.999 967
0.000 01	1414	-117.966	-117.962	0.0042	0.999 964
0.000 005	1946	-117.948	-117.939	0.0082	0.999 930

TABLE V. Diagonal magnetic dipole hyperfine structure parameter A and electric quadrupole parameter B (in MHz) for the $1s^22p\ ^2P_{3/2}$ state of $^9_4\mathrm{Be}^+$ as a function of the increasing active set of orbitals. SDT means single, double, and triple substitutions from the reference $1s^22p$ configuration. Notation $3s2p1d$ in the first column means expansions formed by substitutions from reference configurations to virtual space constructed from three orbitals of the s symmetry, two orbitals of the p symmetry, and one orbital of the d symmetry. Column 3 gives the number of configurations.

Orbital set	Type	NCF	$A_{3/2}$	$B_{3/2}$
$2s$	(DF)	1	-1.870 167	2.461 15
$2s1p$	SDT	8	0.770 225	2.466 79
$3s2p1d$	SDT	110	-0.532 098	2.279 42
$4s3p2d1f$	SDT	645	0.655 401	2.340 26
$5s4p3d2f1g$	SDT	2478	-1.142 384	2.517 67
$6s5p4d3f2g$	SDT	6439	-0.522 170	2.309 47
$7s6p5d4f3g$	SDT	4033	-1.105 021	2.495 94
$8s7p6d5f3g$	SD	4813	-0.903 526	2.356 73
$9s8p7d6f3g$	SD	4475	-1.065 163	2.441 19
$10s9p8d6f3g$	SD	4591	-0.993 753	2.390 96
$11s10p9d6f3g$	SD	4194	-0.973 272	2.432 31
$12s11p9d6f3g$	SD	4668	-0.962 516	2.432 29
$13s12p9d6f3g$	SD	4300	-0.973 616	2.432 32
$14s12p9d6f3g$	SD	4445	-0.963 934	2.432 32
$15s12p9d6f3g$	SD	4593	-0.969 628	2.432 32
$16s12p9d6f3g$	SD	4434	-0.967 444	2.432 32
$17s12p9d6f3g$	SD	4588	-0.968 772	2.432 32
CI		12047	-0.004(4)	0.0004(4)
Bohr-Weisskopf			0.0004(2)	
Nuclear recoil			0.000 18	-0.000 40
Breit			0.0005(7)	-0.0004(1)
$g_s/2$			-0.0068	
Total			-0.978(4)	2.4319(4)
MBPT[a]			-1.04(1)	
FCPC[b]				2.2890[c]
Experiment[d]			$\|A\|<0.6$	

[a] Reference [5].

[b] Reference [53].

[c] Not corrected for nuclear size and relativistic effects.

[d] Reference [26].

4. Neglected virtual orbitals

The effect of omitted orbitals on the calculated hfs constant was evaluated for neutral lithium by Tong *et al.* [1] by performing an l extrapolation. Since the correction arising from the extrapolation is very small and its dependence on relativistic effects is negligible, we assume that the l extrapolation in the relativistic framework would yield a similar value. The correction for Be^+ has been based on another assumption, which holds that the correction scales as Z^2 near the neutral end of the isoelectronic sequence [49]. An estimate of the accuracy of this correction can be obtained from the observation, that the ratio of the calculated hyperfine constants $A_{\mathrm{Be}^+}/A_{\mathrm{Li}}=625.04/401.75$ deviates from the scaling factor $Z^2_{\mathrm{Be}}/Z^2_{\mathrm{Li}}=16/9$ by about 15%. We have taken this deviation as an uncertainty associated with the l extrapolation.

5. QED

The only non-negligible QED correction arises from the anomalous magnetic moment of the electron, for which the factor $g_s/2=1.001\ 159\ 652\ 193$ has been used [50].

6. Summary of small corrections

The three largest corrections to the CI value arise from the QED effects, Bohr-Weisskopf correction, and the nuclear motion effects. The effects of the Breit interaction and of the neglected orbitals in the virtual space are about an order of magnitude smaller than the three leading corrections. The dominant source of uncertainty comes from the nuclear magnetization distribution. The final accuracy of the calculated A value is comparable to that achieved for neutral lithium [3], as can be expected, and the agreement with experiment indicates, likewise, that further progress depends primarily on advances in modeling the structure of nuclear electromagnetic moments.

B. $2p\ ^2P_{1/2}$ state of Be^+

Table III presents the calculated value of the hyperfine constant A for the $2p\ ^2P_{1/2}$ state, compared with other theoretical, as well as with the experimental results. The calculations for this level were done in a similar way as those for $^2S_{1/2}$. The configuration expansions were generated with the

TABLE VI. The effect of the Breit interaction on the calculated diagonal magnetic dipole hyperfine structure parameter A (in MHz) for the $1s^22p\ ^2P_{3/2}$ state of $^9_4\mathrm{Be}^+$. Column 2 gives the number of configurations which survived the condensing procedure for six different values of threshold.

Threshold	NCF	MCDF	MCDF+Breit	Correction	Factor
0.1	1	-18.701 667	-18.701 667	0.0	1.0
0.01	4	-19.083 849	-19.083 849	0.0	1.0
0.001	76	0.498 694	0.502 256	0.003 562	1.007 14
0.0001	524	-1.094 031 0	-1.093 932	0.000 099	0.999 909 8
0.000 01	1844	-1.049 600	-1.049 781	-0.000 181	1.000 172 4
0.000 003	3285	-0.909 699	-0.909 231	0.000 468	0.999 485 5

use of exactly the same scheme as described in Sec. III A. The Breit correction for the hyperfine constant A has been evaluated by scaling the mass-corrected A value by a Breit factor obtained in a procedure similar to that for the $^2S_{1/2}$ state. The Breit factor for the $^2P_{1/2}$ state was equal to 0.999 930. It had not converged very well (see Table IV), so we have not extrapolated it, but instead we have taken the difference between the last two values of the correction factor as the estimate of the error associated with the Breit correction. The nuclear motion corrections were estimated in the same way as before. The only QED correction employed for the $^2P_{1/2}$ state was the electron anomalous magnetic moment correction. The procedure for this correction differs from that used in the case of the $^2S_{1/2}$ state, because the hyperfine Hamiltonian for the p symmetry involves the *orbital* interaction between the magnetic moment generated by the *orbital* motion of the electronic cloud and the nucleus. In the nonrelativistic framework this corresponds to the *orbital* term in the hyperfine Hamiltonian (7). For these states for which there is a nonzero *orbital* term the QED correction is obtained by multiplying the *spin-dipolar* and *Fermi-contact* terms with a factor $g_s/2$, but not the *orbital* term. The relativistic hyperfine Hamiltonian (8) does not separate out the *orbital* term. Following the arguments employed for lithium [3], we have applied the $g_s/2$ correction calculated in the nonrelativistic framework. The nuclear magnetization distribution correction due to Zemach [41] has been derived for s states and in the case of other orbital symmetries the Bohr-Weisskopf effect for the *orbital* term in the hyperfine interaction Hamiltonian is obtained by replacing $1/r^2$ in Eq. (8) by r/R^3 inside the nucleus [40]. An exact determination of this effect depends on the radial shape of magnetization distribution of the nucleus, which is unknown. Therefore, we have neglected the spherical asymmetry of the *orbital* term but instead we have taken the entire *orbital* term contribution as uncertainty associated with the Bohr-Weisskopf effect. It is worth noting that our computed value of A is in good agreement with the result of the many-body perturbation theory (MBPT), and both are well within (relatively large) experimental uncertainty (see Table III).

C. 2p $^2P_{3/2}$ state of Be$^+$

Table V presents the calculated values of hyperfine constants A and B for the $2p\ ^2P_{3/2}$ state, compared with other theoretical, as well as with the experimental result. The MCDF calculations for the $^2P_{3/2}$ level were carried out in exactly the same manner as those for the $^2P_{1/2}$. The nuclear recoil and Breit corrections were estimated in the same way as before, and the multiplicative Breit factor for the magnetic dipole hyperfine constant A was equal to 0.999 485 5 (see Table VI), while that for the electric quadrupole constant B was equal to 0.999 828 (Table VII). In both cases the procedure for obtaining the Breit correction factor did not converge very well, particularly in the case of A constant, for which it oscillated around zero. Therefore, as in the case of the $^2P_{1/2}$ state, we have taken the difference between the last two values of the correction factor as the estimate of the error associated with the Breit correction. The QED correction for the hyperfine constant A for the $^2P_{3/2}$ state has been evaluated in the same manner as that for $^2P_{1/2}$, by employing the correction calculated in nonrelativistic formalism. Similarly, the nuclear magnetization correction has been evaluated by employing the Zemach [41] factor, with the *orbital* term contribution treated as uncertainty. Our calculated A value agrees reasonably well with the result of the MBPT theory, but both are outside the experimental upper limit.

D. 2s $^2S_{1/2}$ state of F^{+6}

Table VIII presents the calculated value of the hyperfine constant A for the $2s\ ^2S_{1/2}$ state of F^{+6}, compared with the

TABLE VII. The effect of the Breit interaction on the calculated diagonal electric quadrupole hyperfine structure parameter B (in MHz) for the $1s^22p\ ^2P_{3/2}$ state of $^9_4\mathrm{Be}^+$. Column 2 gives the number of configurations which survived the condensing procedure for four different values of threshold.

Threshold	NCF	MCDF	MCDF+Breit	Correction	Factor
0.01	4	2.374 66	2.374 66	0.0	1.0
0.001	76	2.090 86	2.090 52	-0.000 330 175	0.999 833
0.0001	524	2.344 26	2.343 94	-0.000 298 213	0.999 865
0.000 01	1844	2.280 65	2.280 26	-0.000 370 117	0.999 828

TABLE VIII. Diagonal magnetic dipole hyperfine structure parameter A (in MHz) for the $1s^22s\ ^2S_{1/2}$ state of $^{19}_{9}\mathrm{F}^{6+}$, as the function of orbital set. SDT means single, double, and triple substitutions from the reference $1s^22s$ configuration. Column 2 gives the number of configurations. Notation $3s2p1d$ in the third column means expansions formed by substitutions from reference configurations to virtual space constructed from three orbitals of the s symmetry, two orbitals of the p symmetry, and one orbital of the d symmetry.

Type	NCF	Orbital set	A
(DF)	1	$2s$	81 914
SDT	8	$2s1p$	81 847
SDT	79	$3s2p1d$	88 483
SDT	410	$4s3p2d1f$	87 546
SDT	1463	$5s4p3d2f1g$	88 017
SDT	3710	$6s5p4d3f2g$	87 863
SD	3989	$7s6p5d4f3g$	87 964
SD	2631	$8s7p6d5f3g$	87 912
SD	2992	$9s8p7d6f3g$	87 939
SD	3323	$10s9p8d6f3g$	87 931
SD	3701	$11s10p9d6f3g$	87 937
SD	3989	$12s11p9d6f3g$	87 931
SD	4313	$13s12p9d6f3g$	87 936
SD	4513	$14s12p9d6f3g$	87 933
SD	4741	$15s12p9d6f3g$	87 936
CI	7017	$15s12p9d6f3g$	0
Bohr-Weisskopf			-39(13)
Nuclear recoil			-8
Breit			18
$g_s/2$			102
Total			88 009(13)
Hylleraas[a]			87 307
FCPC[b]			89 550[c]
Experiment[d]			88890(1800)

[a] Reference [51].

[b] Reference [53].

[c] Not corrected for nuclear size and relativistic effects.

[d] Reference [52].

variational result by King [51], as well as with the experimental value by Randolph *et al.* [52], obtained with nuclear quantum beats technique. The corrections have been evaluated in a manner similar to that used for the Be^+ ion. As indicated in Table IX, the multiplicative Breit factor for the magnetic dipole hyperfine constant A was equal to 1.000 21. The Bohr-Weisskopf effect has been estimated even more crudely than in the case of Be^+, because there are no data on magnetization distribution for $^{19}_{9}\mathrm{F}$ nucleus. We have interpolated among the values for neighboring nuclei from the tables of de Jager, de Vries, and de Vries [42], and arrived at $\langle r\rangle_m = 2.9$ fm, as the effective radius of the magnetization distribution within the nucleus [see Eq. (11)]. The effect of neglected high-l orbitals is expected to be relatively much smaller than in the case of neutral or singly ionized species, because electron correlation effects on hyperfine interaction become strongly dominated by s orbitals with the increase of

TABLE IX. The effect of the Breit interaction on the calculated diagonal magnetic dipole hyperfine structure parameter A (in MHz) for the $1s^22s\ ^2S_{1/2}$ state of $^{19}_{9}\mathrm{F}^{6+}$. Column 2 gives the number of configurations which survived the condensing procedure for five different values of threshold.

Threshold	NCF	MCDF	MCDF+Breit	Correction	Factor
0.01	1	81555	81555	0	1.0
0.001	32	88681	88760	79	1.000 89
0.0001	197	87933	88012	80	1.000 91
0.000 01	793	87937	87962	26	1.000 29
0.000 001	1887	87936	87957	21	1.000 24
		extrapolated			1.000 21

TABLE X. Diagonal magnetic dipole hyperfine structure constants A (in MHz) for the $1s^22s\ ^2S_{1/2}$ state of $^{7}_{3}\mathrm{Li}$, $^{9}_{4}\mathrm{Be}^{+}$, and $^{19}_{9}\mathrm{F}^{6+}$.

Method	$^{7}_{3}\mathrm{Li}$	$^{9}_{4}\mathrm{Be}^{+}$	$^{19}_{9}\mathrm{F}^{+6}$
MCDF[a]	401.765		
MCHF[b]	401.71		
MCHF[c]	401.76		
FE-MCHF[d]	401.60		
CCSD[e]	400.903		
RMBPT[f]	402.47		
Hylleraas[g]	401.79[h]		
Hylleraas[i]	401.89[j]		
Hylleraas[k]	401.71		
FCPC[l]	401.35[m]		
Experiment[n]	401.7520433(5)		
Experiment[o]	401.81(25)		
MCDF[p]		-625.04(8)	
RMBPT[q]		-625.63(9)	
Hylleraas[r]		-625.022(60)	
FCPC[s]		-624.51[t]	
Experiment[u]		-625.008837048(10)	
MCDF[v]			88 009(13)
Hylleraas[w]			87 307
FCPC[x]			89 550[y]
Experiment[z]			88 802

[a] Reference [3].
[b] Reference [29].
[c] Reference [1].
[d] Reference [54].
[e] Reference [55].
[f] Reference [5].
[g] Reference [51].
[h] Not corrected for relativistic effects.
[i] Reference [56].
[j] Not corrected for nuclear size and relativistic effects.
[k] Reference [4].
[l] Reference [53].
[m] Not corrected for nuclear size and relativistic effects.
[n] Reference [57].
[o] Reference [58].
[p] This work.
[q] Reference [5].
[r] Reference [4].
[s] Reference [53].
[t] Not corrected for nuclear size and relativistic effects.
[u] Reference [24].
[v] This work.
[w] Reference [51].
[x] Reference [53].
[y] Not corrected for nuclear size and relativistic effects.
[z] Reference [52].

the atomic number Z. Boucard and Indelicato [17] have determined that the relative contribution of the $1s2s3s$ configuration to the total electron correlation increased from less than 60% near the neutral end, to 90% near $Z=10$, to 98% for $Z=92$.

The variational result by King [51], when corrected for relativistic effects, yields 87 976 MHz, which is in very good agreement with our value of 88 009 MHz (the relative discrepancy is of the order of 0.04%), and both are within the error bars of the experimental value by Randolph *et al.* [52].

TABLE XI. Diagonal magnetic dipole hyperfine structure constants A (in MHz) for the $1s^2 2p\ ^2P_{1/2}$, $^2P_{3/2}$ states and electric quadrupole constant B (in MHz) for the $1s^2 2p\ ^2S_{3/2}$ state of $^9_4\mathrm{Be}^+$.

Method	A for $2p_{1/2}$ $^9_4\mathrm{Be}^+$	A for $2p_{3/2}$ $^9_4\mathrm{Be}^+$	B for $2p_{3/2}$ $^9_4\mathrm{Be}^+$
MCDF[a]	-117.91(3)	-0.978(4)	2.4319(4)
MBPT[b]	-117.94(1)	-1.04(1)	
FCPC[c]	-117.25[d]		2.2890[d]
Experiment[e]	-118.6(36)		
Experiment[f]		$\|A\|<0.6$	

[a] This work.
[b] Reference [5].
[c] Reference [53].
[d] Not corrected for nuclear size and relativistic effects.
[e] Reference [25].
[f] Reference [26].

IV. CONCLUSIONS

We have calculated the magnetic dipole hyperfine constants A for the three lowest states of Be^+ ion, the electric quadrupole constant B for the $2p\ ^2P_{3/2}$ state of Be^+, and the magnetic dipole constant A for the $2s\ ^2S_{1/2}$ state of F^{+6}. Tables X and XI present a survey of theoretical and experimental magnetic dipole hyperfine constants for the ground $1s^2 2s\ ^2S_{1/2}$ state of $^7_3\mathrm{Li}$, $^9_4\mathrm{Be}^+$, and $^{19}_9\mathrm{F}^{6+}$, for the excited $1s^2 2p\ ^2P_{1/2}$ and $^2P_{3/2}$ states of $^9_4\mathrm{Be}^+$, as well as the electric quadrupole constant B for the $1s^2 2p\ ^2P_{3/2}$ state of $^9_4\mathrm{Be}^+$. The agreement between our calculation and experiment for the hyperfine constant A of the ground state of Be^+ is of the order of 0.005%, and indicates that the algorithm used in the present paper yields results close to what might be termed as the MCDF ''no-pair'' limit. The accuracy of the present calculation is essentially limited by the knowledge (or lack thereof) of the magnetization distribution inside the nuclei. The hyperfine constants for excited states of $^9_4\mathrm{Be}^+$, as well as for the ground state of $^{19}_9\mathrm{F}^{6+}$, are less accurately measured, though, and do not permit a meaningful comparison with theory.

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