Theory of hyperfine interactions in lithiumlike systems

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Using relativistic many-body perturbation theory, we have investigated the valence, exchange core polarization, and correlation contributions to the magnetic hyperfine constants in the ground states of the lithiumlike ions Be^+ , B^{2+} , C^{3+} , N^{4+} , O^{5+} , F^{6+} , Ne^{7+} , and Bi^{80+} . Radiative corrections have also been investigated. Both the exchange core polarization and the correlation contributions as fractions of the valence-electron contribution decrease rapidly as one goes to more highly charged ions, the decrease being more drastic for the correlation effect. The radiative effect, on the other hand, increases very rapidly with increasing charge, becoming of the same order of magnitude as the correlation effect in O^{5+} , F^{6+} , and Ne^{7+} . For Bi^{80+} the radiative effect is larger than the correlation contribution, being about 0.3% of the hyperfine field from the valence 2s electron. The significance of these results and trends will be discussed, and comparisons will be made between the net hyperfine fields obtained in the present work and available experimental results as well as with the results of earlier calculations.

I. INTRODUCTION

The linked-cluster many-body perturbation theory, in its nonrelativistic¹ (LCMBPT) and relativistic² (RLCMBPT) forms, has been applied extensively to study hyperfine properties of atomic systems. A particular advantage of this procedure is that one can use it to obtain the contributions from individual mechanisms,^{1,2} such as valence, exchange core polarization (ECP), correlation, and related mechanisms, to the hyperfine constant, thereby providing useful physical insights into the importance of these effects. In this context, it is helpful to study the trends in these contributions over a series of closely related atoms, such as the alkali-metal atoms^{3,4} and the alkaline-earth ions,^{4,5,6} and the various series of ions with increasing charges which are isoelectronic with particular neutral atoms.

The lithiumlike ions are particularly important to study in this respect because they are relatively small systems allowing one to study the contributions from different mechanisms accurately. In particular, since some of the ions even in the second period, such as Ne^{7+} , involve sizeable effective nuclear charges, one has to examine the importance of radiative effects⁷ relative to the other contributions to the hyperfine constant. Such an examination is also necessary because of planned experiments at the Gesellschaft für Schwerionenforschung Darmstadt (Federal Republic of Germany)⁸ in highly stripped lithiumlike ions such as Bi⁸⁰⁺. Two other additional incentives for studying the lithiumlike ions at the present time are the following. The first is the availability of accurate experimental $data^{9-11}$ on the hyperfine constants in a number of such systems, allowing for a verification of the theory. A second reason for studying these systems by the RLCMBPT procedure is that nonrelativistic calculations have been carried out earlier for the lithiumlike series by a differential-equation (DE) approach.^{12,13} One thus has an opportunity to make a detailed comparison between the results from two rather different theoretical procedures.

Section II presents a few details of the RLCMBPT procedure, which has been discussed extensively in the literature.^{2,14} The important many-body diagrams corresponding to the various physical effects are discussed in Sec. II. The role of radiative effects in influencing the hyperfine interaction constants is discussed and the expression^{7(b)} used to obtain the radiative corrections presented in Sec. III is given. Section III presents our results for the lithiumlike ions from the second-period atoms and the highly ionized system Bi⁸⁰⁺. The trends in different physical effects and the nature of agreement with available experimental data are discussed in Sec. III. Further, a comparison is made in Sec. III between our results and the results from earlier investigations.^{12,13}

II. PROCEDURE

There are two main aspects of the procedure we have utilized to obtain the hyperfine constants for the lithiumlike systems that have been studied in the present work. The first aspect deals with the various one-electron and many-body contributions to the hyperfine constant within the framework of RLCMBPT^{2,14} and the second is concerned with the influence of radiative effects.⁷ The reason for using RLCMBPT rather than the nonrelativistic version LCMBPT is that we shall be considering some strongly ionized systems; for instance, Ne⁷⁺ and Bi⁸⁰⁺, for which relativistic effects could be rather pronounced. Since the RLCMBPT procedure has been described extensively in the literature, 2,5,14 we do not need to discuss it in detail here. However, a few relevant points about this procedure will be presented for the sake of completeness.

The relativistic many-electron Hamiltonian for an atomic system^{7(a), 15} excluding radiative effects is given by

$$\mathcal{H} = \sum_{i=1}^{N} \left[c \boldsymbol{\alpha}_{i} \cdot \mathbf{p}_{i} + \beta_{i} m c^{2} - \frac{\zeta e^{2}}{r_{i}} \right] + \sum_{i>j} \frac{1}{r_{ij}} , \qquad (1)$$

where α_i and β_i are the Dirac matrices for the *i*th electron, \mathbf{p}_i is its momentum operator, \mathbf{r}_i is its radius vector measured from the nucleus with charge ζe , and r_{ij} is the distance between electrons *i* and *j*.

The exact many-particle eigenfunction for this Hamiltonian is difficult to calculate; therefore, in RLCMBPT^{2, 14} one separates \mathcal{H} into two parts as in

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \ . \tag{2}$$

In Eq. (2),

$$\mathcal{H}_{0} = \sum_{i=1}^{N} h_{0}(i) = \sum_{i=1}^{N} \left[c \boldsymbol{\alpha}_{i} \cdot \mathbf{p}_{i} + \beta_{i} m c^{2} - \frac{\zeta e^{2}}{r_{i}} \right] + \sum_{i=1}^{N} V_{i}^{(N-1)} .$$
(3)

 $V^{(N-1)}$, as explained in earlier literature,^{2,5,14} is given by

$$\langle a | \mathcal{V}^{(N-1)} | b \rangle = \sum_{n=1}^{N-1} \left[\left\langle an \left| \frac{e^2}{r_{12}} \right| bn \right\rangle - \left\langle an \left| \frac{e^2}{r_{12}} \right| nb \right\rangle \right],$$
(4)

and the perturbation Hamiltonian is given by

$$\mathcal{H}' = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_{i} V_i^{(N-1)} .$$
 (5)

In the summation over n in Eq. (4), usually the outermost valence orbital is the one that is omitted. The major advantage of using $V^{(N-1)}$ over V^N , the usual Hartree-Fock potential, as has been discussed in earlier literature, ^{1,15} is that the former is more physical for excited states. We would also like to remark that in the present work, in keeping with the procedure used in recent work¹⁴ by our group in other systems, we have obtained the one-electron ground and excited states for the V^{N-1} potential using a nucleus with a distributed charge.

In RLCMBPT, the exact eigenfunction Ψ of the many-particle Hamiltonian \mathcal{H} is derived from the eigenfunction Φ_0 (energy eigenvalue E_0) of \mathcal{H}_0 by the linked-cluster expansion:¹⁶

$$\Psi = \sum_{n}^{(L)} \left[\frac{\mathcal{H}'}{E_0 - \mathcal{H}_0} \right]^n \Phi_0 .$$
 (6)

For the magnetic hyperfine interaction, the electronnuclear hyperfine interaction Hamiltonian is given in relativistic theory¹⁷ by

$$\mathcal{H}_{e\mathcal{N}}^{\prime} = \sum_{i=1}^{N} ec \, \boldsymbol{\alpha}_{i} \cdot \frac{\boldsymbol{\mu}_{I} \times \mathbf{r}_{i}}{r_{i}^{3}} , \qquad (7)$$

where μ_I is the magnetic moment of the nucleus. The theoretical expression for the experimentally measured hyperfine constant is^{1,17}

$$A_{J} = \frac{1}{IJ} \left\langle \Psi_{I,J,M_{I}=I,M_{J}=J} | \mathcal{H}_{e\mathcal{N}}' | \Psi_{I,J,M_{I}=I,M_{J}=J} \right\rangle$$
$$= \sum_{m,n}^{(L)} \left\langle \Phi_{0} \right| \left[\frac{\mathcal{H}'}{E_{0} - \mathcal{H}_{0}} \right]^{m} \mathcal{H}_{e\mathcal{N}}' \left[\frac{\mathcal{H}'}{E_{0} - \mathcal{H}_{0}} \right]^{n} \left| \Phi_{0} \right\rangle. \quad (8)$$

The various terms in Eq. (8) corresponding to different values of m and n are referred to as belonging to orders (m,n). These various order terms are expressed in terms of diagrams, ^{1,2,17} the evaluation of these diagrams involving the use of the identity operator given by

$$\sum_{k} \Phi_k \Phi_k^{\dagger} = I \quad , \tag{9}$$

the summation being carried out over the ground state (k=0) and all excited many-electron states corresponding to \mathcal{H}_0 . These many-electron states Φ_k are represented by determinantal wave functions built out of the complete set of bound and continuum one-electron states ϕ_i which are eigenfunctions of h_0 in Eq. (3).

The diagrams which have been found^{1,3} to make the major contributions to the hyperfine constant in lithium and other alkali-metal atoms and which are also found to be the leading contributors for the lithiumlike ions are shown in Fig. 1. These are, respectively, the valence [Fig. 1(a)], ECP [Fig. 1(b)], and correlation [Figs. 1(c) and 1(d)] diagrams.^{1,2,15} The algebraic expressions associated with their contributions to the hyperfine constant in MHz are given, respectively, by²

$$A_J^{\text{val}} = K_J \rho(2s; 2s) ,$$
 (10)



FIG. 1. Diagrams representing (a) valence and (b) leading exchange core polarization and correlation contributions, both (c) direct and (d) exchange, to the hyperfine constants in lithium-like systems.

 $A_{I}^{\rm corr}({\rm exch})$

$$= -2K_J \sum_{m,n,k} \frac{\rho(ks;2s)I(2s,1s;m,n)I(n,m;ks,1s)}{(\varepsilon_{2s} + \varepsilon_{1s} - \varepsilon_m - \varepsilon_n)(\varepsilon_{2s} - \varepsilon_{ks})},$$
(13)

where

$$K_J = \frac{8\pi}{3} \frac{\mu_B \mu_I}{I J a_B^3 h} \times 10^{-6} , \qquad (14)$$

$$\rho(ms;ns) = -\frac{1}{2\pi\alpha} \left[\int_0^\infty \frac{P_{ms}Q_{ns}}{r^2} dr + \int_0^\infty \frac{P_{ns}Q_{ms}}{r^2} dr \right],$$
(15)

$$I(ms, ns; j, k) = \left\langle \phi_{ms}(1)\phi_{ns}(2) \middle| \frac{e^2}{r_{12}} \middle| \phi_j(1)\phi_k(2) \right\rangle, \quad (16)$$

with the ε_m referring to the energy eigenvalues of the one-electron states. In the expression for K_J , μ_B and μ_I refer to the Bohr magneton and the nuclear magnetic moment of the nucleus of interest, with I and J the nuclear spin and total electronic angular momentum, respectively, and a_B is the Bohr radius. In Eq. (15), the P_{ns} and Q_{ns} refer to the radial parts of the large and small components¹⁷ of the relativistic wave function ϕ_{ns} . The states ϕ_i and ϕ_k in Eq. (16) have the same orbital angular momentum (in the relativistic sense)¹⁵ which depends on the multipole component of $1/r_{12}$ used in the matrix element. In the present work, as in most earlier investigations,^{2,3} we have considered multipole moments up to l=2. As will be discussed in Sec. III, dealing with results, the contributions from higher multipole moments to the hyperfine interaction in the present systems are quite small.

In addition to the major diagrams in Figs. 1(a)-1(d), we have also studied additional classes of diagrams representing other physical effects, such as exclusionprinciple violating (EPV), phase space, and consistency diagrams that have been discussed in an earlier detailed investigation¹ of the lithium atom. Typical diagrams in these classes are presented in Figs. 2-4. The EPV diagrams arise out of the choice of the $V^{(N-1)}$ potential used to generate the excited states. The phase-space diagrams result from the fact that the 2s state with down spin (-)is empty in these systems and is therefore available as an excited state, while the up-spin (+) valence-electron state is occupied. The consistency diagrams represent the influence of the change produced by the excitation of one orbital on the potential seen by another. For instance, in Fig. 4(a), the effect described is the influence of the perturbation produced in the 1s⁺ state by the ECP effect on the 2s valence-electron density at the nucleus.



FIG. 2. Typical EPV diagrams contributing to the hyperfine constant in lithiumlike systems.



FIG. 3. Phase-space diagram contributing to the hyperfine constant in lithiumlike systems.



FIG. 4. Typical consistency diagrams contributing to the hyperfine constant in lithiumlike systems.

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Finally, we would like to discuss the role of radiative effects⁷ on the hyperfine interaction of the lithiumlike ions considered here. For light and neutral atoms these effects are expected to be quite small and within the error range of many-body investigations. However, in some of the highly charged ionic systems discussed here, this effect could be significant and should be estimated, especially for an ion like Bi^{80+} . In addition, for these three-electron atoms the accuracy of the many-body contributions is expected to be very good¹ (about 1%), so that the accuracy in the net hyperfine effect would be even better (on the order of 0.1% or better). These considerations make the analysis of radiative effects desirable. It is not

our purpose here to make a very accurate analysis of the role of various types of radiative effects⁷ that can contribute to the hyperfine interaction. We mainly want to make an estimate of radiative corrections within an accuracy of about 20%. The major effect is expected to arise out of the radiative correction to the valence-electron contribution to the spin density at the nucleus. For a hydrogenic atom, this effect can be described as the influence of photon emission and reabsorption¹⁷ processes on the wave function of the electron, which will influence the strength of its hyperfine interaction with the magnetic moment of the nucleus. The expression for the radiative correction in a hydrogenic atoms is given by^{7(b)}

$$\Delta A_{\rm rad} = A_J^{\rm val} (1 + m/M)^{-3} (\alpha(\zeta \alpha) [\ln(2) - \frac{5}{2}] + (\alpha/\pi) (\zeta \alpha)^2 \{ -\frac{2}{3} \ln^2 [(\zeta \alpha)^{-2}] + [-\frac{16}{3} \ln(2) + \frac{7}{2} + \frac{37}{72} + \frac{4}{15}] \ln[(\zeta \alpha)^{-2}] + 12.788 \} \} .$$
(17)

In the corresponding expression (1.7) in Ref. 7(b), there were several additional terms with constants appropriate for the 2s valence state in the bold parentheses which have already been included in our work and do not need to be considered again. Two of these terms refer to the radiative anomaly in the electronic magnetic moment which has been incorporated in the hyperfine interaction contributions through the use of the corrected Bohr magneton μ_B , in the multiplying constant K_J [Eq. (14)] for A_I^{val} in Eq. (10). Next, there was a term taking account of the distributed nuclear charge which has been included in our work through the use of basis states corresponding to a distributed nucleus. Thirdly, there was a term $\left[\frac{3}{2}(\zeta \alpha)^2\right]$ in Ref. 7(b) which has to be considered when one uses a nonrelativistic value for A_J^{val} , but which is not necessary here since we have used a relativistic result for A_J^{val} . The factor $(1 + m/M)^{-3}$ refers to the influence of the conventional mass effect on the spin density. It is quite small but comparable in magnitude to the small radiative contributions for Li⁰ and Be⁺ (Table I). It gets progressively weaker as one goes to heavier nuclei, being virtually negligible for Bi⁸⁰⁺.

In an atom with more than one electron, for a rigorous incorporation of radiative effects for the valence-electron contribution, one has to include these effects within the framework of Hartree-Fock theory,¹⁸ which is a difficult task. Since in the present work we were mainly interested in an estimate of the radiative correction to the hyperfine interaction, we have made use of Eq. (17) employing an effective nuclear charge ζ for the 2s electrons of the various lithiumlike systems considered. The value of ζ is given by $(Z - \Delta Z)$, where Z is the nuclear charge

TABLE I. Contributions $(10^{-1} \text{ T})^a$ from different mechanisms to the hyperfine field at the nucleus in systems isoelectronic with lithium. The numbers in square brackets denote 10^n .

		ECP ^b		Total			
System	Valence		Correlation	Radiative	This work	DE result ^c	Expt. ^d
Li ⁰	86.23	30.21	5.19	-0.01	121.62	121.4	121.398 46
Be^{1+}	417.00	90.13	12.73	-0.10	519.76	523.4	522.205(2)
B^{2+}	1113.0	163.83	17.02	-0.39	1293.5	1317.0	
C^{3+}	2301.7	279.00	23.02	-1.04	2602.7	2625.0	
N^{4+}	4109.7	447.61	28.50	-2.29	4583.5	4572.0	
O ⁵⁺	6667.1	583.02	34.30	-4.38	7280.0	7281.0	
F^{6+}	10 105	780.23	40.12	-7.61	10918	10 889	11 100(230)
Ne ⁷⁺	14 556	1090.10	45.51	-12.34	15679		
Bi ⁸⁰⁺	2.7931[7]	5.3740[5]	3.304[4]	7.184[4]	2.8573[7]		

^aThe results quoted in 10^{-1} T in this table can all be converted to MHz using Eq. (20) which leads to $H_{hyp} = 6.559\,355$ (A/g_I)× 10^{-2} T. Values of g_I for atomic nuclei can be found in Fuller and Cohen (Ref. 24). A more recent compilation by Raghavan is scheduled to appear (Ref. 25).

^bRefers to the sum of all one-electron perturbation contributions ECP, EPV, phase-space, and consistency effects as discussed in the text.

^cReference 21.

^dThe values in 10^{-1} T listed here are obtained using (A/g_1) listed in Table 2 of Ref. 10 and applying the conversion factor in Eq. (20).

and ΔZ is a shielding parameter which represents the influence of the screening of the nuclear charge by the 1s electrons. The value of ΔZ could be chosen in several different ways. One is to use the standard prescription for the shielding parameter in earlier literature.¹⁹ Alternatively, one could attempt to fit the relativistic Hartree-Fock energy for the 2s state or different features of the 2s wave function to the corresponding properties for a shielded hydrogenic atom in relativistic theory. We have chosen to fit the relativistic 2s state energies, which for a hydrogenic atom, are given by²⁰

$$E_{2s} = mc^{2} \left[1 + \left[\frac{\zeta \alpha}{1 + (1 - \zeta^{2} \alpha^{2})^{1/2}} \right]^{2} \right]^{-1/2} - mc^{2} . \quad (18)$$

This choice is preferred because it represents an average fit over all regions of space, rather than a specific point or region of r. In Sec. III, we shall see how this choice compares with the standard choice in earlier literature. To study the dependence of the radiative correction on the choice of shielding parameter, we have also made use of a third choice, involving complete screening by the two 1s electrons, leading to $\Delta Z = 2$. This choice is justified only at very large distances from the nucleus and thus represents a somewhat extreme approximation.

Before proceeding to a discussion of our results, we would like to point out that instead of analyzing the hyperfine constants and various contributions to them, it is often more convenient to consider the hyperfine fields at the nucleus, especially when discussing trends over related systems. The hyperfine field is related to the hyperfine constant by the expression³

$$H_{\rm hyp} = \left[\frac{2\pi}{\gamma_I}\right] A J , \qquad (19)$$

where J is the net electronic angular momentum and $\gamma_I = \mu_I / I\hbar$ is the magnetogyric ratio of the nucleus, μ_I being the nuclear moment. For the lithiumlike systems of interest here, J is equal to the electronic spin S, which has the value $\frac{1}{2}$ for the present systems. Since the experimental results for the hyperfine constants are often quoted¹⁰ in terms of A/g_I where $g_I = \gamma_I \hbar / \mu_N = (1/I)(\mu_I / \mu_N)$, μ_N being the nuclear magneton, it is convenient to express H_{hyp} in the form

$$H_{\rm hyp} = \left[\frac{\pi\hbar}{\mu_N}\right] \left[\frac{A}{g_I}\right] = (6.559\,355) \left[\frac{A}{g_I}\right] \times 10^{-2} \,\mathrm{T} \,.$$
(20)

The numerical factor in Eq. (20) has been obtained using⁷ $\mu_N = 5.050951 \times 10^{-27}$ J/T, $\hbar = 1.0545919 \times 10^{-34}$ J sec and A in units of MHz.

The hyperfine field, unlike the hyperfine constant A, is independent of the nuclear magnetic moment and spin, involving only the unpaired electron-spin density in the vicinity of the nucleus, and is therefore the pertinent quantity to study in analyzing the variations in the electron distributions over related systems. The relation (19) also applies to individual contributions to the hyperfine field, the quantity A on the right-hand side now referring to the corresponding contributions [as in Eqs. (10)-(13)] to the hyperfine constant.

III. RESULTS AND DISCUSSION

The various contributions to the hyperfine field at the nucleus discussed in Sec. II are listed in Table I for the different lithiumlike systems we have investigated. Also listed for ready reference are the experimental results for the hyperfine constants in the systems where they are available,^{9,10,11} and the results of earlier theoretical work^{13,21} by the differential-equation approach. For the radiative contribution, only the results for the choice of shielding parameters from a consideration of the relativistic Hartree-Fock 2s state energies are included in Table I. A comparison of results from this choice with other choices is presented in Table IV and will be discussed later in this section. Before discussing the nature of the agreement between the theoretical and experimental results for the hyperfine fields, we would like to describe a few features of the individual contributions.

The ECP, EPV, consistency, and phase-space contributions are grouped together (and referred to as ECP in Table I) because they all represent one-electron effects beyond the zeroth-order valence contribution. To show the relative importance of these various effects, we have listed their individual contributions for a few selected systems in Table II. It can be seen from Table II that the combined effect of the other three contributions besides ECP is quite significant, ranging from about 30% of the net one-electron perturbation contribution in Li⁰, to about 20% at the end of the second period at Ne^{7+} . The results in Table II show some interesting trends. Thus, while EPV is the leading contributor outside of ECP and valence effects in Li⁰, it is superseded by the phase-space contribution in the case of Ne⁷⁺, this trend being continuous as one moves to the right in the second period. The consistency effect is seen to be the least important from a quantitative point of view. In the rest of the paper we shall refer to the net one-electron perturbation contributions as the ECP effect, as listed in Table I.

The correlation contributions arise primarily from the diagrams in Figs. 1(c) and 1(d). The exchange contribution from diagram 1(d) is consistently smaller in magnitude (and opposite in sign) than the direct contribution from diagram 1(c), as can be seen from Table III where we have listed the direct- and exchange-correlation contributions in B^{2+} and Ne^{7+} from various multipole components l of the electron-electron interaction. The feature of larger contribution from the direct terms is in

TABLE II. Breakdown of various contributions (10^{-1} T) to net one-electron perturbation effect.

	Li ⁰	Be ⁺	Ne ⁷⁺
ECP	20.85	71.41	850.82
Phase space	1.02	7.42	162.31
EPV	7.92	9.95	60.05
Consistency	0.42	1.35	16.91
Total	30.21	90.13	1090.10

TABLE III. Contributions (10^{-1} T) to the correlation effect from various multipole components of the electron-electron interaction.

		Sys	tem
		B ²⁺	Ne ⁷⁺
Monopole	Direct	14.10	37.28
	Exchange	-6.78	- 17.87
	Total	7.32	19.41
Dipole	Direct	13.06	35.80
	Exchange	-4.52	-12.71
	Total	8.54	23.09
Quadrupole	Direct	1.95	5.11
	Exchange	-0.79	-2.10
	Total	1.16	3.01
Octupole	Direct	0.54	1.52
	Exchange	-0.23	-0.67
	Total	0.31	0.85

keeping with the results found for the alkali-metal $atoms^{3,4}$ and alkaline-earth ions,^{4,5,6} all of which have valence s electrons in their ground states. Another interesting feature is the relative importance of various multipole contributions to correlation effects arising from the corresponding multipole components of the electronelectron interaction vertices in Figs. 1(c) and 1(d). As can be seen from Table III, for the two systems shown, namely, B^{2+} and Ne^{7+} , the dipole (l=1) and monopole (l=0)contributions have comparable importance, with the dipole contribution somewhat stronger. The quadrupole component (l=2) is significantly smaller than both monopole and dipole contributions and the octupole component (l=3) is substantially weaker than the quadrupole component. These features were also observed in earlier investigations on the lithium atom¹ and apply for all the systems we have studied here. We have, therefore, included contributions only as far as the quadrupole component for the correlation results in Table I. The higher lcomponents are expected to make contributions well within the confidence limits of our calculated hyperfine

fields discussed at the end of this section.

It can be seen from Table I that the ECP contribution is always more important than the correlation contribution. The correlation contribution is in turn larger than the radiative effect up to and including the Ne⁷⁺ ion, although from O^{5+} onwards to Ne^{7+} it is comparable in order of magnitude to the correlation effect. For Bi^{80+} , the radiative effect is about two times larger in magnitude than the correlation effect and of the same order of magnitude as the ECP effect, being smaller by a factor of about 7. It is about 0.26% of the valence contribution as compared to the ECP effect, which is about 1.90% of the valence effect. The rapid increase in the radiative contribution as one goes to the more highly charged systems is a consequence of the occurrence of powers of $(\zeta \alpha)$ in Eq. (17). An interesting feature is the reversal in sign of the radiative effect in Bi⁸⁰⁺ as compared to the systems of the second period, due to the change in sign of the coefficient of the $(\zeta \alpha)^2$ term in Eq. (17) for larger ζ .

Table IV presents the three sets of shielding parameters ΔZ we have worked with and the corresponding radiative corrections for the lithiumlike series of systems studied here. The trends just described for the variation of the radiative effect over the series and its relative importance with respect to other contributions can be seen from Table IV to apply to the results with all three choices of shielding constants. It is interesting that the shielding parameters obtained by the more sophisticated choice of fitting our calculated relativistic Hartree-Fock 2s energies to relativistic hydrogenic atom energies are not too different from the constant value obtained from earlier literature.¹⁹ There is, however, a significant decrease in ΔZ with the former choice as one goes to heavier ions, especially to Bi⁸⁰⁺, perhaps due to the greater importance of relativistic effects. As expected, the contributions ΔA_{rad} from the radiative effect are much closer for the first two choices of ΔZ in Table IV corresponding to those obtained from relativistic energy fitting and the convention in earlier literature¹⁹ than those from the more extreme choice of complete shielding by core electrons.

A somewhat better insight into the trends in the ECP, correlation, and radiative contributions can be obtained,

	Rel	lativistic energy fit	Con sł	iventional hielding	Complete shielding		
System	ΔZ	$\Delta A_{\rm rad}$	ΔZ	$\Delta A_{\rm rad}$	ΔZ	$\Delta A_{\rm rad}$	
Li ⁰	1.75	-0.01	1.7	-0.01	2	-0.01	
Be ⁺	1.69	-0.10	1.7	-0.10	2	-0.09	
B^{2+}	1.67	-0.39	1.7	-0.38	2	-0.35	
C^{3+}	1.65	-1.04	1.7	-1.03	2	-0.96	
N^{4+}	1.64	-2.29	1.7	-2.26	2	-2.14	
O ⁵⁺	1.63	-4.38	1.7	-4.33	2	-4.14	
F^{6+}	1.63	-7.61	1.7	-7.55	2	-7.25	
Ne ⁷⁺	1.62	-12.34	1.7	-12.33	2	-11.83	
Bi ⁸⁰⁺	1.50	71 839	1.7	70 861	2	69 381	

TABLE IV. Radiative corrections (10^{-1} T) to the hyperfine fields for various choices of shielding parameter

as in earlier work³ on the alkali-metal series, by considering the ratios of these contributions to the valence effect in the various lithiumlike ions we have considered. This allows one to eliminate the effects³ of the varying spin densities at the nucleus due to the valence and core electrons and concentrate on the relative importance of various types of electron-electron interaction effects involved in the different contributions to the hyperfine field. These ratios are listed in Table V, including those for Bi^{80+} . In Figs. 5–7, these ratios are presented graphically for the lithiumlike systems of the second period together with the corresponding available ratios for the ECP and correlation effects up to F^{6+} from the earlier investigation¹³ involving the differential equation based perturbation approach.

From Table V and Fig. 5, the fractional ECP contribu-



FIG. 5. Variation in the fractional contribution to the hyperfine field from the ECP effect (relative to the valence effect) over the lithiumlike systems of the second period. The solid curve refers to results from present work and the dashed curve to results from Ref. 13.

tion is seen to decrease quite rapidly with increasing charge on the ions. This is to be expected, since the fractional contribution for each of these ions is a reflection of the different perturbations in the wave functions of the up- and down-spin core electrons as a consequence of their different exchange interactions with the valence electrons [Fig. 1(b)]. This is a polarization-type effect which is expected to diminish in importance as the core electrons get more tightly bound. The fractional correlation contribution is seen from Table V and Fig. 6 to diminish even more rapidly than the fractional ECP effect. This behavior can be understood by referring to Figs. 1(b) and 1(c), the latter involving a second-order polarization effect due to correlation between the core and valence electrons, while the ECP effect in Fig. 1(b) represents a first-order polarization effect. In contrast, the fractional contribution from the radiative effect (Table V and Fig. 7, where only the results for the energy choice of shield-



FIG. 6. Variation in the fractional contributions to the hyperfine field from the correlation effect (relative to the valence effect) over the lithiumlike systems of the second period. The solid curve refers to results from the present work and the dashed curve to results from Ref. 13.

	ECP/Valence		Corr./Valence		Radiative/Valence	Total/Valence	
System	This work	DE result ^a	This work	DE result ^a	This work	This work	DE result
Li ⁰	35.03	37.14	6.02	4.15	-0.01	141.04	141.22
Be ⁺	21.61	23.79	3.02	2.35	-0.02	124.64	126.14
\mathbf{B}^{2+}	14.72	17.50	1.53	1.30	-0.03	116.22	118.80
C ³⁺	12.12	13.18	1.00	0.85	-0.05	113.08	114.65
N ⁴⁺	10.89	11.40	0.69	0.58	-0.06	111.53	112.00
O ⁵⁺	8.74	9.72	0.53	0.44	-0.07	109.19	110.15
F ⁶⁺	7.72	8.47	0.40	0.33	-0.08	108.04	108.74
Ne ⁷⁺	7.49		0.31		-0.08	108.28	
Bi ⁸⁰⁺	1.92		0.12		0.26	102.31	

TABLE V. Fractional importance (percentage) of various contributions to the hyperfine field relative to the valence.

^aThese results are obtained using the entries in Table 1 of Ref. 13.

ing parameter are given, in keeping with Table I) increases as one goes to heavier atoms, because powers of $(\zeta \alpha)$ are involved in the expression (17) for the radiative correction, as discussed before. In view of this opposing trend of variation with respect to change of the fractional contribution from the radiative effect as compared to both correlation and ECP, the radiative effect becomes of the same order of magnitude as the correlation effect for O⁵⁺ and becomes a larger fraction of the correlation contribution as one goes to F^{6+} and Ne^{7+} . In the highly charged Bi⁸⁰⁺ ion system, on the other hand, the fractional radiative contribution is seen from Table V to be of comparable order as the ECP effect, although smaller in magnitude, as mentioned before. The fractional correlation contribution in this case is seen to be the weakest as compared to the other two effects.

In Fig. 5, the fractional contributions from the ECP effect obtained by our RLCMBPT investigation are compared with those from the DE approach¹³ for Li^0 to F^{6+} , the lithiumlike ions for which DE calculations have been carried out. There is another set of results¹² for the fractional ECP effect from DE investigations, but we have compared our results only with those from Ref. 13 in Fig. 5 since this latter calculation also dealt with correlation



FIG. 7. Variation in the fractional contribution to the hyperfine field from the radiative effect (relative to the valence effect) over the lithiumlike ions of the second period.

effects. The fractional ECP contributions from our investigation are seen to compare quite well with the DE results. However, there are some small but finite quantitative differences, nearly 5% for Li^0 to F^{6+} , the DE results being larger than ours. For the correlation effect, on the other hand, the DE results¹³ are seen from Fig. 6 to be somewhat smaller than ours, the difference ranging from about 30% for Li⁰ to 15% for F^{6+} . The relatively small percentage difference between the RLCMBPT and the DE results for the ECP effect suggests that phase-space, consistency, and EPV effects are in principle included in the ECP result obtained by the DE procedure.¹³ As regards the correlation contributions obtained by the DE procedure, an inspection of Table III indicates that the differences with the RLCMBPT results (Fig. 6) cannot be explained by the possibility that quadrupole terms may not have been included in the DE procedure. The difference between the correlation results by the two procedures probably arises from differences in the monopolar and dipolar contributions. Unfortunately, no breakdown in the correlation contributions from various multipole components is available for the DE results¹³ as in Table III to decide this point. It is hoped that in future work in other systems a more detailed comparison will be possible between the correlation results by the **RLCMBPT** and **DE** procedures.

In making comparisons with experiment, it should be pointed out that the results for the correlation contribution in Table I involve effects up to second order in electron-electron interactions. An examination of typical third- and higher-order diagrams^{1,2} suggests that they would make no larger than 10% of the calculated contributions to the correlation and consistency effects in Table I. It is more difficult to make a quantitative assessment of the confidence limit for the radiative contribution. Equation (17), which is used for the evaluation of the latter contribution, is based on a hydrogenic approximation. A proper treatment of electron-electron interactions at both the one-electron (Hartree-Fock) (Ref. 22) and many-electron levels, which would be rather difficult, could in principle affect the radiative contributions significantly. However, from Tables I and V, the radiative effect is found to have the same order of magnitude as the correlation effect only for O^{5+} and more highly ionized ions. Since in these ions, with only three electrons and substantial nuclear charges, the electronelectron interaction effects in general are expected to be weak compared to the influence of the nuclear Coulomb potential, one could conservatively assume a confidence limit of 20% for the radiative effect. The confidence limit for our net result would thus be expected from Tables I and V to be less than 1% for Li^0 and somewhat better for the heavier ions of the second period like Ne⁷⁺, since the combined effect of the correlation and radiative corrections becomes progressively smaller for heavier ions. With these considerations, it can be seen from Table I that there is very good agreement between theory²³ and experiment within the confidence limit of the former and the range of error in the latter.

In concluding, it can be seen from Table V that for

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Bi⁸⁰⁺ the radiative effect makes a significant contribution to the hyperfine interaction, being about 0.3% of the latter, as compared to 2% for the ECP and 0.1% for correlation. It is clear, then, that a measurement of the 209 Bi hyperfine constant to an accuracy better than 0.1% will provide an opportunity to make a quantitative test of the estimation of the radiative contribution used in the present work. An accurate evaluation of the radiative correction to the hyperfine field will require the incorporation of electron-electron interaction effects at the one-electron and many-electron levels in the diagrams' in quantum electrodynamics contributing to the radiative effect. Equivalently, one could incorporate the influence of electron-photon field interactions and Breit interactions in the diagrams in Figs. 1-4 representing the valence, ECP, and correlation effects.

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