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Theoretical Analysis of the Hyperfine Structure of Alkali Atoms*

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The hyperfine interaction in the alkali-atom series has been investigated quantitatively. In particular, both core-polarization and relativistic effects have been taken into consideration explicitly. The former effect was studied using the moment-perturbation procedure while relativistic Hartree-Fock theory was used for the latter. The core polarization contribution was found to be nearly constant for all the alkali atoms at about 23% of the nonrelativistic restricted Hartree-Fock value. Relativistic corrections were found to be 0.25, 0.68, 2.18, 15.6, and 20.5%, respectively, for lithium, sodium, potassium, rubidium, and cesium. The theoretical results are compared with experimental hyperfine constants to obtain an assessment of the importance of many-body effects in these atoms.

I. INTRODUCTION

Apart from their intrinsic interest, the hyperfine constants in atoms provide a sensitive tool to test the accuracy of atomic wave functions.[1] Owing to recent advances[2] in methods for computing wave functions, it is not unreasonable to aspire for quantitative agreement between theoretical and experimental hyperfine-structure constants. Alkali atoms and metals are some of the simplest systems in nature for which accurate hyperfine data[3] are available. It is therefore desirable not only to try to explain the experimental results quantitatively, but also to understand the relative importance of various contributions[4-6] to the hyperfine interactions. This paper will deal with alkali atoms and a subsequent paper will deal with the metals.

Prior to the present investigation, several attempts[7] have been made to understand the origin of the hyperfine constants in some of the alkali atoms. For some of the atoms, Hartree-Fock wave functions were available and utilized for hyperfine-effect studies while for the heavier ones, no such functions were available, and one could only make semiquantitative estimates. It was therefore not possible to arrive at over-all conclusions regarding the contributions to the hyperfine constants for the entire series of atoms. Recently, Hartree-Fock wave functions have been calculated for all the alkali atoms by a number of different authors.[8] These wave functions and the corresponding energies compare quite closely with each other giving confidence in their accuracy. The differences between hyperfine constants calculated from these wave functions and experimental values can thus be aptly regarded as representative of contributions from sources that are neglected in nonrelativistic restricted Hartree-Fock (NR-RHF) theory. This is therefore an opportune time to attempt at a quantitative understanding of various factors that can contribute to hyperfine effects in the entire series of alkali atoms.

Foremost among the mechanisms neglected in the NR-RHF theory is the core-polarization (CP) effect.[5] Calculations for this effect using Unrestricted Hartree-Fock (UHF) theory[4] have shown that it can have drastic effects on the hyperfine constants for atoms with *p* and *d* valence electrons. In particular, in the case of half-filled *p*, *d*, and *f* shells, NR-RHF theory leads to zero hyperfine constants while finite hyperfine effects have been obtained experimentally. The UHF theory, on the other hand, leads to nonzero hyperfine constants in these cases. For the alkali atoms, there is a finite contribution to the hyperfine constant from the valence *s* states in the NR-RHF approximation. While the role of CP in these atoms is thus less dramatic, it is yet quite substantial, as demonstrated by UHF calculations[4] for lithium, sodium, and potassium. These latter calculations have indicated that CP has a nearly constant percentagewise effect relative to that from NR-RHF theory. It is worthwhile to examine whether similar features hold for the heavier alkali atoms rubidium and cesium, another reason for the interest in these two atoms being the expected importance of relativistic effects.

The earliest attempt at an understanding of relativistic effects on atomic hyperfine structure was made by Casimir.[6] Since relativistic Hartree-Fock wave functions were not available at the time, Casimir had utilized hydrogenic wave functions for a study of relativistic corrections. Further, Casimir in his analysis had confined himself to atoms with *p* valence electrons, where available fine-structure data could be utilized to obtain some of the matrix elements for the hyperfine interaction. Subsequently, Schwartz[9] has also analyzed relativistic effects for the *p*-state hyperfine interaction using Dirac wave functions obtained from an empirical Tietz-type potential. The hyperfine-structure analysis is rather involved for atoms with more than one valence electron. Sandars and Beck[10] and Bordarier, Judd, and Klapisch[11] have studied the influence of relativistic effects on the coupling of valence electrons in such atoms and their consequence on hyperfine properties. With the recent availability of relativistic wave functions, utilizing both Hartree-Fock[12] and Slater exchange potentials,[13] one can now make a meaningful quantitative analysis of relativistic effects.

The third important effect that could contribute significantly to hyperfine structure is the correlation among atomic electrons. A quantitative study of this effect, particularly for atoms with a large number of electrons, is rather difficult. In our present work, we shall be concerned with a careful analysis of CP and relativistic effects on hyperfine structure. The results of this analysis will be compared with experiment to obtain estimates of correlation corrections to the hyperfine constants. It is hoped that these estimates of correlation effects will stimulate interest in the application of current many-body theories[14-16] for atoms to obtain such effects from first principles.

Section II will deal with the calculation of the CP effect. In Sec. III, the calculation of relativistic effects and results will be discussed. Finally, in Sec. IV, the combined contributions from core-polarization and relativistic effects will be compared with experiment, and possible improvements and the role of correlation effects will be analyzed.

II. CORE-POLARIZATION EFFECT

Core-polarization effects are associated with the interaction between the core and the valence electrons with unpaired spins. For purposes of further discussion in this section, we shall define "up" core states as those which have their spins parallel to the spin of the valence electrons, while "down" refers to antiparallel spin states. Electrons in up core states experience a stronger exchange force than those in down core states. This leads to different radial densities for up and down core electrons resulting in a net spin density at the nucleus. In the UHF procedure,[4] one utilizes different orbitals for up and down spin states, which are obtained from a minimization of the total energy. Alternatively, one can utilize perturbation procedures,[17,18] which have the advantage of dealing with small numbers directly rather than with the differences of large numbers associated with the spin densities of up and down core states. There are two variants of the perturbation approach. In one, referred to as the exchange perturbation (EP) procedure, the core states are perturbed by the exchange potential due to the valence electrons and then used to obtain the expectation value of the hyperfine Hamiltonian $\mathcal{H}_{\text{hfs}}$. In the moment-perturbation procedure (MP), the core states are perturbed by $\mathcal{H}_{\text{hfs}}$ and then utilized to calculate the exchange energy. Both procedures have been found to give results in reasonable agreement with each other. The MP procedure has the added advantage of being flexible enough to be extended to the case of metals without much additional complication. It is worthwhile to mention here two features of interest in this work, that are characteristic of UHF and perturbation procedures. First, the UHF procedure incorporates self-consistency while the perturbation procedures do not. However in a recent analysis of many-body effects in hyperfine structure, using a Brueckner-Goldstone diagrammatic[16] approach, it has been shown that consistency effects are associated with higher-order perturbation diagrams. These diagrams have been found to produce less than a 5% correction for lithium, and there is no reason to expect larger errors for other alkali atoms. In addition, wherever results are available for atoms by both UHF and perturbation procedures the two agree very well.[19] There is the further consideration associated with the UHF procedure, namely that the single-determinantal wave function usually utilized is not an eigenfunction of S^2, the total-spin operator. The consequences of this approximation have been discussed by several authors,[20,21] who have shown by fairly general arguments that there is no serious error involved in this approximation. Further, a quantitative evaluation of the diagrams in many-body theory[16] which restore the S^2-eigenfunction character, indicates that the upper limit to the contribution from such diagrams is only of the order of 5%. In our analysis of the alkali atoms, we have used the MP procedure, which will now be briefly described.

The general equation for the first-order perturbation to the wave function in Hartree-Fock theory has been developed by several authors.[22,23] For our present purposes, Method (3) of Ref. 23 is convenient and adequate and leads to the following equations for the first-order perturbations to the *ns* core states of the alkali atoms:

$$\begin{aligned}(h_{ns}{}^0-\epsilon_{ns}{}^0)\delta u_{ns}+h'u_{ns}{}^0&=\textstyle\sum_{n'}[\langle u_{n's}{}^0\,|\,\delta u_{ns}\rangle(\epsilon_{n's}{}^0-\epsilon_{ns}{}^0)u_{n's}{}^0\\&\quad+\langle u_{n's}{}^0\,|\,h^1\,|\,u_{ns}{}^0\rangle u_{n's}{}^0+\langle u_{n's}{}^0\,|\,\delta u_{ns}\rangle\\&\qquad\times\langle u_{ns}{}^0\,|\cdot|\,u_{n's}{}^0\rangle u_{ns}{}^0]\,.\end{aligned}\tag{1}$$

where h^1 is the perturbation Hamiltonian experienced by an electron because of the contact hyperfine interaction and is given by

$$h^1=\tfrac{16}{3}\pi\gamma_N\gamma_e\hbar^2\vec{\mathrm{I}}\cdot\vec{\mathrm{S}}\delta(\vec{\mathrm{r}})\tag{2}$$

$h_{ns}{}^0$ and $\epsilon_{ns}{}^0$ are the one-electron Hamiltonian and energy for the core *ns* state in the restricted Hartree-Fock approximation. $u_{ns}{}^0$ and δu_{ns} are, respectively, the zero-order and first-order wave functions, and

$$\begin{aligned}\langle u_{ns}{}^0\,|\cdot|\,u_{n's}{}^0\rangle u_{ns}{}^0&=\int u_{ns}{}^0(\vec{\mathrm{r}}\,')u_{n's}(\vec{\mathrm{r}}\,')\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\tau' u_{ns}{}^0(\vec{\mathrm{r}})\\&\quad-\int u_{ns}{}^0(\vec{\mathrm{r}}\,')u_{ns}{}^0(\vec{\mathrm{r}}\,')\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\tau' u_{n's}{}^0(\vec{\mathrm{r}}).\end{aligned}\tag{3}$$

In Eq. (1), the summation over n' refers to the other *s* cores of the atom. In carrying out the numerical solution of Eq. (1), we have utilized a local approximation to the unperturbed Hamiltonian $h_{ns}{}^0$, namely,

$$h_{ns}{}^0=-\nabla^2+(u_{ns}{}^0)^{-1}\nabla^2u_{ns}{}^0+\epsilon_{ns}{}^0.\tag{4}$$

The local approximation[24] considerably simplifies the computational procedure without introducing significant error.[23] In general, Eq. (1) is integrodifferential in character. For the case of a single-core state, however, the integral terms are absent and Eq. (1) is easy to solve by conventional procedures.[17] For the case of multiple cores, as in our present work, it is convenient to utilize a noniterative procedure[23] for solving integrodifferential equations. The adaptation of this noniterative procedure to our problem is discussed in Appendix A. In carrying out the numerical solution of the differential equation, we found that a method developed by Froese[25] combining Numerov's procedure for outward integration together with a special "tailing" technique was particularly useful from the point of view of both accuracy and speed.

To obtain the core-polarization component of the hyperfine constant, we have to determine that part of the second-order energy which is composed[17] of one order in the hyperfine interaction and one order in core-valence exchange:

$$\begin{aligned}E_{eN}{}^{(2)}=-2\textstyle\sum_n[\iint u_{\mathrm{val}}{}^0(\vec{\mathrm{r}})\delta u_{ns}(\vec{\mathrm{r}})&\\\times u_{ns}{}^0(\vec{\mathrm{r}}\,')u_{\mathrm{val}}{}^0(\vec{\mathrm{r}}\,')\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\tau d\tau'&\\-\textstyle\sum_{n'}\langle u_{n's}{}^0\,|\,\delta u_{ns}\rangle\iint u_{\mathrm{val}}{}^0(\vec{\mathrm{r}})u_{ns}{}^0(\vec{\mathrm{r}})&\\\times u_{\mathrm{val}}{}^0(\vec{\mathrm{r}}\,')u_{n's}{}^0(\vec{\mathrm{r}}\,')\,|\vec{\mathrm{r}}-\vec{\mathrm{r}}\,'|^{-1}d\tau d\tau'],&\end{aligned}\tag{5}$$

where $u_{\mathrm{val}}{}^0$ represents the valence-electron wave function. In the case of alkali atoms, we have only a single-valence electron. When the atom has more than one valence electron, one has to sum over all the occupied valence states. For an atom with total electronic angular momentum J and nuclear spin I, a_{CP} is given by

$$a_{\mathrm{CP}}=E_{eN}{}^{(2)}/2\pi\hbar IJ.\tag{6}$$

For the zero-order functions $u_{ns}{}^0$ and $u_{\mathrm{val}}{}^0$ appropriate to the ground state ${}^2S_{1/2}$ of the alkali atoms, we have made use of available Hartree-Fock wave functions. Thus, for the lighter atoms lithium, sodium, and potassium, Clementi's analytic wave functions[6] were employed. For some of the inner cores these analytic wave functions exhibit spurious nodes in the tail region because of the limited basis set used in the expansion. To avoid errors in the numerical solution of Eq. (1) associated with these spurious nodes, it was found necessary to adjust the wave functions at large r to have the correct asymptotic behavior. For rubidium and cesium atoms, Froese's numerical Hartree-Fock wave functions[26] were used. These functions were tabulated in a ln$r$ scale and thus required a recasting of the differential Eqs. (1) in terms of the ln$r$ variable. The ln$r$ scale is particularly desirable from the point of view of speed and accuracy in the numerical solution of (1), especially near the origin where there is rapid variation in the wave function. For rubidium and cesium, numerical wave functions have also been obtained by Mann[27] in the regular r scale. These functions compare very well with Froese's wave functions.

The results[28] of our calculation of a_{CP} are presented in Table I. This table includes a_{CP}, the sum of a_{CP} and the direct term a_{d},$(a_{\mathrm{d}}+a_{\mathrm{CP}})$, the UHF values of a where available and experimental results. For a detailed understanding of the nature of a_{CP} we have included in Table I the contributions from individual core states. These results indicate that for all the atoms, the outermost core state makes the dominant contribution to a_{CP}. It is difficult to make *a priori* prediction concerning the relative contributions of the various core states, since the inner cores have diminished exchange with the valence electrons but larger densities near the nucleus. The results in Table I show that the former effect predominates. This behavior plus the fact that all the cores have positive contributions give us confidence about the reliability of the total a_{CP}. This situation is in contrast to the case of atoms with incomplete p shells, for example, in nitrogen and phosphorus atoms, where a_{CP} is composed of comparable contributions of varying signs from the various cores. We would also like to remark on the influence of nonorthogonality effects associated with the perturbed cores on a_{CP}. In carrying out the numerical solution for δu_{ns}, we demand the condition[23]

$$\langle u_{ns}{}^0\,|\,\delta u_{ns}\rangle=0.\tag{7}$$

However, $u_{ns}{}^0+\delta u_{ns}$ need not necessarily be orthogonal to the other core functions $u_{n's}{}^0+\delta u_{n's}$, and this is the reason for the occurrence of terms

TABLE I. Results for the core-polarization contribution to the hyperfine constant a_{CP} in Mc/sec. The UHF results are from D. A. Goodings (Ref. 4) and experimental values from a table by Ramsey (Ref. 3).

	Core States								
Atom	1s	2s	3s	4s	5s	Total a_{CP}	$a_{\mathrm{d}}+a_{\mathrm{CP}}$	a_{UHF}	a_{exp}
Li	94.02					94.02	378.02	390.00	401.80
Na	36.77	104.77				141.54	764.54	764.00	885.70
K	4.43	7.20	23.86			35.49	179.00	178.81	231.54
Rb	7.86	10.40	23.12	88.76		130.14	635.94		1011.90
Cs	8.37	10.53	16.78	38.93	152.64	227.25	1211.05		2298.20

involving $\langle u_{n's}{}^0 | \delta u_{ns}\rangle$ in both Eqs. (1) and (5). The nonorthogonality terms in (1) are composed of some terms that were present in Dalgarno's earlier formulation and the two additional ones as presented in Eq. (3), which were obtained in the recent revised formulation of the nonorthogonal theory by Duff.[23] From our calculations we found that these latter correction terms do not influence the results significantly since the two terms give mutually cancelling effects. In the exchange energy expression in Eq. (15), the fractional importance of nonorthogonality terms was found to be more important for the innermost cores, and steadily decreased on proceeding towards the outermost ones. This trend can be understood as follows. On expanding the MP function for the outermost core states (like 5s in cesium), the major components are the unoccupied higher s states which are orthogonal to the other occupied core states, while the reverse is true for the MP functions of the inner cores. On adding up all the nonorthogonality terms, the net contribution was found to be only about 6 to 7% of the total a_{CP} in all cases. Columns 7 and 8 of Table I show the interesting feature that a_{CP} is about 23% of the direct term a_{d} for all the atoms. This is not surprising since the contribution to a_{CP} was found to arise in all cases from the exchange between the outermost core and the valence electrons. While the inclusion of core-polarization effects enhances the theoretical results substantially, the sum of the direct and core-polarization contributions $(a_{\mathrm{d}}+a_{\mathrm{CP}})$ are seen to be consistently smaller than the experimental values, particularly for the heavier atoms. It is reassuring that for the atoms for which UHF results are available (Column 9) there is very good agreement with the numbers for $(a_{\mathrm{d}}+a_{\mathrm{CP}})$ in Column 8. The difference between theory and experiment appears to increase in the order lithium to cesium. This would seem to indicate the importance of an additional mechanism which increases with atomic number. Relativistic effects provide such a mechanism and will be considered next.

III. RELATIVISTIC EFFECTS

Since hyperfine interactions arise primarily from regions close to the nuclei where the kinetic energy of the electrons is greatest, these interactions are likely to be subject to relatively strong relativistic effects as compared to other properties. There are two alternative approaches that one can adopt to study such effects. One procedure is to handle the relativistic effect on the wave function as a perturbation in the spirit of the Foldy-Wouthuysen transformation.[29] The other approach is to work with Dirac-Hartree-Fock (DHF) Eqs.[30] for the electrons and handle all operators in a completely relativistic manner.[6,9] We have adopted the latter procedure both as it permits a definitive estimate of relativistic corrections and because for heavy elements one would have to go to rather high orders in the perturbation approach. However, er, the perturbation procedure does have the merit of allowing a convenient visualization of different types of relativistic effects, and we shall establish contact with it subsequently in this section.

The one-electron DHF wave functions are conveniently expressed in the four-component spinor form:

$$\varphi_{n\kappa\mu} = \begin{pmatrix} r^{-1} g_{n\kappa}(r)\ \psi_{\kappa\mu} \\ i r^{-1} f_{n\kappa}(r)\ \psi_{-\kappa\mu} \end{pmatrix}, \tag{8}$$

where $\psi_{\kappa\mu}$ are two-component spinors given by

$$\psi_{\kappa\mu} = \sum_{m=\pm\frac{1}{2}} C(l\tfrac{1}{2}j;\,\mu-m,m)\,Y_l^{\mu-m}(\theta,\varphi)\,\chi(m) \tag{9}$$

in terms of Clebsch-Gordan coefficients,[31] spherical harmonics, and the Pauli spinors

$$\chi(\tfrac{1}{2}) = \binom{1}{0}, \quad \chi(-\tfrac{1}{2}) = \binom{0}{1}. \tag{10}$$

The wave functions $\varphi_{n\kappa\mu}$ are characterized by the eigenvalues of energy, the total angular momentum and its z component j and μ, respectively, and parity. The parity and j dependence are both described by the quantum number κ which is related to j by the relation

$$\kappa = \mp (j+\tfrac{1}{2}) \tag{11}$$

for even and odd parity, respectively. Instead of the conventional Fermi-contact, orbital, and dipole-dipole operators of nonrelativistic theory, one now has to use the relativistic hyperfine operator

$$\mathcal{H}_{\text{hfs}}^{\text{Rel}} = e\vec{\alpha}\cdot\vec{\text{A}}, \tag{12}$$

where $-e$ is the electronic charge, the components of $\vec{\alpha}$ are the first-three Dirac matrices and $\vec{\text{A}}$ is the magnetic vector potential produced by the nuclear moment $\vec{\mu}_I$

$$\vec{\text{A}} = \vec{\mu}_I \times \vec{\text{r}}/r^3. \tag{13}$$

For a system with more than one electron, the hyperfine operator in Eq. (12) has to be summed over all the electrons. Similarly to the case of the nonrelativistic Hartree-Fock approximation, one also works with determinantal wave functions in the relativistic case and the sum over electrons reduces to a sum of the expectation values over the one-electron states. Further, as in the nonrelativistic case, if one uses the restricted Hartree-Fock approximation, the closed shells do not contribute to the hyperfine matrix element, and only valence electrons have to be considered. Since our present work is concerned with alkali atoms, we have only single-valence electron states and the algebra for the matrix elements is analogous to that worked out by Rose[29] and others[6,9] for hydrogen-like atoms. We shall not therefore repeat the algebraic procedure but only list the final expressions for the matrix elements of $\mathcal{H}_{\text{hfs}}^{\text{Rel}}$ between states $(n\kappa\mu)$ and $(n\kappa'\mu')$, where the n dependence is unimportant since we have a single-valence electron. If the direction of the nuclear moment is chosen as along the z axis, one can show that J_z commutes with $\mathcal{H}_{\text{hfs}}^{\text{Rel}}$ and therefore only matrix elements with $\mu = \mu'$ need to be considered. For the study of atomic hyperfine structure, only the case $\kappa = \kappa'$ is of interest. However, we are also interested in hyperfine effects in metals where because of the crystalline field there is mixing of l states in the nonrelativistic approximation and j states in relativistic theory so that the matrix elements with $\kappa = \kappa'$ are of interest. Commensurate with the notation for the wave functions in (8), the matrix elements are

$$\langle \kappa\mu | e\vec{\alpha}\cdot\vec{\text{A}} | \kappa'\mu\rangle = -ieR_{\kappa\kappa'}A_{\kappa\kappa'}^{\mu}, \tag{14}$$

where

$$R_{\kappa\kappa'} = \int_0^\infty r^{-2}(g_\kappa f_{\kappa'} + g_{\kappa'} f_\kappa)dr, \tag{15}$$

$$A_{\kappa\kappa'}^{\mu} = \langle \psi_{\kappa\mu} | (\vec{\sigma}\times\hat{r})_z | \psi_{-\kappa'\mu}\rangle, \tag{16}$$

and $\vec{\sigma}$ represents the two-component Pauli matrices. Equation (16) can be reduced further using Eq. (9). The diagonal elements defined by $\kappa = \kappa'$ are given by

$$\begin{aligned} A_{\kappa\kappa}^{\mu} &= 4il\mu/(4l^2-1), & j &= l-\tfrac{1}{2}, \\ A_{\kappa\kappa}^{\mu} &= -[4i(l+1)\mu/(2l+1)(2l+3)], & j &= l+\tfrac{1}{2}. \end{aligned} \tag{17}$$

For the nondiagonal elements $\kappa \neq \kappa'$, we can have two cases:

Case 1: Matrix elements between states with same l composition, for example, $(p_{1/2}, p_{3/2})$, $(d_{3/2}, d_{5/2}), \ldots$, and

Case 2: Matrix elements between states with different l composition, $(s_{1/2}, d_{3/2})$, $(p_{3/2}, f_{5/2}), \ldots$. Equation (16) then yields

$$\begin{aligned} A_{\kappa\kappa'}^{\mu} &= i[(l+\tfrac{1}{2})^2-\mu^2]/(2l+1) \quad \text{Case 1}, \\ A_{\kappa\kappa'}^{\mu} &= -i[(l+\tfrac{3}{2})^2-\mu^2]/(2l+3) \quad \text{Case 2}. \end{aligned} \tag{18}$$

For atoms, one obtains from experiment the hyperfine constant a in the spin Hamiltonian $a\vec{\text{I}}\cdot\vec{\text{J}}$. The theoretical value of a may be obtained from the hyperfine matrix element by the relation

$$a = -(ie\gamma_I/\pi)A_{\kappa\kappa}^{\mu}R_{\kappa\kappa}, \tag{19}$$

where γ_I is the magnetogyric ratio $\mu_I/I\hbar$. The evaluation of a thus requires a knowledge of the radial integrals $R_{\kappa\kappa}$. For this purpose, we need the radial functions $g_\kappa(r)$ and $f_\kappa(r)$. While formulations of the DHF equations were available for sometime, only recently have solutions of such equations become available.[12,13] The complexities of the procedure for solving DHF equations can be appreciated by noting first that one now has twice the number of coupled eigenvalue equations that occur in nonrelativistic theory. Secondly, because the large and small components vary by orders of magnitude over various ranges of r, the demands on numerical accuracy are considerably larger in the relativistic case. In their work, Liberman, Waber, and Cromer[13] (LWC) have utilized the Slater approximation (henceforth referred to as DHFS). Herman and Skillman[32] had also utilized the Slater approximation in their extensive nonrelativistic (NR-HFS) calculations. While one could compare results obtained from LWC's wave functions with those obtained using Herman-Skillman functions to assess the importance of relativistic effects, there is some question about the applicability of the Slater approximation to systems with rapidly varying densities as in atoms. The Slater approximation is more justifiable in the solid state, where the densities have lesser fluctuations. Coulthard[12] has recently obtained wave functions for a number of atoms without making use of the Slater approximation (referred to henceforth as DHF). The results that we obtain using his wave functions are more appropriate for quantitative comparisons with experiment and nonrelativistic theory.

In utilizing the available DHF and DHFS functions to evaluate $R_{\kappa\kappa}$ in Eq. (15), one has to be cautious about the difference in phase conventions due to Rose[29] that we have adopted and those by other authors.[12,13] From the forms of the equations employed by these authors the following relationships are seen to hold between the various choices of phase.

$$\left.\begin{aligned} g_{\text{Rose}} &= g_{\text{LWC}} = g_{\text{Coulthard}}, \\ f_{\text{Rose}} &= f_{\text{LWC}} = -f_{\text{Coulthard}} \end{aligned}\right\} \quad j = l-\tfrac{1}{2};$$

$$\left.\begin{aligned} g_{\text{Rose}} &= g_{\text{LWC}} = g_{\text{Coulthard}}, \\ f_{\text{Rose}} &= -f_{\text{LWC}} = -f_{\text{Coulthard}} \end{aligned}\right\} \quad j = l+\tfrac{1}{2}.$$

In relativistic theory, all states with $j=\frac{1}{2}$ exhibit a weak (but square-integrable) divergence of f and g. As a result, the integrand gf/r^2 occurring in the matrix element of $\mathcal{H}_{\mathrm{hfs}}{}^{\mathrm{Rel}}$ is singular at the origin. The occurrence of this divergence can be understood physically as follows. In the nonrelativistic Schrödinger equation, it is the centrifugal term $l(l+1)/r^2$ which determines the r^{l+1} behavior of the radial wave functions at small r. On the other hand, in the relativistic case at small r, there is a partial cancellation of the centrifugal potential by a relativistic term of the form $(z\alpha/r)^2$ which leads to an r dependence of the type

$$r^{1-(\kappa^2-Z^2\alpha^2)^{1/2}}$$

that is responsible for the divergence of the $j=\frac{1}{2}$ states. To avoid errors due to this apparent divergence, we have evaluated the integral (15) for a number of cutoffs (r_0) at small r. The behavior of the integral was studied as a function of r_0 and was found to have a linear dependence on r_0, a typical case was for the cesium ${}^6S_{1/2}$ state, being as shown in Fig. 1. A linear extrapolation to $r_0 \rightarrow 0$ was therefore quite justified.

Using this limiting procedure for the evaluation of in (15), we have obtained the hyperfine constants for the ${}^2S_{1/2}$ states of all the alkali atoms using DHF wave functions. The results are listed in Table II and compared with the results from nonrelativistic Hartree-Fock theory and experiment. The differences between the relativistic and nonrelativistic values of the hyperfine constants are in the right direction to improve agreement with experiment. Further, as anticipated, the percentage corrections are substantial for the heavier atoms rubidium and cesium, and decrease steadily as one goes to the lighter atoms. However, it is clear from this table that relativistic effects alone cannot produce perfect agreement with experiment, and other factors such as the core-polarization effect of the previous section will have to be included. In the next section we shall combine the core-polarization and relativistic effects and try to draw conclusions from the nature of the agreement between theory and experiment.

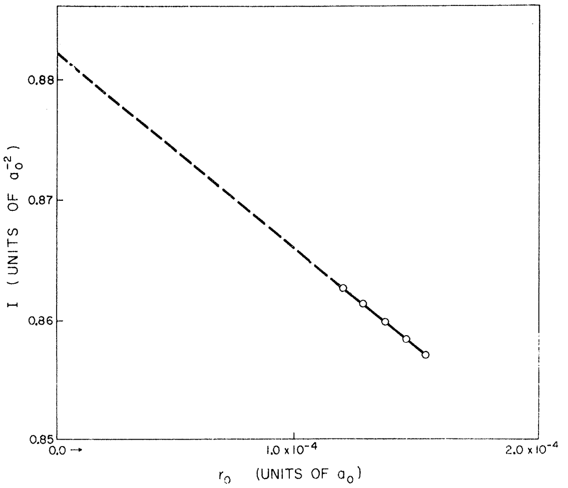

FIG. 1. The hyperfine integral $\mathrm{I}=\int_{r_0}^{\infty} r^{-2}\, gf\, dr$ for cesium as a function of the cutoff parameter r_0.

TABLE II. Hyperfine constants a obtained from nonrelativistic Hartree-Fock (NR-RHF), relativistic Hartree-Fock (DHF), and experiment in Mc/sec.

Atom	a(NR-RHF)	a(DHF)	a(EXP)
Li	284.00	285.00	401.80
Na	629.00	635.00	885.70
K	144.00	149.00	230.90
Rb	505.80	663.40	1011.90
Cs	983.80	1456.20	2298.20

In the remainder of this section, we would like to make some comparison between the purely relativistic theory of hyperfine effects that has been used here and the perturbation approach for handling relativistic effects starting from the nonrelativistic limit. This is important for two reasons. First there have been recent calculations on hyperfine structure in some other atomic systems,[10,11] and we would like to comment on their relationship to our analysis. Secondly it is useful to have some nonrelativistic limits for hyperfine matrix moments which could be used to check solid-state calculations to be reported later.

There are two alternate ways of relating the relativistic theory to a perturbation expansion starting with the nonrelativistic limit. One can either take the relativistic matrix elements of the type in Eq. (14) and make a Breit reduction[33] in various orders of parameters such as $Z\alpha$ and $\hbar/mc$. The other procedure is to perform a Foldy-Wouthuysen transformation on the total Hamiltonian $\mathcal{H}^{\mathrm{Rel}}$,

$$\mathcal{H}^{\mathrm{Rel}}=\mathcal{H}_0{}^{\mathrm{Rel}}+\mathcal{H}_{\mathrm{hfs}}{}^{\mathrm{Rel}},$$

to obtain an expansion in various orders of relativistic effects. In the lowest order, $\mathcal{H}_{\mathrm{hfs}}{}^{\mathrm{Rel}}$ reduces to the form

$$\mathcal{H}_{\mathrm{hfs}}{}^{\mathrm{Rel}}=\frac{8\pi}{3}\mu_B\vec{\mu}_I\cdot\vec{\sigma}\,\delta(\vec{\mathrm{r}})-\mu_B[(\vec{\mu}_I\cdot\vec{\sigma}/r^3)$$

$$-3(\vec{\mu}_I\circ\vec{\mathrm{r}})(\vec{\sigma}\cdot\vec{\mathrm{r}})/r^5]+2\mu_B(\vec{\mu}_I\cdot\vec{\mathrm{L}}/r^3), \quad (20)$$

which consists of conventional Fermi-contact, electron-nucleus dipole-dipole, and nuclear-moment-electron-orbital terms. The Hamiltonian $\mathcal{H}_0{}^{\mathrm{Rel}}$ can be reduced in the nonrelativistic approximation to a sum of three operators given by

$$\mathcal{H}_0{}^{\mathrm{Rel}}=\mathcal{H}_0{}^{\mathrm{NR}}+\mathcal{H}_{\mathrm{SO}}+\mathcal{H}', \quad (21)$$

where $\mathcal{H}_0{}^{\mathrm{NR}}$ is the conventional nonrelativistic Hamiltonian, $\mathcal{H}_{\mathrm{SO}}$ gives the contribution of spin-orbit and spin-other-orbit effects, and $\mathcal{H}'$ represents additional contributions, for example, the mass-velocity term which does not explicitly depend on the angular momentum. It is this term which restores the degeneracy between equal j states in the hydrogen atom after the spin-orbit effect is applied. There is some uncertainty as to the exact form of the spin-orbit potential for many-electron systems in the presence of exchange. In the case of more than one valence electron outside of closed shells, a portion of the spin orbit term $\mathcal{H}_{SO}$ leads to a mixing between states of different orbital angular momentum (but of the same j values). This has been referred to in the literature[10] as the BDLSC effect. However, in the case of alkali atoms, we have only one valence electron and the BDLSC effect is insignificant. The main difference between nonrelativistic results in our case is therefore a reflection of the influence of the mass-velocity term on the radial part of the one-electron valence wave function.

For the sake of illustration, we have listed in Table III the nonrelativistic limit for matrix elements of the hyperfine operator between those $\kappa\mu$ states which reduce in NR theory $p_{3\mu/2}$ and $p_{\mu/2}$ states. These are determined by both the above procedures, namely, by taking the expectation values of $\mathcal{H}_{hfs}{}^{NR}$ over the nonrelativistic states and also by Breit reduction[33] of the matrix elements of Eq. (14) (see Appendix B). As mentioned earlier, this table as well as corresponding ones for s and d states will be of use in solid-state calculations where off-diagonal $(j\mu, j'\mu)$ elements can occur because of the mixing of orbital states by the crystal potential.

It should be pointed out that in our relativistic calculations, the effect of the Breit interaction between electrons has not been included since this effect was not incorporated in the DHF wave functions[12] which we have used. Since the Breit interaction[34] is essentially a two-electron effect, one would not expect it to have significant influence on one-electron properties like the hyperfine interaction as has in fact been demonstrated in earlier calculations.[10]

IV. DISCUSSION

Theoretical values for the hyperfine constants a in all the alkali atoms including the NR-RHF, CP, and relativistic contributions are tabulated in Table IV and compared with the experimental results. To facilitate discussion, the individual contributions from these sources are also included. By relativistic contribution is meant the difference between the DHF and NR-RHF results from Columns 3 and 2 of Table II. The differences between the experimental and theoretical values of a in Table IV are seen to increase from about 6% for lithium to 26% for cesium. From the trend of these differences, it is tempting to ascribe them to errors in the relativistic calculation. However, one can dispense with this source as a major contributor by itself, since the remaining discrepancies between theory and experiment are much larger than the entire relativistic correction (Column 4 of Table IV) for the lighter atoms. As regards errors in the CP contribution, it could be argued that by using a perturbation approach (MP), we may be neglecting higher-order perturbation effects. However, CP contributions from UHF calculations in lithium, sodium, and potassium are seen from Table I to compare quite favorably with those by the MP procedure. As a matter of fact, any appreciable difference in the results by the two procedures occurs only in the case of the lightest atom lithium, and can be understood by the fact that exchange potential is a larger fraction of the total Hamiltonian in the lighter atoms. Therefore it seems reasonable to assume that the MP results for rubidium and cesium are a good representation of the actual nonrelativistic core-polarization effect. It is then interesting to inquire whether a relativistic treatment of the CP effect would lead to any substantial

TABLE III. Reduction of relativistic hyperfine matrix elements.

Bra and ket	Relativistic hfs matrix element	Breit reduced[a] matrix element	Matrix elements of $\mathcal{H}_{hfs}{}^{NR}$		
$\langle j\mu\|\ \ \|j'\mu\rangle$			Dipolar	Orbital	Total
$\langle\frac{1}{2}\ \frac{1}{2}\|\ \ \|\frac{1}{2}\ \frac{1}{2}\rangle$	$\frac{4}{3}e\mu_I\int_0^\infty\frac{g_{1/2}f_{1/2}}{r^2}dr$	$\frac{8}{3}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$\frac{4}{3}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$\frac{4}{3}\mu_B\mu_I\langle\frac{1}{r3}\rangle$	$\frac{8}{3}\mu_B\mu_I\langle\frac{1}{r3}\rangle$
$\langle\frac{3}{2}\ \frac{3}{2}\|\ \ \|\frac{3}{2}\ \frac{3}{2}\rangle$	$-\frac{8}{5}e\mu_I\int_0^\infty\frac{g_{3/2}f_{3/2}}{r^2}dr$	$\frac{8}{5}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$-\frac{2}{5}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$2\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$\frac{8}{5}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$
$\langle\frac{3}{2}\ \frac{1}{2}\|\ \ \|\frac{3}{2}\ \frac{1}{2}\rangle$	$-\frac{8}{15}e\mu_I\int_0^\infty\frac{g_{3/2}f_{3/2}}{r^2}dr$	$\frac{8}{15}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$-\frac{2}{15}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$\frac{2}{3}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$\frac{8}{15}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$
$\langle\frac{1}{2}\ \frac{1}{2}\|\ \ \|\frac{3}{2}\ \frac{1}{2}\rangle$ + $\langle\frac{3}{2}\ \frac{1}{2}\|\ \ \|\frac{1}{2}\ \frac{1}{2}\rangle$	$\frac{2^{3/2}}{3}e\mu_I\int_0^\infty\frac{g_{3/2}f_{1/2}+g_{1/2}f_{3/2}}{r^2}dr$	$\frac{2^{3/2}}{3}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$-\frac{2^{3/2}}{3}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$\frac{2^{5/2}}{3}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$	$\frac{2^{3/2}}{3}\mu_B\mu_I\langle\frac{1}{r^3}\rangle$

[a] $\langle 1/r3\rangle$ in this column and subsequent ones refers to the matrix element of r^{-3} over the radial part of the nonrelativistic p wave function.

TABLE IV. Various contributions to the theoretical value of a and comparison with experiment.

Atom	$a_{\text{NR-RHF}}$	a_{CP}	a_{Rel}[a]	a_{Total}	a_{Exp}
Li	284.00	94.02	1.00	379.02	401.80
Na	629.00	141.54	6.00	777.54	885.70
K	144.00	35.49	5.00	184.49	230.90
Rb	505.80	130.14	157.60	793.54	1011.90
Cs	983.80	227.25	472.40	1683.45	2298.20

[a] $a_{\text{Rel}} = a_{\text{DHF}} - a_{\text{NR-RHF}}$.

correction to the nonrelativistic result. In the relativistic case, the UHF approximation would imply different radial functions (both large and small components) for different one-electron m_j states analogous to the difference in the radial functions for different m_s states in the nonrelativistic approximation. A relativistic MP calculation will of necessity be more complicated, since one has to solve coupled perturbation equations for the large and small components. Furthermore the demands on computational accuracy will be much more severe because of the expected order of magnitude difference between the radial functions for large and small components. In the absence of actual relativistic CP calculations, we can only speculate on the magnitude of relativistic corrections to the CP effect. From Table I the nonrelativistic CP effect is seen to be about 23% of the NR-RHF contribution for all the atoms. If it is assumed that the relativistic CP effect will also have the same percentage importance relative to the DHF result, we get only 39.89 Mc/sec and 122.42 Mc/sec for $\Delta a_{\text{cp}} = a_{\text{cp}}{}^{\text{Rel}} - a_{\text{cp}}{}^{\text{NR}}$ for rubidium and cesium and negligible corrections for the lighter atoms. Thus the nature of the agreement between experiment and theory would be essentially unaltered by incorporating relativistic effects in the CP calculation.

From these considerations, we are led to believe that the residual difference between experiment and theory can only be explained by including correlation effects explicitly. There are two types of correlation effects which could influence the theoretical result. One type is the correlation between the valence electron and the cores which can lead to a change in the valence-electron wave function near the nucleus. A second effect can arise from the intra- and inter-shell correlations among the core electrons. The latter type of correlation can influence the hyperfine constant indirectly through its influence on the CP effect. Many-body calculations[16] on lithium atom using Breuckner-Goldstone theory indicates that of the two types, the one involving the valence electron is more important. This feature is expected to hold for all the alkali atoms.

V. CONCLUSION

Various possible contributions to the hyperfine constant have been analyzed for the alkali atoms. The core-polarization contribution appears to be the main source of correction to restricted Hartree-Fock approximation. Relativistic effects are found to be insignificant for the three lighter alkali atoms but comparable to the core-polarization effect for the heavier atoms rubidium and cesium. The explanation of the remaining discrepancy between theory and experiment would require explicit consideration of correlation effects.

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APPENDIX A: NONITERATIVE PROCEDURE FOR SOLVING INTEGRODIFFERENTIAL EQUATIONS OF SECTION II

We shall present here a generalization of the noniterative procedure[23] for solving an integrodifferential equation when more than one core states are involved. In most general form, Eq. (1) in Sec. II can be written as

$$M\varphi = f_0 + \sum_{i=1}^{n} \gamma_i \langle \chi_i | \varphi \rangle f_i, \tag{A-1}$$

where M is the differential operator and f_0 is the inhomogeneous part of the equation; the f_i are radial functions which may in particular cases be identical to χ_i, and the γ_i are multiplying constants. In general, the f_i are nonorthogonal,

$$\langle f_i | f_j \rangle \neq \delta_{ij}. \tag{A-2}$$

For an atom with t cores (including the one which is being perturbed) n is equal to $3(t-1)$. One demands the solution of Eq. (A-1) in the form

$$\varphi = \sum_{i=0}^{n} C_i \varphi_i \tag{A-3}$$

with $C_0 = 1$ and the φ_i satisfying the equations

$$M\varphi_i = f_i \tag{A-4}$$

Substituting for φ from Eq. (A-3) in (A-1) and using (A-4), one obtains

$$\sum_{i=1}^{n} C_i \Bigg(\langle f_i | f_k \rangle - \sum_{j=1}^{n} \gamma_j \langle \chi_j | \varphi_i \rangle \times \langle f_j | f_k \rangle) = \sum_{i=1}^{n} \gamma_i \langle \chi_j | \varphi_0 \rangle \langle f_i | f_k \rangle \Bigg). \tag{A-5}$$

In deriving Eq. (A-5), the linear independence of the source functions f_i have been utilized. Defining the square matrix $[A]$ by

$$A_{ki} = \langle f_i | f_k \rangle - \sum_{j=1}^{n} \gamma_j \langle \chi_j | \varphi_i \rangle \langle f_j | f_k \rangle \tag{A-6}$$

and two column matrices $[C]$ and $[S]$, the latter being defined as

$$S_k = \sum_{i=1}^{n} \gamma_i \langle \chi_i | \varphi_0 \rangle \langle f_i | f_k \rangle, \tag{A-7}$$

one obtains the desired coefficients C_i in Eq. (A-3) from the equation

$$C_i = \sum_{j=1}^{n} [A]_{ik}{}^{-1} S_k. \tag{A-8}$$

In Eq. (A-8), i takes the values from 1 to n, C_0 being equal to unity. In practice, therefore, one solves the $(n+1)$ differential Eqs. (A-4) with appropriate boundary conditions and then obtains the perturbed solution φ using (A-6), (A-7), (A-8), and (A-3). The normalization of the total perturbed function is achieved by adding to it a suitable multiple of the solution of the homogeneous equation

$$M\varphi = 0. \tag{A-9}$$

APPENDIX B

We are interested in the nonrelativistic reduction of the radial part of the relativistic hyperfine matrix element given in Eq. (15) of the main text.

$$R_{\kappa\kappa'} = \int_0^\infty r^{-2}(g_\kappa f_{\kappa'} + g_{\kappa'} f_\kappa)\, dr, \tag{B-1}$$

where g_κ and f_κ are the large and small radial components of the Dirac wave functions for the state under investigation. The functions g_κ and f_κ satisfy the following radial equations:

$$\frac{dg_\kappa}{dr} + \kappa \frac{g_\kappa}{r} = \left[\frac{2\pi}{\Lambda}\left(1 + \frac{E}{mc^2}\right) - V\right] f_\kappa, \tag{B-2}$$

$$\frac{df_\kappa}{dr} - \kappa \frac{f_\kappa}{r} = \left[\frac{2\pi}{\Lambda}\left(1 - \frac{E}{mc^2}\right) + V\right] g_\kappa, \tag{B-3}$$

$$\frac{dg_{\kappa'}}{dr} + \kappa' \frac{g_{\kappa'}}{r} = \left[\frac{2\pi}{\Lambda}\left(1 + \frac{E}{mc^2}\right) - V\right] f_{\kappa'}, \tag{B-4}$$

$$\frac{df_{\kappa'}}{dr} - \kappa' \frac{f_{\kappa'}}{r} = \left[\frac{2\pi}{\Lambda}\left(1 - \frac{E}{mc^2}\right) + V\right] g_{\kappa'}, \tag{B-5}$$

where $\Lambda = h(mc)^{-1}$. The terms involving E and V on the right may be eliminated by multiplying Eq. (B-3) by $f_{\kappa'}$ and Eq. (B-4) by g_κ and adding the two

$$\begin{aligned}\frac{4\pi}{\Lambda}\int_0^\infty \frac{g_\kappa f_{\kappa'}}{r^2} dr &= \int_0^\infty \frac{1}{r^2}(g_\kappa dg_{\kappa'} + f_{\kappa'} df_\kappa) \\ &\quad + \int_0^\infty \frac{1}{r^3}(\kappa' g_\kappa g_{\kappa'} - \kappa f_\kappa f_{\kappa'})\, dr.\end{aligned} \tag{B-6}$$

By an equivalent procedure using Eqs. (B-2) and (B-5), one obtains a similar equation involving $g_{\kappa'}$ and f_κ.

$$\begin{aligned}\frac{4\pi}{\Lambda}\int_0^\infty \frac{g_{\kappa'} f_\kappa}{r^2} dr &= \int_0^\infty \frac{1}{r^2}(g_{\kappa'} dg_\kappa + f_\kappa df_{\kappa'}) \\ &\quad + \int_0^\infty \frac{1}{r^3}(\kappa g_\kappa g_{\kappa'} - \kappa' f_\kappa f_{\kappa'})\, dr.\end{aligned} \tag{B-7}$$

On adding (B-6) and (B-7), the matrix element $R_{\kappa\kappa'}$ in (B-1) is expressed in terms of products of large and small components by themselves, a form particularly suitable for the nonrelativistic reduction process.

$$\begin{aligned}\frac{4\pi}{\Lambda}\int_0^\infty \frac{1}{r^2}(g_\kappa f_{\kappa'} + g_{\kappa'} f_\kappa)\, dr &= \int_0^\infty \frac{1}{r^2}[(d/dr)(g_\kappa g_{\kappa'} + f_\kappa f_{\kappa'})]\, dr \\ &\quad + \int_0^\infty \frac{1}{r^3}[(\kappa + \kappa')(g_\kappa g_{\kappa'} - f_\kappa f_{\kappa'})]\, dr.\end{aligned} \tag{B-8}$$

In order to take into account the fact that the nucleus has finite size, one has to subtract from the Eq. (B-8) the contribution to the integrals from a small region 0 to r_0, given by

$$\begin{aligned}\frac{4\pi}{\Lambda}\int_0^{r_0} \frac{1}{r^2}(g_\kappa f_{\kappa'} + g_{\kappa'} f_\kappa)\, dr &= \int_0^{r_0} \frac{1}{r^2}[(d/dr)(g_\kappa g_{\kappa'} + f_\kappa f_{\kappa'})]\, dr \\ &\quad + \int_0^{r_0} \frac{1}{r^3}[(\kappa + \kappa')(g_\kappa g_{\kappa'} - f_\kappa f_{\kappa'})]\, dr.\end{aligned} \tag{B-9}$$

Subtracting (B-9) from (B-8), one obtains after partial integration

$$\begin{aligned}\int_0^\infty \frac{1}{r^2}(g_\kappa f_{\kappa'} + g_{\kappa'} f_\kappa)\, dr &= \int_0^{r_0} \frac{1}{r^2}(g_\kappa f_{\kappa'} + g_{\kappa'} f_\kappa)\, dr \\ &\quad + \frac{\Lambda}{4\pi}\int_0^\infty [g_\kappa g_{\kappa'}(\kappa + \kappa' + 2) - f_\kappa f_{\kappa'}(\kappa + \kappa' - 2)]\frac{dr}{r^3} \\ &\quad - \frac{\Lambda}{4\pi}\frac{1}{r_0^2}(g_\kappa g_{\kappa'} + f_\kappa f_{\kappa'})\Big|_{r_0}.\end{aligned} \tag{B-10}$$

In the nonrelativistic limit the first term on the right goes to zero, the second yields the conventional dipolar interaction for non-s states, and the first part of the third term goes over to the Fermi-contact interactions for s states.

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Spin-Extended Wave Functions for First-Row Atoms*

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An extension of Brillouin's theorem, stating that matrix elements of $H-EI$ between the spin-extended Hartree-Fock (SEHF) function and the projected singly-excited functions derived from it vanish, is used to calculate the SEHF function itself. Functions are reported for C, N, O, and F, using two basis sets for each atom. Results are compared with earlier calculations for other first-row atoms. Appreciable energy reductions with respect to the restricted Hartree-Fock results were obtained only for the closed-shell atoms He and Be, and a spin density in good agreement with experiment was obtained only for Li. It is suggested that larger basis sets may be required to span the SEHF functions.

I. INTRODUCTION

The method most widely used for obtaining atomic wavefunctions is the Hartree-Fock approximation,[1,2] in which the best solution to the Schrödinger equation representable as an antisymmetrized product of one-electron functions is found. The exact eigenfunctions of the nonrelativistic, spin-free Hamiltonian are also eigenfunctions of the spin and orbital angular momentum operators