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Spin densities of first-row atoms calculated from polarization wave functions with accurate numerical methods

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Fermi contact spin densities of the first-row atoms B–F having open-shell p electrons are systematically calculated with simple, physically interpretable wave-function models that include only the dominant configurations together with relevant single excitations that describe polarization effects. All orbitals involved are optimized self-consistently by accurate numerical grid methods to obviate any questions about basis-set incompleteness. It is found that spin polarization of the $1s$, $2s$, and $2p$ shells (the latter for oxygen and fluorine only) together with orbital polarization of the $2s$ shell are the important effects. Core and valence contributions are separately large in magnitude, but nearly cancel one another leading to much smaller net spin densities. The results show good semiquantitative agreement with experiment, implying that true electron-correlation effects play a secondary role in determining the spin densities of these first-row atoms.

INTRODUCTION

Despite many recent advances in electronic structure theory, accurate *ab initio* calculation of Fermi contact spin densities that determine isotropic electron spin resonance (ESR) hyperfine parameters in polyatomic free radicals remains an elusive problem.[1] Including the important polarization effects through simple methods based on unrestricted Hartree-Fock (UHF) wave functions, with or without subsequent spin projection, has proven unreliable in some cases.[2] More successful methods for including the same polarization effects while maintaining correct wave-function symmetry often correspond to variations on the theme of augmenting the restricted open-shell Hartree-Fock (ROHF) wave function with certain important singly excited configurations.[3–6] In those free radicals where such simple single-excitation configuration-interaction (SECI) methods have failed, it has generally not been clear to what extent the discrepancies with experiment have been due to the wave-function model itself, which neglects true electron-correlation effects that are described by double and higher excitations, or to deficiencies of the Gaussian basis sets normally employed to approximate the solutions.

In an effort to address these problems separately, we report here a comprehensive theoretical study on the first-row ground-state atoms B–F having open-shell p electrons. Any questions about basis-set incompleteness are obviated by solving the multiconfiguration self-consistent-field (MCSCF) equations of the single-excitation model accurately with numerical grid methods. Thus, this study provides a benchmark demonstrating the inherent efficacy of the single-excitation model for these atoms.

The calculation of spin densities in the first-row atoms is, of course, also an interesting problem in its own right and has been the subject of numerous previous studies that have recently been reviewed.[7] The Fermi contact term is one of several hyperfine parameters required to analyze the spectra of light atoms. The others, corresponding to orbital and spin-dipolar magnetic dipole interactions and to electric quadrupole interactions, are generally well described by simple wave functions[7] and consequently will not be further considered here.

The Fermi contact spin density reported in this work is defined in atomic units as

$$Q(0)/N=\left\langle\Psi\left|\sum_i \delta(\mathbf{r}_i)2\mathcal{S}_{zi}\right|\Psi\right\rangle\Big/\left\langle\Psi\left|\sum_i 2\mathcal{S}_{zi}\right|\Psi\right\rangle ,$$

where the electronic wave function Ψ has quantum numbers $J=L+S$ and $M_J=J$. The denominator is simply the number of unpaired electrons, normalizing the spin density to a per electron basis. It can be seen from entry G of Table I that this particular definition has the advantage of showing a monotonic increase in the experimental spin density upon moving across the period from B to F. In fact, the variation is so smooth that it has been used to estimate the unknown experimental value for C $[^3P]$ by fitting the differences between calculated and experimental values for the other atoms.[8,10] Simple graphical interpolation of the known experimental values also leads to essentially the same result.

The calculations reported in this work were carried out with the numerical atomic MCSCF program of Froese

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TABLE I. Fermi contact spin density $Q(0)/N$ in atomic units for ground states of first-row atoms. Different row entries correspond to inclusion of different polarization effects. The most complete calculation for each atom is marked with an asterisk.

	Polarization Spin[a]	Orbital[b]	B $[^2P]$	C $[^3P]$	N $[^4S]$	O $[^3P]$	F $[^2P]$
A	$1s,2s$		−0.0076	0.0027	0.0162	0.0012	−0.0035
B	$1s,2s$	$1s,2s$	0.0155*	0.0238*	0.0336*	0.0279	0.0291
C	$1s,2s,2p$					0.0224	0.0334
D	$1s,2s,2p$	$1s,2s$				0.0450	0.0610
E	$1s,2s,2p$	$1s,2s,2p$				0.0456*	0.0622*
F[c]	$1s,2s,2p$	$1s,2s$	0.0153	0.0218	0.0309	0.0406	0.0555
G	experiment		0.0081[d]	(0.020)[f]	0.0324[h]	0.0569[i]	0.0717[i]
			0.013[e]	(0.0192)[g]			

[a]This column indicates the shells for which spin polarization configurations were included.
[b]This column indicates the shells for which orbital polarization configurations were included.
[c]In entry F, minor terms are removed from the most sophisticated calculation for each atom (see text for full explanation).
[d]Reference 8 (gas phase value).
[e]Reference 9 (Ar matrix value).
[f]Reference 8 (estimated value—see text).
[g]Reference 10 (estimated value—see text).
[h]Reference 11.
[i]Reference 12.

Fischer,[13] together with related Hamiltonian[14] and spin-density[15] matrix-element evaluation programs. Some modifications were made to interface these programs with one another and to allow for calculations with predetermined linear combinations of configurations.

Previous comprehensive atomic calculations were generally carried out with Slater basis sets,[7,16] with the important exception of one numerical UHF study.[17] While this manuscript was in preparation, an additional theoretical study by Feller and Davidson appeared.[18] That work utilizes Gaussian basis sets in conjunction with large-scale multireference configuration interaction (MRCI) wave functions, made tractable by perturbation-theory configuration selection. In contrast, the focus in the present work is to assess the effects of true electron correlation indirectly by first determining the inherent accuracy of the simple single-excitation model.

The results of this work show that the single-excitation model, at least when treated by accurate numerical methods, can indeed provide a semiquantitatively correct description of the first-row atom spin densities. This implies that true electron-correlation effects are of secondary importance. The plethora of terms involved in most other methods is avoided here by utilizing a short configuration list built from a small number of well-chosen orbitals determined self-consistently, thereby allowing for clear assessment of each of the physical effects important for the spin density. It is found that spin polarization effects in the $1s$, $2s$, and $2p$ shells (the latter for oxygen and fluorine only) and orbital polarization effects in the $2s$ shell must all be described properly to obtain good results. The core and valence contributions are separately large in magnitude but opposite in sign, nearly canceling one another to give a much smaller net spin density. Therefore, small relative errors in any of these separate important terms can lead to large final errors in the spin density.

SPIN POLARIZATION OF s SHELLS

The dominant configuration for each of the ground-state first-row atoms under consideration can be expressed as

$$\Psi_0 = 1s^2\,2s^2\,2p^n\ ,$$

where $n=1$ for B, 2 for C, etc. Throughout this work we adopt the convention that configurations are always properly antisymmetrized net eigenfunctions of $\mathcal{S}^2$ and $\mathcal{L}^2$ and, unless explicitly indicated otherwise, have $2p$-shell electrons coupled to yield the same term as the overall atomic state under consideration. Note that the dominant configuration alone would give zero spin density since each unpaired electron is in a p orbital having a node at the nucleus.

The most important corrections influencing the spin densities correspond to spin polarization of the $1s$ and $2s$ orbitals via $(s\rightarrow s)$-type single excitations. These configurations have the form

$$\Psi_1 = 1s\,s^{**}\,[^3S]\,2s^2\,2p^n\ ,$$

$$\Psi_2 = 1s^2\,2s\,s^{*}\,[^3S]\,2p^n\ ,$$

where the term symbol in brackets indicates the intermediate coupling of the immediately preceding singly occupied orbitals. Since the "excited" or "virtual" s^{**} and s^* orbitals are optimized self-consistently, each can be regarded as representing an entire class of excitations in a conventional CI picture. Most of the spin density in this three-configuration wave function arises from the off-diagonal terms coupling Ψ_1 and Ψ_2 to Ψ_0 in the spin-density matrix.

Note the omission of configurations similar to Ψ_1 and Ψ_2, but with $[^1S]$ intermediate spin coupling of the two singly occupied s orbitals. The major effect of such excitations is already automatically included in Ψ_0 itself via

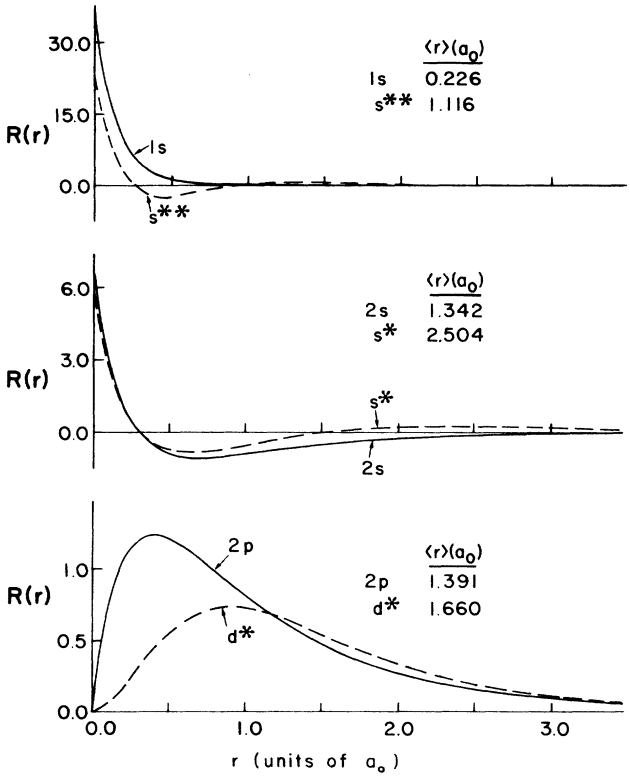

FIG. 1. Plots of radial functions for N [^4S] orbitals.

the SCF optimization of the $1s$ and $2s$ orbitals. Explicit inclusion of such configurations is therefore unnecessary and, in fact, undesirable since their inclusion would be detrimental to the stability of the MCSCF optimization procedure. Such considerations do not apply to Ψ_1 and Ψ_2, since the [^3S] intermediate spin coupling of the two singly occupied s orbitals requires a concomitant spin flip of a p-shell electron, making the nominal single excitation actually a double excitation when viewed in terms of spin orbitals.

Radial plots of the optimum numerical $1s$, $2s$, s^*, and s^{**} orbitals for the nitrogen atom are shown in Fig. 1. The positions of the inner nodes of the slightly occupied "excited" s^{**} and s^* orbitals are primarily determined by the requirements of orthogonality to their highly occupied partners, the $1s$ and $2s$ orbitals, respectively. The s^{**} and s^* orbitals are largely localized in the core and valence regions, respectively, but each is somewhat more diffuse than its highly occupied partner. Similar features are found in the analogous plots for the other atoms as well.

Results from this simple three-configuration model are given as entry A in Table I. The spin densities are seen to be uniformly much smaller than experiment, even being negative in some instances. It should not be concluded, however, that the $s \rightarrow s$ spin polarization effects are unimportant—quite the opposite is true. For example, the net calculated spin density of 0.0162 in N [^4S] is composed of a -0.1325 core contribution and a 0.1487 valence contribution. Similarly in all the atoms, the negative core and positive valence contributions are separately much larger than the experimental result, but nearly cancel one another to provide net results much smaller than experiment. Thus, the terms that separately provide the largest spin-density contributions collectively yield little net spin density. This "accidental" near cancellation will probably not be as severe in polyatomic free radicals, since chemical bonding effects should alter the valence more than the core contributions. Nevertheless, it is clear that for the first-row atoms one must look beyond the $s \rightarrow s$ spin polarization excitations to obtain good results.

ORBITAL POLARIZATION OF s SHELLS

Orbital polarization of the $1s$ and $2s$ orbitals via $s \rightarrow d$ single excitations is also important in the first-row atoms. For boron and fluorine the possible net [^2P] configurations can be represented by

$$\Psi_3 = 1s\, d^{**}\, [^3D]\, 2s^2\, 2p^n\ ,$$

$$\Psi_3' = 1s\, d^{**}\, [^1D]\, 2s^2\, 2p^n\ ,$$

$$\Psi_4 = 1s^2\, 2s\, d^*\, [^3D]\, 2p^n\ ,$$

$$\Psi_4' = 1s^2\, 2s\, d^*\, [^1D]\, 2p^n\ .$$

We will continue to use the term orbital polarization since the usage is firmly entrenched, but it should be recognized that configurations such as Ψ_3 and Ψ_4 (as well as analogous configurations for the other atoms) actually refer to simultaneous orbital and spin polarization.

For carbon and oxygen there are several possible intermediate couplings of $s \rightarrow d$ single excitations that can ultimately lead to a net [^3P] state. It is convenient here to write the configurations in the form

$$\Psi_3 = 1s\, d^{**}\, [^3D]\, 2s^2\, 2p^n \{a[^3P] + b[^1D]\}\ ,$$

$$\Psi_3' = 1s\, d^{**} [^1D]\, 2s^2\, 2p^n [^3P]\ ,$$

$$\Psi_3'' = 1s\, d^{**}\, [^3D]\, 2s^2\, 2p^n \{-b[^3P] + a[^1D]\}\ ,$$

$$\Psi_4 = 1s^2\, 2s\, d^*\, [^3D]\, 2p^n \{a[^3P] + b[^1D]\}\ ,$$

$$\Psi_4' = 1s^2\, 2s\, d^*\, [^1D]\, 2p^n [^3P]\ ,$$

$$\Psi_4'' = 1s^2\, 2s\, d^*\, [^3D]\, 2p^n \{-b[^3P] + a[^1D]\}\ ,$$

where $a = \sqrt{2}/\sqrt{5}$ and $b = \sqrt{3}/\sqrt{5}$ are chosen to produce certain desirable linear combinations of the possible couplings of electrons in the $2p$ shell. These combinations are constructed such that Ψ_3'' and Ψ_4'' have vanishing Hamiltonian matrix elements with Ψ_0. These configurations do not connect with Ψ_0 in the spin-density matrix either. Consequently, they should have only a small effect and will be ignored.

For nitrogen, the only possible $s \rightarrow d$ single excitations that can lead to a net [^4S] state involve spin and orbital polarization of the s shells, accompanied by a recoupling of the $2p$-shell electrons in configurations of the form

$$\Psi_3 = 1s\, d^{**}\, [^3D]\, 2s^2\, 2p^3\, [^1D]\ ,$$

$$\Psi_4 = 1s^2\, 2s\, d^*\, [^3D]\, 2p^3\, [^1D]\ .$$

The results of including both spin and orbital polariza-

tion of the s shells are seen in entry B of Table I. Comparison to entry A shows that inclusion of $s \rightarrow d$ orbital polarization significantly increases the spin densities. Indeed, the carbon and nitrogen results are now in semiquantitative agreement with experiment. The absolute agreement is actually not so bad for boron either, but the fact that the gas-phase experimental result is so near zero makes the relative error seem large in that case. Our calculated result for boron is in much better agreement with the experimental value reported in an Ar matrix at 4 K.[9] Only the oxygen and fluorine results still have large errors at this level.

This section, which includes the influence of both spin and orbital polarization of the $1s$ and $2s$ shells, provides our most complete calculations for B–N. For O–F there is an additional possibility of polarizing the more than half-filled $2p$ shell. That effect will be considered in the following sections.

SPIN POLARIZATION OF p SHELL

In the boron, carbon, and nitrogen atoms explicit $2p \rightarrow p^*$ single excitations can be omitted because their influence is already largely included via self-consistent optimization of the $2p$ orbitals. However, for oxygen and fluorine with a more than half-filled $2p$ shell, such terms can be important. For O $[^3P]$ it is convenient to form linear combinations of the possible $2p$ shell couplings as in the configurations

$$\Psi_5 = 1s^2 2s^2 2p^3 \{c[^4S] + d[^2D] - e[^2P]\} p^* ,$$

$$\Psi_5' = 1s^2 2s^2 2p^3 \{-f[^4S] + e[^2D] - g[^2P]\} p^* ,$$

$$\Psi_5'' = 1s^2 2s^2 2p^3 \{h[^4S] + c[^2D] + f[^2P]\} p^* ,$$

with $c = \sqrt{5}/3$, $d = \frac{1}{6}$, $e = \sqrt{5}/\sqrt{12}$, $f = 1/\sqrt{3}$, $g = \frac{1}{2}$, and $h = \frac{1}{3}$. For F $[^2P]$ the convenient linear combinations are

$$\Psi_5 = 1s^2 2s^2 2p^4 \{i[^1S] + j[^1D] - k[^3P]\} p^* ,$$

$$\Psi_5' = 1s^2 2s^2 2p^4 \{l[^1S] + f[^1D] + m[^3P]\} p^* ,$$

$$\Psi_5'' = 1s^2 2s^2 2p^4 \{n[^1S] - o[^1D] + q[^3P]\} p^* ,$$

with $i = \sqrt{8}/\sqrt{15}$, $j = 1/\sqrt{6}$, $k = \sqrt{3}/\sqrt{10}$, $l = 1/\sqrt{15}$, $m = \sqrt{3}/\sqrt{5}$, $n = \sqrt{2}/\sqrt{5}$, $o = 1/\sqrt{2}$, and $q = 1/\sqrt{10}$. With these particular choices, Ψ_5'' has, by construction, a vanishing Hamiltonian matrix element with Ψ_0. Also, the Ψ_5' configuration has only a small Hamiltonian matrix element with Ψ_0 (it would be zero by Brillouin's theorem if Ψ_0 were the ROHF wave function). Furthermore, none of these configurations connect to Ψ_0 in the spin-density matrix. We therefore neglect Ψ_5'' and Ψ_5', leaving only Ψ_5 to be considered as a possibly important $p \rightarrow p$ spin polarization configuration in the oxygen and fluorine atoms.

In Table I two sets of results are given to show the importance of the Ψ_5 terms. In entry C they augment only the $s \rightarrow s$ spin polarization results of entry A. This is of some academic interest since it shows the limiting accuracy of the single-excitation model when only s and p functions are included. In entry D the Ψ_5 terms augment the $s \rightarrow s$ spin polarization plus $s \rightarrow d$ orbital polarization results of entry B. Comparison of these various entries in Table I indicates that the $p \rightarrow p$ spin polarization effect in oxygen and fluorine is comparable in importance to the $s \rightarrow d$ orbital polarization effect. Furthermore, the two contributions are roughly additive and, taken together with the $s \rightarrow s$ spin polarization, bring these two atoms into semiquantitative agreement with experiment.

ORBITAL POLARIZATION OF p SHELL

For atoms with a more than half-filled $2p$ shell, there is also the possibility of orbital polarization in the p shell via $p \rightarrow f$ single excitations. The relevant configurations are

$$\Psi_6 = 1s^2 2s^2 2p^3 [^2D] f^*$$

for O $[^3P]$ and

$$\Psi_6 = 1s^2 2s^2 2p^4 [^1D] f^*$$

for F $[^2P]$. Augmenting the model of entry D with these terms provides the results in entry E of Table I and represents our most complete calculations for these two atoms. Comparison with entry D shows that the $p \rightarrow f$ excitations increase the spin density, leading to improved agreement with experiment. However, the effect is quite small and it must be concluded that orbital polarization of the $2p$ shell has a minor influence on the spin density. The results at this level show good semiquantitative agreement with experiment.

REMOVAL OF MINOR TERMS

It has been shown in the previous sections that the single-excitation model is capable of giving semiquantitative agreement with experimental spin densities when all conceivably important polarization terms are included. This encompasses some configurations that during the course of the calculations have empirically been found to have a minor effect. For example, it has already been demonstrated that the $p \rightarrow f$ orbital polarization excitations that can contribute in the oxygen and fluorine atoms are of little importance. Detailed examination of the results shows that in addition, for all the atoms, the $s \rightarrow d$ $[^1D]$ excitations can be neglected in both the $1s$ and $2s$ shells, as can the $1s \rightarrow d^{**}$ $[^3D]$ excitations. This leaves only the $1s \rightarrow s^{**}$ $[^3S]$ spin polarization configuration Ψ_1 as important in the core region. In the valence region we are left with the $2s \rightarrow s^*$ $[^3S]$ spin polarization configuration Ψ_2, the $2s \rightarrow d^*$ $[^3D]$ spin and orbital polarization configuration Ψ_4, and, for oxygen and fluorine only, the $2p \rightarrow p^*$ spin polarization configuration Ψ_5.

The results after removal of all these minor terms are shown as entry F in Table I. Comparison with the most complete results for each atom, namely, entry B for boron, carbon, and nitrogen and entry E for oxygen and fluorine, shows that the removal leads to some decrease in spin density, but there is still satisfactory semiquantitative agreement with experiment. Thus, good results can be obtained from very compact wave functions, just four configurations for B–N and five for O–F.

TABLE II. Comparison with literature results for Fermi contact spin density $Q(0)/N$ in atomic units for ground states of first-row atoms.

Source	B [^2P]	C [^3P]	N [^4S]	O [^3P]	F [^2P]
POL-CI[a]	0.0073	0.0139	0.0243	0.0305	0.0470
This work[b]	0.0155	0.0238	0.0336	0.0456	0.0622
MRCI[c]	0.0044	0.0159	0.0311	0.0480	0.0678
Experiment[d]	0.0081	(0.020)	0.0324	0.0569	0.0717
	0.013	(0.0192)			

[a]Slater basis-set results of Ref. 16.
[b]Most complete results of this work. See text for full explanation.
[c]Gaussian basis-set results of Ref. 18.
[d]See footnotes to Table I for experimental references.

DISCUSSION

This work shows clearly that the single excitation model is capable of providing semiquantitative accuracy for the Fermi contact spin densities of the first-row atoms B–F. Spin polarization of the 1*s* and 2*s* shells gives the largest individual contributions, but these terms nearly cancel one another to give net results much smaller than experiment. Orbital polarization of the 2*s* shell and, for oxygen and fluorine, spin polarization of the 2*p* shell are additional important effects that must also be included.

For the simple wave-function models considered here, the MCSCF orbitals are the natural orbitals. Since there are no ambiguous cross terms, it is then possible to cleanly separate core from valence contributions in the spin-density matrix. Our most complete results for each atom then break down into core contributions of −0.0492, −0.0837, −0.1271, −0.1782, and −0.2403 and valence contributions of 0.0647, 0.1075, 0.1607, 0.2238, and 0.3025 for B, C, N, O, and F, respectively. Thus, the separate contributions are consistently about three to five times larger in magnitude than the net spin density, and show a similar monotonic increase with atomic number. An important consequence of the "accidental" near cancellation of core and valence contributions is that a small relative error in either separate contribution can become magnified into a large error in the final result.

Comparison of the present results with some other relevant calculations is provided in Table II. The polarization-CI (POL-CI) study[16] corresponds to a ROHF+SECI model and was carried out with Slater basis sets that are presumably large enough for convergence of the spin density. The results do not compare as well with experiment, particularly for oxygen and fluorine which are much too small. That calculation is similar in spirit to the present one insofar as reliance is placed on a single-excitation model. In fact, by expressing that wave function in terms of its natural orbitals, it can be collapsed to a small number of configurations, each analogous to one discussed in the present work. While a full investigation into the source of the different results obtained is beyond the scope of the present work, it is still worthwhile to speculate on the matter. It seems improbable that the configurations omitted here because of their expected small effect would contribute much to the differences found. A more likely explanation lies in the different forms of the orbitals used to build the configurations. Full MCSCF optimization of all orbitals as carried out here allows for higher-order relaxation effects to come in, causing significant differences both in the highly occupied 1*s*, 2*s*, and 2*p* orbitals and in the slightly occupied polarizing orbitals of the two models.

The recent large scale MRCI results of Feller and Davidson[18] carried out with large Gaussian basis sets are also included in Table II. They show some improvement over the present results when compared with experiment. However, the residual errors are still comparable to the differences between the two calculations. It therefore appears that the influence of true electron-correlation effects on atomic spin densities will be exceedingly difficult to recover accurately.

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