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Gaussian basis sets for calculation of spin densities in first-row atoms

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Summary. The suitability of Gaussian basis sets for *ab initio* calculation of Fermi contact spin densities is established by application to the prototype first-row atoms B—F having open shell *p* electrons. Small multiconfiguration self-consistent-field wave functions are used to describe relevant spin and orbital polarization effects. Basis sets are evaluated by comparing the results to highly precise numerical grid calculations previously carried out with the same wave function models. It is found that modest contracted Gaussian basis sets developed primarily for Hartree-Fock calculations can give semi-quantitative results if augmented by diffuse functions and if further uncontracted in the outer core–inner valence region.

Key words: Spin density — Gaussian basis sets — First row atoms — Polarization wave function

1. Introduction

The suitability of Gaussian basis sets for *ab initio* calculation of spin densities that determine electron spin resonance isotropic hyperfine coupling constants in polyatomic free radicals is a prominent question. The Fermi contact spin density depends on the wave function only at a single point in space, the nucleus. It is therefore of some concern that computational results might be highly sensitive to minor changes in the exponents and/or contraction coefficients of the several highly peaked *s* Gaussian functions required to describe the inner core region, thus making reliable spin density calculations difficult. An additional concern relates to the fact that Gaussians have zero radial slope at the nucleus and are therefore inherently unable to satisfy the correct nuclear cusp condition.

These potential problems have contributed to the viewpoint that the large errors often encountered in theoretical calculations of spin densities in polyatomic free radicals may be due to the use of Gaussian basis functions. Satisfactory resolution of the basis set problem is clearly a prerequisite for further progress in this field.

In this work we present a comprehensive study of spin densities in the first-row atoms B—F calculated by *ab initio* methods with Gaussian basis sets. By virtue of having open shell *p* electrons, these atoms can be regarded as analogous to molecular π radicals. In such cases, the highly occupied spin-restricted reference determinant makes no direct contribution to the contact spin density and additional configurations must be included. The description of spin density can therefore become intimately entangled with the description of electron correlation. It would be desirable to separate the extent to which any disagreement with experiment may be due to Gaussian basis set limitations rather than to shortcomings of the wave function models employed. This ambiguity is resolved here by determining the requirements on Gaussian basis sets necessary to reproduce results obtained from the same simple polarization wave function models implemented with highly precise numerical grid methods. The interesting effects of true electron correlation, which are not overly large in this case, can then be regarded as a separate question.

Early studies on first-row atom spin densities have been critically reviewed [1], so we only briefly mention some of the more recent works here. Comprehensive spin-unrestricted Hartree-Fock (UHF) calculations have been carried out numerically by Bagus et al. [2]. Extensions of such a model have been reported with Slater basis sets by Goddard [3], and with Gaussian basis sets by Meyer [4]. A number of studies have been reported using spin-restricted methods with large Slater basis sets. These include the polarization and first-order configuration interaction calculations carried out by Schaefer et al. [5, 6], which have been further analyzed by Larsson et al. [7], and the symmetry-adapted cluster calculations of Nakatsuji et al. [8]. None of the above studies obtained overall satisfactory agreement with the known experimental spin densities.

Good agreement with experiment has been reached only recently in several works that appeared while this manuscript was in the final stages of preparation. The multi-reference configuration interaction (MR-CI) calculations of Feller and Davidson [9], and the various large CI calculations on nitrogen by Bauschlicher et al. [10] were based on spin-restricted models. Carmichael [11] used more modest CI expansions based on spin-unrestricted models. These studies have shown that good results can be obtained from large Gaussian basis sets in the context of highly correlated wave functions.

Whilst these recent works [9–11] have demonstrated sufficient methods for quantitative spin density determination, they have not clarified the minimum conditions necessary for semiquantitative accuracy. That remains an important question, since it would be desirable to have useful yet practical methods that can be applied to larger molecular free radicals. This is our motivation for going to the opposite extreme and considering the simplest possible wave functions and basis sets necessary for reasonable description of Fermi contact spin density within a spin-restricted framework.

Our recent benchmark numerical multi-configuration self-consistent-field (MCSCF) study [12] on the atoms B—F provides the basis for this work. It was shown there that reasonably good spin density results can be obtained from simple wave functions including only the highly occupied reference configuration and those few singly excited configurations expected on theoretical grounds to be connected to it by significant Hamiltonian matrix elements. These single excitations represent spin and orbital polarization of the highly occupied 1*s*, 2*s* and 2*p* orbitals. Since analogous configurations are implicit in the UHF model, we prefer to distinguish these polarization and relaxation effects from true electron correlations that would require double and higher excitations.

The reasonably good agreement with experiment obtained from such simple wave function models [12] may, of course, be somewhat fortuitous. However, that possibility does not vitiate the present work. We utilize here the same configuration lists and MCSCF orbital optimization methods as in the earlier [12] numerical study. This allows attention to be diverted from the wave function models employed and focused instead on the requirements for Gaussian basis sets to reproduce precise numerical grid results. As an additional advantage, the demands can be examined separately for each class of angular momentum basis functions.

To summarize our findings, it is shown here that properly constructed modest Gaussian basis sets are quite capable of providing semiquantitative spin density results for the first-row atoms. In surprising contrast to the considerations discussed in the opening paragraph above, it is found that the major deficiencies of common Gaussian basis sets do not lie in the region very close to the nucleus, where standard contractions of standard basis sets are actually found to be quite satisfactory. Rather, the problems lie in the lack of primitive functions in the diffuse region [13] and in overcontraction of *s* functions describing the outer core–inner valence region. Simple explanations of these results are found upon examination of the slightly occupied polarizing orbitals. These are crucial for spin density determination but are not well represented by common contracted Gaussian basis sets designed only to fit the highly occupied Hartree-Fock orbitals.

It should be emphasized that basis sets are considered here within the context of a simple wave function model that describes only the lowest order spin and orbital polarization effects. They may not be well balanced for description of true electron correlation effects, which can significantly affect the spin densities in some systems. Proper description of electron correlation makes additional demands on the basis set and lies outside the scope of this study.

2. Computational methods

In our development of appropriate Gaussian basis sets, the distribution of primitive exponents and their contraction schemes are both considered. To be specific, the study is based on the commonly used (9*s*5*p*) primitive Gaussian basis set of Huzinaga [14] and various segmented contractions of it recommended by Dunning [15]. However, the general conclusions that emerge are likely to be applicable to many other commonly used basis sets.

All MCSCF calculations over Gaussian basis sets were carried out with the ALIS [16] series of programs. To ensure proper L^2 (angular momentum) eigenfunctions, a program option to enforce equivalence restrictions on the degenerate orbital components of a shell was utilized. The program determines the correct variational minimum for such an orbitally constrained wave function [17]. The ALIS programs automatically construct Serber-type spin eigenfunctions. Multiplication of a simple orbital product by a Serber function yields, after antisymmetrization, a configuration called a SAAP [18]. A program feature allows the relative weights of several SAAPs to be fixed *a priori* throughout the MCSCF optimization. This was found useful in constructing alternate desired S^2 (spin) eigenfunctions for certain $2p \rightarrow p^*$ configurations and more generally in forming the linear combinations of SAAPs corresponding to L^2 eigenfunctions. The $3s$ components of the six cartesian d basis functions were eliminated, leaving only true five-component d functions to be included in the calculations. As a consequence of these constructions, the wave function models used here correspond exactly to those of our earlier study [12]. This then allows us to focus on the essential difference of representing the radial forms of the orbitals in terms of Gaussian basis functions rather than the earlier [12] numerical grid representations.

Additional programs were written to evaluate Fermi contact spin densities from the MCSCF wave functions. The actual expression used is based on expectation values according to

$$Q(0)/N = \langle \Psi | \sum_i \delta(r_i) 2S_{zi} | \Psi \rangle / \langle \Psi | \sum_i 2S_{zi} | \Psi \rangle$$

which gives the spin density per unpaired electron in atomic units.

In practice, the major factor limiting the precision of MCSCF spin densities obtained from Gaussian basis sets comes in determination of the s^{**} orbital associated with spin polarization of the $1s$ shell. The configuration in which the s^{**} orbital appears has a coefficient of only 0.001–0.002 in the various first-row atoms. The total energy is therefore somewhat insensitive to this orbital and program convergence thresholds must be set stringently to allow precise determination of the amplitude of s^{**} at the nucleus. This problem is most severe for calculations with the fully uncontracted Gaussian basis sets. By carrying out selected equivalent calculations with other programs at our disposal, it has been verified that the spin densities in this work have been correctly determined to more than the number of significant digits actually reported.

To minimize confusion, the notation and configuration numbering used here is carried over from our earlier work [12], which should be consulted for more detailed discussions of why certain configurations are kept and others are omitted. Throughout this work we adopt the convention that configurations are always properly antisymmetrized net eigenfunctions of S^2 and L^2 and, unless explicitly indicated otherwise, have $2p$ shell electrons coupled to yield the same term as the overall atomic state.

3. Development of *sp* basis sets

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

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

where n is 1 for B, 2 for C, etc. By itself this configuration would give zero contact spin density since each unpaired electron is in a p orbital having a node at the nucleus. The most important corrections for the present purposes [12] come from spin polarization of the s shells via $1s \to s^{**}$ and $2s \to s^*$ excitations. These are described by configurations of the form

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

and

$$\Psi_2 = 1s^2 2ss^*[^3S]2p^n$$

where the term symbol in brackets indicates the intermediate coupling of the immediately preceding singly occupied orbitals [19]. For atoms with the p shell more than half filled there is also the possibility of spin polarization by $2p \to p^*$ excitations. This effect is represented in O [^3P] by the configuration

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

with $c = \sqrt{5}/3$, $d = 1/6$, $e = \sqrt{5/12}$, and in F [^2P] by the configuration

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

with $i = \sqrt{8}/\sqrt{15}, j = 1/\sqrt{6}, k = \sqrt{3}/\sqrt{10}$. Note that in each case the configuration is actually a linear combination of three possible intermediate couplings of the $2p^{n-1}$ shell electrons. In was argued in our earlier work [12] that the other two possible linear combinations should have only a small effect and can be omitted, since they have small or vanishing connections with Ψ_0 in the Hamiltonian and spin density matrices. All the results discussed in this section correspond to MCSCF wave functions composed only of the dominant configurations Ψ_0 together with the spin polarization configurations Ψ_1 and Ψ_2 and, for oxygen and fluorine, Ψ_5.

Comparison with experiment is not made in this section, since important orbital polarization effects have not yet been included in the wave functions. It was emphasized in our earlier study [12] that whilst the $1s$ and $2s$ spin polarization effects are separately large in magnitude, they are opposite in sign and nearly cancel one another in all the first-row atoms. The net results at this level are therefore much smaller than experiment. However, meaningful comparisons can be made to the numerical results obtained with the same wave function models.

Performance of the primitive ($9s5p$) basis set with standard [$4s2p$] and [$5s3p$] contractions and also fully uncontracted is shown at the top of Table 1. Comparing to the numerical results quoted at the bottom of the table, it is seen that the [$4s2p$] contraction gives reasonable results. However, more detailed

Table 1. MCSCF results with *sp* Gaussian basis sets[a] for ground state first-row atom Fermi contact spin densities $Q(0)/N$ in atomic units. Wave functions include only spin polarization effects

Basis set	B $[^2P]$	C $[^3P]$	N $[^4S]$	O $[^3P]$	F $[^2P]$
$[4s2p]$	−0.0019	0.0084	0.0193	0.0242	0.0323
$[5s3p]$	0.0133	0.0331	0.0557	0.0753	0.1002
$(9s5p)$	−0.0098	−0.0027	0.0062	0.0121	0.0220
$(9s5p)$ + diff *sp*	−0.0066	0.0032	0.0161	0.0233	0.0335
$(9s5p)$ + diff *ss′pp′*	−0.0067	0.0032	0.0160	0.0222	0.0332
$[3s2p]$ + diff *sp*	−0.0201	−0.0285	−0.0372	−0.0666	−0.0947
$[4s2p]$ + diff *sp*	−0.0017	0.0097	0.0225	0.0254	0.0323
$[5s3p]$ + diff *sp*	0.0132	0.0340	0.0584	0.0760	0.0996
$[5's2p]$ + diff *sp*	−0.0079	0.0012	0.0123	0.0146	0.0222
$[6s3p]$ + diff *sp*	−0.0079	0.0018	0.0149	0.0214	0.0325
Numerical[b]	−0.0076	0.0027	0.0162	0.0224	0.0334

[a] All *sp* Gaussian basis sets are based on the $(9s5p)$ primitive basis of [14]. The $[3s2p]$, $[4s2p]$ and $[5s3p]$ contractions are from [15] while the $[5's2p]$ and $[6s3p]$ contractions are closely related as described in the text. Diffuse functions are given in [25]

[b] Numerical result from [12] obtained with same wave function model

examination of the $[4s2p]$ calculations reveals that in all the atoms the coefficient of Ψ_1 is much too small and the amplitude of s^{**} at the nucleus is much too large. These discrepancies are both of the order of 300%, but since the spin density depends approximately linearly on their product there is a fortuitous rough cancellation of these two large separate errors. Despite being more flexible, the $[5s3p]$ contraction gives poor results. This is due primarily to large errors again in the coefficient of Ψ_1 and in the amplitude of s^{**} at the nucleus, but here the errors do not happen to be the same size and their cancellation is not so complete. The coefficients and orbital amplitudes all become approximately correct only for the fully uncontracted $(9s5p)$ basis. Even so, agreement with the precise numerical results is still not completely satisfactory in most cases. This indicates that the primitive $(9s5p)$ basis itself is deficient in some respect for spin density calculations.

A clue to the difficulty with this primitive basis comes from the observation made in the previous study [12] that the s^* polarizing orbital is more diffuse than its $2s$ partner in all the atoms. Similarly, the p^* polarizing orbital in oxygen and fluorine is more diffuse than its $2p$ partner. Since the $(9s5p)$ basis set and its contractions were developed to fit only the highly occupied $1s$, $2s$ and $2p$ orbitals, it may be deficient in the diffuse region. This hypothesis was tested by adding one and then two shells of diffuse s and p functions, with exponents chosen [25] to continue the approximate geometric progression of the outermost functions in the $(9s5p)$ basis. These results are shown in the middle of Table 1. It is seen that adding one shell of diffuse functions leads to good agreement with the numerical results. Further, it is seen that adding a second shell of still more diffuse functions has little additional effect. It can be concluded that adding just one shell of diffuse *s* and *p* functions is sufficient. The diffuse *p* functions may not actually be needed for the atoms B—N, where there is no spin polarization of the $2p$ shell.

Adopting the $(9s5p)$ + diffuse *sp* basis as a suitable set of primitive functions, we now reconsider the question of contraction schemes. Results from Dunning's $[3s2p]$, $[4s2p]$ and $[5s3p]$ contractions, all augmented with one shell of freely varying diffuse functions, are given in the middle of Table 1. Among this group, only the $[4s2p]$ + diffuse *sp* results are reasonable, and that is again due to fortuitous cancellation of large separate errors (this time of the order of 50%) in the coefficient of Ψ_1 and in the amplitude of s^{**} at the nucleus. The $[3s2p]$ + diffuse *sp* and $[5s3p]$ + diffuse *sp* spin densities are erratic and generally inaccurate.

It was suspected that the problem with the contracted sets may lie in the description of the s^{**} polarizing orbital, which is known to be more diffuse than its $1s$ partner [12]. If so, a proper representation might require additional variational flexibility in the outer core–inner valence region. This hypothesis was tested by manufacturing two new contractions of the *s* space. The first, labelled $[5's]$ is closely related to Dunning's $[4s]$ set, differing only in allowing the outer member of the innermost six-function contraction to float freely, the remaining five inner functions being left contracted in their original ratios. In another common and obvious notation, this corresponds to a (5,1,1,1,1) contraction scheme. The second new set, labelled $[6s]$, is a similar modification of Dunning's original $[5s]$ set, corresponding to a (4,1,1,1,1,1) contraction scheme. It is seen in the bottom part of Table 1 that the new $[5's2p]$ + diffuse *sp* basis does reasonably well and that the new $[6s3p]$ + diffuse *sp* basis set gives quite good agreement both with the numerical results and with the uncontracted $(9s5p)$ + diffuse *sp* results.

It can be concluded that the $(9s5p)$ basis provides a good starting point for description of the *sp* space, but it must be augmented by at least one shell of diffuse functions and must not be overcontracted in the important outer core–inner valence region. These considerations lead to a new $[6s3p]$ + diffuse *sp* basis that performs well for spin density calculations.

4. Development of *d* basis sets

In our previous work [12] it was found that orbital polarization of the $2s$ shell via configurations involving $2s \rightarrow d^{*}$ $[^3D]$ excitations were very important for spin density determination. Analogous configurations found to be of minor significance [12] include $2s \rightarrow d^{*}$ $[^1D]$ excitations, all orbital polarization of the $1s$ shell via both $1s \rightarrow d^{**}$ $[^1D]$ and $[^3D]$ excitations, and $2p \rightarrow f^{*}$ orbital polarization of the $2p$ shell. All these configurations of minor significance will be excluded here.

The $2s \rightarrow d^{*}$ orbital polarization configuration of importance for spin density takes the form

$$\Psi_4 = 1s^2 2s\, d^*[^3D] 2p^n \qquad \text{for B and F,}$$

$$\Psi_4 = 1s^2 2s\, d^*[^3D] 2p^n \{a[^3P] + b[^1D]\} \qquad \text{for C and O,}$$

where $a = \sqrt{2}/\sqrt{5}$ and $b = \sqrt{3}/\sqrt{5}$, and

$$\Psi_4 = 1s^2 2s\, d^*[^3D]2p^3[^1D] \quad \text{for N.}$$

Note that a linear combination of two intermediate spin couplings for the $2p^n$ shell electrons is considered for C and O. It was argued in our earlier work [12] that the other independent linear combination has vanishing connections with Ψ_0 in the Hamiltonian and spin density matrices so has only a small effect and can be omitted. All results presented in this section correspond to a wave function including the dominant and spin polarization configurations discussed in the previous section together with the orbital polarization configuration Ψ_4.

The effect of augmenting the $[6s3p]$ + diffuse *sp* basis developed in the previous section with a single shell of *d* functions of various exponent is shown in the top portion of Table 2. It is seen that a single *d* function with an optimized exponent [26] chosen to minimize the total energy gives results in fairly good agreement with the analogous numerical calculations, which are quoted at the bottom of the table. However, this is somewhat fortuitous since the spin density is actually a sensitive function of the Gaussian *d* exponent. This is clearly demonstrated in the table, where significantly different results are seen upon increasing or decreasing the optimum single *d* exponent by just 20%.

Over this limited variation of *d* exponent, the spin density appears to be approximately linear. In actual fact, as the *d* exponent gets smaller the spin density soon reaches a maximum, e.g., $Q(0)/N = 0.0515$ a.u. for exponent 0.31 in nitrogen, and for still more diffuse exponents it gradually falls off to the value found in the absence of *d* functions. As the exponent gets larger, the spin density

Table 2. MCSCF results with *spd* Gaussian basis sets[a] for ground state first-row atom Fermi contact spin densities $Q(0)/N$ in atomic units. Wave functions include both spin and orbital polarization effects

d exponent	B $[^2P]$	C $[^3P]$	N $[^4S]$	O $[^3P]$	F $[^2P]$
One *d*					
opt + 20%	0.0077	0.0115	0.0181	0.0259	0.0379
opt	0.0140	0.0198	0.0279	0.0370	0.0508
opt − 20%	0.0199	0.0282	0.0383	0.0488	0.0642
Two *d*					
opt + 20%	0.0139	0.0202	0.0288	0.0387	0.0532
opt	0.0143	0.0212	0.0304	0.0408	0.0559
opt − 20%	0.0150	0.0224	0.0321	0.0429	0.0585
Three *d*					
opt	0.0139	0.0205	0.0296	0.0398	0.0550
Numerical[b]	0.0153	0.0218	0.0309	0.0406	0.0555

[a] All *sp* Gaussian basis sets are based on the $[6s3p]$ + diffuse *sp* set developed in this work (see text). One, two or three *d* functions are added with exponents obtained from the energy-optimized (opt) single *d* values listed in [26]. See text for additional details

[b] Numerical result from [12] obtained with same wave function model

passes through a minimum, e.g., $Q(0)/N = -0.0281$ for exponent 2.8 in nitrogen, before approaching the no-*d* value. Analogous widely ranging behavior is also found for each of the other atoms.

This high sensitivity to the *d* exponent is undesirable, since the serendipitously good value found here may not transfer well to other situations. Nevertheless, be this as it may, the results obtained with a single *d* exponent chosen to minimize the total energy are found to be consistently good for the spin densities of all the first-row atoms.

To see whether the single *d* results obtained above are actually representative of a more saturated *d* basis, results obtained with two *d* Gaussians are presented in the middle part of Table 2. We employ the common practice of obtaining the exponents by multiplying and dividing the energy-optimized single *d* exponent by a factor of two. It is seen that little change occurs in the spin density upon passing to the two *d* representation. However, the results are now much more stable to variations of the exponents, as demonstrated by the small changes obtained on increasing or decreasing the two exponents by 20%. Moving on to include three Gaussian *d* functions, obtained by again multiplying and dividing the two *d* exponents by a factor of two, is seen at the bottom of Table 2 to cause little additional change in the results. This suggests that just two Gaussian *d* functions are adequate for reasonable description of the d^* polarizing orbital.

It is concluded that a single Gaussian *d* function can reproduce the 2*s* orbital polarization effect for spin densities of the first-row atoms, provided that the *d* exponent is chosen to minimize the total energy. However, this criterion may not carry over to other cases. At least two Gaussian *d* functions are required for a truly satisfactory representation of the *d* space.

5. Discussion

The most important finding of this work is that modest Gaussian basis sets are quite capable of providing a reasonably good description of Fermi contact spin densities. However, typical standard basis sets designed for Hartree-Fock calculations must be altered in certain ways to make this possible. A shell of diffuse *s* and *p* functions must be added to describe the $2s \rightarrow s^*$ and $2p \rightarrow p^*$ spin polarizations properly. The outer core–inner valence region must be left uncontracted to provide sufficient flexibility for description of the $1s \rightarrow s^{**}$ spin polarization. Fortunately, and somewhat surprisingly, the inner core region is well described by standard contractions of standard basis sets for the innermost few *s* functions. A single *d* function can describe the important $2s \rightarrow d^*$ orbital polarization, but the *d* exponent must be very carefully chosen. In the case of the first-row atoms, minimization of the total energy is found to be a suitable criterion, although it is possible that this may not carry over to other cases. The results become insensitive to small changes in the *d* exponents only if two or more *d* functions are used.

These conclusions were based on finding Gaussian basis sets that reproduce numerical results obtained from simple MCSCF polarization wave functions involving only the most important single excitations. It is seen in Table 3 that this also provides a reasonable semiquantitative description of the experimentally observed spin densities of the first-row atoms. Further small changes, usually improvements, are seen for the numerical MCSCF results [12] quoted in Table 3, which include other minor orbital polarization effects that have been neglected here.

Comparison to selected other basis set calculations is also given in Table 3. The polarization [5] (POL), first order [6] and symmetry adapted cluster [8] (SAC) CI results each show fair agreement with experiment for B—N, but less so for O and F. These were all obtained with large and apparently satisfactory Slater basis sets, so whatever shortcomings they might have are likely to be due to the wave function models employed.

The recent comprehensive MR-CI study [9] is seen in Table 3 to have obtained very good results with large uncontracted Gaussian basis sets and long configuration lists. An excellent result of $Q(0)/N = 0.0321$ a.u. was obtained for nitrogen in another recent detailed study [10] that examined various large CI wave functions with both uncontracted and contracted Gaussian basis sets. The latter work emphasized the role of diffuse functions for spin density determination, and also found the energy-optimized $(9s5p)$ primitive sp basis used here to be more efficient than even-tempered Gaussian sets. Since both the present work and the recent MR-CI study [9] find all the first-row atoms to show very similar dependence of spin density on basis set variations, it seems likely that many of

Table 3. Comparison to other literature results and to experiment for Fermi contact spin density $Q(0)/N$ in atomic units for ground states of first-row atoms

Calculation	B $[^2P]$	C $[^3P]$	N $[^4S]$	O $[^3P]$	F $[^2P]$
MCSCF[a]	0.0139	0.0205	0.0296	0.0398	0.0550
MCSCF[b]	0.0155	0.0238	0.0336	0.0456	0.0622
POL-CI[c]	0.0073	0.0139	0.0243	0.0305	0.0470
First order-CI[d]	0.0041	0.0114	0.0238	0.0314	0.0496
SAC-CI[e]	0.0147	0.0244	0.0392	0.0356	0.0305
MR-CI[f]	0.0044	0.0159	0.0311	0.0480	0.0678
Experiment	0.0081[g] 0.013[h]	(0.020)[i] (0.0192)[j]	0.0324[k]	0.0569[l]	0.0717[l]

[a] This work, with $[6s3p3d]$ + diffuse sp Gaussian basis (see text for details)

[b] Best numerical results from [12]. These differ slightly from the results quoted in Table 2 due to inclusion of several minor terms in the wave function that are omitted in the present work

[c] [5], with large Slater basis sets

[d] [6], with large Slater basis sets

[e] [8], with large Slater basis sets

[f] [9], with large uncontracted Gaussian basis sets

[g] [20]

[h] [21]

[i] [20] (estimated value)

[j] [22] (estimated value)

[k] [23]

[l] [24]

the conclusions reached in the nitrogen study [10] will carry over to the other first-row atoms as well. Both these recent papers [9, 10] should be consulted for detailed discussions of the coupling between Gaussian basis sets and high order electron correlations for description of atomic spin densities, a matter which is beyond the scope of the present study.

Those small but nonnegligible discrepancies with experiment that remain in the present results are likely to be due primarily to additional electron correlation effects that are omitted from the wave functions of this work. The recent highly accurate studies discussed above [9, 10] have shown that basis set requirements for proper description of electron correlation contributions to spin density are more demanding than those found here, particularly as regards the role of *d* functions. In fact, as they stand, the basis sets developed here are not even appropriate for treatment of true electron correlation in large scale CI calculations [27]. They have been developed in the context of a simple wave function model that only describes the spin and orbital polarizations affecting the spin density in lowest order. This should be regarded as a minimal starting point that will be necessary, although not always sufficient, for proper treatment of spin density. Even so, we can settle on the guardedly optimistic conclusion that modest contracted Gaussian basis sets, if properly prepared, are capable of describing reasonably well the spin and orbital polarization effects that are most important for spin density determination in many systems.

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19. It is interesting to note that the Serber spin functions are particularly convenient for calculations in open shell systems. In the present context, the unpaired electrons in each important ($s \rightarrow s$) single excitation configuration with triplet intermediate spin coupling (such as occurs in Ψ_1 and Ψ_2) can be expressed with a single Serber function multiplying an appropriately ordered product of spatial functions. Other choices, e.g. a genealogical construction, would generally require a linear combination of spin eigenfunctions to form such a configuration for an overall triplet or quartet state
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25. The shells of diffuse exponents used here have values
    B (0.0330*s*, 0.0106*s*, 0.0226*p*, 0.0073*p*);
    C (0.0479*s*, 0.0150*s*, 0.0358*p*, 0.0122*p*);
    N (0.0667*s*, 0.0208*s*, 0.0517*p*, 0.0162*p*);
    O (0.0862*s*, 0.0261*s*, 0.0648*p*, 0.0196*p*);
    F (0.1101*s*, 0.0334*s*, 0.0828*p*, 0.0251*p*).
26. The total energy was minimized with respect to the *d* exponent for the $[6s3p]$ + diffuse *sp* basis set described in this work with an MCSCF wave function consisting of terms Ψ_0, Ψ_1, Ψ_2, Ψ_4 and, for O and F only, Ψ_5. The optimum single *d* exponent was found to have the values:B (0.32*d*), C (0.51*d*), N (0.73*d*), O (1.01*d*), and F (1.33*d*).
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