Spin density in first-row atoms from the Hiller–Sucher–Feinberg identity

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Summary. The performance of delta function and Hiller–Sucher–Feinberg (HSF) operators is compared for calculations of the electronic spin density at the nucleus, which determines the observed Fermi contact hyperfine splitting. Calculations are performed on the ground states of the first-row open-shell atoms boron through fluorine. The wavefunctions include low order spin polarization effects calculated through the multiconfigurational self-consistent-field procedure. It is shown that while delta function and HSF operators give nearly the same results when essentially exact numerical grid methods are used, the HSF operator gives a significant advantage when contracted Gaussian type basis sets are utilized.

Introduction

Recently, there has been interest in using the Hiller–Sucher–Feinberg (HSF) identity [1] for calculation of the electronic spin density in open shell systems [2–9]. The usual formulation of this property in terms of a delta function operator depends only on the error in the wavefunction at the particular point of interest. Unfortunately, for many kinds of approximate wavefunctions this error may be large, particularly in the calculation of magnetic hyperfine coupling constants where the relevant point is the position of a nucleus. By contrast, the analogous HSF operator is global in nature and so distributes the error over all of space. Since most methods for determination of approximate wavefunctions are based on calculation of the total energy, which is also represented by a global operator, it seems possible that the HSF formulation may reduce the spin density error and improve its rate of convergence as the wavefunction is systematically improved.

The observed Fermi contact hyperfine coupling constant for a magnetic nucleus located at the origin is proportional to $q(0)/N$, which is the electronic spin density at the nucleus $q(0) = \rho_\alpha(0) - \rho_\beta(0)$ normalized to the number of unpaired

electrons N. The spin density can be expressed through the delta function operator as an expectation value over the electronic wavefunction ψ as

$$q^\delta(0)/N = \langle\psi|\sum_i^{\text{electrons}} \delta(r_i)2s_{zi}|\psi\rangle/N. \tag{1}$$

The works of Hiller et al. [1], Sucher and Drachman [2], and Harriman [3] have shown that the delta function operator above may be replaced by a global operator as in

$$q^{\text{HSF}}(0)/N = \langle\psi|\sum_i^{\text{electrons}} \left(\frac{\partial V}{\partial r_i} - \frac{L_i^2}{r_i^3}\right)2s_{zi}|\psi\rangle/2\pi N. \tag{2}$$

This latter expression utilizing the HSF operator can be considered as a sum of three terms. One arises from the L_i^2/r_i^3 part, where L_i^2 is the total orbital angular momentum operator for the ith electron, and will be abbreviated as the L term. The others arise from the $\partial V/\partial r_i$ part, where V is the potential energy operator appearing in the total nonrelativistic Hamiltonian. The one and two electron portions of V then lead to contributions that are abbreviated as the U and V terms, respectively.

When evaluated with an exact eigenfunction of the total Hamiltonian, $q^\delta(0)/N$ and $q^{\text{HSF}}(0)/N$ give identical results [1–3]. It is also found that these operators give identical results in the case of both spin and total electron density for any wavefunction found through spin-unrestricted Hartree–Fock [5], or more general unrestricted multiconfigurational self-consistent-field (MCSCF) optimization (see Appendix I), provided that calculations are done with a complete basis set. Usually, certain restrictions are imposed on the MCSCF procedure, such as a requirement for the wavefunction to be an eigenfunction of the total spin operator S^2. This restriction may cause the spin density values of delta function and HSF operators to be different from one another, although the total electron density values remain identical (see Appendix I).

The finite size of the basis set can also be viewed as a restriction on the MCSCF procedure. In this case the use of a global operator in $q^{\text{HSF}}(0)/N$ may give an improved calculation of both the total electron and spin densities. On the other hand, the HSF formulation is more difficult to implement, particularly due to the two-electron term. Calculations on real systems are required to determine whether or not the HSF formulation carries any advantage in practice.

The HSF formulation has been tested in several previous spin density studies [4–9]. Most of these [5–7] have utilized the spin-unrestricted Hartree–Fock (UHF) wavefunction. These studies have shown that HSF usually performs better than the delta function in that situation. In some cases the improvement is up to an order of magnitude, while in other cases there is little or no improvement. One calculation on BeH [8] has reported HSF spin density results with correlated wavefunctions, but no comparison with delta function results was provided.

It should also be noted that Challacombe and Cioslowski [10–12] have presented several interesting formal and computational results on use of the HSF identity for calculation of total electron densities, i.e., $\rho_\alpha(r) + \rho_\beta(r)$, at various spatial locations r not just limited to the position of the nucleus. Particularly interesting is their demonstration that the HSF operator can provide a cusp in the density at the nucleus even with the use of Gaussian basis functions that are cuspless in the usual delta function formulation [10].

We have recently compared [9] delta function and HSF spin densities in the [^{2}S] ground and [^{2}P] first excited states of the Li atom. The wavefunctions

considered were based on spin-restricted open-shell Hartree-Fock (ROHF), augmented with single-excitation configurations appropriate to describe spin polarization (SP) and spin + orbital polarization (SOP) effects. When the wavefunctions were determined by highly precise numerical grid methods, it was found that the delta function and HSF approaches gave very similar results, with HSF being slightly closer to experiment. For approximations to these wavefunction models expanded within finite Slater and Gaussian basis sets, the HSF results were generally significantly better than those from the delta function.

These findings have encouraged us to continue a systematic study of use of the HSF identity for spin density calculations. In the present work, we report analogous calculations on the ground states of the remaining open-shell first-row atoms boron [²P], carbon [³P], nitrogen [⁴S], oxygen [³P], and fluorine [²P]. This closely parallels our earlier delta function studies [13–15] on these systems.

Several other groups have recently calculated delta function spin density results for these atoms, including Feller and Davidson [16], Bauschlicher et al. [17], Carmichael [18], Sundholm and Olsen [19], Engels [20], Jönsson and Fischer [21], Kong et al. [22], and Perera et al. [23]. Those works have generally focused on the higher-order effects of dynamical electron correlation, which are indeed required to attain truly quantitative accuracy. Our motivation is different, in that the ultimate goal is to develop efficient computational methods that can be applied to study spin densities in large polyatomic free radicals. There is evidence [24, 25] that useful semiquantitative results can be obtained by including just the most important low-order effects in relatively simple uncorrelated wavefunctions such as are considered here. In this connection, it is also desired to develop small to moderately large Gaussian basis sets appropriate for spin density calculations.

The various ROHF, SP and SOP wavefunction models considered are discussed in the next section. Then the inherent accuracy of each, as compared to experiment, is examined by first carrying out highly precise determinations of the wavefunctions with numerical grid methods. These correspond to the limiting results that could be obtained from essentially complete basis sets. In that context, they are very useful as benchmarks for the subsequent studies that utilize Gaussian basis sets. Finally, the concluding section provides a summary and discussion of the important findings from this work.

Wavefunction models

The ROHF configuration for each of the ground-state first-row atoms considered in this work can be expressed as

$$\psi^{ROHF} = |1s^2 \, 2s^2 \, 2p^n|, \tag{3}$$

where the $n = 1$–5 electrons in the open $2p$ shell are coupled to the same term as the overall state symmetry. LS coupling is assumed throughout this work, and the requirement that all wavefunctions be proper eigenfunctions of the S^2, S_z, L^2, and L_z angular momentum operators necessitates that many of the configurations discussed below be fixed linear combinations of several Slater determinants. The $1s, 2s$, and $2p$ orbitals are optimized by a SCF procedure [26].

In the following, ψ_0 will denote a wavefunction having the same generic form as ψ^{ROHF} but differing by virtue of having the orbitals optimized in a more general multiconfiguration (MC) SCF that includes the effects of other configurations.

Explicit expressions for the remaining configurations have been given previously [15] and discussed at some length, so they will only be briefly described below.

Spin polarization effects can be introduced through wavefunctions of the form

$$\psi^{SP} = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 (\, + c_3\psi_3) \tag{4}$$

that augment the dominant configuration ψ_0 with either two or three singly excited configurations ψ_1, ψ_2, and possibly ψ_3. Due to Brillouin's theorem [27], the only two $s \rightarrow s$ excitations that need be considered are the $1s \rightarrow s^{**}$ and $2s \rightarrow s^*$ promotions having triplet intermediate spin coupling of the unpaired s electrons, i.e.,

$$\psi_1 = |1s\,s^{**}[^3S]\,2s^2\,2p^n[W]|, \tag{5}$$

$$\psi_2 = |1s^2\,2s\,s^*[^3S]\,2p^n[W]|, \tag{6}$$

with consequent intermediate recoupling of the $2p$ electrons to produce the correct overall state symmetry, i.e., $[W] = [^2P]$ for B and F, $[W] = [^3P]$ for C and O, and $[W] = [^4S]$ for N. Note that for simplicity of notation we omit the trivial $[^1S]$ coupling of any complete shell. Those shells of electrons having the particular intermediate couplings indicated are, of course, finally coupled together to give an overall state of the desired symmetry. For O and F a third spin polarization configuration is included to treat the more than half-filled p shell, corresponding to a $2p \rightarrow p^*$ promotion, i.e.,

$$\psi_3 = |1s^2\,2s^2\,2p^{n-1}[X]p^*|, \tag{7}$$

with a particular intermediate coupling of the $n - 1\ 2p$ electrons given by $[X] = \{\sqrt{20}[^4S] + [^2D] - \sqrt{15}[^2P]\}/6$ for O and $[X] = \{4[^1S] + \sqrt{5}[^1D] - 3[^3P]\}/\sqrt{30}$ for F. The other two possible intermediate couplings of the $2p$ electrons are not included because the Hamiltonian and spin density matrix elements with ψ_0 either vanish by construction or are quite small due to the fact that the $1s$, $2s$, and $2p$ orbitals are close to the ROHF ones so that Brillouin's theorem is approximately satisfied [28].

Orbital polarization effects can be introduced through wavefunctions of the form

$$\psi^{SOP} = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 (\, + c_3\psi_3) + c_4\psi_4 + c_5\psi_5 \tag{8}$$

that augment the SP wavefunction discussed above with two additional singly excited configurations ψ_4 and ψ_5. For all the atoms these are the $1s \rightarrow d^*$ and $2s \rightarrow d^*$ promotions having triplet intermediate spin coupling of the unpaired s and d electrons, i.e.,

$$\psi_4 = |1s\,d^*[^3D]2s^2\,2p^n[Y]|, \tag{9}$$

$$\psi_5 = |1s^2\,2s\,d^*[^3D]2p^n[Y]|, \tag{10}$$

where the appropriate intermediate recoupling of the $2p^n$ electrons is $[Y] = [^2P]$ for B and F, $[Y] = \{\sqrt{2}[^3P] + \sqrt{3}[^1D]\}/\sqrt{5}$ for C and O, and $[Y] = [^1D]$ for N. Note that the same d^* polarization orbital is used for both the $1s$ and $2s$ shells. In our earlier work [13] a distinct orthogonal d^{**} orbital was used in ψ_4 for $1s$ polarization, and in that case ψ_4 was found to play only a minor role in the wavefunction. However, a later reexamination [15] in which the possible non-orthogonality of d^{**} and d^* was considered showed that they indeed overlap

Table 1. Spin densities of ground state first-row atoms from various wavefunctions determined numerically. All results are given in atomic units

	Boron	Carbon	Nitrogen	Oxygen	Fluorine
ROHF					
L	− 0.2469	− 0.5385	− 0.9866	− 1.5833	− 2.4017
U	0.4217	0.8519	1.4887	2.3157	3.4302
V	− 0.1811	− 0.3241	− 0.5185	− 0.7532	− 1.0548
$q^{HSF}(0)/N$	− 0.0063	− 0.0108	− 0.0164	− 0.0208	− 0.0263
$q^{\delta}(0)/N$	0	0	0	0	0
Spin polarization					
L	− 0.2509	− 0.5462	− 0.9990	− 1.6810	− 2.5952
U	0.4305	0.8827	1.5473	2.4979	3.7517
V	− 0.1869	− 0.3332	− 0.5312	− 0.7919	− 1.1184
$q^{HSF}(0)/N$	− 0.0073	0.0033	0.0171	0.0250	0.0382
$q^{\delta}(0)/N$	− 0.0076	0.0027	0.0162	0.0224	0.0334
Spin + orbital polarization					
L	− 0.2509	− 0.5407	− 0.9879	− 1.6657	− 2.5800
U	0.4497	0.8884	1.5399	2.4859	3.7408
V	− 0.1880	− 0.3323	− 0.5286	− 0.7886	− 1.1155
$q^{HSF}(0)/N$	0.0108	0.0154	0.0234	0.0317	0.0453
$q^{\delta}(0)/N$	0.0096	0.0138	0.0214	0.0279	0.0392
Experiment[a]	0.0081	0.0173	0.0324	0.0569	0.0717

[a] B expt [30]; C expt [31]; N expt [32]; O expt [33]; F expt [33]

considerably and that in fact a single common d^* polarizing orbital, as considered here, is sufficient to treat the orbital polarization of both the $1s$ and $2s$ shells. In that case, both ψ_4 and ψ_5 are significant contributors to the wavefunctions. The various other possible orbital polarization configurations that can be written but are omitted here have been shown by explicit numerical testing [13] to have only minor effects.

In this work, all the orbitals $1s$, s^{**}, $2s$, s^*, $2p$, p^*, and d^*, along with the linear configuration interaction (CI) coefficients c_i, are fully optimized through MCSCF calculations. All spin densities in this paper are obtained from expectation values, as in either Eq. (1) or Eq. (2), and are reported in atomic units.

Numerical calculations

Highly precise calculations of the wavefunctions described above were first carried out with Fisher's program [29] that is based on numerical grid methods. This obviates any questions about basis set completeness and allows for unambiguous evaluation of the inherent utility of the ROHF, SP and SOP wavefunctions for spin density determination. The numerical grid results for delta function and HSF spin densities of the first-row atoms are given in Table 1.

Since the open-shell electrons are in p orbitals that have nodes at the nuclei, the delta function formulation gives exactly zero ROHF spin density for all the atoms considered here. However, the ROHF spin density need not be zero for HSF. The

individual L, U, and V contributions to $q^{HSF}(0)/N$ are in fact quite large. U is the largest and is consistently positive, while L and V are each a little smaller and are both consistently negative. Considerable cancellation occurs when these contributions are added together, to the extent that the net results are about two orders of magnitude smaller than the individual contributions. The final values of $q^{HSF}(0)/N$ are all opposite in sign and substantially smaller in magnitude than the positive experimental values. Clearly, at the ROHF level neither delta function nor HSF results give a useful account of the experimental values for these atoms.

With SP wavefunctions, the delta function results become nonzero but still considerably underestimate experiment. For HSF, the individual L, U, and V contributions each become slightly larger in magnitude than with ROHF wavefunctions and lead to positive net spin density values for all atoms except boron. The magnitudes are still significantly lower than experiment, although HSF values are generally better than delta function values.

With SOP wavefunctions the delta function results become comparable to experiment, with boron being 19% too large and the other atoms ranging from 27% to 51% too small. For HSF, small further changes (some positive, some negative) in the individual L, U, and V contributions make all the net spin density values more positive. As with the delta function, the net HSF results are now comparable to experiment, with boron being 33% too large and the other atoms ranging from 18% to 44% too small. For all atoms except boron, the HSF results are closer than the delta function values to experiment.

A common feature of these numerical grid results for different wavefunction models is very similar performance of the delta function and HSF approaches for spin densities. That is, the differences between results from the two formulations is generally much smaller than the deviations of either from experiment. Even so, with the larger SP and SOP wavefunctions the HSF results are usually slightly better than those from the delta function.

Gaussian basis sets

Spin polarization for carbon

In this section we consider the utility of various contracted Gaussian basis sets for spin density determination. We have already considered above the inherent limiting performance of each wavefunction model in comparison to experiment. Here it is more illuminating to compare the basis set results to the corresponding numerical grid results obtained from the same wavefunction model, rather than to experiment. This allows us to more clearly judge the separate question of the relative performance of each basis set in comparison to the limiting values that could be obtained from a complete basis set.

All basis set calculations were performed using the ALIS program [34].

We start with a detailed case study of the carbon atom using a wide variety of basis sets. Results with SP wavefunction, which only requires s and p functions, are given in Table 2.

The smallest set, designated $[4s2p]$ is the common $(9s5p)$ primitive set of Huzinaga [35] as contracted to double zeta size by Dunning [36]. Compared to the corresponding numerical results (see the final column of Table 2), the delta function result is too large by about a factor of three. The HSF contributions are

Table 2. Spin density of ground state carbon atom from spin polarization wavefunctions with various Gaussian basis sets. All results are given in atomic units

	$[4s2p]$	$[6s3p]$	$[6^+s3^+p]$	$(11s7p)$	$(13s9p)$	$(15s10p)$	Numerical
L	− 0.5332	− 0.5352	− 0.5447	− 0.5444	− 0.5452	− 0.5460	− 0.5462
U	0.8950	0.8800	0.8817	0.8825	0.8826	0.8826	0.8827
V	− 0.3322	− 0.3329	− 0.3328	− 0.3329	− 0.3329	− 0.3332	− 0.3332
$q^{HSF}(0)/N$	0.0296	0.0119	0.0042	0.0052	0.0045	0.0034	0.0033
$q^{\delta}(0)/N$	0.0084	0.0012	0.0014	0.0036	0.0034	0.0019	0.0027

somewhat too positive for L and U, while V is described quite well, leading to a net result that is too large by about a factor of nine.

In an earlier study utilizing the delta function [14], it was found that considerable improvement could be obtained by uncontracting the outermost primitive s member from the innermost contraction group, thereby allowing for a better description of the outer core-inner valence region spanned by the s^{**} polarizing orbital. It was also necessary to add an uncontracted diffuse s function to allow for a better description of the outer valence region spanned by the s^* polarizing orbital. A diffuse p function was also added, leading to the basis designated here as $[6s3p]$ [37]. With this basis, the delta function result is now too small by about a factor of two. The HSF contributions show a small improvement for L, a considerable improvement in U, and a slight improvement in the already good value for V, leading to a net result that is too large by about a factor of four.

A strong inverse r dependence (r^{-3} for the L term and r^{-2} for the U term) makes the HSF operator very sensitive to the representation of the wavefunction near the nucleus, and of course the delta function operator should also be sensitive to that region. Therefore tight, i.e., very high exponent, s and p functions were added to the basis, leading to the basis designated $[6^+s3^+p]$. Here the dagger superscript indicates the addition of a tight primitive function that is contracted in with the existing innermost group from the previous $[6s3p]$ basis. Details of the procedure used to obtain the values of the tight exponents are given in the Appendix II. The tight functions lead to only a small change in the delta function result, which is still too small by nearly a factor of two. The HSF contributions show a considerable improvement in the value for L, which is attributed mainly to the effect of the tight p function, an improvement in the already fairly good value for U, which is attributed mainly to the effect of the tight's function, and no change in the value of V, leading to a net result that is now fairly good, being only 26% too large. However, this is due somewhat to an accidental cancellation of errors in the separate L and U contributions.

At this stage, the effect of fully uncontracting the basis was examined, leading to the basis designated $(11s7p)$, i.e., the $(9s5p)$ Huzinaga basis with both diffuse and tight s and p functions added. This leads to a significant change in the delta function result, which is now too large by 33%. The HSF contributions show that L becomes slightly worse, U improves to nearly its converged value, and V changes only slightly. This leads to a net HSF result that is now not as good, being almost 60% too large due to the disappearance of the previously noted accidental cancellation of errors.

To investigate possibilities for the nature of the remaining errors, additional tighter and more diffuse s and p functions were added to the fully uncontracted basis, leading to the basis designated $(13s9p)$, i.e., the $(9s5p)$ Huzinaga basis with two diffuse and two tight s and p functions added [38]. This leads to a small change in the delta function result, which is now too large by 26%. The HSF contributions show a small improvement in L, with no change in either U or V. This leads to a net result that is now fairly good, being too large by 35%.

Finally, a somewhat larger $(13s8p)$ primitive basis due to van Duijneveldt [39] was considered. Compared to the $(9s5p)$ basis on which the above studies were based, the innermost functions are significantly tighter, the outermost functions are comparable, and more functions are distributed between these limits. To this, additional very tight and diffuse s and p functions were added, leading to the fully uncontracted basis designated $(15s10p)$ [40]. This leads to a significant change in the delta function result, which is still not converged, being now too small by about 30%. By contrast, the HSF contributions are now each separately nearly converged to their corresponding numerical values, as is the net result that is only slightly too large.

These studies on the SP wavefunction show that the requirements on s and p basis functions needed to reach true convergence are very demanding. In fact, the delta function result has still not converged even with the largest basis considered. The HSF result, on the other hand, is well converged with the largest basis and shows reasonably smooth convergence behaviour with the various large bases considered. Interestingly, the various HSF contributions converge at different rates. The slowest convergence is shown by the L term, which is well described only in the largest basis considered here. The U term converges more rapidly and is already fairly well described in the $[6^+s3^+p]$ basis. The V term, which is computationally the most difficult to implement, converges very rapidly, being reasonably well described even in the smallest $[4s2p]$ basis.

Orbital polarization for carbon

Inclusion of orbital polarization effects requires extension of the basis set into the d space. We again select the carbon atom for a detailed case study. The smallest basis considered above that provided semiquantitative results for the SP wavefunction was $[6^+s3^+p]$, and therefore that was selected as a starting point. Either one or two shells of d functions were added, with exponents taken from an earlier study [14], to produce the sets designated $[6^+s3^+p1d]$ and $[6^+s3^+p2d]$, respectively. True five component spherical harmonic d functions were used throughout. Results with the SOP wavefunction are given in Table 3.

As compared to the analogous numerical results, the delta function values are fairly good, being too small by 22% with one d function and by 11% with two d functions. The absolute error with two d shells is essentially the same as that found for the SP wavefunction with the $[6^+s3^+p]$ basis. This suggests that the remaining error may be attributed mainly to the treatment of the spin polarization part of the wavefunction that is described by the sp part of the basis and that the orbital polarization effect is described quite well with just one d function and extremely well with two d functions.

The HSF contributions are each consistently too large in magnitude, in contrast to the SP wavefunction where they were consistently too small. With one d function the L and U terms show significant errors while the V term is given quite

Table 3. Spin density of ground state carbon atom from spin + orbital polarization wavefunctions with various Gaussian basis sets. All results are given in atomic units

	$[6^+s3^+p1d]$	$[6^+s3^+p2d]$	Numerical
L	-0.5468	-0.5452	-0.5407
U	0.8935	0.8925	0.8884
V	-0.3334	-0.3330	-0.3323
$q^{HSF}(0)/N$	0.0133	0.0144	0.0154
$q^{\delta}(0)/N$	0.0107	0.0125	0.0138

Table 4. Spin densities of ground state first-row atoms from spin polarization wavefunctions determined with the $[6^+s3^+p]$ basis set. All results are given in atomic units. The relative error of each result, as compared to the corresponding limiting numerical grid result, is indicated in parentheses

	Boron	Carbon	Nitrogen	Oxygen	Fluorine
L	-0.2499	-0.5447	-0.9970	-1.6936	-2.6248
	(-0.41%)	(-0.26%)	(-0.20%)	(0.75%)	(1.14%)
U	0.4298	0.8817	1.5453	2.5058	3.7751
	(-0.16%)	(-0.11%)	(-0.13%)	(0.32%)	(0.62%)
V	-0.1866	-0.3328	-0.5307	-0.7927	-1.1211
	(-0.17%)	(-0.11%)	(-0.10%)	(0.11%)	(0.25%)
$q^{HSF}(0)/N$	-0.0066	0.0042	0.0176	0.0195	-0.0292
	(-8.9%)	(26%)	(2.8%)	(-28%)	(-23%)
$q^{\delta}(0)/N$	-0.0081	0.0014	-0.0130	0.0153	0.0239
	(6.6%)	(-47%)	(-20%)	(-32%)	(-40%)

well. Due to an accidental cancellation of errors from the separate L and U terms, the net result is quite good, being just 14% too small. With two d functions there is a small improvement in the L term and even smaller improvements in the U and V terms. Significant accidental cancellation of errors from the separate L and U terms remains so that the net result is again quite good, being just 7% too small. We have observed similar behavior in test calculations on boron and nitrogen, suggesting that such a cancellation of errors is consistent with this basis set.

Results for first-row atoms

The $[6^+s3^+p]$ basis set was selected to examine the behavior of the various first-row atoms with spin polarization wavefunctions. Results are presented in Table 4, which also lists the percent error of each result as compared to the corresponding limiting numerical result.

The delta function values range from being 47% too low to 7% too high. The HSF values are slightly too small in magnitude for B, C, and N and are slightly too large in magnitude for O and F. The errors are largest for the L terms. As already discussed above in connection with carbon, there are significant error

Table 5. Spin densities of ground state first-row atoms from spin + orbital polarization wavefunctions determined with the $[6^+s3^+p1d]$ basis set. The relative error of each result, as compared to the corresponding limiting numerical grid result, is indicated in parentheses

	Boron	Carbon	Nitrogen	Oxygen	Fluorine
L	− 0.2556	− 0.5468	− 0.9944	− 1.6872	− 2.6190
	(1.86%)	(1.12%)	(0.65%)	(1.29%)	(1.51%)
U	0.4541	0.8935	1.5447	2.5011	3.7714
	(0.99%)	(0.57%)	(0.32%)	(0.61%)	(0.82%)
V	− 0.1892	− 0.3334	− 0.5295	− 0.7907	− 1.1192
	(0.61%)	(0.35%)	(0.17%)	(0.26%)	(0.33%)
$q^{HSF}(0)/N$	0.0094	0.0133	0.0209	0.0233	0.0332
	(− 13%)	(− 14%)	(− 11%)	(− 27%)	(− 27%)
$q^{\delta}(0)/N$	0.0082	0.0017	0.0160	0.0185	− 0.0270
	(− 14%)	(− 22%)	(− 25%)	(− 33%)	(− 31%)

cancellations, particularly between the L and U contributions, to produce net results that range from being 28% too low to 26% too high. The net result for nitrogen is accidentally extremely good. With the exception of boron, the HSF results are closer to their limiting numerical values than are the delta function results.

The $[6^+s3^+p1d]$ basis set was selected to examine the behavior of the various first-row atoms with spin + orbital polarization wavefunctions. Results are presented in Table 5, which again lists the percent error of each result as compared to the corresponding numerical result.

The delta function values are all too small in magnitude, with errors ranging from 14% to 33%. The HSF values are slightly too large in magnitude, with the largest errors again occurring in the L terms. And again there are significant error cancellations between the L and U contributions to produce net results having errors ranging from 11%–27%, all consistently too low. The HSF results are better converged than the delta function ones for every atom. The cancellation of HSF errors is thus even more systematic than in the case of the SP wavefunction.

Conclusions

The numerical grid calculations demonstrate that the delta function and HSF operators give comparable results for the exact SP and SOP wavefunctions, with HSF usually being slightly better. The SOP results are in semi-quantitative agreement with experiment.

Comparison of the numerical results with calculations utilizing Gaussian basis sets shows several notable features. The delta function results converge slowly with basis set extension, and in fact are still not converged even with the largest basis sets considered here. By comparison, the HSF net results converge to their limiting values significantly more rapidly.

The most computationally intensive contribution to the HSF result comes from the two-electron V term. Fortunately, this term converges very rapidly, being given

quite well even with rather small basis sets. This observation suggests the possibility of an efficient hybrid computational procedure that uses a relatively small basis set for evaluation of the difficult V term together with a larger basis set for the easier one-electron L and U terms.

Common double zeta basis sets require augmentation by diffuse functions and some uncontraction of the innermost s group in order to describe the spin polarization orbitals adequately. Due to the strong dependence of the L and U terms in the HSF operator on inverse powers of r, it is also necessary to extend common primitive Gaussian basis sets with tight functions. One set of tight s (for U) and tight p (for L) functions contracted into the existing innermost groups, as for example in the $[6^+s3^+p1d]$ basis considered here, seems to be enough to produce reasonable results. This arises in part from some error cancellation between the separate L and U contributions, which actually require fairly large basis sets for true convergence. This accidental cancellation appears to be systematic throughout the first-row atoms. Since the cancellation occurs from inner region contributions which are likely to be insensitive to the effects of chemical bonding, it is possible that it will also systematically occur in polyatomic systems as well.

In conclusion, this work shows that the HSF formulation has some significant advantage over the traditional delta function approach for spin density calculation by allowing for the use of smaller basis sets to achieve satisfactory accuracy. Additional studies on polyatomic systems are in progress to investigate this topic further.

Appendix I

The derivation of the HSF relation is based on the hypervirial theorem [41]

$$\langle\psi|[H, W]|\psi\rangle = 0, \tag{A1}$$

where $[H, W]$ is the commutator of some operator W with the Hamiltonian of the system for which ψ is an exact eigenfunction. We show here that for *any* one-electron operator W the hypervirial theorem is true not only for the exact wavefunction, but also for any unrestricted MCSCF wavefunction obtained within a complete basis set.

For simplicity assume the wavefunction ψ to be real. Then Eq. (A1) can be rewritten as

$$\langle\psi|H(W - \tilde{W})|\psi\rangle = 0, \tag{A2}$$

where $\tilde{W}$ is the transpose operator to W, i.e., the complex conjugate of the Hermitian adjoint to W, or $(W^+)^*$. It is convenient to use the second quantization notation, in which any one-electron operator W can be expressed as

$$W = \sum C_{pq}a_p^+ a_q, \tag{A3}$$

where C_{pq} are the coefficients in the expansion of W through the creation and annihilation operators a_p^+ and a_q acting on spin-orbitals. Then Eq. (A2) becomes

$$\sum C_{pq}\langle\psi|H(a_p^+ a_q - a_q^+ a_p)|\psi\rangle = 0 \tag{A4}$$

which is satisfied because every term in the sum vanishes due to the generalized Brillouin theorem that holds for an unrestricted MCSCF wavefunction [42]. In other words, the variational principle makes an unrestricted MCSCF wavefunction ψ stable to first order against all single excitations that preserve orbital orthonormality to first order. In particular, it will then be stable to the variation $(W - \tilde{W})\psi$ when W is a one-electron operator.

Often a restriction is applied to the wavefunction that can be expressed in the form of an operator (representing some constant of the motion) that commutes with H, e.g., an angular momentum operator. The above hypervirial theorem is still satisfied in such a restricted MCSCF procedure if the operator representing the restriction also commutes with $(W - \tilde{W})$.

The equivalence of delta function and HSF results for an unrestricted MCSCF wavefunction is now obtained by the specific choice of the nonhermitian operator $W = \sum \partial/\partial r_i$ (for total electronic density) or $W = \sum s_{zi} \partial/\partial r_i$ (for spin density), where summation is carried over all electrons, as in the original HSF derivations [1–3].

In the more common situation of a spin-restricted MCSCF procedure, the generalized Brillouin theorem contains variations with respect to spatial orbitals only [43]. In this case, Eq. (A4) will still be valid if W is a spin-free one-electron operator and, therefore, can be represented through creation and annihilation operators acting in the space spanned by spatial orbitals, similar to Eq. (A3). Consequently, the delta function and HSF total electronic densities will agree with one another in both spin-restricted and spin-unrestricted MCSCF wavefunctions, including UHF and ROHF.

On the other hand, the generalized Brillouin theorem appropriate for a spin-restricted MCSCF procedure is not strong enough for the above proof to work for the spin-dependent operator $W = \sum s_{zi} \partial/\partial r_i$, because this does not commute with S^2. Thus, while delta function and HSF spin densities will still agree for spin-unrestricted MCSCF wavefunctions (including UHF), they may differ from one another for spin-restricted MCSCF wavefunctions (such as ROHF).

Because L^2 commutes with both H and $(W - \tilde{W})$, constraining the wavefunctions in the present study to be eigenfunctions of L^2 does not affect our proofs regarding the relationships between delta function and HSF densities at the nucleus.

Finally, it should be emphasized that the proofs given in this appendix apply only to exact MCSCF wavefunctions, i.e., obtained either within a complete basis set or by essentially exact numerical methods. This is required to ensure that $(W - \tilde{W})\psi$ lies within the space spanned by the basis set.

Appendix II

In order to optimize the values of the tight Gaussian exponents, simple model calculations were performed. The single Slater s type function $\exp(-Zr)$, which has a cusp at the nucleus, was selected as a standard. This was approximated with the original primitive $(9s)$ Gaussian basis of Huzinaga plus one added tight s function. The value of the tight exponent as well as the expansion coefficients of all the primitive Gaussian functions were least squares optimized in calculations of average values of operators having the form r^{-n} $(1 \leqslant n \leqslant 3)$. That is, the integral

$$\int_0^\infty [\exp(-Zr) - C_t \exp(-\alpha_t r^2) - \sum_i C_i \exp(-\alpha_i r^2)]^2 r^{-n} r^2 \, dr$$

Table 6. The $[6^+s3^+p1d]$ contracted Gaussian basis sets for the first-row atoms

	Boron		Carbon		Nitrogen	
	Exp	Coefficient	Exp	Coefficient	Exp	Coefficient
	24805.	0.00016525	37721.	0.00015918	52630.	0.00015744
	2788.41	0.0022700	4232.61	0.0021940	5909.44	0.0021675
	419.039	0.0186417	634.882	0.0180604	887.451	0.0178182
s	96.4683	0.089462	146.097	0.087043	204.749	0.085615
	28.0694	0.301214	42.4974	0.296851	59.8376	0.292595
	9.3760	0.682240	14.1892	0.688199	19.9981	0.693037
	3.4062	1.0	5.1477	1.0	7.1927	1.0
	1.3057	1.0	1.9666	1.0	2.6860	1.0
	0.3245	1.0	0.4962	1.0	0.7000	1.0
	0.1022	1.0	0.1533	1.0	0.2133	1.0
	0.033	1.0	0.0479	1.0	0.0667	1.0
	64.4	0.0012133	103.3	0.0012020	152.0	0.0011631
	11.3413	0.017156	18.1557	0.017683	26.7860	0.017408
p	2.4360	0.111078	3.9864	0.116138	5.9564	0.117093
	0.6836	0.381319	1.1429	0.383982	1.7074	0.387782
	0.2134	0.649276	0.3594	0.641956	0.5314	0.639200
	0.0701	1.0	0.1146	1.0	0.1654	1.0
	0.0226	1.0	0.0358	1.0	0.0517	1.0
d	0.32	1.0	0.51	1.0	0.73	1.0

	Oxygen		Fluoride	
	Exp	Coefficient	Exp	Coefficient
	69560.	0.00015826	88860.	0.00015751
	7816.54	0.0021757	9994.79	0.0021615
	1175.82	0.0178341	1506.03	0.0176803
	273.188	0.084419	350.269	0.083746
	81.1696	0.284028	104.053	0.282894
	27.1836	0.701313	34.8432	0.702877
s	9.5322	1.0	12.2164	1.0
	3.4136	1.0	4.3688	1.0
	0.9398	1.0	1.2078	1.0
	0.2846	1.0	0.3634	1.0
	0.0862	1.0	0.1101	1.0
	199.6	0.0012348	251.4	0.0013074
	35.1832	0.018658	44.3555	0.019820
	7.9040	0.124885	10.0820	0.130751
p	2.3051	0.391806	2.9959	0.395739
	0.7171	0.629950	0.9383	0.620612
	0.2137	1.0	0.2733	1.0
	0.0648	1.0	0.0828	1.0
d	1.01	1.0	1.33	1.0

was minimized with respect to α_t and C_t (the exponent and coefficient of the added tight function), and all the C_i (the coefficients of the functions from the original Huzinaga basis). In a similar manner, the radial dependence of the single Slater p type function $r\exp(-Zr/2)$ was approximated with the original primitive $(5p)$ Gaussian basis of Huzinaga plus one added tight p function.

It turns out that the optimized values of the tight exponents α_t are nearly the same, within 10%, regardless of the value of n considered. This implies that the tight exponent which is best suited for improvement of the total energy of the system (as represented by $n = 1$) is also nearly optimal for the one electron terms in the HSF density (as represented by $n = 2$ or 3). Even so, the improvement of the HSF value is much greater than for the energy. For example, in carbon atom SP calculations the difference in total energies between the $[6s3p]$ and $[6^+s3^+p]$ sets corresponds to a relative change of just 0.003%, while the difference in L contributions to the HSF result corresponds to a much larger relative change of 2%.

The values of the tight functions found in this manner are given in Table 6. For reference, the full specifications for the $[6^+s3^+p1d]$ bases that are emphasized in this work are also given there. The contraction coefficients were determined in the usual way by carrying out ROHF calculations with the fully uncontracted basis, taking relative weights from their coefficients in the $1s$ or $2p$ orbital, and renormalizing. Note that the addition of primitive tight functions to the basis set in this manner does not make the wavefunction calculations significantly longer, because the number of contracted functions remains unchanged.

It is interesting to note some regularities in the values of the tight exponents that were determined. The ratio of the added tight exponent to the highest exponent from the original Huzinaga basis is 8.90 ± 0.01 for s and 5.68 ± 0.01 for p in all five atoms. A similar regularity may be seen in the ratio of the two largest exponents in the original Huzinaga basis sets.

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