J. Phys. Chem. A **1997,** *101,* 4633−4636

Atomic Spin Densities from Correlation-Consistent Basis Sets[†]

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Received: January 31, 1997; In Final Form: April 16, 1997[⊗]

Recently introduced correlation-consistent (cc-) basis sets are used together with the quadratic configuration interaction (QCISD) correlation recovery technique and a hybrid density functional method, including both gradient corrections and a Hartree−Fock exchange contribution, to calculate the isotropic hyperfine coupling, *a*, in the electronic ground states of the atoms B−F. As expected, valence-only cc-basis sets are found to be inappropriate for spin density calculation with either of the above methods. Results from core-valence cc-basis sets converge satisfactorily toward experiment at QCISD, but the asymptotes of the density functional calculations match experiment only for nitrogen. At the complete basis set limit, the corresponding density functional values for the spin density at the nucleus is substantially overestimated for B and C but underestimated for O and F.

Introduction

The computation of accurate and reliable hyperfine coupling constants remains one of the more challenging areas of modern *ab initio* electronic structure theory.

Recently, however, several high-level electron correlation approaches have begun to produce results of a predictive quality suitable to be of some use to experimenters in high-resolution gas-phase and matrix-isolation spectroscopy, for example.[1−12] A common thread in the implementation of these methods is the exacting demand placed on available computer facilities. Further taxing the computational burden of these extensive correlation treatments is the requirement that, for the desired level of accuracy, large basis sets are often necessary.

On the other hand, several density functional treatments of hyperfine coupling have appeared which purport to produce results of a similar quality with much less computational exertion.[13−21]

Our initial coupled-cluster study of the hyperfine interactions in atoms[22] was stimulated by the success of Sekino and Bartlett,[23] who employed finite (Fermi-contact)-field coupled-cluster calculations (CCSD) with modest (double-ζ plus polarization) basis sets to calculate reasonably accurate hyperfine coupling constants in a range of small radicals. Perera *et al.*[12] recently extended this earlier CCSD work, using much larger basis sets and calculating the splittings directly from the relaxed coupled-cluster density. With the largest basis sets, the results obtained by Perera *et al.* for the atoms B−F are in close accord with the values reported in our previous quadratic configuration interaction (QCISD) study[24] and presumably with experiment. (Although the value for boron is not settled, that for carbon has been obtained in conjunction with a theoretical parameter, and substantial experimental error remains in the reported couplings at oxygen and fluorine.)

Dunning and co-workers have recently introduced correlation-consistent basis sets, first to describe the valence-space electron correlation[25] and later to address core and core−valence correlation effects.[26] Here we employ these correlation-consistent basis sets to evaluate the spin density at the nuclei for the atoms B−F from quadratic configuration interaction calculations.

Of the many choices of density functionals used in the literature, the nonlocal hybrid density functional, B3LYP,[27] appears to be particularly useful for the computation of spin densities.[14] The B3LYP model includes a contribution from Hartree−Fock exchange in addition to both local[28] and nonlocal[29] exchange functionals and both local[30] and nonlocal[31] correlation corrections. Similar calculations of unpaired spin density have been performed with a range of the correlation-consistent basis sets for this functional.

Computational Details

All calculations were performed with a modified version of the Gaussian 94 suite of programs.[32] The quadratic configuration interaction scheme was introduced by Pople *et al.*,[33] and the particular choice of hybrid density functional, UB3LYP,[27] was employed as implemented in Gaussian 94. Basis sets used were downloaded from the Extensible Computational Chemistry Environment Basis Set Database.[34]

Results and Discussion

The correlation-consistent polarized valence sets, cc-pVXZ (X = D, T, Q, 5), were designed to form a systematic sequence particularly suited to the recovery of valence-electron correlation effects.[25] Supplementary (more diffuse) functions, giving basis sets denoted aug-cc-pVXZ, were introduced[35] and used with correlation procedures sufficiently extensive to allow satisfactory computation of electron affinities, for example. Properties calculated from these sets were demonstrated to converge (exponentially) to the basis set limit. Assuming an adequate treatment of electron correlation, whether or not the basis set limit achieved at this level of theory is related to the experimental value for a particular property, depends on the sensitivity of this property to the inclusion of core and core−valence electron correlation effects. Core−valence cc-basis sets, cc-pCVXZ, were subsequently developed[26] to address this issue. Extrapolation of the results obtained from calculations with systematic sequences of these cc-basis sets removes any uncertainty associated with specific values derived from particular segmented basis sets.

[†] This is Document No. NDRL-3979 from the Notre Dame Radiation Laboratory.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

S1089-5639(97)00402-7 CCC: $14.00

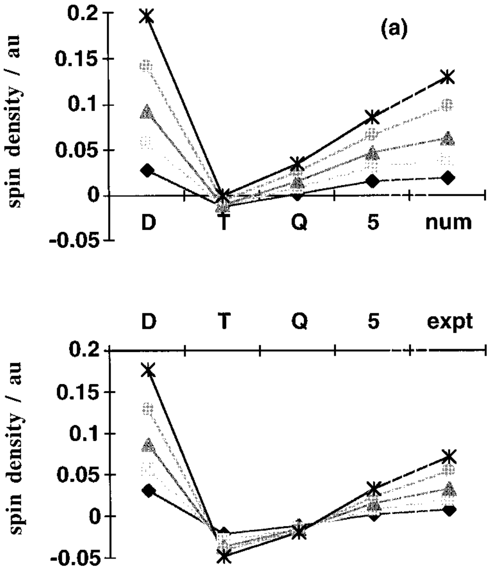

Figure 1. Computed spin density (au) at the atoms B (◆), C (■), N (▲), O (●), and F (*) from valence-only correlation-consistent basis sets, cc-pVXZ (X = D, T, Q, 5): (a) UHF (num = numerical UHF), (b) QCISD (expt = experimental).

TABLE 1: QCISD(full) Atomic Isotropic Splittings (in MHz) from Valence-Only Correlation-Consistent Basis Sets, cc-pVXZ

	B	C	N	O	F
pVDZ	45.8	62.8	28.3	−77.9	748
pVTZ	−29.3	−30.8	−11.4	24.5	−195
pVQZ	−16.5	−15.7	−4.9	9.9	−74.5
pV5Z	4.1	9.1	5.0	−14.3	141
aug-pVDZ	61.0	84.1	37.5	−102	959
aug-pVTZ	−22.6	−19.9	−6.0	10.4	−66.2
aug-pVQZ	−15.6	−14.0	−4.0	7.6	−52.9
aug-pV5Z	4.6	10.0	5.5	−15.5	152
expt	11.6(7)	(19.5)	10.45	−34.5(69)	302(18)

Isotropic hyperfine coupling constants, *a*, are determined by the unpaired electron spin density, $Q_0(N)$, at the location of the magnetic nucleus, N.

$$a(N) = (8\pi/3)(g_e/g_0)g_N\beta_N Q_0(N)/n_e \qquad (1)$$

In eq 1, g_e/g_0 is the ratio of the isotropic *g* value for the species to that of the free electron, here taken as unity, g_N and β_N are the nuclear magnetogyric ratio and nuclear magneton, respectively, and n_e is the number of unpaired electrons.

In an isolated atom this spin density is contributed solely by the electron distribution in s-orbitals which typically produces large and oppositely signed contributions from the K- and L-shells. A balanced description of core- and valence-correlation effects is therefore essential for obtaining reliable values. Immediate evidence of this assertion is provided in Table 1, which list the QCISD/cc-pVXZ values for the isotropic splitting in the atoms B−F. The reported values do not approach the known experimental couplings even at the quintuple-ζ level and are clearly of little useful predictive value. With the cc-pV5Z basis sets the derived spin densities are still only about 50% of the observed values.

The trends observed in the QCISD/cc-pVXZ calculations are already present in the spin densities computed directly from the underlying UHF reference determinant, as seen in Figure 1. The asymptotes against which the UHF values are compared in Figure 1b are obtained from fully numerical solutions to the UHF equations. As expected, with regard to the satisfactory calculation of isotropic coupling constants even at the UHF level, the cc-VXZ basis sets are overcontracted in the core region.

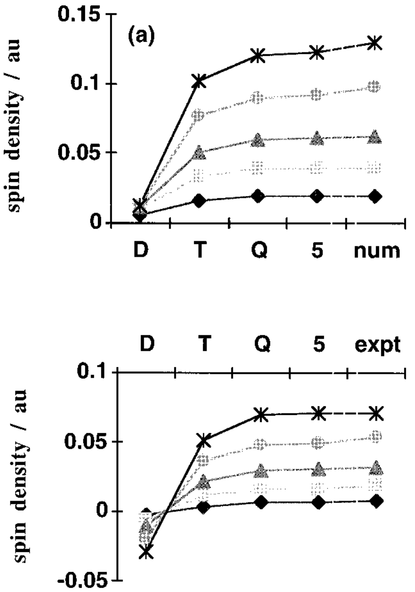

Figure 2. Computed spin density (au) at the atoms B (◆), C (■), N (▲), O (●), and F (*) from augmented core−valence correlation-consistent basis sets, aug-cc-pCVXZ (X = D, T, Q, 5): (a) UHF (num = numerical UHF), (b) QCISD (expt = experimental).

TABLE 2: QCISD(full) Atomic Isotropic Splittings (in MHz) from Core−Valence Correlation-Consistent Basis Sets, cc-pCVXZ

	B	C	N	O	F
pCVDZ	−3.4	−6.4	−3.3	11.5	−123
pCVTZ	4.8	12.7	7.1	−22.6	216
pCVQZ	9.3	18.4	9.6	−29.4	294
pCV5Z	9.4	18.7	10.0	−30.3	298
aug−pCVDZ	10.5	11.8	4.4	−9.0	55.0
aug−pCVTZ	8.0	18.4	10.1	−30.7	292
aug−pCVQZ	10.0	19.8	10.4	−31.6	315
aug−pCV5Z	9.7	19.4	10.3	−31.1	306
expt	11.6(7)	(19.5)	10.45	−34.5(69)	302(18)

A much different picture emerges with the core−valence basis sets, cc-pCVXZ, however, as seen in Figure 2. As the quality of the basis set is improved, the UHF values converge smoothly toward the numerical UHF results for the atoms in a manner reminiscent of the properties determined by Kendall *et al.*[35] Similarly, the QCISD values converge smoothly toward the putative experimental results. This behavior is perhaps more clearly demonstrated in Table 2. It is noteworthy that the effects of the addition of the supplementary functions (cc- → aug-cc) become much less important as the basis set is systematically enlarged and that the percent difference (between cc-pVXZ and cc-pCVXZ) in the correlation recovery is large only for the smallest basis sets and is independent of "aug-" addition. Accurate calculations of isotopic splitting in a number of small molecular species with similarly adapted cc-basis sets have also been reported by Feller and co-workers[6,36,37]

So far, we have focused on basis set improvement as the main route to approach accord with the observed splittings. The assumption has been that little change would ensue beyond the QCISD level. This is checked in Table 3 where the effects, as estimated at fifth order in perturbation theory, of mixing in configurations reached by triple substitutions in the UHF determinant are reported, QCISD(T). Spin densities at QCISD(T) are computed by finite-field perturbation theory, as previously.[24] Only small corrections to the QCISD values are found,

TABLE 3: QCISD(T)(full) Atomic Isotropic Splittings (in MHz) from Core−Valence Correlation-Consistent Basis Sets, cc-pCVXZ

	B	C	N	O	F
pCVDZ	−2.9	−6.3	−3.3	11.8	−126
pCVTZ	5.4	13.0	7.2	−22.5	214
pCVQZ	9.9	18.8	9.8	−29.6	294

TABLE 4: UB3LYP Atomic Isotropic Splittings (in MHz) from Segmented Contracted Basis Sets

	B	C	N	O	F
[4s2p1d]	20.0	25.6	8.9	−18.1	97.3
[7s4p2d]	16.0	23.1	9.6	−26.8	219
[8s5p4d1f]	16.6	23.6	9.9	−27.4	223

TABLE 5: UB3LYP Atomic Isotropic Splittings (in MHz) from Correlation-Consistent Basis Sets

	B	C	N	O	F
pCVDZ	6.4	0.3	−3.0	15.3	−208
pCVTZ	9.7	16.3	7.0	−20.9	173
pCVQZ	17.0	23.6	9.4	−24.2	195
pCV5Z	18.6	25.0	9.6	−24.1	191
aug−pCVDZ	11.9	8.5	0.6	6.1	−129
aug−pCVTZ	12.9	20.9	9.0	−26.0	217
aug−pCVQZ	17.7	24.8	10.0	−25.9	210
aug−pCV5Z	18.2	25.6	9.9	−24.7	197
expt	11.6(7)	(19.5)	10.45	−34.5(69)	302(18)

and these corrections generally move the computed values closer to experimental observations.

As mentioned previously, the nonlocal hybrid density functional denoted UB3LYP has proved particularly useful for estimating spin densities in a number of radicals.[13,14,18] In general, these studies have employed conventional energy-optimized segmented contracted basis sets, perhaps modified to enhance suitability for spin density computation.

Results for hyperfine coupling in the atoms B−F computed from UB3LYP with three unenhanced sets employed in previous work[24] are displayed in Table 4. For the nitrogen atom the computed splitting is relatively insensitive to the chosen basis set and is fortuitously close to experiment. For B and C the computed values overestimate experiment, while for O and F substantial underestimates are found.

To distinguish whether these trends are an artifact of the limited flexibility inherent in the particular choice of these basis sets or pertain to the particular form of the density functional, extensive series of calculations were carried out with the cc-pVXZ and cc-pCVXZ basis sets and the results extrapolated to the basis set limit.

For the core−valence cc-basis sets, cc-pCVXZ, computed spin densities with this particular density functional are displayed in Table 5. As the basis set is improved, the calculated coupling constants once again converge in the familiar fashion. However, only for the nitrogen atom does this convergence lead to the experimental value. For boron and carbon the asymptotes are high, while for O and F convergence leads to values far below experiment, echoing the findings with the segmented basis sets.

In general, then, the successful calculation of hyperfine coupling constants using the UB3LYP functional thus depends on fortuitous cancellation of errors arising from both the particular form of the functional adopted and the limited flexibility of the particular basis set employed. No doubt a different choice of density functional could be made more appropriate to the reliable computation of spin densities. However, it is emphasized here that such a choice should not depend on results gained through the use of limited basis sets.

TABLE 6: Atomic Isotropic Splittings (in MHz) from Valence-Only Correlation-Consistent pVQZ Basis Set

	B	C	N	O	F
UHF	2.6	10.5	5.1	−15.6	145
UB3LYP	0.82	−4.7	−4.2	15.8	−193
UQCISD	−16.5	−15.7	−4.9	9.9	−74.5

As a footnote, Table 6 points out that valence-only cc-basis sets are also inappropriate for calculation of spin density with the UB3LYP functional.

Conclusion

Extrapolation of the results from cc-pCVXZ basis sets produces an accurate description of the spin density distribution in the atoms B−F when coupled with a sufficiently thorough treatment of the effects of electron correlation. The success of a currently popular density functional treatment for rapid computation of hyperfine coupling constants is shown to rely on fortuitous cancellation of errors.

Acknowledgment. The research described herein has been supported by the Office of Basic Energy Sciences of the United States Department of Energy.

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