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Assessment of Procedures for Calculating Radical Hyperfine Structures

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The effects of different basis sets and computational methods on calculated isotropic hyperfine couplings have been investigated for a set of representative small radicals (OH, H_2O^+, CN, HCN^-, FCN^-, $HCCH^-$, CH_3, CH_4^+, NH_2, NO_2, and H_2CO^+). Particular emphasis has been placed on the performance of the QCISD approach, when used in combination with moderately large basis sets. It is found that the 6-311+G(2df,p) basis set generally gives good results and that the IGLO-III basis set performs nearly as well. The cc-pVXZ and aug-cc-pVXZ basis sets, on the other hand, display large and unpredictable fluctuations in hyperfine couplings even at the cc-pVQZ level. As noted previously, the reason for this erroneous behavior can be traced to the contraction of the *s*-shell. The error due to the unbalanced nature of the pVXZ basis sets is greatly reduced on going to the core-valence correlated aug-cc-pCVXZ sets. The calculated hyperfine coupling constants are very sensitive to changes in geometry. In turn, the geometries of radical anion systems in particular are sensitive to level of theory. The 6-311+G(2df,p) basis set has also been tested with other spin-unrestricted methods (UHF, UMP2, UQCID, and five DFT functionals), but none of these are found to perform comparably to QCISD. Inclusion of triple excitations (QCISD(T)) leads to hyperfine couplings that generally lie within 2−3 G of the QCISD results.

Introduction

The calculation of radical hyperfine properties has received extensive attention in recent years.[2−5] With the rapid improvement in computer technology, combined with increasingly accurate computational schemes, theoretical predictions of radical hyperfine structures (hfs) are today serving an important role in the understanding of the properties of radicals and their reactions. Due to the high reactivity of most radical systems, relatively little experimental information can, in general, be obtained on such species. Theory may be of assistance through comparisons of observed and computed hyperfine coupling constants (hfcc's), which may lead to the assignment of plausible geometries and the identification of reaction products. Further analysis of the theoretical data also enables us to answer questions regarding reaction barriers, transition states, charge and spin distributions, and various other properties.

Isotropic hfcc's ($a^{\mathrm{N}}_{\mathrm{iso}}$) arise from a direct contact interaction between the electron and the magnetic nuclei in the radical. They are calculated by evaluating the spin density at the nucleus in question (N), multiplied by the nuclear (g_{N}) and electronic (g) *g*-factors, the Bohr magneton (β) and the nuclear magneton (β_{N}):

$$a^{\mathrm{N}}{}_{\mathrm{iso}} = (8\pi/3)g\beta g_{\mathrm{N}}\beta_{\mathrm{N}} \sum_{\mu,\nu} P^{\alpha-\beta}_{\mu,\nu}\langle\psi_{\mu}(r_{k\mathrm{N}})|\delta(r_{k\mathrm{N}})|\psi_{\nu}(r_{k\mathrm{N}})\rangle$$

It is only recently, however, that it has become possible to obtain a detailed understanding of the various factors involved in computing hyperfine parameters of radicals. It has been found that high recovery of electron correlation, as well as the use of a basis set that accurately describes the spin density at the nucleus of interest (see, for example, refs 3, 5, 6), is of great importance in the quantitative prediction of hyperfine couplings. It has been found in particular, in a number of studies,[3−6] that basis sets of double-ζ-plus-polarization (DZP) quality or lower are generally quite inadequate, except for specific cases in which fortuitous cancellation of errors occurs. As a result, success to date has been achieved by applying large basis sets, often fully uncontracted or very loosely contracted, specially developed for hfcc calculations.

Of the many conventional *ab initio* approaches, it is essentially only multireference configuration interaction (MRCI), quadratic configuration interaction (QCI), and coupled-cluster (CC) techniques, in conjunction with large basis sets, that consistently have proven able to generate hfcc's of high accuracy.[5,7−12] One problem with such approaches is that they are computationally quite expensive even for moderately sized systems, hence restricting studies to date to relatively small systems.

An alternative approach for calculating hfcc's is represented by density functional theory (DFT),[13] for which the computational cost and memory requirements are considerably less than those of conventional correlated *ab initio* procedures. As a consequence, the number of basis functions, and hence atoms, is not nearly as limiting a factor at the DFT level as it is for the latter approaches. A problem with DFT methods, including the gradient-corrected variants, is that we cannot as yet systematically improve the functionals. Nevertheless, because of empirical demonstrations of their good performance, DFT methods are today becoming a serious alternative to conventional *ab initio* calculations in the computation of hfcc's. In addition, because of their lower cost and hence their ability to treat larger systems, DFT methods may be used to obtain more realistic descriptions of the interactions between radical systems and their surroundings by explicit consideration of the latter. Furthermore, in DFT we are able to accurately include atoms (*e.g.*, some transition metals) for which the simpler HF-based methods generally face significant problems.

In the present work, we have chosen to investigate the ability of large, yet "standard", basis sets to predict accurate hfcc's, in particular when used in combination with spin-unrestricted QCI or DFT techniques.

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Theoretical Procedures

Calculations were performed using the Gaussian 92/DFT,[14] Gaussian 94,[15] and ACES II[16] programs. Geometry optimizations were performed for the complete set of 11 radicals (OH, H_2O^+, CN, HCN^-, FCN^-, *trans*-$HCCH^-$, CH_3, CH_4^+, NH_2, NO_2 and H_2CO^+) at the unrestricted second-order Møller−Plesset (UMP2) and quadratic configuration interaction (UQCISD) levels of theory with the 6-31G(d) and 6-311+G(2df,p) basis sets. More extensive studies were also performed on a subset of four radicals (OH, H_2O^+, CN and HCN^-). For the sake of brevity, we refer to the full set of 11 radicals as R1 and the subset of four radicals as R2. The frozen-core (fc) approximation was employed in all geometry optimizations.

The hyperfine coupling constant (hfcc) calculations were performed using unrestricted Hartree−Fock (UHF), UMP2, UQCID (which is identical to UCCD), UQCISD, and UQCISD(T) procedures. A variety of different DFT approaches were also employed (see below). The basis sets used represent three distinct groups: the Pople 6-31G and 6-311G series, up to 6-311+G(2df,p);[17] the IGLO-III basis set of Kutzelnigg *et al.*;[18] and the correlation-consistent polarized-valence basis sets (cc-pVXZ) of Dunning *et al.*,[19] including their analogues augmented by diffuse functions (aug-cc-pVXZ; X = D, T, Q), and the corresponding core-valence correlated aug-cc-pCVXZ (X = D, T) basis sets. For the hfcc calculations employing correlated *ab initio* methods, all electrons were correlated. The symbols U (unrestricted), fc (frozen core), and FULL (all electrons included) are hereafter neglected for simplicity.

The IGLO-III basis set is known from various density functional theory studies to generally produce quite accurate hyperfine data when used in combination with certain gradient-corrected functionals.[4,20−22] Hence, it is also of interest to investigate its performance when used in conjunction with high-level *ab initio* methods such as QCISD, to see whether the good performance of the basis set is due to fortuitous cancellation effects when used in combination with particular DFT approaches or if it is a property inherent to the basis set itself. The 6-311+G(2df,p) basis was chosen as a representative of a large, yet widely used, Pople set with a view to seeing whether we need specially tailored basis sets to obtain quantitatively accurate hfcc's or if standard high-quality contracted basis sets are sufficient. The final group of basis sets that we have examined is the correlation-consistent polarized-valence basis sets of Dunning and co-workers.[19] These are known to yield very accurate valence properties and have been previously used in modified and partially decontracted forms in MRCI,[8] QCI,[8−10] and MCSCF[23] studies of radical hfcc's. To improve the balance in the cc-pVXZ basis sets, core-valence correlation-consistent basis sets (cc-pCVXZ) have also been developed[19d] and are included in some of the comparisons in the present work.

As the final part of the present study, we also include an examination of the performance of five different DFT approaches in computing hfcc's for the R2 subset of radicals (OH, H_2O^+, CN, HCN^-). The functionals employed are the local density approach using the Slater exchange[24] together with the Vosko−Wilk−Nusair local density parametrization of the correlation contribution (S-VWN),[25] and combinations of the gradient-corrected exchange functional of Becke (B)[26] or his three-parameter hybrid exchange functional (B3)[27] together with the gradient-corrected correlation functional of Lee, Yang, and Parr (LYP)[28] or of Perdew (P86).[29] The gradient-corrected approaches were used in a total of four combinations: B-LYP, B3-LYP, B-P86, and B3-P86 as implemented in the Gaussian 92/DFT[14] and Gaussian 94[15] programs. For all DFT calculations of hyperfine coupling constants, we have used QCISD/6-31G(d) optimized geometries. The 6-311+G(2df,p) basis set, in both its standard contracted form and with decontraction of the heavy-atom functions, and the standard IGLO-III basis set were employed.

The 11 radicals and radical ions of the R1 set constitute a wide variety of geometric structures, radical types, charges, and spin distributions. For most of these, there is a sufficient amount of previous theoretical and experimental data to enable a proper evaluation of the performance of the present approaches. The R2 subset was used for a majority of the preliminary calculations that examined the performance of different basis sets and theoretical methods, whereas the final and best calculations were carried out for the full R1 set.

Results and Discussion

1. Optimized Geometries. Table 1 lists the optimized geometries, obtained at the MP2/6-31G(d), QCISD/6-31G(d), and QCISD/6-311+G(2df,p) levels. Also included are results obtained previously[20b,c,21c,30] with DFT calculations at the gradient-corrected PW-P86/IGLO-III level.

The QCISD/6-31G(d) geometries are in good agreement with the available experimental structural data.[31−34] There is also good overall agreement between the MP2/6-31G(d) and QCISD/6-31G(d) geometries, with a general feature being that QCISD usually generates slightly longer bonds. The largest differences in structure occur for CN and HCN^-, the QCISD structure for CN being in better agreement with experiment. The QCISD calculated geometries of OH, H_2O^+, CN, CH_3, CH_4^+ and NH_2 show only minor changes on increasing the basis set from 6-31G(d) to 6-311+G(2df,p). Slightly larger changes are shown by $HCCH^-$, NO_2, and H_2CO^+, but the effects are more significant for HCN^- and FCN^-. In the case of HCN^-, this appears primarily to reflect the effects of diffuse functions for this anionic species.[35] However, for FCN^-, it is the inclusion of f-functions that appears to be very important.[36] The QCISD/6-31G(d) structures generally compare well with the PW-P86/IGLO-III structures. The largest differences are found for the bond angle in HCN^-, the F−C bond length in FCN^-, and the C−O bond length in H_2CO^+. Apart from these, the bond lengths agree to within 0.02 Å, and the bond angles to within 2−3 degrees. We note, however, that there is a large difference between the PW-P86/IGLO-III and QCISD/6-311+G(2df,p) H−C lengths in HCN^- and F−C lengths in FCN^-.

Table 2 presents the spin contamination values of the UHF wave functions, for the R2 set, at the geometries listed. There is a non-negligible degree of spin contamination for all systems, the contamination being particularly large for the CN radical. The high spin contamination can be expected to have an adverse influence on the results, primarily at the lower levels of theory in which higher excitations are not explicitly included. No spin projection techniques, to annihilate the effects of higher excitations in the UHF wave function, were employed in the present work. As shown, for example, by Chipman,[6] the use of spin projection generally improves UHF-based results, although significant errors can still occur.

In the remaining parts of this paper, we will be using QCISD/6-31G(d) geometries, unless otherwise noted.

2. Hyperfine Coupling Constants. *2.1 Basis Set Selection.* We begin by investigating the performance of the Pople basis sets,[17] improved by successive addition of valence functions, diffuse functions, and polarization functions, from 6-31G(d) to 6-311+G(2df,p). The 6-311+G(2df,p) results are then compared with results obtained using other basis sets of similar quality (*e.g.*, IGLO-III,[18] cc-pVXZ, aug-cc-pVXZ, and aug-cc-pCVXZ[19]).

TABLE 1: Optimized Geometries[a]

species	symmetry	parameter	MP2/6-31G(d)	QCISD/6-31G(d)	QCISD/6-311+G(2d,f,p)	PW-P86/IGLO-III[b]	exptl
OH	$C_{\infty v}$	r(O−H)	0.979	0.984	0.972	0.985	0.970[c]
H_2O^+	C_{2v}	r(O−H)	1.011	1.013	1.001	1.017	0.999[c]
		∠(H−O−H)	109.9	109.5	109.9	108.6	110.5
CN	$C_{\infty v}$	r(C−N)	1.135	1.181	1.167	1.174	1.172[c]
HCN^-	C_s	r(H−C)	1.230	1.217	1.163	1.211	
		r(C−N)	1.210	1.233	1.221	1.219	
		∠(H−C−N)	129.8	120.7	123.1	124.2	
FCN^-	C_s	r(F−C)	1.607	1.616	1.531	1.718	
		r(C−N)	1.201	1.205	1.197	1.192	
		∠(F−C−N)	130.6	129.1	128.1	131.3	
$HCCH^-$	C_{2h}	r(C−C)	1.325	1.324	1.305	1.310[d]	
		r(C−H)	1.114	1.119	1.097	1.108	
		∠(H−C−C)	120.2	120.4	125.2	123.5	
CH_3	D_{3h}	r(C−H)	1.079	1.084	1.081	1.083	1.079[e]
CH_4^+	C_{2v}	r(C−H1)	1.084	1.087	1.084	1.087[f]	
		r(C−H2)	1.174	1.178	1.187	1.195	
		∠(H1−C−H1)	123.6	123.7	125.4	125.1	
		∠(H2−C−H2)	58.4	58.6	55.2	56.1	
NH_2	C_{2v}	r(N−H)	1.028	1.034	1.028	1.036[g]	1.024[h]
		∠(H−N−H)	103.3	102.9	103.5	102.9	103.3
NO_2	C_{2v}	r(N−O)	1.217	1.209	1.189	1.210	1.194[i]
		∠(O−N−O)	133.7	134.2	134.9	133.0	133.9
H_2CO^+	C_{2v}	r(C−O)	1.209	1.213	1.197	1.189	
		r(C−H)	1.108	1.113	1.115	1.129	
		∠(H−C−O)	118.4	119.2	119.5	118.0	

[a] Bond lengths are in angstroms; angles are in degrees. [b] Taken from ref 20b unless otherwise indicated. [c] Reference 31. [d] Reference 30. [e] Reference 32. [f] Reference 20c. [g] Reference 21c. [h] Reference 33. [i] Reference 34.

TABLE 2: Spin-Squared Expectation Values ($\langle S^2 \rangle$) in the UHF Wave Functions for the OH, H_2O^+, CN, and HCN^- Radicals at Various Geometries[a]

species	MP2/6-31G(d)	QCISD/6-31G(d)	QCISD/6-311+G(2df,p)
OH	0.755	0.756	0.757
H_2O^+	0.758	0.758	0.758
CN	1.033	1.203	1.138
HCN^-	0.791	0.818	0.809

[a] The spin contamination is reflected in the deviation of $\langle S^2 \rangle$ from the ideal value for a doublet of 0.750.

The QCISD isotropic hfcc's for OH, H_2O^+, CN and HCN^-, computed with the Pople basis sets, are compared with experimental values[37−40] in Table 3. All calculations were performed using the QCISD/6-31G(d) geometries given in Table 1. With few exceptions, the 6-31G(d) and 6-31G(d,p) basis sets considerably overestimate the magnitudes of the experimental a_{iso} values. Particularly poor performance is noted for ^{13}C in HCN^- and for ^{17}O in H_2O^+. Enlarging the basis set from double-ζ valence to triple-ζ valence[41] to give 6-311G(d,p) leads to a uniform improvement in the calculated hfcc's. Further improvement is observed on adding a set of diffuse functions (6-311+G(d,p)), the effect being particularly large for HCN^-. The additions to 6-311G(d,p) of a first set of f-functions (6-311G(df,p)) and of a second set of d-polarization functions (6-311G(2df,p)) are of less importance. The carbon coupling in HCN^- still differs by more than 30 G from the experimental value using the latter basis set. Clearly, inclusion of diffuse functions, as in 6-311+G(2df,p), is essential. With the exception of HCN^-, a_{iso} values obtained with the 6-311G(2df,p) and 6-311+G(2df,p) basis sets are very similar. The former basis set should generally provide suitable accuracy for radical cations and most neutral radicals. For anions and neutral radicals with very diffuse electron distributions, the 6-311+G(2df,p) basis set is our preferred choice. For larger systems, 6-311G(d,p) for cations and most neutrals and 6-311+G(d,p) for anions and neutrals with lone-pair electrons would represent reasonable compromises between accuracy and computational expense. The mean absolute deviations from experiment at the QCISD/6-311+G(d,p) and QCISD/6-311+G(2df,p) levels are 3.3 and 2.5 G, respectively.

Also included in Table 3 are hfcc values obtained at the QCISD level with the IGLO-III basis set. The results are generally quite similar to those obtained with 6-311+G(2df,p), but there are some poorer cases (*e.g.*, ^{13}C in HCN^-) and the mean absolute deviation from experiment is increased to 4.5

TABLE 3: Effect of Basis Set on QCISD Calculated a_{iso} Values (G) for the OH, H_2O^+, CN, and HCN^- Radicals[a]

	OH		H_2O^+		CN		HCN^-			
basis set	^1H	^{17}O	^1H	^{17}O	^{13}C	^{14}N	^{13}C	^{14}N	^1H	$\lvert \Delta a_{iso} \rvert$[b]
6-31G(d)	−29.9	−21.1	−30.1	−38.9	200.4	−3.2	121.4	6.9	146.5	9.6
6-31G(d,p)	−29.3	−21.1	−30.1	−38.8	200.4	−3.2	124.7	6.9	142.4	9.4
6-311G(d,p)	−28.8	−15.3	−29.9	−28.0	208.8	−2.1	110.7	5.6	128.3	6.7
6-311+G(d,p)	−28.7	−16.5	−29.8	−27.5	214.8	−2.4	75.2	7.4	125.0	3.3
6-311G(df,p)	−27.0	−14.8	−28.2	−27.2	204.9	−2.6	110.0	5.2	128.7	6.8
6-311G(2df,p)	−26.7	−16.2	−27.5	−28.2	212.5	−3.3	108.2	5.9	130.6	5.5
6-311+G(2df,p)	−26.7	−17.3	−27.5	−28.0	215.4	−3.5	76.2	7.3	126.4	2.5
IGLO−III	−26.4	−18.1	−27.2	−29.0	222.6	−2.9	92.4	7.4	130.4	4.5
exptl	−26.2[c]	−18.3[c]	−26.1	−29.7	210.0	−4.5	75.4	7.1	137.2	
exptl ref	37, 38		39		40		40			

[a] QCISD/6-31G(d) optimized structures used throughout. [b] Mean absolute deviation between theoretical and experimental values. [c] For other experimental values, see ref 37.

TABLE 4: Effect of Choice of Geometry on Calculated QCISD/6-311+G(2df,p) a_{iso} Values (G) for the OH, H_2O^+, CN, HCN^-, FCN^- and $HCCH^-$ Radicals

species	atom	MP2/ 6-31G(d)	QCISD/ 6-31G(d)	QCISD/ 6-311+ G(2df,p)	exptl
OH	^{17}O	−17.3	−17.3	−17.3	−18.3[a]
	^{1}H	−26.6	−26.7	−26.5	−26.2[a]
H_2O^+	^{17}O	−28.0	−28.0	−29.0	−29.7[b]
	^{1}H	−27.5	−27.5	−27.5	−26.1[b]
CN	^{13}C	223.3	215.4	217.8	210.0[c]
	^{14}N	−2.4	−3.5	−3.2	−4.5[c]
HCN^-	^{13}C	85.7	76.2	63.9	75.4[c]
	^{14}N	7.9	7.3	7.8	7.1[c]
	^{1}H	118.6	126.4	112.9	137.2[c]
FCN^-	^{13}C	235.8	234.0	203.8	231.1[c]
	^{14}N	7.0	6.4	7.7	6.4[c]
	^{19}F	539.5	522.3	546.6	486.4[c]
$HCCH^-$	^{13}C	18.1	18.3	12.1	14.5[d]
	^{1}H	50.5	50.6	46.2	48[d]
$\lvert\Delta a_{iso}\rvert$[e]		8.2	4.9	10.1	

[a] References 37, 38. [b] Reference 39. [c] Reference 40. [d] Reference 42. [e] Mean absolute deviation between theoretical and experimental values.

G. As for the 6-311+G(2df,p) results, the main part of the deviations can be traced to a few atoms with large errors.

To examine the effect on calculated hfcc's of the choice of geometry, calculations were also performed for OH, H_2O^+, CN, HCN^-, FCN^-, and $HCCH^-$ at the QCISD/6-311+G(2df,p) level, using MP2/6-31G(d) and QCISD/6-311+G(2df,p) optimized geometries. The geometries of OH and H_2O^+ do not change significantly with level of theory (Table 1), and it is therefore not surprising that their hfcc's are not very dependent on choice of optimized geometry (Table 4). However, large changes can be seen for the hfcc's of ^{13}C in CN, ^{13}C and ^{1}H in HCN^-, ^{13}C and ^{19}F in FCN^-, and ^{13}C in $HCCH^-$. Results with MP2/6-31G(d) geometries are poorer than those with QCISD/6-31G(d) geometries, as might have been expected. However, it is less clear why the use of QCISD/6-311+G(2df,p) geometries should also lead to poorer results, particularly for the two anionic systems, HCN^- and FCN^-.[43] The main conclusion to be reached is that calculated hfcc's are highly sensitive to changes in geometry.

QCISD/6-311+G(2df,p) a_{iso} values for the OH radical are compared with QCISD results obtained with the IGLO-III, cc-pVDZ, aug-cc-pVDZ, aug-cc-pCVDZ, cc-pVTZ, aug-cc-pVTZ, aug-cc-pCVTZ, and cc-pVQZ basis sets in Table 5. Also examined in Table 5 are the effects of full or partial decontraction of the oxygen basis sets. We can see that the proton hfcc in OH is well described for all the contracted basis sets tested. In addition, decontracting the various basis sets for oxygen has negligible effects upon the proton hfcc.

However, large variations in isotropic hfcc's are found for oxygen, with values ranging from +1.5 G (cc-pVTZ) to −46.1 G (aug-cc-pVDZ)! We can see that poorest agreement with the experimental value of −18.3 G[37,38] is found for the correlation-consistent basis sets, whereas both the 6-311+G(2df,p) and the IGLO-III basis sets give results in good agreement with experiment. The changes resulting from decontracting these latter two basis sets are minor, especially for IGLO-III, suggesting that these contraction schemes are well balanced. The importance of balancing the inner shell and valence correlation contributions to a_{iso}, which are of opposite sign but are roughly equal in magnitude, has been investigated in great detail, for example, by Engels *et al.*[7b,g,i]

All the standard contracted correlation-consistent valence basis sets (cc-pVXZ) give poor values of a_{iso} for ^{17}O. Decontraction of the s-shell significantly improves the results in all cases. Decontracting the p-shell without decontracting the s-shell has only a minor effect (not shown),[44] as does a decontraction of the p-shell with the *s*-shell already decontracted. Best agreement with experiment for the cc-pVXZ basis sets is found for the s- or sp-decontracted aug-cc-pVTZ sets. Clearly, the standard contraction schemes employed in the cc-pVXZ basis sets are unsuitable for hfcc calculations. For the core-valence correlation-consistent basis sets, on the other hand, it is only the aug-cc-pCVDZ basis that displays a contraction dependence. The aug-cc-pCVTZ basis set performs very similarly to the 6-311+G(2df,p) and IGLO-III basis sets.

TABLE 5: QCISD Calculated a_{iso} Values (G) for the OH Radical[a]

basis set	^{1}H	^{17}O
6-311+G(2df,p)	−26.6	−17.3
IGLO-III	−26.3	−18.1
cc-pVDZ	−25.2	−39.8
aug-cc-pVDZ	−27.0	−46.1
aug-cc-pCVDZ	−27.1	−10.9
cc-pVTZ	−26.9	1.5
aug-cc-pVTZ	−25.8	−2.0
aug-cc-pCVTZ	−25.7	−17.8
cc-pVQZ	−25.6	−4.9
us-6-311+G(2df,p)[b]	−26.6	−17.1
us-IGLO-III[b]	−26.3	−18.3
us-cc-pVDZ[b]	−25.3	−14.1
us-aug-cc-pVDZ[b]	−27.1	−20.1
us-aug-cc-pCVDZ[b]	−27.1	−20.0
us-cc-pVTZ[b]	−26.9	−15.1
us-aug-cc-pVTZ[b]	−25.7	−17.7
us-aug-cc-pCVTZ[b]	−25.7	−18.5
usp-6-311+G(2df,p)[c]	−26.5	−16.9
usp-IGLO-III[c]	−26.3	−18.3
usp-cc-pVDZ[c]	−25.5	−13.1
usp-aug-cc-pVDZ[c]	−27.2	−19.0
usp-aug-cc-pCVDZ[c]	−27.2	−19.1
usp-cc-pVTZ[c]	−26.8	−15.2
usp-aug-cc-pVTZ[c]	−25.7	−17.7
usp-aug-cc-pCVTZ[c]	−25.7	−18.5
exptl[d,e]	−26.2	−18.3

[a] MP2/6-31G(d) geometry used throughout. [b] us: uncontracted oxygen s-shell. [c] usp: uncontracted oxygen s- and p-shells. [d] References 37, 38. [e] For other experimental values, see reference 37.

Modified versions of the aug-cc-pVXZ basis sets have previously been used by Feller *et al.* in QCI and MRCI studies of F_2^-, NO, H_2CN, and H(HO)CN.[8,10d] Additional diffuse functions were added to each shell, and the outermost member of each innermost contracted s- and p-function was split off. The QCISD and QCISD(T) calculations, using this "mod-aug-cc-pVTZ" basis set, generated accurate hfcc's. The conclusion made by Feller *et al.*, that the crucial aspect of these basis set modifications is the decontraction of the s-shell, is supported by the present work. Similar findings were also made in an MCSCF study of the CN and CP radicals by Fernández *et al.*[23] Using the sp-decontracted cc-pVTZ basis set, they obtained reasonable agreement with experiment, although additional diffuse p- and d-functions, and four tight s-functions, had to be added in order for the calculations to achieve convergence with respect to the hfcc's. The somewhat slow convergence with respect to basis set size, and strong dependence on active space in MCSCF hfcc calculations has been noted previously.[46]

Table 6 compares the QCISD/6-311+G(2df,p) and QCISD(T)/6-311+G(2df,p) hfcc's for the full R1 set of radicals, with experimental[6,37−40,42,46−50] and previously calculated[3,7h,11,20b,c,21b−d,23,30,46,47,51−53] values. With a few exceptions, the computed hfcc's are within 3−4 G of experimental values. The most pronounced differences compared with experiment

TABLE 6: Comparison of QCISD/6-311+G(2df,p) and QCISD(T)/6-311+G(2df,p) Calculated a_{iso} Values (G) with Other Calculated and Experimental Values

species	atom	QCISD[a]	QCISD[b]	QCISD(T)[c]	previous calc	exptl
OH	^{17}O	−17.3	−17.3	−17.0	−17.7[d], −15.1[e], −17.5[f]	−18.3[g]
	^{1}H	−26.7	−26.5	−25.8	−21.1[d], −24.5[e], −24.6[f]	−26.2[g]
H_2O^+	^{17}O	−28.0	−29.0	−27.3	−24.1[d], −20.6[h]	−29.7[i]
	^{1}H	−27.5	−27.5	−26.8	−22.2[d], −23.8[h]	−26.1[i]
CN	^{13}C	215.4	217.8	189.8	200.9[d], 210.4[j]	210.0[k]
	^{14}N	−3.5	−3.2	−5.5	−3.1[d], −8.1[j]	−4.5[k]
HCN^-	^{13}C	76.2	63.9	65.0	111.7[d]	75.4[k]
	^{14}N	7.3	7.8	7.1	4.5[d]	7.1[k]
	^{1}H	126.4	112.9	112.2	118.3[d]	137.2[k]
FCN^-	^{13}C	234.0	203.8	200.6	254.7[d]	231.1[k]
	^{14}N	6.4	7.7	7.1	4.0[d]	6.4[k]
	^{19}F	522.3	546.6	552.5	450.5[d]	486.4[k]
$HCCH^-$	^{13}C	18.3	12.1	10.1	29.9[l]	14.5[m]
	^{1}H	50.6	46.2	45.9	48.9[l]	48[m]
CH_3	^{13}C	25.2	24.9	23.7	32.8[d], 16.3[h], 28.9[n]	27[o]
	^{1}H	−25.2	−25.2	−24.3	−20.8[d], −26.3[h], −25.7[n]	−25.0[o]
CH_4^+	^{13}C	8.5	11.7	11.1	24.2[d]	
	$^{1}H1$	−20.1	−20.8	−20.3	−18.9[d], −17[p]	−14.6[p]
	$^{1}H2$	128.7	113.7	113.7	127.9[d], 137.0[p]	121.7[p]
NH_2	^{14}N	9.4	9.4	9.1	9.8[q], 9.8[r]	10.0[s]
	^{1}H	−24.2	−24.1	−23.5	−18.0[q], −24.5[r]	−24.0[s]
NO_2	^{14}N	51.4	50.9	50.4	58.4[d], 50.2[t]	54.7[u]
	^{17}O	−18.8	−20.8	−22.5	−20.5[d], −12.0[t]	−16.8[u]
H_2CO^+	^{13}C	−36.0	37.7	36.9	−31.8[d], −24.7[h], −38.2[v], −37.1[w]	−38.8[x]
	^{17}O	−19.6	−20.4	−19.7	−13.4[d], −12.6[h], −23.9[v], −22.5[w]	
	^{1}H	103.1	109.9	113.1	133.3[d], 86.2[h], 113.6[v], 115.7[w]	132.7[x]
$\lvert\Delta a_{iso}\rvert$[y]		5.0	8.0	9.0	8.5[d,l,q]	

[a] QCISD/6-311+G(2df,p)//QCISD/6-31G(d). [b] QCISD/6-311+G(2df,p)//QCISD/6-311+G(2df,p). [c] QCISD(T)/6-311+G(2df,p)//QCISD/6-311+G(2df,p). QCISD(T) calculations performed using the ACES II program, see ref 16. [d] PW-P86/IGLO-III, ref 20b,c. [e] MCSCF, ref 45. [f] UCCD(ST), ref 51. [g] References 37, 38. [h] CISD, ref 52. [i] Reference 39. [j] MCSCF, ref 23. [k] Reference 34. [l] PW-P86/IGLO-III, ref 30. [m] Reference 42. [n] MRCISD, ref 3. [o] References 6, 46. Experimental values corrected by Chipman for the inversion motion to give a value for the planar form, see ref 46a for more details. [p] CISD, ref 47. [q] PW-P86/IGLO- III, ref 21b,c. [r] MRCISD, ref 7h. [s] Reference 48. [t] CISD, ref 21d. [u] References 37, 49. [v] MRD-CI/B$_k$, ref 53. [w] CCSD, ref 11. [x] Referemce 50. [y] Mean absolute deviation between theoretical and experimental values.

are found for the proton couplings in H_2CO^+ (20−30 G), HCN^- (10−15 G), and CH_4^+ (5−8 G), the ^{13}C coupling in CN (5−20 G), and the ^{19}F coupling in FCN^- (36−66 G). As we have seen (Table 4), at least in some of these systems, these errors are likely to be related to the difficulty in predicting a sufficiently accurate geometry. This is demonstrated in Table 6 by the differences in QCISD/6-311+G(2df,p) hfcc's computed using the QCISD/6-31G(d) optimized geometries on one hand and QCISD/6-311+G(2df,p) geometries on the other. The mean absolute differences from experiment are 5.0 G (QCISD/6-311+G(2df,p)//QCISD/6-31G(d)) and 8.0 G (QCISD/6-311+G-(2df,p)//QCISD/6-311+G(2df,p)).

As noted by Feller *et al.*,[8] QCISD gives hfcc's that compare favorably with those obtained from other high-level correlated *ab initio* methods. There is a general improvement over the conventional CISD approach in the computed hfcc's, and the results usually fall within 1 G of MRCISD values (cf. Table 6). Further improvement has been achieved in earlier work on the NO radical by approximate inclusion of triple excitations (QCISD(T)).[8b] The effects of triple excitations on the present molecule set are included in Table 6. The QCISD(T) results are, with a few exceptions, within 2−3 G of the QCISD results calculated using the same (QCISD/6-311+G(2df,p)) geometries. The most pronounced differences are again for C in CN (28 G), F in FCN^- (6 G) and H in H_2CO^+ (3 G). We note that for CN, the apparent discrepancy may be due in part to the large spin contamination found for this species (see Table 2). When the CCSD(T) procedure is used in place of QCISD(T), the calculated hfcc's of ^{13}C and ^{14}N in CN are 197.5 and −7.1 G, respectively. The mean absolute deviation of 9.0 G for QCISD-(T)/6-311+G(2df,p)//QCISD/6-311+G(2df,p) is slightly greater than at the QCISD/6-311+G(2df,p) level using the same geometries (8.0 G).

Comparing our QCISD/6-311+G(2df,p)//QCISD/6-31G(d) results with those from earlier PW-P86/IGLO-III calculations on the R1 set of radicals shows generally reasonable agreement, but there are some very significant differences. The mean absolute difference between the two sets of results is 10.4 G, with a very large maximum difference of 71.8 G. The PW-P86 method generally predicts larger values of the carbon couplings, although CN is an exception in this respect. The fluorine coupling in FCN^- is underestimated by PW-P86 to roughly the same extent that it is overestimated by QCISD/6-311+G(2df,p). The mean absolute difference from experiment of the PW-P86/IGLO-III calculated hfcc's for the R1 set is 8.5 G.

2.2. Comparison with Other Spin-Unrestricted ab Initio Methods. As a next step in the present investigation, the 6-311+G(2df,p) basis set was used in a comparison of the UQCISD method with three other spin-unrestricted schemes: UHF, UMP2, and UQCID. The results for the R2 set are presented in Table 7. Unrestricted approaches have an advantage over restricted open-shell (ROHF) based methods in that spin-polarization effects are included explicitly. This is essential in the case of π-radicals, unless higher excitations are taken into account (see, for example, ref 6). However, as mentioned above, the disadvantage of UHF-based methods is an uncertainty in the quality of the wave function because of spin contamination.

Consistent with results from earlier work, we find that UHF itself generates isotropic hyperfine couplings that are generally far too large, by as much as a factor of 2 or more. The mean absolute deviation from experimental values is 41.1 G. The reason for the failure of the UHF method may be attributed to the lack of electron correlation, core correlation in particular. This is crucial in accurately describing the electron and spin

TABLE 7: Calculated a_{iso} Values (G), Using Various UHF-Based Methods, for the R2 Set of Radicals with the 6-311+G(2df,p) Basis Set[a]

species	atom	UHF	MP2	QCID	QCISD	exptl
OH	^{17}O	−32.8	−15.2	−15.6	−17.3	−18.3[b]
	^{1}H	−38.6	−24.5	−24.1	−26.7	−26.2[b]
H_2O^+	^{17}O	−49.7	−24.8	−25.8	−28.0	−29.7[c]
	^{1}H	−40.0	−25.7	−25.0	−27.5	−26.1[c]
CN	^{13}C	459.5	198.8	257.6	215.4	210.0[d]
	^{14}N	−15.0	1.8	−1.2	−3.5	−4.5[d]
HCN^-	^{13}C	46.8	144.9	111.5	76.2	75.4[d]
	^{14}N	19.5	−11.2	−2.8	7.3	7.1[d]
	^{1}H	145.1	127.2	124.1	126.4	137.2[d]
$\|\Delta a_{iso}\|$[e]		41.1	13.9	13.3	2.5	

[a] QCISD/6-31G(d) optimized geometries used throughout. [b] References 37, 38. [c] Reference 39. [d] Reference 40. [e] Mean absolute deviation between theoretical and experimental values.

TABLE 8: DFT a_{iso} Values (G) for the R2 Set of Radicals Calculated Using Various Functionals in Conjunction with the 6-311+G(2df,p) Basis Set

species	atom	S-VWN	B-LYP	B3-LYP	B-P86	B3-P86	exptl
OH	^{17}O	6.7	−7.4	−11.4	0.2	−4.9	−18.3[c]
		(−1.0)	(−12.6)	(−15.7)	(−6.6)	(−10.5)	
	^{1}H	−20.4	−21.2	−22.8	−20.8	−22.8	−26.2[c]
		(−20.3)	(−21.2)	(−22.7)	(−20.7)	(−22.5)	
H_2O^+	^{17}O	4.3	−12.7	−18.6	−5.5	−12.4	−29.7[d]
		(−4.1)	(−18.3)	(−23.4)	(−12.7)	(−18.5)	
	^{1}H	−21.2	−22.4	−24.3	−21.7	−23.7	−26.1[d]
		(−21.1)	(−22.4)	(−24.2)	(−21.7)	(−23.7)	
CN	^{13}C	163.9	172.2	187.3	163.7	189.9	210.0[e]
		(167.0)	(171.6)	(185.0)	(165.4)	(187.5)	
	^{14}N	−3.3	−3.1	−6.9	−5.3	−8.8	−4.5[e]
		(−2.0)	(−2.0)	(−5.7)	(−4.1)	(−7.6)	
HCN^-	^{13}C	81.0	86.6	86.3	80.9	83.8	75.4[e]
		(81.7)	(86.8)	(85.8)	(81.0)	(82.6)	
	^{14}N	1.1	4.2	5.5	2.3	3.7	7.1[e]
		(2.5)	(5.0)	(6.3)	(3.4)	(4.9)	
	^{1}H	102.0	118.2	123.6	110.2	118.1	137.2[e]
		(101.9)	(118.1)	(123.6)	(110.1)	(118.5)	
$\|\Delta a_{iso}\|$[f]		18.2	12.1	8.3	15.2	10.2	
		(16.2)	(11.0)	(7.3)	(13.3)	(8.8)	

[a] The 6-311+G(2df,p) basis set was used in both its standard contracted form and, in parentheses, uncontracted on the heavy atoms. [b] QCISD/6-31G(d) geometries used throughout. [c] Reference 37, 38. [d] Reference 39. [e] Reference 40. [f] Mean absolute deviation between theoretical and experimental values.

TABLE 9: DFT a_{iso} Values (G) for the OH, H_2O^+, CN, and HCN^- Radicals Calculated Using Various Functionals in Conjunction with the IGLO-III Basis Set

species	atom	S-VWN	B-LYP	B3-LYP	B-P86	B3-P86	exptl
OH	^{17}O	−2.0	−12.4	−15.6	−6.8	−10.7	−18.3[b]
	^{1}H	−19.7	−20.6	−22.3	−19.7	−21.8	−26.2[b]
H_2O^+	^{17}O	−5.1	−18.0	−23.1	−12.8	−18.6	−29.7[c]
	^{1}H	−20.5	−22.1	−23.8	−20.6	−22.8	−26.1[c]
CN	^{13}C	177.1	181.2	196.9	174.5	201.4	210.0[d]
	^{14}N	−1.9	−2.0	−6.0	−4.1	−7.9	−4.5[d]
HCN^-	^{13}C	96.7	105.0	102.3	99.3	97.9	75.4[d]
	^{14}N	2.4	4.6	6.0	3.1	4.6	7.1[d]
	^{1}H	109.0	127.3	131.0	117.8	124.6	137.2[d]
$\|\Delta a_{iso}\|$[e]		14.7	11.2	7.1	13.7	8.4	

[a] QCISD/6-31G(d) geometries used throughout. [b] Reference 37, 38. [c] Reference 39. [d] Reference 40. [e] Mean absolute deviation between theoretical and experimental values.

distributions at the nuclei, especially for atoms with more than one shell. Incorporating electron correlation in the form of MP2 theory improves the results considerably. The mean absolute deviation from experiment is now 13.9 G. There are some poor predictions, however, such as the ^{13}C coupling in HCN^- and the wrong sign predicted for the nitrogen a_{iso} values in both CN and HCN^-. It has been suggested[54] that UMP2 performs particularly poorly in predicting isotropic hfcc's when the underlying UHF wave function is not the uniquely dominating reference.

We have already seen that QCISD generally performs well in predicting hfcc's. However, when single excitations are not included, as in QCID, the results are not very encouraging (Table 7). The mean absolute deviation from experiment is now 13.3 G. The a_{iso} values are typically 2 G lower than the corresponding values predicted by QCISD, although in some cases the deviations are far greater, *e.g.*, ^{13}C in CN and HCN^-. In addition, QCID/6-311+G(2df,p) predicts the wrong sign for the nitrogen hfcc in HCN^-. A similar shortcoming has been found by Feller *et al.*[8b] in QCID calculations on the NO radical (-6.9 G compared with the experimental value of +7.9 G[55]). The inclusion of single excitations (QCISD, CCSD) was shown to be the crucial factor in correcting this problem, leading to only small errors in the final calculated hfcc's. The present results support those findings. The mean absolute deviation from the experimental values for the R2 set at the QCISD/6-311+G(2df,p) level is just 2.5 G.

2.3. DFT Calculations. Density functional theory, in its modern LCAO form, has only recently been employed in hfcc calculations of small radical systems.[4,20−22,53,56,57] Barone has investigated the performance of the functionals employed in the present study, using a larger, partly modified, TZP basis set.[56a,f] He concluded that B3-LYP generally provides the most accurate hfcc's, and that these are comparable in accuracy to high-level CI-based methods (MRCI, QCISD). In previous work, it has also been shown that the gradient corrections according to Perdew and Wang for the exchange (PW)[58] and by Perdew for the correlation (P86),[29] together with the IGLO-III basis set, provide a very effective combination for calculating radical properties to reasonable accuracy. The PW exchange functional is not implemented in the Gaussian series of programs, the LCGTO-DFT program deMon[59] being utilized. A third previous approach, by Ishii and Shimitzu,[57] uses Slater-type orbitals rather than Gaussian functions to calculate hfs parameters.

The results from the DFT calculations for the R2 set of radicals are listed for the 6-311+G(2df,p) and IGLO-III basis sets in Tables 8 and 9, respectively. Both the contracted and the uncontracted (heavy atoms only) forms of the 6-311+G(2df,p) basis set have been used. In agreement with previous findings, the local density approach (S-VWN) is found here to be generally reasonable for proton couplings, but quite inadequate for hfcc's of heavier atoms. This is particularly evident for the OH and H_2O^+ radicals. Adding the various gradient corrections (B, B3) improves the results over those of S-VWN. Decontracting the basis set for the heavy atoms generally has only a minor effect but can lead to improvements of up to 6 G. Best results are found when the LYP correlation functional is employed. We also note that the B3 exchange functional performs better than the B functional (*e.g.*, comparing B3-LYP with B-LYP). The IGLO-III and uncontracted 6-311+G(2df,p) basis sets perform very similarly. Slight differences are observed for the carbon atom in CN and the proton in HCN^-, where IGLO-III performs better, and the C and N nuclei in HCN^-, where use of the uncontracted 6-311+G(2df,p) basis set generates more accurate data. The best overall accuracy of the DFT approaches tested here is found for B3-LYP using either of these two basis sets, for which the results are better than QCID but not nearly as good as QCISD, as reflected in the tabulated mean absolute deviations. Some improvement might be achieved with even larger basis sets.[56a] Due to the cost effectiveness of the DFT-based methods, increasing the

TABLE 10: Spin-Squared Expectation Values (⟨S^2⟩) for the DFT Calculations Listed in Table 8[a,b]

species	S-VWN	B-LYP	B3-LYP	B-P86	B3-P86
OH	0.752	0.752	0.753	0.752	0.752
H_2O^+	0.752	0.752	0.753	0.752	0.753
CN	0.754	0.754	0.757	0.755	0.759
HCN^-	0.752	0.754	0.757	0.753	0.756

[a] Results from the calculations using the contracted 6-311+G(2df,p) basis set are listed; the value of ⟨S^2⟩ are not significantly different in the calculations using the uncontracted basis set. [b] The spin contamination is reflected in the deviation of ⟨S^2⟩ from the ideal value for a doublet of 0.750.

basis set sizes is still possible without the calculations becoming intractable from a computational point of view.

The spin contamination values in the DFT calculations, using both the contracted and uncontracted 6-311+G(2df,p) basis sets, are reflected in the ⟨S^2⟩ values given in Table 10. The spin contamination can be seen to be very low, even for the CN radical, where conventional *ab initio* methods generate values of ⟨S^2⟩ larger than 1 (see Table 2). The ⟨S^2⟩ values obtained from DFT calculations using the IGLO-III basis set (not shown) are very similar to those reported in Table 10.

Conclusions

In the present study, we have investigated the basis set dependence of isotropic hyperfine coupling constants for a representative set of radicals, evaluated using the QCISD approach. It is found that the standard 6-311+G(2df,p) basis set, in conjunction with geometries determined at the QCISD/6-31G(d) level, generally gives good hfcc's. The inclusion of diffuse functions on the heavy atoms is found to be particularly important for hfcc predictions for anionic systems. The 6-311+G(2df,p) results are somewhat better than those obtained using the IGLO-III basis set and often lie within 1−2 G of experiment, though there are occasional large errors. The 6-311+G(d,p) basis set is somewhat less reliable than 6-311+G(2df,p) but could be used for larger systems for which the latter basis set might become prohibitively expensive. Effects of triple excitations were examined through the use of QCISD(T), using the 6-311+G(2df,p) basis set. Compared with the corresponding QCISD calculations, the effects are in most cases very minor.

The standard correlation-consistent basis sets (cc-pVXZ), including also the aug-cc-pVXZ basis sets, are found to perform poorly in the prediction of hfcc's. However, modification by decontracting the s-shell on oxygen leads to substantial improvement in the hfcc calculated for the OH radical. Further decontraction of the p-shell does not have a significant effect. The core-valence correlation-consistent basis sets perform well for OH already at the standard contracted aug-cc-pCVTZ level. For the double-ζ basis, s-shell decontraction is required.

The calculated hfcc's are very sensitive to geometry. It is not clear why in some cases best agreement with experimental hfcc's is achieved for geometries optimized at intermediate levels rather than at the highest levels of theory. The possibility that the experimental results are influenced by crystal field effects needs to be considered.

Finally, the 6-311+G(2df,p) basis set was employed in conjunction with UHF, UMP2, UQCID, and various DFT approaches for a subset of four test systems: OH, H_2O^+, CN, and HCN^-. The UHF approach is found to yield poor hfcc's, sometimes twice the experimental value. Use of the MP2 and the QCID approaches results in marked improvements over UHF, but large errors can occur in some instances. None of the DFT methods (S-VWN, B3-LYP, B3-P86, B-LYP, and B-P86) examined using the 6-311+G(2df,p) basis set generate hfcc's of accuracy comparable to QCISD. However, moderate accuracy is achieved, and due to the considerably lower cost, methods such as B3-LYP may be useful for hfcc calculations for larger systems.

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