Improved Description of Nuclear Magnetic Resonance Chemical Shielding Constants Using the M06-L Meta-Generalized-Gradient-Approximation Density Functional

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Improved Description of Nuclear Magnetic Resonance Chemical Shielding Constants Using the M06-L Meta-Generalized-Gradient-Approximation Density Functional

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Received: May 23, 2008; Revised Manuscript Received: June 13, 2008

The performance of the M06-L density functional has been tested for four databases of NMR isotropic chemical shielding constants. Comparison with the B3LYP, BLYP, HCTH, KT1, KT2, LSDA, OPBE, OLYP, PBE, TPSS, and VSXC functionals shows that M06-L has improved performance for calculating NMR chemical shielding constants, especially for highly correlated systems. We also found that VSXC and M06-L have encouraging accuracy for calculating ^{13}C chemical shielding constants, and both functionals perform very well for the chemical shielding constants in the *o*-benzyne molecule.

I. Introduction

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful experimental techniques to study the structure and dynamics of complex molecules. The accurate calculation of nuclear magnetic resonance chemical shielding constants is an active and important research area in theoretical chemistry.[1–8] Auer et al.[9] have shown that highly correlated wave function theory (WFT), e.g., CCSD(T), is very accurate for predicting gas-phase ^{13}C nuclear magnetic chemical shielding constants; however, its computational cost is too demanding to be applied to large molecules or condensed-phase systems. Density functional theory (DFT) is more robust than correlated WFT due to its excellent performance-to-cost ratio, but the local spin density approximation (LSDA) and most generalized gradient approximations (GGAs) are usually less accurate than correlated WFT for calculating NMR chemical shielding constants; LSDA and GGAs tend to predict nuclei that are too deshielded.[10–22] Furthermore, hybrid GGAs, such as the popular B3LYP functional, are less accurate than local density functionals (such as LSDA or GGAs) for calculating NMR chemical shielding constants. Maximoff and Scuseria[18] showed how to make meta-GGAs gauge invariant without affecting their zero-field behavior and showed that a meta-GGA, VSXC[23] (also called VS98), has improved performance as compared to a GGA, two hybrid GGAs (including B3LYP), and two other meta-GGAs. Until now, though, the most accurate DFT models for NMR are the KT1 and KT2 GGAs developed by Keal and Tozer,[16] which are designed specifically to provide accurate main-group NMR chemical shielding constants.

Recently, we developed a meta-GGA, M06-L,[24,25] that is designed for main-group thermochemistry, transition-metal bonding, thermochemical kinetics, and noncovalent interactions. The M06-L functional has been shown to give good performance for predicting gas-phase thermochemistry (including attractive noncovalent interaction) of ruthenium carbene metathesis,[26,27]

for predicting magnetic coupling (i.e., singlet−triplet splitting) in organic and inorganic molecules,[28] for calculating interactions in zeolite model compounds,[29] for calculating host−guest interactions in supramolecular complexes in a hydrocarbon nanoring[30] and concave−convex $\pi\cdots\pi$ interactions in buckyball tweezers,[31] and for describing stereoelectronic effects in ligated monocopper dioxygen complexes[32] and mechanisms for O_2-induced decarboxylation and arene subsituent hydroxylation of a series of copper(I)−α-ketocarboxylate complexes.[33] More generally, it has better average accuracy than the popular B3LYP hybrid functional for main-group and transition-metal thermochemistry and noncovalent interactions.

Because M06-L, VSXC, KT1, and KT2 do not involve Hartree−Fock exchange, they are well suited for calculations on large molecules where more efficient algorithms[34–42] can be employed in the absence of Hartree−Fock exchange.

In the present study, we assess the performance of M06-L and VSXC for the prediction of NMR chemical shielding constants. In section II, we describe the test sets, and we present the computational detail in section III. Section IV gives the Results and Discussion, and section V contains concluding remarks.
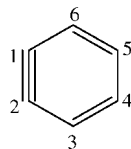
II. Databases

We tested the functionals against four databases, and they are described in this section.

II.A. WTCS32. WTCS32 is a database of 32 absolute NMR isotropic chemical shielding constants in 21 molecules compiled by Wilson and Tozer,[14] based on previous experiments.[43–58] This database has been employed by Keal and Tozer to develop the KT1,[16] KT2,[16] and KT3[20] GGAs, and WTCS32 has also been used to test other density functionals.[18,59–61]

II.B. HCCS8. HCCS8 is a database of 8 NMR chemical shielding constants in 5 highly correlated molecules (CF_4,[47] NO_2^-,[62] *cis*-N_2F_2,[63] *trans*-N_2F_2,[63] and C_6H_6[47]) based on experiments. The reference data have been compiled by Helgaker et al.[13] The union of WTCS32 and HCCS8 is called a set of "diverse chemical shielding" constants (DCS40).

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Figure 1. Nuclei numbering in *o*-benzyne.

II.C. BCCS11. BCCS11 is a database of 11 benchmark ^{13}C chemical shielding constants in 7 organic molecules (C_2H_6, CH_3OH, CH_3CN, CH_3CHO, CH_3COCH_3, and CH_2CCH_2), based on the experiments of Jameson and Jameson.[47] The reference data were taken from Auer et al.,[9] with the zero-point vibrational contributions removed at the MP2/cc-pVTZ//MP2/qz2p level. Merging the 11 chemical shielding constants of BCCS11 with the 8 ^{13}C chemical shielding constants of WTCS32 gives a larger ^{13}C chemical shielding constant database called CCS19.

II.D. BCS5. BCS5 is a database of 5 chemical shielding constants in the *o*-benzyne molecule (Figure 1), including an sp carbon, two sp^2 carbon positions, and two hydrogen positions. The reference data were taken from Helgaker et al.[64] and are based on the previous experiment of Warmuth.[65]

III. Computational Details

III.A. Tested Functionals. Although the main goal of the present study is to test the performance of the M06-L meta-GGA for calculating chemical shielding constants, we include three other functionals, namely, OPBE, VSXC,[23] and TPSS,[66] for all four databases in order to put the present results in a broader perspective. OPBE is a GGA formed by combining the OPTX exchange[67] and PBE correlation functionals,[68] and it is included because it was shown recently by Zhang et al.[21] and Wu et al.[22] to have good performance for NMR chemical shielding constants. VSXC[23] (already mentioned in the Introduction) and TPSS[66] are two high-quality meta-GGAs and, for this reason, are particularly appropriate for comparison to the M06-L meta-GGA. We include some results from the literature for comparison, and we also carried out selected additional calculations with Hartree−Fock (HF) theory to show the effect of neglecting electron correlation and with the BLYP,[69,70] OLYP,[67,70] and PBE[68] functionals because they are interesting to compare to OPBE.

III.B. Software. All density functional calculations were carried out using a locally modified *Gaussian03*[71,72] program. The algorithms for calculating NMR chemical shielding constants in this program are described elsewhere.[11]

III.C. CSGT and GIAO. In the *Gaussian03* program, there are two methods for calculating NMR chemical shielding constants, namely, the continuous set of gauge transformations (CSGT) method[11,73] (which is equivalent to the CTOCD-DZ scheme of Lazzeretti[74,75]) and the gauge-independent atomic orbital (GIAO) method.[11,76−78] Cheeseman et al.[11] have shown that the CSGT and GIAO give very similar results, except that the CSGT method shows slower basis set convergence than the GIAO method. GIAO is much more popular than CSGT in the literature. Unfortunately, the GIAO method in the current version of *Gaussian03* is available only for GGAs and hybrid GGAs, not for meta-GGAs or hybrid meta-GGAs, so we employ the CSGT method for M06-L, VSXC, and TPSS, and we employ the GIAO and CSGT methods for the OPBE GGA.

III.D. Basis Set and Geometries. Calculations of NMR chemical shielding tensors are very sensitive to the quality of the basis sets due to the fact that there are important contributions both from the vicinity of the nucleus and from the valence electron region.[79,80] Furthermore, as shown by Cheeseman et

al.,[11] the CSGT method needs a larger basis set than GIAO, so we employ the aug-pcS-3 basis set developed recently by Jensen,[80] which is of quadruple-ζ quality and is designed specifically for NMR chemical shielding constant calculations.

The geometries for the molecules in the WTCS32 database are experimental or near-experimental geometries for which references are given in refs 12 and 14. The geometries for the HCCS8 and BCS5 databases are consistently optimized with each functional with the 6−311+G(2df,2p) basis set. The geometries in the BCCS11 database are optimized with the QCISD/6−311++G(2df,2p) level of theory, where QCISD is quadratic configuration interaction with single and double excitations.[81]

IV. Results and Discussion

IV.A. WTCS32 Database. Table 1 presents the results for the WTCS32 database. Comparing the results from GIAO-OPBE and CSGT-OPBE, we find that CSGT and GIAO give almost identical chemical shielding constants with the aug-pcS-3 basis set. Our CSGT-TPSS and CSGT-VSXC chemical shielding constants are slightly different from the GIAO calculations of Maximoff and Scuseria;[18] the small differences may be ascribed to using different basis sets.

The mean signed error (MSE) and mean unsigned error (MUE) for the WTCS32 database are shown in Table 2, with some results from the literature. The row labeled WFT is a set of results collected by Keal and Tozer[16] based on various levels of WFT, namely, CCSD(T),[82] MP2,[11,83] CASSCF,[84] CCSD,[85−87] and MP3.[88] Table 2 shows that VSXC give the best performance for ^{13}C chemical shielding constants, followed by KT2 and M06-L. For ^{17}O chemical shielding constants, M06-L is the best density functional, followed by KT1 and KT2. For the ^{15}N chemical shielding constants, KT2 gives the best performance, followed by VSXC and KT1. Overall, KT1, KT2, and M06-L have the smallest MUEs among the 14 density functionals tested for the WTCS32 database, but M06-L has the lowest magnitude of the MSE. The two hybrid GGAs, PBEh and B3LYP, give the largest overall MUEs and largest MUEs for each type of nucleus.

The performance of OPBE in Tables 1 and 2 does not confirm the conclusions in the studies of Zhang et al.[21] and Wu et al.,[22] and this discrepancy is probably due to the fact that the three worst cases for OPBE, namely, PN, O_3, and OF_2, are not in their test set. OPBE is, however, better on average than OLYP or PBE. Hartree−Fock theory is very inaccurate, especially for ozone.

IV.B. HCCS8 Database. The results for the HCCS8 database of 8 chemical shielding constants of "highly correlated" systems (which, in this context, means systems with appreciable near-degeneracy[89−91] correlation) are presented in Table 3. Table 3 shows that M06-L gives the best performance for this database, and it even outperforms the correlated WFT results (MP2[92] and CASSCF[93,94]) collected as "best" in ref 13. VSXC is much less accurate than M06-L, but it outperforms the KT2 functional. OPBE and TPSS give the worst results for this database, and this is consistent with the results in Tables 1 and 2. For N_2F_4, the M06-L results are more accurate than the full-valence CASSCF calculations of ref 94, although the latter involve more than 8×10^5 determinants, whereas M06-L is based on a single determinant.

The last two rows of Table 3 show the MUE averaged over the first two databases in two different ways. We see that M06-L is a considerable improvement over previous functionals. The reason for the improved performance of M06-L is probably its

Letters

J. Phys. Chem. A, Vol. xxx, No. xx, XXXX **C**

TABLE 1: Absolute Isotropic Chemical Shielding Constants (in ppm) for the WTCS32 Database[a]

molecule	nuclei	expt.	M06-L	CSGT-OPBE	GIAO-OPBE	TPSS	VSXC	HF
HF	F	419.7	415.0	411.1	411.1	411.6	413.5	414.0
H_2O	O	357.6	329.3	328.8	328.8	327.4	330.0	327.9
CH_4	C	198.4	189.2	192.4	192.5	188.8	193.5	194.5
CO	C	2.8	0.3	−6.6	−6.5	−2.8	3.9	−25.9
	O	−36.7	−39.9	−72.0	−72.0	−60.1	−53.3	−87.6
N_2	N	−59.6	−63.5	−77.3	−77.3	−70.6	−62.4	−113.1
F_2	F	−192.8	−169.4	−260.5	−260.3	−225.0	−235.5	−171.0
O′OO′	O′	−1290.0	−1233.5	−1419.5	−1419.3	−1309.9	−1313.0	−2824.9
	O	−724.0	−765.6	−845.9	−845.9	−828.9	−821.3	−2748.0
PN	P	53.0	45.4	−0.4	−0.3	22.3	63.2	−85.3
	N	−349.0	−344.8	−382.9	−383.0	−374.0	−358.3	−487.8
H_2S	S	752.0	738.0	731.6	731.6	712.8	740.1	712.3
NH_3	N	273.3	259.9	262.4	262.4	259.2	262.9	261.5
HCN	C	82.1	80.0	76.5	76.6	78.2	83.0	70.4
	N	−20.4	−18.0	−33.6	−33.6	−26.9	−23.6	−51.0
C_2H_2	C	117.2	115.9	113.0	113.0	114.3	117.1	114.6
C_2H_4	C	64.5	62.1	55.4	55.4	57.3	61.1	58.2
H_2CO	C	−4.4	−2.0	−16.5	−16.5	−10.4	−7.0	−7.9
	O	−375.0	−310.6	−413.3	−413.3	−377.8	−378.3	−441.1
N′NO	N′	99.5	103.7	96.7	96.8	94.5	101.9	61.8
	N	11.3	17.3	10.8	10.9	6.0	14.0	−35.1
	O	200.5	179.8	175.4	175.5	176.3	182.3	174.7
CO_2	C	58.8	61.7	58.9	59.0	56.4	62.9	50.1
	O	243.4	222.2	213.3	213.4	214.7	222.0	222.1
OF_2	O	−473.1	−486.8	−620.1	−620.0	−567.8	−585.9	−466.7
H_2CNN'	C	164.5	161.4	164.5	164.5	161.9	165.7	163.9
	N	−43.4	−34.3	−46.9	−46.8	−49.9	−40.3	−14.3
	N′	−149.0	−119.2	−147.6	−147.5	−148.6	−130.9	−302.4
HCl	Cl	952.0	965.3	952.9	953.0	943.1	958.5	950.4
SO_2	S	−126.0	−119.9	−189.7	−189.5	−186.2	−140.7	−334.4
	O	−205.0	−204.9	−263.8	−264.0	−251.6	−234.7	−285.5
PH_3	P	599.9	590.6	590.8	591.0	574.1	601.9	580.2

[a] The aug-pcS-3 basis set is employed for all calculations. The CSGT method is used for M06-L, TPSS, and VSXC.

TABLE 2: Statistical Errors (in ppm) for the WTCS32 Database[a]

	^{13}C		^{17}O		^{15}N		all	
method	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE
WFT[b]	5.0	5.0	4.5	23.0	3.4	5.5	4.5	11.2
KT1[b,c]	3.4	3.9	−22.4	32.1	3.3	7.3	−4.7	13.0
KT2[b,c]	1.8	3.0	−30.9	33.4	−0.4	4.6	−9.5	13.2
M06-L[a,d]	−1.9	3.2	−0.9	27.8	4.8	9.1	0.7	13.3
VSXC[a,d]	−0.5	2.3	−38.9	38.9	0.1	6.5	−12.8	16.1
TPSS[a,d]	−5.0	5.0	−41.7	41.7	−9.1	9.2	−21.7	21.7
OPBE[a,c]	−5.8	5.8	−68.3	68.3	−10.1	10.5	−30.1	30.3
HCTH93[b,c]	−7.4	7.4	−69.2	69.2	−11.9	11.9	−32.4	32.4
OLYP[a,c]	−8.2	8.2	−73.4	73.4	−14.4	14.4	−35.2	35.2
HCTH407[c,e]	−8.2	8.2	−74.2	74.2	−14.1	14.1	−36.2	36.2
PBE[a,c]	−12.8	12.8	−90.5	90.5	−22.2	22.2	−45.2	45.2
BLYP[a,c]	−15.4	15.4	−95.5	95.5	−27.4	27.4	−51.1	51.1
LSDA[b]	−16.2	16.2	−106.6	106.6	−25.2	25.2	−51.8	52.2
PBE0[e,f]	−10.5	10.5	−140.1	140.1	−29.4	29.4	−60.0	60.0
B3LYP[e,f]	−13.4	13.4	−134.1	134.1	−33.1	33.1	−62.4	62.4
HF[a,g]	−8.2	8.2	−425.2	426.6	−55.4	62.7	−147.7	151.3

[a] CSGT results for M06-L, OPBE, TPSS, VSXC, OLYP, PBE, BLYP, and HF with the aug-pcS-3 basis set. GIAO-OPBE gives the same mean errors as CSGT-OPBE. [b] Calculated from the results of ref 16. [c] GGA. [d] meta-GGA. [e] Taken from the results of ref 18. [f] Hybrid GGA. [g] WFT.

broad applicability[95] to both single-reference and multireference molecules, that is, both to systems with negligible near-degeneracy correlation and to systems with significant near-degeneracy correlation effects. M06-L not only outperforms KT1 and KT2 for chemical shielding constants, it is also better for atomization energy. For example, KT1 and KT2 have mean unsigned errors in atomization energies that are larger than those for the B3LYP functional by factors of ∼3.3 and 1.6, respectively,[16,96] whereas, using a different but similar training set, M06-L and VSXC have mean unsigned errors in atomization

energies of 7 and 37%, respectively, smaller than that for B3LYP[95] (M06-L, however, has mean unsigned errors lower than VSXC for barrier heights, noncovalent interactions, and transition-metal thermochemistry by 22%, a factor of 7.3, and 34%, respectively[95]).

IV.C. BCCS11 Database. Table 4 presents the results for the BCCS11 database of 11 benchmark ^{13}C chemical shielding constants in 7 organic molecules. VSXC and M06-L are the two best performers for this database, and HF theory also performs well. The good performance obtained with VSXC and

TABLE 3: Absolute Isotropic Chemical Shielding Constants and Statistical Errors (ppm) for the HCCS8 Database[a]

	atom	exp.[b]	M06-L	WFT[c]	VSXC	KT2[d]	OPBE	TPSS	HF
CF_4	C	64.5	55.1	64.4[e]	51.6	52.2	48.5	41.7	82.5
NO_2^-	N	−368.0	−330.1	−360.0[f]	−341.4	−360.8	−356.9	−370.8	−529.2
	O	−342.0	−347.3	−382.0[f]	−385.4	−409.0	−420.1	−423.2	−393.5
cis-N_2F_2	N	−119.8	−130.7	−100.9[g]	−142.8	−143.2	−145.1	−154.8	−159.8
	F	52.8	52.1	80.7[g]	6.9	21.7	14.3	−10.1	157.1
trans-N_2F_2	N	−181.7	−199.7	−165.5[g]	−210.6	−216.9	−222.5	−224.5	−229.1
	F	95.1	92.6	103.7[g]	57.6	42.9	60.4	36.5	193.0
C_6H_6	C	57.2	60.9	64.0[e]	58.4	59.6	52.7	51.8	55.5
MSE			−0.7	5.8	−20.5	−26.5	−28.4	−38.9	−10.2
MUE			11.1	15.8	27.4	28.9	31.1	38.9	65.3
AMUE[h]			12.2	13.5	21.7	21.0	30.7	30.3	108.3
MUE(DCS40)[i]			12.9	12.1	18.3	16.3	30.4	25.2	134.1

[a] CSGT results for M06-L, OPBE, TPSS, and VSXC with the aug-pcS-3 basis set and DFT/6−311+G(2df,2p) geometries. [b] Taken from ref 13. [c] Taken from refs 92–94, as collected in refs 13 and 19. [d] Taken from ref 19. [e] MP2. [f] CASSCF//MP2.[93] The active space contained all valence orbitals. [g] Full-valence CASSCF at experimental geometry.[94] [h] Average of MUEs for WTCS32 and HCCS8. [i] MUE averaged over the 40 data of WTCS32 and HCCS8.

TABLE 4: Absolute Isotropic Chemical Shielding Constants and Statistical Errors (ppm) for the BCCS11 Database[a]

molecules	exp.[b]	VSXC	HF[c,d]	M06-L	OLYP[c]	OPBE	TPSS	B3LYP[c]	BLYP[c]
C_2H_6	184.6	176.2	183.3	174.1	174	175.9	172.6	172.9	169
CH_3OH	140.5	131.3	143.8	130.6	129.6	130.4	128.2	127.4	122.1
CH_3NH_2	162.3	153.0	163.4	151.5	151.1	152.6	149.7	149.6	144.8
$\underline{C}H_3CN$	190.0	183.9	191.1	181.1	182	182.7	179.8	180.7	177.4
$CH_3\underline{C}N$	75.2	73.1	62.4	71.1	68.1	67.3	67.4	59.0	59.3
$\underline{C}H_3CHO$	160.6	152.8	161.9	154.6	150.5	151.5	149.6	147.6	143.3
$CH_3\underline{C}HO$	−5.5	−8.9	−13.8	−5.8	−15.4	−18.3	−16.8	−27.5	−29.2
$\underline{C}H_3COCH_3$	161.2	155.9	163.4	156.5	153.9	154.5	152.0	150.4	146.8
$CH_3\underline{C}OCH_3$	−12.4	−14.7	−21.7	−11.7	−21.3	−23.3	−25.6	−34.4	−36.1
$\underline{C}H_2CCH_2$	116.7	115.2	113.8	112.2	110.4	109.5	108.4	104.2	102.7
$CH_2\underline{C}CH_2$	−27.7	−29.9	−44.7	−29.0	−36.3	−36.9	−38.1	−52.1	−52.1
MSE (BCCS11)		−5.2	−3.9	−5.5	−9.0	−9.1	−10.8	−15.2	−18.0
MUE (BCCS11)		5.2	5.5	5.6	9.0	9.1	10.8	15.2	18.0
MSE (CCS19)[e]		−3.2	−5.7	−4.0	−8.7	−7.7	−8.3	−14.5	−16.9
MUE (CCS19)[e]		4.0	6.7	4.6	8.7	7.7	8.3	14.5	16.9

[a] CSGT method for M06-L, OPBE, TPSS, and VSXC with the aug-pcS-3 basis set and QCISD/6−311+G(2df,2p) geometries. [b] The reference experimental data were taken from Auer et al.,[9] with the zero-point vibrational contribution removed at the MP2/cc-pVTZ//MP2/qz2p level. [c] Taken from ref 17. [d] WFT (not DFT). [e] CSC19 is the union of BCCS11 and 8 ^{13}C chemical shielding constants in WTCS32.

TABLE 5: Absolute Isotropic Chemical Shielding Constants (ppm) for the BCS5 Database[a]

nuclei[b]	exp.[c]	VSXC	M06-L	TPSS	OPBE
C1	3.7	−0.8	−0.2	−11.1	−13.4
C3	59.5	61.1	61.3	53.9	54.3
C4	48.2	49.7	51.2	42.3	43.1
H3	25.2	24.8	25.1	24.9	24.3
H4	25.8	24.0	24.4	24.2	23.5
MUE		1.9	2.0	5.6	6.1

[a] CSGT results with the aug-pcS-3 basis set and DFT/6−311+G(2df,2p) geometries. [b] See Figure 1 for the numbering of the nuclei in *o*-benzyne. [c] The reference experimental data were taken from Helgaker et al.[64]

TABLE 6: Statistical Errors (ppm) for the BCS5 Database

method	MSE	MUE
VSXC	−0.7	1.9
M06-L	−0.1	2.0
KT1[a]	−0.9	2.9
KT2[a]	0.5	3.2
HF[a,b]	−1.2	4.6
CCSD[a,b]	2.9	4.7
B97-2[a]	−5.1	5.1
OPBE[a]	−5.3	5.3
TPSS	−5.6	5.6
OPBE	−6.1	6.1
B97-1[a]	−7.5	7.5
B3LYP[a]	−9.4	9.4
PBE[a]	−9.8	9.8
PW91[a]	−10.2	10.2
BLYP[a]	−12.2	12.2

[a] Calculated from the GIAO results (optimized geometries) in ref 64. [b] WFT (not DFT).

M06-L is consistent with their good performance for ^{13}C chemical shielding constants in Table 2, as indicated in the last row of the table, but the good performance of HF theory is anomalous. OPBE and OLYP give very similar performance (to each other) but with MUEs for CCS19 about twice as large as those for VSXC and M06-L, and BLYP and B3LYP are the worst performers of the methods tested.

IV.D. BCS5 Database. Table 5 presents the results for the BCS5 database of 5 absolute isotropic chemical shielding constants in *o*-benzyne, and the statistical errors for this database are presented in Table 6. As for CCS19, VSXC and M06-L are

the two best performers for this database, and they even outperform CCSD theory. However, only CCSD theory gives the correct sign of the chemical shielding constant of the sp carbon.

IV.E. Average Error. Table 7 presents an overall assessment of 4 density functionals and Hartree−Fock theory for the

Letters

J. Phys. Chem. A, Vol. xxx, No. xx, XXXX **E**

TABLE 7: Average Errors (in ppm) for All Four Databases

method	WTCS32	HCCS8	BCCS11	BCS5	AMUE
M06-L	13.3	11.1	5.6	2.0	8.0
VSXC	16.1	27.4	5.2	1.9	12.7
OPBE	30.3	31.1	9.1	6.1	19.1
TPSS	21.7	38.9	10.8	5.6	19.3
HF	151.3	65.3	5.5	4.6	56.7

chemical shielding constants in the four databases. The last column in Table 4 is the average mean unsigned error (AMUE), which is the average of the MUEs in four databases. If we use AMUE to judge the performance of these functionals for NMR chemical shielding constants, we can see that M06-L performs the best.

V. Concluding Remarks

In the present study, we tested the M06-L meta-GGA, three other functionals, and (for comparison) Hartree−Fock theory against four databases of NMR chemical shielding constants, and we also compared to other results for subsets of the databases. We found the following:

(1) M06-L has much improved performance for calculating NMR chemical shielding constants, and this is encouraging since (i) there is no NMR data in the training set of the M06-L functional, (ii) M06-L has previously been shown to have better overall performance for energies than the popular B3LYP functional, and (iii) M06-L is a local functional, and hence it can be employed economically to study very large molecules.

(2) OPBE is not as generally accurate for calculating NMR chemical shielding constants as might have been expected from the studies by Zhang et al.[21] and Wu et al.[22]

(3) VSXC and M06-L are the two most promising functionals for calculating ^{13}C chemical shielding constants; both functionals give very good performance in general for these constants and for the chemical shielding constants in the *o*-benzyne molecule.

(4) Only M06-L performs well for highly correlated systems such as in the HCCS8 database, and other functionals give large errors.

We expect that M06-L can be quite useful for calculating NMR chemical shielding constants in organic and inorganic chemistry.

Supporting Information Available: Chemical shielding constants for the WTCS32 database calculated with the BLYP, PBE, and OLYP functionals. This material is available free of charge via the Internet at http://pubs.acs.org.

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