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Assessment of Density Functionals for Predicting One-Bond Carbon−Hydrogen NMR Spin−Spin Coupling Constants

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Abstract: We benchmark the performance of 20 approximate density functionals for the calculation of one-bond carbon−hydrogen NMR spin−spin coupling constants (SSCCs). These functionals range from the simplest local-spin density approximation to novel meta-generalized gradient approximation and hybrid density functionals. Our testing set consists of 72 diverse molecules that represent multiple types of hybridization of the carbon atom corresponding to 96 experimentally measured one-bond carbon−hydrogen SSCCs. Our results indicate that generalized gradient approximations perform best for this type of coupling.

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy has become an indispensable instrument of structural analysis for many experimental chemists, largely because of the high sensitivity of chemical shifts and indirect spin−spin coupling constants (SSCCs) to the chemical environment.

Back in 1970, John Pople and co-workers[1] recognized in a seminal paper the importance of NMR spectroscopy as a powerful tool for structural chemistry and computed the leading contribution to one-bond carbon-proton $^1J_{CH}$ SSCCs (the Fermi contact term) for a series of molecules using the self-consistent perturbation theory based on the INDO approximation, one of the most advanced techniques at the time. Since that paper was published, applied computational quantum chemistry has advanced enormously. The niche previously filled with semiempirical methods has been taken over by rapidly developing approximate approaches based on density functional theory (DFT).[2,3] This remarkable method has received widespread recognition among chemists due to its relatively high accuracy and attractively modest computational cost compared to computationally demanding wave function-based techniques (see ref 4 and references therein). Despite this success, little is known about the accuracy of approximate functionals in predicting SSCCs except for the works of Helgaker, Handy, Cremer, and co-

workers,[5−7] who found that the hybrid B3LYP functional delivers satisfactory accuracy for SSCCs over a small set of molecules. The performance of three functionals for other types of coupling was also reported in ref 8.

Here, we follow Pople's endeavor and present a *comprehensive* benchmark study of various DFT functionals in predicting one-bond C−H SSCCs. We attempt to answer the important practical question of how well approximate functionals predict experimental SSCCs.

2. Spin−Spin Coupling Constants

The basic theory of nonrelativistic SSCCs was outlined by Ramsey back in 1953.[9] He identified four distinct contributions to an isotropic SSCC: the Fermi contact (FC), spin-dipolar (SD), the paramagnetic spin−orbit (PSO), and diamagnetic spin−orbit (DSO) terms. The FC and SD triplet perturbations originate from the interaction between the electronic spin and the nuclear momenta, while the PSO and DSO singlet perturbations arise from the interaction between the electron orbital and the nuclear magnetic momenta. The DSO contribution appears in first-order and is evaluated as an expectation value over the ground state. The remaining FC, SD, and PSO terms appear in second-order and involve the first-order response of the molecular orbital coefficients available from solving the first-order coupled-perturbed equations for 10 external perturbations per coupled atom pair. In many cases, the isotropic FC contribution dominates the total value of SSCC, thus only one external perturbation per

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Table 1: Properties of Approximate Functionals Employed in This Work

functional	class	CPU[a]	refs
LSDA[b]	local approximation	1.0	2,31
PW91	GGA	1.3	32,33
PBE	GGA	1.3	28
BLYP	GGA	1.3	34
OLYP	GGA	1.4	35
BP86	GGA	1.3	36,37
KT2	GGA	1.4	29
HCTH407	GGA	1.4	38
PKZB	meta-GGA	1.8	39
VSXC	meta-GGA	1.9	40
TPSS	meta-GGA	1.8	41
B3LYP[c]	GGA hybrid	6.6	42
B3P86	GGA hybrid	6.5	17
O3LYP	GGA hybrid	6.3	35
PBE0	GGA hybrid	6.7	22,43
B971	GGA hybrid	6.6	44
B972	GGA hybrid	6.6	45
B98	GGA hybrid	6.9	46
B1B95	meta-GGA hybrid	7.3	47
TPSSh	meta-GGA hybrid	6.6	20

[a] We estimate the approximate computational cost (two 900 MHz Intel Itanium2 CPUs) required for the evaluation of all SSCCs in $C_6H_5NO_2$ with 514 basis functions. The quoted computational cost is measured relative to LSDA (162 s). [b] The sum of the Dirac exchange and Vosko-Wilk-Nusair (VWN5) parametrization (formula V of ref 31) of the correlation energy of the homogeneous electron gas. [c] The local component is VWN3 functional (formula I of ref 31) as implemented in Gaussian.[17]

coupled atom pair needs to be considered, dramatically reducing the computational cost. We refer the interested reader to the reviews on the theory of SSCCs by Fukui,[10] Contreras,[11,12] and Helgaker.[13,14]

To calculate SSCCs, we evaluate the four Ramsey's contributions using the algorithms[5,6,15,16] implemented in the Gaussian03 suite of programs.[17] The FC term, characterized by the value of the electron density at the nuclei, imposes stringent requirements on the quality of the basis set in the core region. Therefore, we employ the aug-cc-pVTZ-J basis set designed for the calculation of SSCCs.[18] Peralta et al. have found that this basis set yields SSCCs in satisfactory close agreement to the complete basis set limit for DFT (B3LYP) calculations.[19] In fact, the difference between the basis set limit and the aug-cc-pVTZ-J values is less than 0.3 Hz for $^1J_{CH}$ SSCCs in CH_4, FCH_3, and C_2H_4.[19]

3. Approximate Density Functionals

Among numerous approximations to the exchange-correlation energy available in the literature, we select 20 exchange-correlation functionals for this study. A brief description of these approximations is assembled in Table 1.

The computational cost of an approximate functional is in practice controlled by the nature of the variables included and the complexity of its expression. The simplest functional, the local spin-density approximation (LSDA), depends solely on the electron spin-density. Addition of the density first derivatives leads to Generalized Gradient Approximations (GGAs). Many prominent functionals belong to the meta-

GGA class, a family of functionals that additionally depend on the noninteracting kinetic energy density along with the GGA ingredients. Hybrid functionals introduce a mixture of exact (Hartree−Fock type) exchange, yielding very successful functionals for thermochemistry.[20]

4. Calculation Details

To ensure the validity of our assessment, we benchmark the 20 chosen functionals over an extensive set of 72 chemically diverse molecules that correspond to 96 experimentally measured one-bond C−H couplings involving 22 aromatic, 28 sp³, 34 sp², and 12 sp C atoms (see Supporting Information). All calculated NMR couplings as well as their individual contributions are available as Supporting Information. This set encompasses the original Pople set[1] and also includes additional couplings taken from ref 21. Since accurate experimental geometries are only available for a few molecules in this set, we optimized the geometries of the sample molecules at the hybrid PBE0/6-31+G(2df,p) level of theory,[22] which is deemed sufficiently accurate for the present purpose.

Although rovibrational effects notably impact SSCCs,[23,24] their evaluation is computationally demanding.[25] Lutnaes, Ruden, and Helgaker note, however, that the zero-point vibrational contribution (ZPVCs) prevails in the rovibrational effects.[26] Ruden et al.[25] have shown that the value of the ZPVC for one-bond carbon−hydrogen SSCCs appear to be very close to 5 Hz (within tenths of Hz). Hence, an ad hoc correction of 5 Hz was added to all calculated one-bond C−H SSCCs, to effectively account for the ZPVC.

The experimental SSCCs are measured at temperatures that imply free rotation in flexible species rendering indistinguishable otherwise chemically different atoms. We account for this effect by averaging over equivalent pairs of atoms considering only one conformer, however.

Experimental SSCCs are often measured in solution, while our calculations correspond to an isolated molecule, i.e., solvent effects are neglected.[21,27] We rank the performance of the approximate functionals according to the values of the mean error (ME), the mean absolute error (MAE), the standard deviation (STDEV), and the minimum and maximum deviations with respect to the experimental data. Whenever the sign is important, we assume that the experimental values are subtracted from the theoretical ones. We use accuracy and computational cost as a guide in selecting the most prominent functional. In this comparison, we consider equivalent all errors bellow the margin of ± 2 Hz set by the solvent, geometry, rovibrational, and finite basis set size effects.

5. Results and Discussion

In Table 2 we present the statistics for the complete benchmark set. All GGA functionals improve over the simpler LSDA functional. Accuracy of the nonempirical GGAs PW91 and PBE is similar. This does not come as a surprise since PBE is conceived as a computationally equivalent simplification of the PW91 functional.[28] The PBE0 ab initio hybrid (based on the PBE functional) worsens the overestimation of PBE. PKZB, the meta-GGA extension of

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Table 2: Statistical Results for 96 One-Bond $^1J_{CH}$ Coupling Constants in a Set of 72 Molecules Using Several Functionals (in Hz)[a]

functional	MAE	ME	STDEV	max.(+)	min.(−)
LSDA	23.07	−23.07	4.47		−43.27
PW91	3.54	1.38	5.17	18.80	−11.21
PBE	3.49	−0.26	4.91	15.39	−14.51
BLYP	16.41	16.41	7.47	42.13	
OLYP	4.78	3.91	5.95	24.52	−8.31
BP86	3.90	−1.77	4.79	13.89	−15.60
KT2	20.48	20.48	10.40	58.70	
HCTH407	9.01	−8.56	5.05	5.70	−23.41
PKZB	4.72	−3.45	4.78	10.77	−21.55
VSXC	9.00	−8.72	4.88	6.44	−25.98
TPSS	24.98	24.98	7.56	52.64	
B3LYP	15.89	15.89	6.73	38.26	
B3P86	3.56	2.32	4.75	17.57	−10.01
O3LYP	5.40	4.95	5.68	23.95	−6.94
PBE0	5.51	5.20	4.97	21.35	−7.22
B971	11.94	11.89	4.94	26.94	−2.44
B972	3.51	1.78	4.60	14.79	−12.89
B98	12.42	12.40	5.12	27.65	−1.29
B1B95	7.98	7.83	4.87	23.25	−4.27
TPSSh	26.43	26.43	7.62	53.68	

[a] Individual values can be obtained from the Supporting Information.

Table 3: Statistical Results for 12 One-Bond $^1J_{CH}$ sp-Type Couplings in a Set of 12 Molecules Using Several Functionals (in Hz)[a]

functional	MAE	ME	STDEV	max.(+)	min.(−)
LSDA	23.83	−23.83	4.28		−34.69
PW91	12.08	11.65	5.30	18.80	−2.57
PBE	9.50	8.46	5.40	15.39	−6.25
BLYP	33.87	33.87	4.86	42.13	
OLYP	16.30	16.27	5.97	24.52	−0.19
BP86	8.19	6.93	5.36	13.89	−7.59
KT2	44.73	44.73	8.04	58.70	
HCTH407	3.56	−0.01	5.74	5.70	−16.34
PKZB	5.40	2.89	6.31	10.77	−15.01
VSXC	3.45	−1.21	6.01	6.44	−18.19
TPSS	42.30	42.30	6.12	52.64	
B3LYP	31.50	31.50	4.06	38.26	
B3P86	11.67	11.67	4.50	17.57	
O3LYP	16.82	16.82	5.20	23.95	
PBE0	15.33	15.33	4.52	21.35	
B971	21.47	21.47	3.95	26.94	
B972	10.14	9.66	4.68	14.79	−2.87
B98	22.24	22.24	3.83	27.65	
B1B95	16.82	16.82	4.39	23.25	
TPSSh	44.05	44.05	5.62	53.68	

[a] Individual values can be obtained from the Supporting Information.

the PBE functional, features performance resembling that of PBE. TPSS, a recent attempt to further improve over PKZB, severely overestimates one-bond C−H SSCCs. The semiempirical hybrid fit TPSSh to atomization energies based on TPSS worsens the TPSS performance, too. The combination OLYP of semiempirical exchange functional OPTX of Handy and Cohen and the Lee−Yang−Parr correlation functional outperforms the older and better known combination BLYP. The corresponding hybrid functionals, O3LYP and B3LYP, display a performance pattern similar to that of the parent GGAs OLYP and BLYP. The recently developed KT2 functional, a GGA which is fitted to accurate exchange-correlation potential data and known for its excellent description of NMR shielding tensors,[29] delivers high errors for one-bond C−H SSCCs. Two highly parametrized semiempirical functionals, VSXC and HCTH407, produce very similar results. Becke's hybrid fit B98 and its later revision B971 feature similar performance. The later parametrization B972 that relies on accurate exchange-correlation potential data significantly improves over B98 and B971. Overall, only the GGAs PW91, PBE, and BP86 and the hybrid B3P86 and B972 functionals achieve a MAE smaller than 4 Hz.

Our results for BLYP, B3LYP, and KT2 functionals are in line with the findings of Keal et al. in a set of 11 molecules.[30] Although the number of $^1J_{CH}$ calculated by these authors is too small to draw statistically significant conclusions, they found that calculated one-bond C−H SSCCs are systematically overestimated by these three functionals. These authors[30] report that the error for the KT2 functional ranges from +8 Hz to +38 Hz, while we report a KT2 ME of +20 Hz. Lutnæs et al. have investigated the performance of B3LYP for a set of 10 rigid molecules[26] and concluded that this functional overestimates experimental values by

∼10%, in agreement with our conclusions. Most of the SSCCs in the present study are overestimated. Taking into account that $^1J_{CH}$ couplings are dominated by the FC contribution, it seems this term is responsible for such an overestimation (see Supporting Information).

In Table 3 we present the results for one-bond SSCCs between H and sp-type carbon atoms. Most of the functionals strongly overestimate this type of couplings except for VSXC and HCTH407, which agree fairly well with experiment. The standard deviations from experiment vary for different functionals from 3.8 Hz (B98) to 8.0 Hz (KT2).

In Table 4 we present the statistical results for sp^2-type SSCCs. The performance of PW91, PBE, and BP86 functionals is the best. For this set of 34 $^1J_{CH}$ SSCCs, standard deviations range from 3.0 Hz (B3LYP) to 5.0 Hz (LSDA).

For the sp^3-type SSCCs, five functionals give MAEs of about 2 Hz: PW91, OLYP, and the hybrids B3P86, B972, and O3LYP (see Table 5). Standard deviations for this type of SSCCs range from 2.1 Hz (B3LYP) to 4.8 Hz (LSDA).

For $^1J_{CH}$ SSCCs involving a C atom belonging to an aromatic ring (see Table 6), PW91, PBE, and the hybrid B972 yield MAE below 2 Hz. For this type of SSCCs, all functionals give a standard deviation between 2.3 Hz (OLYP) and 2.9 Hz (TPSS and TPSSh), i.e., the errors for the aromatic SSCCs are confined within a narrow band around their mean value.

Interestingly, the width of the error distribution increases along the series aromatic → sp^3 → sp^2 → sp type of SSCCs.

6. Conclusions

We have computed one-bond C−H SSCCs with 20 distinct approximate density functionals over a comprehensive set of experimental data. All GGA functionals overall outperform LSDA. Meta-GGA and hybrid functionals, however,

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Table 4: Statistical Results for 34 One-Bond $^1J_{CH}$ sp^2-type Coupling Constants in a Set of 21 Molecules Using Several Functionals (in Hz)[a]

functional	MAE	ME	STDEV	max.(+)	min.(−)
LSDA	23.62	−23.62	5.04		−43.27
PW91	2.78	0.36	3.54	6.92	−11.21
PBE	2.64	−1.55	3.75	5.23	−14.51
BLYP	15.46	15.46	3.22	21.84	
OLYP	4.22	3.21	3.56	10.37	−8.31
BP86	3.09	−2.82	3.78	3.98	−15.60
KT2	19.41	19.41	3.55	25.34	
HCTH407	8.76	−8.76	4.16		−23.41
PKZB	4.97	−4.56	4.95	4.11	−21.55
VSXC	9.38	−9.38	4.41		−25.98
TPSS	23.60	23.60	3.52	30.30	
B3LYP	15.29	15.29	2.97	21.75	
B3P86	3.14	1.65	3.36	8.35	−10.01
O3LYP	5.04	4.44	3.42	11.60	−6.94
PBE0	5.12	4.62	3.30	11.41	−7.22
B971	11.50	11.35	3.92	18.74	−2.44
B972	3.40	1.51	3.95	9.25	−12.89
B98	12.12	12.04	3.85	19.22	
B1B95	7.29	7.02	3.34	13.47	−4.27
TPSSh	25.31	25.31	3.38	31.96	

[a] Individual values can be obtained from the Supporting Information.

Table 5: Statistical Results for 29 One-Bond $^1J_{CH}$ sp^3-type Coupling Constants Using Several Functionals (in Hz)[a]

functional	MAE	ME	STDEV	max.(+)	min.(−)
LSDA	23.25	−23.25	4.79		−35.25
PW91	2.23	−1.37	2.54	3.05	−8.79
PBE	3.30	−2.03	3.46	4.55	−10.45
BLYP	11.65	11.65	2.37	16.25	
OLYP	1.73	0.10	2.44	5.33	−6.96
BP86	3.99	−3.90	2.68	0.61	−11.52
KT2	13.27	13.27	3.23	27.79	
HCTH407	11.61	−11.61	2.84		−19.51
PKZB	5.10	−5.07	2.76	0.38	−12.48
VSXC	11.18	−11.18	2.95		−19.04
TPSS	21.54	21.54	3.01	34.11	
B3LYP	11.37	11.37	2.07	15.47	
B3P86	1.69	−0.38	2.34	4.15	−7.25
O3LYP	1.95	1.17	2.33	6.29	−5.68
PBE0	2.60	2.15	2.18	6.74	−4.29
B971	9.17	9.17	2.58	13.94	
B972	2.02	−0.80	2.66	3.82	−8.10
B98	9.72	9.72	2.55	14.57	
B1B95	5.31	5.14	3.56	18.95	−2.45
TPSSh	22.60	22.60	2.96	34.90	

[a] Individual values can be obtained from the Supporting Information.

do not necessarily improve over GGA functionals for this particular type of coupling. Our findings indicate that for one-bond C−H couplings, the most accurate functionals are PW91 and PBE and the semiempirical hybrids B3P86 and B972. In contrast to B3P86 and B972, PW91 and PBE do not require computing an expensive exact exchange component and thus are preferred computationally. The PBE functional gives accurate $^1J_{CH}$ SSCCs involving sp^2, sp^3, and aromatic carbon atoms. The semiempirical HCTH407 and

Table 6: Statistical Results for 21 One-Bond $^1J_{CH}$ Coupling Constants in a Set of 11 Aromatic Molecules Using Several Functionals (in Hz)[a]

functional	MAE	ME	STDEV	max.(+)	min.(−)
LSDA	21.52	−21.52	2.75		−28.38
PW91	1.73	0.94	2.34	8.71	−3.07
PBE	1.68	−0.74	2.33	6.96	−4.70
BLYP	14.52	14.52	2.46	22.42	
OLYP	3.32	3.25	2.30	10.83	−0.78
BP86	2.65	−2.11	2.33	5.62	−5.96
KT2	18.33	18.33	2.77	25.85	
HCTH407	8.93	−8.93	2.32		−12.74
PKZB	3.41	−3.03	2.30	4.00	−7.04
VSXC	8.57	−8.57	2.33		−11.96
TPSS	22.06	22.06	2.88	30.27	
B3LYP	14.18	14.18	2.42	22.13	
B3P86	2.17	1.80	2.35	9.63	−2.17
O3LYP	4.21	4.21	2.31	11.87	
PBE0	4.56	4.56	2.36	12.37	
B971	11.04	11.04	2.38	18.90	
B972	1.95	1.29	2.34	8.96	−2.56
B98	11.49	11.49	2.37	19.36	
B1B95	7.71	7.71	2.37	15.56	
TPSSh	23.44	23.44	2.89	31.68	

[a] Individual values can be obtained from the Supporting Information.

VSXC, however, rival PBE performance for the $^1J_{CH}$ SSCCs involving a sp carbon atom.

Our findings do not support the common belief that hybrid functionals (particularly B3LYP) surpass GGAs for one bond C−H NMR SSCCs.

Supporting Information Available: All calculated NMR couplings and their individual contributions. This material is available free of charge via the Internet at http://pubs.acs.org.

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