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Calculation of Nuclear Spin−Spin Coupling Constants of Molecules with First and Second Row Atoms in Study of Basis Set Dependence

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Abstract: This paper proposes a systematic way to modify standard basis sets for use in NMR spin−spin coupling calculations, which allows the high sensitivity of this property to the basis set to be handled in a manner which remains computationally feasible. The new basis set series is derived by uncontracting a standard basis set, such as correlation-consistent aug-cc-pVTZ, and extending it by systematically adding tight s and d functions. For elements in different rows of the periodic table, different progressions of functions are added. The new basis sets are shown to approach the basis set limit for calculations on a range of molecules containing hydrogen and first and second row atoms.

Introduction

Nuclear magnetic resonance (NMR) is the most useful technique for chemical structure study in solution with extensive flexibility. Among all spectral information, spin−spin coupling constants are one of the most difficult to produce quantitatively.[1,2] Advances in electronic structure theory, such as equation-of-motion coupled cluster theory[3,4] or second-order polarization propagator approximations,[5] are able to predict spin−spin coupling constants in good agreement with experiments. However, formidable computational cost prohibits the use of these methods for large systems.[6]

As an alternative, density functional theory (DFT) is computationally much less expensive with comparable accuracy.[7] Recent studies have shown that DFT, particularly with the Becke three-parameter Lee−Yang−Parr (B3LYP) hybrid functional,[8] provides promising and fast calculation of indirect nuclear spin−spin coupling constants on medium-sized [9,10] and bulky molecules.[11] Evaluations have been made on the capability of B3LYP and linear response methods in spin−spin coupling calculations.[12,13]

There are four isotropic contributions to the NMR coupling constants, Fermi contact (FC), spin-dipolar (SD), paramagnetic spin−orbit (PSO), and diamagnetic spin−orbit (DSO). Usually, the FC term is the major contribution among the four, and with standard basis sets, it has the largest error.

The accuracy of a spin−spin coupling constant calculation is highly dependent on the Gaussian basis set employed.[14,15] The basis sets of quantum chemistry are well-developed for the valence electrons. However, NMR experiments probe the electron density closer to the nuclei, where many standard basis sets of ab initio theory will give erroneous results.[16−18] Because the FC operator requires good characterization of core electrons, its contribution is highly dependent on details of the Gaussian basis sets which are relatively unimportant for most other properties. An analysis of basis set dependence in both complete active space self-consistent field wave functions and the DFT framework has been performed. Within the former, Helgaker et al. reported an extensive study of extending a correlation-consistent Gaussian basis set by uncontracting and augmenting the s-type functions at the tight end.[16]

Peralta et. al.'s recent work investigated the basis set dependence within a DFT framework.[19] Although their study

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had shown the dependence of spin−spin coupling on the core basis set, the systematic examination of how to improve the basis set in an economical manner was not complete. Peralta et al.[20] proposed the use of the cc-pCVXZ-sd (X = D and T) basis set, which is the cc-pCVXZ basis set with all s functions fully uncontracted. This basis set yields good results for the one-bond C−C coupling calculation and has been used successfully in bulky fullerene molecules, such as C70. However, the cc-pCVDZ-sd basis set has not shown promising results for coupling other than one-bond C−C coupling.

The aug-cc-pVTZ-J basis set, developed by Sauer and co-workers, gives a very good description of the FC term, with adequate treatment of the wave functions at the nucleus.[21] The basis set fully uncontracts the aug-cc-pVTZ basis set, then augments it with four tight s-type functions and without the most diffuse second polarization function. Unfortunately, the aug-cc-pVTZ-J basis sets only contains H, four first row atoms (C, N, O, and F), and S (whose basis set includes, in addition to the modifications above, three additional tight d-type functions). Systematic studies for other first and second row atoms were not complete.

The large uncontracted universal Gaussian basis set (UGBS) was first introduced by Silver et al.[22] and later generated by Jorge and de Castro.[23] It provides basis sets for all atoms which are at the basis set limit for valence angular momentum ($l = 0$ and 1). However, calculations using UGBS are very computationally demanding. In this paper, we present a systematic approach for expanding standard valence-oriented basis sets in order to compute spin−spin couplings without large errors arising from the basis set.

2. Theory and Computational Aspects

A variety of molecules containing hydrogen and atoms from the first two rows are studied in our work. All molecules are first optimized at the B3LYP/6-31G* level of theory, using the development version of the Gaussian computational program.[24] Because there are very few spin−spin coupling experimental values obtained in the gas phase, and the goal of this study is to reduce basis set errors, the results of the smaller basis sets derived in this study will be compared to results from very large basis sets for calibration.

The uncontracted UGBS2P basis sets are chosen to be the reference basis sets. UGBS2P includes two additional polarization functions for each function in the UGBS: one p and d function for each s function and one d and f function for each p function. Preliminary study showed that adding two tighter s functions than the tightest s functions in UGBS2P affected the results by less than 1%, compared to the unmodified UGBS2P basis. Therefore, the UGBS2P basis set was used as a reference in this study, and it was not considered necessary to examine the addition of functions tighter than those in UGBS2P to any of the smaller basis sets.

Our approach is to derive a basis set suitable for computation of the FC term from the original basis set, while using the original basis as-is for the rest of the terms in the spin−spin coupling. We uncontract the original basis set and then

Table 1. uTZ-Derived Basis Set Size and Maximum Number of Tighter *s* Functions To Be Added

atoms	number of basis functions in UGBS2P	number of basis functions in uTZ basis set	maximum number of tight *s* functions added
H	60	11	5
C	68		2
N	71	22	2
O	71		2
F	72		3
Si			2
P	84	31	3
S			2
Cl			2

add additional tight functions until the basis set error in the FC term is comparable to that of the other terms.

The added tight s functions have even-tempered exponents starting from the tightest s functions in the small basis set. For hydrogen and first row atoms, a ratio of 3 for successive exponents was used, while for second row atoms, a ratio of 2 was applied.

In section 3, we test this approach using the aug-cc-pVTZ basis sets[25] and determine how many and what type of functions should be added for the FC term. In section 4, we apply the rules developed in section 3 to two smaller basis sets, aug-cc-pVDZ and 6-311+G(d,p). In section 5, we compare our results to previous work on this problem.

3. Addition of Functions to aug-cc-pVTZ

3.1. Notation. We denote the uncontracted aug-cc-pVTZ basis by uTZ and use uTZ-s*n* to denote uTZ augmented by *n* tight s functions. uTZ-w will denote the uTZ basis augmented by the number of s functions found to be sufficient to saturate the core region. uTZ-wd*n* will denote a uTZ-w basis augmented by *n* d functions. A preliminary study indicated that tight p functions had virtually no effect on the FC term, and these are not considered further here.

The basis set sizes of the UGBS2P and uTZ-s*n* series for the first and second row atoms involved in this study are summarized in Table 1. It can be seen that the uTZ-s*n* sets are much smaller in size than the UGBS2P. The table also shows the number of s functions that could be added to the uTZ basis set before reaching the tightest s functions in UGBS2P.

3.2. H and First Row Atoms: HF, NH₃, HCN. The results for one-bond coupling $^1J(^1H^{19}F)$ calculations in the HF molecule are shown in Table 2. The SD, PSO, and DSO terms are calculated using the contracted aug-cc-pVTZ basis set and remain unchanged for all uTZ-s*n* calculations. Compared to the UGBS2P, the PSO term contributes 1.5% of the error to the total contribution. In this and later tables, the optimal choice of *n*s is given in bold face.

As can be seen in Table 2, the FC terms increases in a regular pattern as s functions are added. Also, the third tighter s functions on fluorine and the fifth tighter s functions on hydrogen only have minor effects on the results. Therefore,

Table 2. $^1J(^1H^{19}F)$ Coupling in the HF Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		F uTZ-sn				UGBS2P
		$n=0$	1	2	3	
H uTZ-sn	$n=0$	167.78[a]	169.29	171.97	172.32	
		361.71[b]	363.22	365.90	366.26	
	1	173.27	174.59	177.53	177.78	
		367.21	368.52	371.46	371.71	
	2	180.10	181.65	184.59	184.92	FC: 192.47
		374.04	375.58	378.52	378.86	SD: −3.14
	3	181.67	183.12	186.16	186.44	PSO: 201.31
		375.61	377.05	380.09	380.38	DSO: −0.20
	4	184.12	185.67	**188.70**	189.02	total: 390.44
		378.06	379.60	**382.63**	382.96	
	5	184.49	185.99	189.06	189.36	
		378.43	379.92	382.99	383.30	

[a] Fermi contact contribution. [b] Total spin−spin coupling. SD, PSO, and DSO are respectively −1.41, 195.10, and 0.25 (calculated using contracted aug-cc-pVTZ basis set). Expt.: 412−479 Hz (in various solvents).[27]

Table 3. $^1J(^{14}N^1H)$ Coupling in the NH_3 Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		N uTZ-sn			UGBS2P
		$n=0$	1	2	
H uTZ-sn	$n=0$	36.05[a]	36.42	36.98	
		38.57[b]	38.94	39.50	
	1	37.12	37.50	38.08	
		39.64	40.02	40.60	
	2	38.71	39.11	39.71	FC: 41.05
		41.23	41.63	42.23	SD: 0.17
	3	38.99	39.39	40.00	PSO: 2.34
		41.51	41.91	42.52	DSO: 0.04
	4	39.56	39.97	**40.58**	total: 43.60
		42.08	42.49	**43.10**	
	5	39.62	40.02	40.64	
		42.14	42.54	43.16	

[a] Fermi contact contribution. [b] Total spin−spin coupling. SD, PSO, and DSO are respectively 0.17, 2.30, and 0.05 (calculated using contracted aug-cc-pVTZ basis set). Expt.: 40 ± 1 Hz (neat liquid).[28]

Table 4. $^1J(^{13}C^1H)$ Coupling in the HCN Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		C uTZ-sn			UGBS2P
		$n=0$	1	2	
H uTZ-sn	$n=0$	248.21[a]	250.86	254.70	
		248.52[b]	251.17	255.01	
	1	255.44	258.18	262.13	
		255.75	258.49	262.44	
	2	266.53	269.38	273.50	FC: 283.08
		266.84	269.69	273.81	SD: 0.53
	3	268.36	271.24	275.39	PSO: −0.75
		268.67	271.55	275.70	DSO: 0.39
	4	272.38	275.30	**279.51**	total: 283.24
		272.69	275.61	**279.82**	
	5	272.70	275.62	279.84	
		273.01	275.93	280.15	

[a] Fermi contact contribution. [b] Total spin−spin coupling. Adding tight functions to N has no effect on $^1J(CH)$ coupling calculation in HCN. SD, PSO, and DSO are respectively 0.61, −0.73, and 0.43 (calculated using contracted aug-cc-pVTZ basis set). Expt.: 261−274 Hz (in various solvents).[29]

Table 5. $^1J(^{13}C^{14}N)$ Coupling in the HCN Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		C uTZ-sn			UGBS2P
		$n=0$	1	2	
N uTZ-sn	$n=0$	6.30[a]	6.37	6.46	
		11.69[b]	11.76	11.85	FC: 6.76
	1	6.36	6.43	6.52	SD: 5.40
		11.75	11.82	11.91	PSO: 0.59
	2	6.46	6.53	**6.63**	DSO: −0.03
		11.85	11.92	**12.02**	total: 12.73

[a] Fermi contact contribution. [b] Total spin−spin coupling. Adding tight functions to H has no effect on $^1J(CN)$ calculation in HCN. SD, PSO, and DSO are respectively 4.77, 0.65, and −0.03 (calculated using contracted aug-cc-pVTZ basis set). Expt.: 26.4 Hz (neat liquid).[29] (The experimental spin−spin couplings have been converted from ^{15}N to ^{14}N, which is, within the Born−Oppenheimer approximation, related by the ratio of the nuclear magnetogyric ratios only if rovibrational corrections are neglected.)

uTZ-s2 for fluorine and uTZ-s4 for hydrogen should sufficiently simulate the UGBS2P results.

This combination of a uTZ basis set (uTZ-s4 for hydrogen and uTZ-s2 for first row atoms) is named the "uTZ-w" basis set. Compared to the UGBS2P calculation, the uTZ-w basis set gave 2.0% error in the FC term and 2.1% error in the total contribution.

The results for one-bond coupling calculations in the NH_3 and HCN molecules and two-bond coupling $^2J(^1H^{14}N)$ in HCN are shown in Tables 3−6. [The two-bond $^2J(HH)$ couplings of NH_3 are listed in the next section.]

As with HF, the uTZ-w basis set (uTZ-s4 for hydrogen and uTZ-s2 for first row atoms) produces satisfactory results for NH_3 and HCN. The size of this uTZ-sn series and aug-cc-pVTZ is significantly smaller than that of UGBS2P, but the relative errors of total contribution obtained from uTZ-w basis set and UGBS2P are small. In the case of

$^1J(^{13}C^{14}N)$ and $^2J(^1H^{14}N)$ of HCN, the relative error is a little higher than 5%, but the absolute error is within 0.8 Hz.

The SD, PSO, and DSO terms of these couplings calculated using the aug-cc-pVTZ basis set are also very close to the results of UGBS2P; the absolute errors are all within 0.7 Hz.

The study of molecules of hydrogen and the first row atoms shows that, compared to UGBS2P, the uTZ-sn basis set takes much less computation time for NMR spin−spin coupling constants, yet a specific combination of the uTZ-sn series (uTZ-w) can simulate UGBS2P's results accurately.

3.3. H and Second Row Atoms: SiH_4, PH_3, and H_2S. All of the $^1J(XH)$ (X = Si, P, and S) coupling calculations are shown in Tables 7−9. In the three molecules, the SD, PSO, and DSO terms of $^1J(XH)$ couplings are significantly smaller than the FC term. These three terms of the aug-cc-pVTZ basis set results are very close to the UGBS2P results. Hence, the basis set errors arise primarily from the FC term. Note that, for second row atoms, the added tight s functions

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Table 6. $^2J(^{14}N^1H)$ Coupling in the HCN Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		N uTZ-sn			
		$n=0$	1	2	UGBS2P
H uTZ-sn	$n=0$	2.03^a	2.05	2.09	
		4.76^b	4.78	4.82	
	1	2.09	2.11	2.15	
		4.82	4.84	4.88	
	2	2.19	2.21	2.24	FC: 2.31
		4.92	4.94	4.97	SD: 0.65
	3	2.20	2.22	2.25	PSO: 2.77
		4.93	4.95	4.98	DSO: −0.44
	4	2.23	2.25	**2.29**	total: 5.29
		4.96	4.98	**5.02**	
	5	2.23	2.26	2.29	
		4.96	4.99	5.02	

^{a} Fermi contact contribution. ^{b} Total spin−spin coupling. Adding tight functions to C has no effect on $^2J(^{14}N^1H)$ calculation in HCN. SD, PSO, and DSO are respectively 0.60, 2.56, and −0.43 (calculated using contracted aug-cc-pVTZ basis set). Expt.: 10.5−12.4 Hz (in various solvents).[29] (The experimental spin−spin couplings have been converted from ^{15}N to ^{14}N, which is, within the Born−Oppenheimer approximation, related by the ratio of the nuclear magnetogyric ratios only if rovibrational corrections are neglected.)

Table 7. $^1J(^{29}Si^1H)$ Coupling in the SiH$_4$ Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		Si uTZ-sn			
		$n=0$	1	2	UGBS2P
H uTZ-sn	$n=0$	−188.82^a	−189.23	−190.42	
		−188.22^b	−188.63	−189.82	
	1	−194.65	−195.07	−196.30	
		−194.05	−194.47	−195.70	
	2	−202.87	−203.31	−204.59	FC: −210.04
		−202.27	−202.71	−203.99	SD: −0.17
	3	−204.42	−204.87	−206.15	PSO: 0.32
		−203.82	−204.27	−205.55	DSO: −0.02
	4	−207.38	−207.83	**−209.13**	total: −209.91
		−206.78	−207.23	**−208.53**	
	5	−207.69	−208.14	−209.44	
		−207.09	−207.54	−208.84	

^{a} Fermi contact contribution. ^{b} Total spin−spin coupling. SD, PSO, and DSO are respectively 0.07, 0.55, and −0.02 (calculated using contracted aug-cc-pVTZ basis set). Expt.: −202.5 ± 0.2 Hz (gas phase).[30]

Table 8. $^1J(^{31}P^1H)$ Coupling in the PH$_3$ Molecule Evaluated Using the UTZ-sn Basis Set (Hz)

		P uTZ-sn				
		$n=0$	1	2	3	UGBS2P
H uTZ-sn	$n=0$	141.45^a	141.74	142.62	142.73	
		147.13^b	147.42	148.30	148.41	
	1	145.66	145.96	146.86	146.98	
		151.34	151.64	152.54	152.66	
	2	151.89	152.20	153.14	153.26	FC: 158.43
		157.57	157.88	158.82	158.94	SD: −0.82
	3	152.99	153.30	154.25	154.37	PSO: 6.35
		158.67	158.98	159.93	160.05	DSO: −0.01
	4	155.24	155.55	**156.52**	156.64	total: 163.96
		160.92	161.23	**162.20**	162.32	
	5	155.44	155.75	156.72	156.85	
		161.12	161.43	162.40	162.53	

^{a} Fermi contact contribution. ^{b} Total spin−spin coupling. SD, PSO, and DSO are respectively −1.26, 6.92, and 0.02 (calculated using contracted aug-cc-pVTZ basis set). Expt.: 188.7 Hz (in complex solution)[31] and 182.2 ± 0.3 Hz (neat liquid).[32]

Table 9. $^1J(^{33}S^1H)$ Coupling in the H$_2$S Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		S uTZ-sn				
		$n=0$	1	2	3 (over)	UGBS2P
H uTZ-sn	$n=0$	17.07^a	17.11	17.22	17.24	
		21.57^b	21.61	21.72	21.74	
	1	17.51	17.54	17.66	17.67	
		22.01	22.04	22.16	22.17	
	2	18.30	18.34	18.46	18.48	FC: 19.25
		22.80	22.84	22.96	22.98	SD: −0.06
	3	18.40	18.44	18.56	18.58	PSO: 4.68
		22.90	22.94	23.06	23.08	DSO: −0.01
	4	18.69	18.73	**18.85**	18.87	total: 23.85
		23.19	23.23	**23.35**	23.37	
	5	18.70	18.74	18.86	18.88	
		23.20	23.24	23.36	23.38	

^{a} Fermi contact contribution. ^{b} Total spin−spin coupling. SD, PSO, and DSO are respectively −0.18, 4.68, and 0.00 (calculated using contracted aug-cc-pVTZ basis set).

have a ratio of 2 for successive exponents starting from the tightest s functions in uTZ basis sets. As for Si, a third additional s function would be tighter than the tightest functions in the reference basis, so we only considered adding two s functions. For S and P, a third s function could be tested.

As seen in the results, uTZ-s3 on P and S only gave a marginal improvement to the results compared to uTZ-s2, as was the case for uTZ-s5 on hydrogen to uTZ-s4. Therefore, uTZ-s2 on second row atoms and uTZ-s4 on hydrogen produced reasonable results for the uTZ-sn series. All of the $^1J(XH)$ coupling calculations using this combination are within 2% accuracy to UGBS2P.

All $^2J(HH)$ coupling calculation results (including NH$_3$) are listed in Table 10. Adding tighter s functions to the basis set on the center atoms does not affect the $^2J(HH)$ calcula-

tions. The fifth tight s function on hydrogen is unnecessary, as uTZ-s5 on hydrogen gives very close total contribution results to those of uTZ-s4.

3.4. Second Row and First Row Atoms: SiF$_4$, PF$_3$, SF$_6$, and PCl$_3$. This section extends the basis set dependence study to molecules containing both first and second row atoms. Five molecules, SiF$_4$, PF$_3$, SF$_6$, Cl$_2$O, and PCl$_3$, are studied. The results of $^1J(X^{19}F)$ (X = ^{29}Si, ^{31}P, and ^{33}S) are shown in Tables 11−13, $^2J(^{19}F^{19}F)$ in Table 14, $^1J(^{31}P^{35}Cl)$ in Table 15, and $^2J(^{35}Cl^{35}Cl)$ in Table S1 in the Supporting Information.

For $^1J(X^{19}F)$ coupling, as tight s functions are added to both F and second row atoms, the FC term increments are similar to those of previous results. The SD, PSO, and DSO terms are taken from the unmodified contracted aug-cc-pVTZ basis set results. Among the three terms, PSOs in three $^1J(X^{19}F)$ couplings carry the largest error but are still below

Table 10. $^2J(^1H^1H)$ Coupling in NH_3, SiH_4, PH_3, and H_2S Molecules Evaluated Using the uTZ-sn Basis Set (Hz)[a]

		NH₃	SiH₄	PH₃	H₂S
H uTZ-sn	$n=0$	-10.24^b	3.81	-10.74	-10.49
		-9.10^c	2.64	-10.83	-10.13
	1	-10.86	4.04	-11.37	-11.07
		-9.72	2.87	-11.46	-10.71
	2	-11.80	4.40	-12.38	-12.08
		-10.66	3.23	-12.47	-11.72
	3	-11.98	4.46	-12.55	-12.23
		-10.84	3.29	-12.64	-11.87
	4	**-12.33**	**4.60**	**-12.93**	**-12.61**
		-11.19	**3.43**	**-13.02**	**-12.25**
	5	-12.36	4.61	-12.96	-12.63
		-11.22	3.44	-13.05	-12.27
	SD	0.64	0.08	0.12	0.12
	PSO	5.50	1.09	1.18	2.08
	DSO	-5.00	-2.34	-1.39	-1.84
UGBS2P	FC	-12.51	4.92	-12.87	-12.48
	SD	0.67	0.07	0.11	0.11
	PSO	6.17	2.36	1.57	2.51
	DSO	-5.04	-2.35	-1.40	-1.86
	total	-10.71	5.00	-12.59	-11.71
	expt.	-10.35 ± 0.80^d	2.75 ± 0.15^e	-13.2 ± 0.7^f	

[a] Adding tight functions to N, Si, P, and S has no effect on $^2J(HH)$ coupling calculation. SD, PSO, and DSO remain unchanged (calculated using contracted aug-cc-pVTZ basis set). [b] Fermi contact contribution. [c] Total spin−spin coupling. [d] Neat liquid.[33] [e] Gas phase.[30] [f] Neat liquid.[32]

Table 11. $^1J(^{29}Si^{19}F)$ Coupling in the SiF_4 Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		Si uTZ-sn			UGBS2P
		$n=0$	1	2	
F uTZ-sn	$n=0$	262.79^a	263.36	265.02	
		339.27^b	339.84	341.50	
	1	265.77	266.35	268.02	FC: 262.41
		342.25	342.83	344.50	SD: -4.45
	2	269.56	270.15	**271.84**	PSO:85.67
		346.04	346.63	**348.32**	DSO:-0.55
	3	270.37	270.96	272.67	total: 343.08
		346.85	347.44	349.15	

[a] Fermi contact contribution. [b] Total spin−spin coupling. SD, PSO, and DSO are respectively -4.00, 81.05, and -0.57 (calculated using contracted aug-cc-pVTZ basis set).

Table 12. $^1J(^{31}P^{19}F)$ Coupling in the PF_3 Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		P uTZ-sn				UGBS2P
		$n=0$	1	2	3	
F uTZ-sn	$n=0$	-1261^a	-1264	-1272	-1273	
		-1524^b	-1527	-1535	-1536	
	1	-1274	-1277	-1285	-1286	FC: -1312
		-1537	-1540	-1548	-1549	SD: 38.78
	2	-1293	-1296	**-1304**	-1305	PSO: -322.38
		-1556	-1559	**-1567**	-1568	DSO: 0.76
	3	-1297	-1300	-1307	-1309	total: -1595
		-1560	-1563	-1570	-1572	

[a] Fermi contact contribution. [b] Total spin−spin coupling. SD, PSO, and DSO are respectively 36.00, -299.57, and 0.85 (calculated using contracted aug-cc-pVTZ basis set). Expt.: -1441 Hz (neat liquid).[34]

Table 13. $^1J(^{33}S^{19}F)$ Coupling in the SF_6 Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		S uTZ-sn				UGBS2P
		$n=0$	1	2	3	
F uTZ-sn	$n=0$	-284.37^a	-284.95	-286.63	-286.85	
		-306.91^b	-307.49	-309.17	-309.39	
	1	-287.41	-288.00	-289.70	-289.92	FC: -296.09
		-309.95	-310.54	-312.24	-312.46	SD: 9.99
	2	-291.63	-292.22	**-293.95**	-294.17	PSO: -34.75
		-314.17	-314.76	**-316.49**	-316.71	DSO: 0.39
	3	-292.43	-293.02	-294.75	-294.98	total: -320.46
		-314.97	-315.56	-317.29	-317.52	

[a] Fermi contact contribution. [b] Total spin−spin coupling. SD, PSO, and DSO are respectively 9.17, -32.10, and 0.39 (calculated using contracted aug-cc-pVTZ basis set). Expt.: -250.1 Hz (gas phase).[35]

Table 14. $^2J(^{19}F^{19}F)$ Coupling in SiF_4, PF_3, and SF_6 Molecules Evaluated Using the uTZ-sn Basis Set (Hz)

		SiF₄	PF₃	SF₆(90°)	SF₆(180°)
F uTZ-sn	$n=0$	-59.29^a	-50.57	-66.84	-21.27
		-155.27^b	-34.72	-265.36	-42.81
	1	-60.63	-51.83	-68.39	-21.75
		-156.61	-35.98	-266.91	-43.29
	2	**-62.38**	**-53.24**	**-70.33**	**-22.38**
		-158.36	**-37.39**	**-268.85**	**-43.92**
	3	-62.75	-53.62	-70.77	-22.51
		-158.73	-37.77	-269.29	-44.05
	SD	16.46	59.81	57.05	-7.90
	PSO	-111.23	-43.26	-256.20	-9.72
	DSO	-1.21	-0.70	0.63	-3.92
UGBS2P	FC	-61.30	-54.17	-67.57	-18.19
	SD	16.81	62.97	61.79	-8.47
	PSO	-115.49	-49.35	-267.89	-7.54
	DSO	-1.26	-0.76	0.57	-3.97
	total	-161.24	-41.31	-273.10	-38.17

[a] Fermi contact contribution. [b] Total spin−spin coupling. SD, PSO, and DSO remain unchanged (calculated using contracted aug-cc-pVTZ basis set).

1.5%. The uTZ-w basis set shows good agreement with UGBS2P in total contribution calculation in PF_3 and SF_6.

All $^2J(^{19}F^{19}F)$ coupling calculations are listed Table 14. There are two types of $^2J(^{19}F^{19}F)$ in SF_6; either the F−S−F is 90 or 180°. As seen in the table, $^2J(^{19}F^{19}F)$'s in SiF_4, PF_3, and SF_6 (90°) have similar values. As expected, the FC term increment percentages of all $^2J(^{19}F^{19}F)$'s are approximately the same and twice the $^1J(X^{19}F)$ FC increment of the uTZ-sn series on the F atom.

The uTZ-w basis set yields fairly similar values to the UGBS2P values of $^2J(^{19}F^{19}F)$ coupling in SiF_4 and SF_6 (90°). However, nontrivial errors remain in $^2J(FF)$ calculations of PF_3 and SF_6 (180°), which are 3.92 and 5.75 Hz, respectively, and 9.5% and 15% in relative error. In the case of PF_3, this

is due to the basis set error in the aug-cc-pVTZ basis for the PSO and DSO terms.

The uTZ-w basis sets for the $^1J(^{31}P^{35}Cl)$ couplings in PCl_3 produce very good agreement with UGBS2p. Adding tight s functions to uTZ basis set had very little effect on the small two-bond $^2J(ClCl)$ calculations in PCl_3.

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Table 15. $^1J(^{31}P^{35}Cl)$ Coupling in the PCl$_3$ Molecule Evaluated Using the uTZ-sn Basis Set (Hz)

		P uTZ-sn			
		$n = 0$	1	2	3	UGBS2P
Cl uTZ-sn	$n = 0$	−100.72[a]	−100.93	−101.55	−101.63	FC: −103.25
		−125.95[b]	−126.16	−126.78	−126.86	SD: 11.06
	1	−100.91	−101.12	−101.74	−101.82	PSO: −37.54
		−126.14	−126.35	−126.97	−127.05	DSO: 0.05
	2	−101.49	−101.71	**−102.32**	−102.41	total: −129.67
		−126.72	−126.94	**−127.55**	−127.64	

[a] Fermi contact contribution. [b] Total spin−spin coupling. SD, PSO, and DSO are respectively 9.86, −35.15, and 0.06 (calculated using contracted aug-cc-pVTZ basis set). Expt. $^1J(^{31}P^{35}Cl)$ −120 Hz (neat liquid).[36]

In some cases, when compared to the uTZ basis set, uTZ-w produced poorer results for the FC terms, such as $^1J(SiF)$ in SiF$_4$ and both $^1J(SF)$'s in SF$_6$. In other words, adding tight s functions moves the FC term away from the UGBS2P results. Preliminary results demonstrated that this is because tight d functions are also important in these cases. Therefore, we generated uTZ-wd$n$ basis sets by adding more d functions to the uTZ-w basis set. This problem only occurs in systems containing second row atoms; these additional d functions are tested for these atoms. The additional d functions have progressive exponents of 2 with reference to the tightest d function in the uTZ basis for that atom.

3.5. Overall Results for uTZ-Based Basis Sets. Table 16 lists all of the couplings in this study and the results of FC term and total contributions using UGBS2P, contracted

aug-cc-pVTZ, uTZ, uTZ-w, uTZ-wd2, and uTZ-wd4 basis sets. The average absolute error (AAE) and maximum absolute error (MAE) are also listed. Table 17 shows the relative errors of the same coupling calculations using these basis sets and includes the average relative error (ARE) and maximum relative error.

Both absolute and relative errors are shown because each evaluates the calculation results from a different perspective. In some cases, the relative error is fairly high, while the actual difference between UGBS2P and a small basis set can be as low as 0.25 Hz [e.g., $^2J(^{35}Cl^{35}Cl)$ in PCl$_3$]. In other cases, the absolute error is large [e.g., $^1J(PF)$ of PF$_3$], but relative error is consistent with the other results.

Because the SD, PSO, and DSO terms are calculated using the unmodified aug-cc-pVTZ basis set, they remain unchanged for all aug-cc-pVTZ-derived basis calculations. The extended uTZ basis sets improve the total spin−spin coupling by improving the FC term. It is interesting to note that, in some cases, the FC term is improved but the total contribution is worsened. This is due to the cancellation of basis set errors between the FC term and the others. For some cases, in which the errors are modest in size and opposite in sign, improving just the FC term makes the overall results slightly worse.

From the tables, it can be seen that the unchanged aug-cc-pVTZ has very poor agreement with UGBS2P, with 23.65 Hz in AAE and 17.94% in ARE in total spin−spin coupling. The uTZ basis shows minor improvement yet still produces inadequate results, with 11.21 Hz in AAE and 10.77% in ARE. With tighter s functions added, the uTZ-w basis set

Table 16. Absolute Values of FC Term and Total Spin−Spin Coupling Calculations Using Different Basis Set Series (Hz)

		UGBS2P		contracted TZ		uTZ		uTZ-w		uTZ-wd2		uTZ-wd4	
		FC	total	FC	total	FC	total	FC	total	FC	total	FC	total
HF	$^1J(HF)$	192.47	390.44	195.80	389.74	167.78	361.71	188.70	382.63	188.70	382.63	188.70	382.63
NH$_3$	$^1J(NH)$	41.05	43.60	36.57	39.09	36.05	38.57	40.58	43.10	40.58	43.10	40.58	43.10
	$^2J(HH)$	−12.51	−10.71	−11.16	−10.02	−10.24	−9.10	−12.33	−11.19	−12.33	−11.19	−12.33	−11.19
HCN	$^1J(HC)$	283.08	283.24	273.70	274.01	248.21	248.52	279.51	279.82	279.51	279.82	279.51	279.82
	$^2J(HN)$	2.31	5.29	4.61	7.34	2.03	4.76	2.29	5.02	2.29	5.02	2.29	5.02
SiH$_4$	$^1J(SiH)$	−210.04	−209.91	−159.44	−158.85	−188.82	−188.22	−209.13	−208.53	−208.56	−207.96	−208.50	−207.90
	$^2J(HH)$	4.92	5.00	3.33	2.17	3.81	2.64	4.60	3.43	4.84	3.67	4.88	3.71
PH$_3$	$^1J(PH)$	158.43	163.96	115.03	120.71	141.45	147.13	156.52	162.20	157.19	162.87	157.14	162.82
	$^2J(HH)$	−12.87	−12.59	−10.51	−10.60	−10.74	−10.83	−12.93	−13.02	−12.67	−12.76	−12.63	−12.72
H$_2$S	$^1J(SH)$	19.25	23.85	15.13	19.63	17.07	21.57	18.85	23.35	19.15	23.65	19.16	23.65
	$^2J(HH)$	−12.48	−11.71	−10.15	−9.78	−10.49	−10.13	−12.61	−12.25	−12.31	−11.94	−12.26	−11.90
HCN	$^1J(CN)$	6.76	12.73	6.70	12.10	6.30	11.69	6.63	12.02	6.63	12.02	6.63	12.02
SiF$_4$	$^1J(SiF)$	262.41	343.08	164.76	241.24	262.79	339.27	271.84	348.32	264.96	341.44	264.14	340.62
	$^2J(FF)$	−61.30	−161.24	−70.52	−166.48	−59.29	−155.27	−62.38	−158.36	−61.12	−157.09	−60.97	−156.94
PF$_3$	$^1J(PF)$	−1312	−1595	−1165	−1427	−1261	−1524	−1304	−1567	−1301	−1564	−1300	−1563
	$^2J(FF)$	−54.17	−41.31	−79.08	−63.24	−50.57	−34.72	−53.24	−37.39	−53.38	−37.54	−53.42	−37.57
SF$_6$	$^1J(SF)$	−296.09	−320.46	−249.95	−272.49	−284.37	−306.91	−293.95	−316.49	−293.46	−316.00	−293.32	−315.86
	$^2J(FF)$ 90°	−67.57	−273.10	−84.64	−283.15	−66.84	−265.36	−70.33	−268.85	−66.98	−265.49	−66.54	−265.06
	$^2J(FF)$ 180°	−18.19	−38.17	−19.06	−40.61	−21.27	−42.81	−22.38	−43.92	−18.45	−40.00	−17.98	−39.53
PCl$_3$	$^1J(ClP)$	−103.25	−129.67	−119.91	−145.14	−100.72	−125.95	−102.32	−127.55	−102.97	−128.20	−102.98	−128.21
	$^2J(ClCl)$	−0.07	2.58	0.75	3.15	−0.06	2.33	−0.06	2.33	−0.07	2.32	−0.07	2.32
	average absolute error			23.13	23.65	8.96	11.21	1.97	3.61	1.41	3.54	1.46	3.64
	maximum absolute error			147.00	168.00	51.00	71.00	9.43	28.00	11.00	31.00	12.00	32.00
	average H coupling absolute error			11.39	11.13	10.25	10.65	1.07	1.70	1.03	1.59	1.04	1.59
	average no H coupling absolute error			36.04	37.41	7.55	11.83	2.96	5.71	1.84	5.69	1.92	5.89

Table 17. Relative Errors of the FC Term and Total Spin−Spin Coupling Calculations Using Different Basis Set Series

		UGBS2P		contracted TZ		uTZ		uTZ-w		uTZ-wd2		uTZ-wd4	
		FC (Hz)	total (Hz)	FC error	total error	FC error	total error	FC error	total error	FC error	total error	FC error	total error
HF	^1J(HF)	192.47	390.44	1.73%	0.18%	12.83%	7.36%	1.96%	2.00%	1.96%	2.00%	1.96%	2.00%
NH_3	^1J(NH)	41.05	43.60	10.91%	10.34%	12.18%	11.54%	1.14%	1.15%	1.14%	1.15%	1.14%	1.15%
	^2J(HH)	−12.51	−10.71	10.79%	6.44%	18.15%	15.03%	1.44%	4.48%	1.44%	4.48%	1.44%	4.48%
HCN	^1J(HC)	283.08	283.24	3.31%	3.26%	12.32%	12.26%	1.26%	1.21%	1.26%	1.21%	1.26%	1.21%
	^2J(HN)	2.31	5.29	99.57%	38.75%	12.12%	10.02%	0.87%	5.10%	0.87%	5.10%	0.87%	5.10%
SiH_4	^1J(SiH)	−210.04	−209.91	24.09%	24.32%	10.10%	10.33%	0.43%	0.66%	0.70%	0.93%	0.73%	0.96%
	^2J(HH)	4.92	5.00	32.32%	56.60%	22.56%	47.20%	6.50%	31.40%	1.63%	26.60%	0.81%	25.80%
PH_3	^1J(PH)	158.43	163.96	27.39%	26.38%	10.72%	10.26%	1.21%	1.07%	0.78%	0.66%	0.81%	0.70%
	^2J(HH)	−12.87	−12.59	18.34%	15.81%	16.55%	13.98%	0.47%	3.42%	1.55%	1.35%	1.86%	1.03%
H_2S	^1J(SH)	19.25	23.85	21.40%	17.69%	11.32%	9.56%	2.08%	2.10%	0.52%	0.84%	0.47%	0.84%
	^2J(HH)	−12.48	−11.71	18.67%	16.48%	15.95%	13.49%	1.04%	4.61%	1.36%	1.96%	1.76%	1.62%
HCN	^1J(CN)	6.76	12.73	0.89%	4.95%	6.80%	8.17%	1.92%	5.58%	1.92%	5.58%	1.92%	5.58%
SiF_4	^1J(SiF)	262.41	343.08	37.21%	29.68%	0.14%	1.11%	3.59%	1.53%	0.97%	0.48%	0.66%	0.72%
	^2J(FF)	−61.30	−161.24	15.04%	3.25%	3.28%	3.70%	1.76%	1.79%	0.29%	2.57%	0.54%	2.67%
PF_3	^1J(PF)	−1312	−1595	11.20%	10.53%	3.89%	4.45%	0.61%	1.76%	0.84%	1.94%	0.91%	2.01%
	^2J(FF)	−54.17	−41.31	45.98%	53.09%	6.65%	15.95%	1.72%	9.49%	1.46%	9.13%	1.38%	9.05%
SF_6	^1J(SF)	−296.09	−320.46	15.58%	14.97%	3.96%	4.23%	0.72%	1.24%	0.89%	1.39%	0.94%	1.44%
	^2J(FF) 90°	−67.57	−273.10	25.26%	3.68%	1.08%	2.83%	4.08%	1.56%	0.87%	2.79%	1.52%	2.94%
	^2J(FF) 180°	−18.19	−38.17	4.78%	6.39%	16.93%	12.16%	23.03%	15.06%	1.43%	4.79%	1.15%	3.56%
PCl_3	^1J(ClP)	−103.25	−129.67	16.14%	11.93%	2.45%	2.87%	0.90%	1.63%	0.27%	1.13%	0.26%	1.13%
	^2J(ClCl)	−0.07	2.58	1171.43%	22.09%	14.29%	9.69%	14.29%	9.69%	0.00%	10.08%	0.00%	10.08%
	average relative error			76.76%	17.94%	10.20%	10.77%	3.38%	5.07%	1.06%	4.10%	1.07%	4.00%
	maximum relative error			1171.43%	56.60%	22.56%	47.20%	23.03%	31.40%	1.96%	26.60%	1.96%	25.80%
	average H coupling relative error			24.41%	19.66%	14.07%	14.64%	1.67%	5.20%	1.20%	4.21%	1.19%	4.08%
	average no H coupling relative error			134.35%	16.06%	5.95%	6.52%	5.26%	4.93%	0.89%	3.99%	0.93%	3.92%

shows a decent improvement in total spin−spin coupling, with a 5.07% ARE and 3.61 Hz AAE compared to UGBS2P. The AAE of the FC term reduced 6.99 Hz from that of the uTZ basis set, and the AAE of total contribution reduced 7.60 Hz. The 0.6 Hz difference is from error cancellation. Going from the uTZ basis to uTZ-w produces a greater improvement in the couplings involving H atoms than in the couplings involving only heavy atoms.

For the contracted aug-cc-pVTZ basis set, the overall MAE occurs for the ^1J(PF) in PF_3 and is 147 and 168 Hz, for the FC and total contribution, respectively. uTZ reduces these to 51 and 71 Hz (for FC and total, respectively). The uTZ-w basis again substantially improved these to 8 and 28 Hz, respectively, for the FC and total contribution. This makes the error in ^1J(SiF) in SiF_4, 9.43 Hz, the MAE of the FC contribution for uTZ-w.

For a few couplings involving second row atoms, such as ^1J(SiF) in SiF_4 and both ^2J(FF)'s in SF_6, adding tighter d functions made modest improvements in the FC term compared to uTZ-w. For both ^2J(FF)'s in SF_6, the absolute error reduced by about 2−4 Hz and the relative error was slightly reduced. In the case of ^2J(FF) in SF_6 (90°), the FC term was improved while the total spin−spin coupling became slightly worse because of the cancellation of errors among four terms. The uTZ-wd2 and uTZ-wd4 basis sets also slightly improved the average error of the FC term for coupling without H atoms present: the AAE of coupling without H atoms, using the uTZ-wd2 basis set, improved by 1.12 Hz, and the ARE improved from 5.26% to 0.89%, compared to that in the uTZ-w basis set. However, the uTZ-

wd*n* basis sets provide very modest improvements to the overall results of spin−spin coupling calculations and, therefore, are not suggested by the authors for practical application.

4. Tests on Smaller Basis Sets

Two smaller basis sets, aug-cc-pVDZ and 6-311+G(d,p), have been tested using the same scheme.

Table 18 lists the results of all spin−spin couplings (the FC term and total coupling) using aug-cc-pVDZ-derived basis sets, compared to those using UGBS2P. The FC term was calculating using DZ (contracted aug-cc-pVDZ), uDZ, uTZ-w, and uTZ-wd2. The prefix "u" indicates an uncontracted basis set. The suffix "-w" stands for the same scheme of adding tight s functions as in uTZ-w, that is, four s functions to hydrogen with progressive exponents of 3, two s functions to first row atoms with exponents of 3, and two s functions to second row atoms with exponents of 2. The suffix "-wd2" means two tight d functions for second row atoms with progressive exponents of 2 are added, in addition to tight s functions. The SD, PSO, and DSO terms were calculated using the contracted aug-cc-pVDZ basis set. Table 19 shows the results for couplings using 6-311+G(d,p)-derived basis sets (uG, uG-w, etc.)

As can been seen from the AAEs and MAEs in the tables, the regular contracted basis sets produced generally poor results compared to those of UGBS2P. The uncontracted uDZ and uG basis sets both reduce the AAE to less than 20 Hz and MAE to less than 100 Hz for the total spin−spin

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Table 18. FC Term and Total Spin−Spin Coupling Calculation Results Using aug-cc-pVDZ-Derived Basis Set (Hz)

		UGBS2P		aug-cc-pVDZ		uDZ		uDZ-w		uDZ-wd2	
		FC	total	FC	total	FC	total	FC	total	FC	total
HF	^1J(HF)	192.47	390.44	406.18	579.05	149.24	322.11	181.80	354.67	181.80	354.67
NH$_3$	^1J(NH)	41.05	43.60	46.04	48.15	33.20	35.31	40.08	42.19	40.08	42.19
	^2J(HH)	−12.51	−10.71	−12.12	−11.96	−8.76	−8.59	−11.98	−11.81	−11.98	−11.81
HCN	^1J(HC)	283.08	283.24	312.25	312.39	230.30	230.44	277.67	277.81	277.67	277.81
	^2J(HN)	2.31	5.29	0.66	2.63	1.92	3.89	2.30	4.27	2.30	4.27
SiH$_4$	^1J(SiH)	−210.04	−209.91	−174.39	−174.07	−178.00	−177.68	−211.02	−210.69	−208.32	−208.00
	^2J(HH)	4.92	5.00	1.78	0.26	2.81	1.30	3.97	2.45	4.69	3.17
PH$_3$	^1J(PH)	158.43	163.96	138.34	141.34	134.12	137.11	158.84	161.84	158.16	161.16
	^2J(HH)	−12.87	−12.59	−12.12	−12.36	−9.82	−10.06	−13.22	−13.46	−12.61	−12.85
H$_2$S	^1J(SH)	19.25	23.85	13.75	17.42	16.33	20.00	19.40	23.07	19.69	23.36
	^2J(HH)	−12.48	−11.71	−11.98	−11.86	−9.03	−8.90	−12.19	−12.07	−11.54	−11.42
HCN	^1J(CN)	6.76	12.73	7.11	11.30	6.57	10.76	6.93	11.12	6.93	11.12
SiF$_4$	^1J(SiF)	262.41	343.08	165.32	228.55	297.02	360.26	310.56	373.79	286.16	349.39
	^2J(FF)	−61.30	−161.24	−13.24	−102.31	−62.62	−151.69	−66.39	−155.46	−62.53	−151.59
PF$_3$	^1J(PF)	−1312	−1595	−1093	−1325	−1266	−1499	−1323	−1556	−1308	−1540
	^2J(FF)	−54.17	−41.31	19.68	42.42	−48.36	−25.63	−51.33	−28.59	−52.31	−29.57
SF$_6$	^1J(SF)	−296.09	−320.46	−197.59	−218.56	−277.54	−298.51	−290.00	−310.97	−288.83	−309.79
	^2J(FF) 90°	−67.57	−273.10	−6.56	−194.83	−68.84	−257.13	−73.02	−261.30	−66.72	−255.01
	^2J(FF) 180°	−18.19	−38.17	−8.39	−26.99	−27.90	−46.50	−29.57	−48.17	−21.74	−40.34
PCl$_3$	^1J(ClP)	−103.25	−129.67	−79.25	−103.01	−93.02	−116.77	−95.79	−119.55	−97.03	−120.80
	^2J(ClCl)	−0.07	2.58	1.02	3.37	0.05	2.40	0.05	2.40	0.04	2.39
	average absolute error			45.16	49.70	14.46	19.27	5.64	8.74	3.35	8.41
	maximum absolute error			219.00	270.00	52.78	96.00	48.15	39.00	23.75	55.00
	H coupling average absolute error			28.69	26.93	15.99	18.63	1.88	4.74	1.95	4.76
	non-H coupling average absolute error			63.28	74.74	12.78	19.97	9.78	13.14	4.90	12.43

Table 19. FC Term and Total Spin−Spin Coupling Calculation Results Using 6-311+G(d,p)-Derived Basis Set (Hz)

		UGBS2P		contracted G		uG		uG-w		uG-wd2	
		FC	total	FC	total	FC	total	FC	total	FC	total
HF	^1J(HF)	192.47	390.44	132.02	320.15	146.41	334.54	165.55	353.68	165.55	353.68
NH$_3$	^1J(NH)	41.05	43.60	36.54	38.86	35.36	37.68	40.18	42.49	40.18	42.49
	^2J(HH)	−12.51	−10.71	−11.43	−10.88	−10.11	−9.57	−12.06	−11.52	−12.06	−11.52
HCN	^1J(HC)	283.08	283.24	266.67	267.00	246.19	246.52	279.78	280.11	279.78	280.11
	^2J(HN)	2.31	5.29	2.55	5.02	2.04	4.50	2.30	4.77	2.30	4.77
SiH$_4$	^1J(SiH)	−210.04	−209.91	−188.24	−187.90	−189.08	−188.74	−210.95	−210.61	−210.02	−209.91
	^2J(HH)	4.92	5.00	4.04	2.86	3.61	2.43	4.34	3.16	4.57	3.39
PH$_3$	^1J(PH)	158.43	163.96	131.39	136.26	140.32	145.18	156.22	161.09	157.36	162.23
	^2J(HH)	−12.87	−12.59	−10.29	−10.58	−10.33	−10.63	−12.36	−12.66	−12.23	−12.53
H$_2$S	^1J(SH)	19.25	23.85	14.13	18.47	16.45	20.80	18.20	22.54	18.75	23.10
	^2J(HH)	−12.48	−11.71	−10.20	−10.16	−9.58	−9.53	−11.39	−11.35	−11.10	−11.06
HCN	^1J(CN)	6.76	12.73	10.18	15.23	6.12	11.17	6.56	11.61	6.56	11.61
SiF$_4$	^1J(SiF)	262.41	343.08	327.35	409.59	308.53	390.77	324.23	406.47	316.85	399.10
	^2J(FF)	−61.30	−161.24	−72.13	−179.06	−66.53	−173.45	−71.10	−178.02	−70.02	−176.94
PF$_3$	^1J(PF)	−1312	−1595	−1250	−1534	−1229	−1513	−1292	−1576	−1287	−1571
	^2J(FF)	−54.17	−41.31	−62.98	−39.53	−49.60	−26.16	−53.03	−29.59	−52.89	−29.45
SF$_6$	^1J(SF)	−296.09	−320.46	−283.27	−304.67	−273.42	−294.82	−287.20	−308.60	−287.55	−308.95
	^2J(FF) 90°	−67.57	−273.10	−71.46	282.15	−70.37	−281.05	−75.24	−285.92	−70.71	−281.40
	^2J(FF) 180°	−18.19	−38.17	−32.34	−49.06	−34.42	−51.14	−36.80	−53.52	−30.11	−46.82
PCl$_3$	^1J(ClP)	−103.25	−129.67	−87.38	−114.17	−85.51	−112.30	−88.33	−115.13	−91.05	−117.84
	^2J(ClCl)	−0.07	2.58	−0.17	2.45	0.13	2.74	0.13	2.74	0.13	2.75
	average absolute error			16.15	42.84	16.15	17.76	8.63	10.30	7.67	9.35
	maximum absolute error			64.94	555.25	83.00	82.00	61.82	63.39	54.44	56.02
	H coupling average absolute error			12.94	13.86	12.72	13.65	3.45	4.50	3.23	4.28
	non-H coupling average absolute error			19.68	74.72	19.92	22.27	14.33	16.67	12.56	14.92

coupling. The smaller uG basis sets generate slightly better results than uDZ.

The uDZ-w and uG-w basis sets, with tight s functions added, improved the results in most couplings. The uDZ-w basis sets considerably reduced the AAE to 8.74 Hz and the MAE to 39 Hz, in total contribution. The uG-w basis sets had an AAE of 10.30 Hz and an MAE of 63.30 Hz, which is only a modest improvement from those of the uG basis sets. Adding d functions in both uDZ-w and uG-w basis sets produced no significant reduction in absolute errors.

In general, uTZ-derived basis sets produced the most accurate results, in comparison to UGBS2P. The uDZ- and uG-derived basis sets had only moderately good and barely adequate results, respectively. Hence, use of the uTZ-w basis set is strongly recommended. If the computational cost of uTZ-w is prohibitive, then uDZ-w and uG-w give qualitatively reasonable results at a substantially lower cost, although care should be used in making quantitative predictions using these basis sets.

The MAEs for aug-cc-pVTZ, uTZ, and uDZ-w basis sets are 168, 71, and 39 Hz, respectively, and so, uDZ-w is both much cheaper and more accurate than aug-cc-pVTZ or uTZ.

For all three basis sets examined in this paper, the procedure described here produces a substantial improvement in the reliability of the predicted spin–spin couplings over that of the unmodified basis. We expect the procedure to be applicable to other basis sets as well.

5. Comparison with cc-pCVXZ-sd and aug-cc-pVTZ-J Basis Sets

Different research groups have recently derived small basis sets for use in spin–spin coupling calculations. For comparison, results using two such basis sets, the cc-pCVXZ-sd (X = D and T) basis set (developed by Peralta et. al.)[19] and the aug-cc-pVTZ-J basis sets (developed by Sauer et. al.),[21] have been examined for the molecules used in this study.

The cc-pCVXZ-sd basis sets have been successfully applied in one-bond C–C coupling calculations.[20] The results using cc-pCVXZ-sd (X = D and T) basis sets are listed in Table S2 in the Supporting Information and are compared to those of the uXZ-w (X = D and T) and UGBS2P basis sets. It can be seen that uXZ-w (X = D and T) basis sets have smaller AAEs and MAEs in all couplings, by factors of 2–4.

Table S3 in the Supporting Information shows the results using aug-cc-pVTZ-J (TZ-J) basis sets, compared to those of uTZ-w and uTZ-wd2 basis sets. As can be seen in the table, TZ-J and uTZ-wd2 basis sets generate very comparable results; thus, both basis set series are appropriate for spin–spin coupling calculations. However, the TZ-J basis sets have been generated for only six elements (H, C, N, O, F, and S), while our uTZ-derived basis sets are applicable to at least all of the first and second row elements. Furthermore, our modification scheme is general and can be applied to other basis sets, such as aug-cc-pVQZ.

The scheme described in this paper has been implemented in the Gaussian 03 program, revision D,[26] with keyword "NMR = Mixed". One should also specify "CPHF = Conv = 10" and "Int = ultrafine" as options.

6. Conclusion

In this paper, we have presented a general scheme of basis set modification in NMR spin–spin coupling constant calculation. The basis set used to compute the FC term is derived by uncontracting the original basis and then adding tighter s functions. The added tight s functions have even-tempered exponents starting from the tightest s functions in original basis set. For hydrogen and first row atoms, a ratio

of 3 for successive exponents was found to be optimal, while for second row atoms, a ratio of 2 was preferable.

Four tighter s functions are added for hydrogen and two tighter s functions for first and second row atoms. Tight d functions can also be added to second row atoms, in the same way as s functions, with a progressive exponent of 2 to the tightest d function in original basis sets, but produce marginal improvements. The SD, PSO, and DSO terms are calculated using an unmodified contracted basis set.

The three basis set series derived from aug-cc-pVTZ, aug-cc-pVDZ, and 6-311+G(d,p) have different accuracies in spin–spin coupling calculations. The uTZ-w basis sets produced an AAE of 3.61 Hz and an MAE of 28 Hz (total contribution), compared to 23.65 and 168 Hz, respectively, for the original aug-cc-pVTZ. The uDZ-w basis sets have an AAE and MAE of 8.74 and 39 Hz, respectively, compared to 49.70 and 270 Hz for the unmodified aug-cc-pVDZ. The AAE and MAE of uG-w are 10.30 and 63.39 Hz, respectively, compared to 42.84 and 555.25 Hz for the unmodified 6-311+G(d,p) basis set.

The uTZ-w basis produces spin–spin coupling constants, which are close to the basis set limit at moderate cost, and is the choice we strongly recommend. If uTZ-w is too expensive, then uDZ-w is a much better choice than the unmodified or uncontracted aug-cc-pVTZ basis set.

Supporting Information Available: A summary of the calculated geometries and absolute energies of all molecules at the B3LYP/6-31G* level, tabulated calculation results of $^1J(^{35}Cl^{35}Cl)$ coupling, and comparison results of uTZ-derived basis sets with cc-pCVXZ-sd (X = D and T) and aug-cc-pVTZ-J (TZ-J) basis sets. This information is available free of charge via the Internet at http://pubs.acs.org.

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