

Pople Style Basis Sets for the Calculation of NMR Spin–Spin Coupling Constants: the 6-31G-J and 6-311G-J Basis Sets

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 Supporting Information

ABSTRACT: We present a modification of the small and popular Pople basis sets, 6-31G and 6-311G, for density functional theory calculations of Fermi contact dominated NMR indirect nuclear spin–spin coupling constants. These new basis sets, 6-31G-J and 6-311G-J, contain twice the number of contracted s-type functions but the same number of contracted p-type functions as the original Pople basis set. For our test set of 12 one-, two- and three-bond coupling constants, the new basis sets augmented with the standard diffuse and polarization functions, i.e., the 6-31+G*-J and 6-311++G**-J basis sets, lead to a maximum deviation of 5 and 2 Hz, respectively, compared to results obtained with the 6 or more times larger aug-pcJ-4 basis set. In correlated wave function calculations using the second-order polarization propagator approximation, the deviations with respect to the aug-ccJ-pVQZ basis set are 8 and 3 Hz and thus slightly larger.

1. INTRODUCTION

It is well-known, that standard one-electron Gaussian basis sets are in general not suited for the calculation of NMR indirect nuclear spin–spin coupling constants (SSCC), while basis sets specially optimized for SSCCs are often too large for routine calculations on larger organic or biological molecules.^{1–18} In the Ramsey formulation,¹⁹ the SSCC is the sum of four different contributions, the Fermi contact (FC), the spin dipolar (SD), the paramagnetic spin–orbit (PSO), and the diamagnetic spin–orbit (DSO) terms. Standard basis sets are typically optimized for energies and are therefore not necessarily optimal for calculations of other properties, which is especially true for SSCCs. Calculations of SSCCs demand basis sets with higher exponents than included in standard basis sets. In particular s-type functions with very high exponents are required for the FC term, as it depends on the electron density at the nucleus. The PSO term requires additional tight p-type functions and the SD term tight p-, d- and f-type functions. The FC term is often the dominant contribution, especially for one-bond couplings between less electronegative atoms, and several basis sets have thus been made to improve the description of the FC term. This includes the cc-pVXZ-Cs and cc-pVXZ-sun basis sets⁵ and the HuzIV-su4^{20–24} and the aug-cc-pVTZ-J^{6,8–10,17,18} basis sets, which all include additional tight s-type functions. In addition there are also basis sets designed to describe all the contributions to the coupling constants accurately. This includes the pcJ-n, aug-pcJ-n^{14,16} and ccJ-pVXZ¹⁵ families of basis sets, which include tight s-, p-, d-, and sometimes even f-type functions. The pcJ-n and aug-pcJ-n basis sets are developed for calculations at the density functional theory (DFT) level, while the ccJ-pVXZ basis sets are designed for correlated wave function methods.

Unfortunately all of these basis sets are rather large; the pcJ-2 basis set, e.g., is of approximately the same size as the aug-pVTZ-J basis set. Consequently these basis sets cannot be used routinely for larger systems like larger organic or biological molecules. Instead, much smaller basis sets, such as the very popular Pople

style^{25,26} or Ahlrichs TZVP and qzp basis sets,^{27,28} are used for larger molecules, even though these basis sets are clearly not adequate for the calculation of SSCCs.

In this study, we will present and test improvements to the Pople basis sets 6-31G and 6-311G for the calculation of FC dominated coupling constants. We only address FC dominated couplings, as most organic and biological couplings are FC dominated. Also, when we only consider FC dominated couplings, we primarily have to focus on the addition of tight s-type functions. Therefore we do not attempt to generate the best possible SSCC basis set, because such basis sets already exist, for example, the aug-pcJ-4 basis set. On the contrary, we want to generate a basis set, which gives acceptable results while still being reasonably small and which can consistently be used together with the Pople basis sets 6-31G and 6-311G. These basis sets should be suitable for organic or biological systems, where larger basis sets cannot be used in routine applications. Finally one should mention that Barone and co-workers²⁹ have recently presented in a similar study new basis sets for the calculation of electron paramagnetic resonance hyperfine coupling constants at the B3LYP level, called N07D. The N07D basis sets are also based on the 6-31G basis sets but are augmented with only one set of core–valence s-, p-, and d-type functions.

We restrict ourselves here to basis sets for hydrogen, carbon, nitrogen, and oxygen to be used in calculations of ¹J(CH), ¹J(NH), ¹J(CN), ¹J(CC), ¹J(CO), ¹J(OH), ²J(HH), and ³J(HH) couplings, as these are the most important FC dominated couplings relevant for organic and biological systems. However, one should note that the ¹J(CO), ¹J(OH), ²J(HH), and ³J(HH) couplings are not completely dominated by the FC term but have also significant contributions from primarily the PSO term as well as non-negligible contributions from the SD and DSO terms. For the development of the basis sets we have studied the

Received: August 4, 2011

Published: October 24, 2011

Table 1. Composition of the Basis Sets Discussed in This Paper

	hydrogen		C, N, O	
	primitives	contracted	primitives	contracted
6-31G	4s	2s	10s4p	3s2p
6-31G-J	7s	4s	13s5p	6s2p
6-31+G*-J	7s	4s	14s6p1d	7s3p1d
6-311G	5s	3s	11s5p	4s3p
6-311G-J	8s	6s	14s6p	8s3p
6-311++G**-J	9s1p	7s1p	15s7p1d	9s4p1d
pcJ-1*	6s1p	4s1p	9s5p1d	5s4p1d
pcJ-1	6s2p	4s2p	9s5p2d	5s4p2d
pcJ-2*	8s2p1d	5s2p1d	12s7p2d1f	7s5p2d1f
aug-cc-pVTZ-J	13s3p1d	6s3p1d	21s8p3d1f	9s5p3d1f
pcJ-2	8s3p2d	5s3p2d	12s7p3d2f	7s5p3d2f
ccJ-pVTZ	7s3p2d	5s3p2d	12s6p3d1f	7s4p3d1f
aug-ccJ-pVQZ	9s5p4d2f	7s5p4d2f	15s8p5d3f2g	10s6p5d3f2g
aug-pcJ-4	13s8p5d3f2g	9s8p5d3f2g	20s13p8d5f3g2h	12s10p8d5f3g2h

corresponding couplings in methane, ethane, ammonia, water, and formamide (FMA), while the final basis sets were also tested in calculations of the $^1J(\text{NH})$ coupling constant of *N*-methylacetamide.

2. COMPUTATIONAL DETAILS

In all calculations of the SSCCs we employed the Dalton program package.³⁰ In the development of the basis set, the calculations were carried out at the DFT level with the B3LYP exchange–correlation functional,^{31–34} while some of the benchmark calculations were performed at the level of the second-order polarization propagator approximation (SOPPA).^{6,35–40} The B3LYP functional was chosen, as this functional had been used for the development of the (aug-)pcJ-*n* family of basis sets¹⁴ and as B3LYP generally gives good results for SSCCs.^{11,23,24,41–51} All DFT calculations will be benchmarked against the aug-pcJ-4 result, as this basis set is the best possible basis set for DFT calculations and all SOPPA calculations against the aug-ccJ-pVQZ basis set. The geometries of all molecules were optimized by B3LYP/6-311++G**.

3. BASIS SET GENERATION

The 6-31G and 6-311G basis sets are very small (see, e.g., Table 1). There are only s-type functions on hydrogen, and for the second-row atoms, there are only s- and p-type functions. Polarization and diffuse functions can be added using the standard notations. We will base our basis set development on the 6-31G and 6-311G basis sets and add polarization and diffuse functions only, when we have obtained the new 6-31G-J and 6-311G-J basis sets. In Section 3.1 we will thus describe how the new 6-31G-J and 6-311G-J basis sets are generated. We will primarily discuss how the 6-31G-J basis sets were made, as the same procedure was used for the 6-311G-J basis sets.

3.1. Uncontracted Basis Sets. To improve the Pople style basis sets, we first decontracted the basis sets completely. For the 6-31G basis set the differences between the results obtained with the contracted (6-31G) and uncontracted (6-31Guc) basis sets are considerable, differing up to 30 Hz, while the differences

Table 2. Exponents of the s- and p-Type Functions Added to the 6-31G and 6-311G Basis Sets

atom	s ₁	s ₂	s ₃	p ₁
6-31G				
H	186.51684197	2789.59214924	62666.02044953	
C	30750.99553738	469897.3134792	10873731.57976	39.81711939
N	42052.27768090	641872.0643321	14841521.17252	60.55463459
O	55205.88661614	841553.7695902	19428536.09300	81.54048672
6-311G				
H	340.31345127	5170.23631942	118753.0892189	
C	46416.99275025	717812.0184378	16876193.13942	121.32953805
N	63798.90182836	988674.6264273	23421322.38384	175.03570330
O	86856.41933057	1341747.480166	31660948.43265	238.82507403

between the results from the 6-311G and 6-311Guc basis sets are smaller with a maximum difference of 15 Hz. Interestingly, the results obtained with the uncontracted basis sets deviate generally much more from the aug-pcJ-4 results than the ones from the contracted basis sets, which implies that the Pople basis sets in their contracted form benefit from a very fortunate error cancelation as far as SSCCs are concerned.

The uncontracted basis sets were then augmented with s-type functions with large exponents until convergence. The exponents were chosen according to

$$a_{i-1} = \frac{(a_i/a_{i+1})^2}{a_{i+1}/a_{i+2}} a_i \quad (1)$$

where a_i , a_{i+1} , and a_{i+2} are the previously largest, second, and third largest exponents, and a_{i-1} is the new exponent. This implies that the ratio between the exponents are increased, and not kept fixed as in the even-tempered or aug-cc-pVTZ-J basis sets.^{6,8–10,17,18} The exponents are listed in Table 2. Addition of the first tight s-type function is very important, contributing up to 25 Hz, while addition of the second and third s-type function is less important and the fourth s-type function no longer improves the results considerably. Afterward the carbon, nitrogen, and oxygen basis sets were augmented with p-type functions until convergence. It was only necessary to add one tight p-type function to the second-row atoms. The addition of three tight s-type functions and one p-type function defines the 6-31G-Juc basis set. The 6-311Guc basis set was improved in the same way leading to the 6-311G-Juc basis set, however, is it worth noticing that the two basis sets, 6-31G-Juc and 6-311G-Juc, give almost the same results, the largest difference is 1 Hz. In this context it is important to stress that we did not only consider the total SSCC but also the four individual contributions and that we found that the good correspondence between the results obtained with the uncontracted 6-31G-Juc and 6-311G-Juc basis sets is not due to fortunate error cancelations but to a good description of all four terms.

3.2. Contracted Basis Sets. The optimal uncontracted basis sets were then contracted again. Contrary to the aug-cc-pVTZ-J basis sets,^{6,8–10,17,18} we did not employ molecular orbital coefficients of the simplest hydrides of each atom but natural orbital coefficients from complete active space (CAS) calculations on the atoms. For the second-row atoms all electrons were included in the CAS-space, while all orbitals were included for hydrogen. However, the orbital coefficients of the relevant orbitals obtained from the CAS calculations do not differ significantly from those

Table 3. DFT/B3LYP Results for the Coupling Constants in Hz in the Test Set as a Function of the One-Electron Basis Set Employed

basis	$^1J(\text{CC})$	$^1J(\text{CN})$	$^1J(\text{CO})$	$^1J(\text{CH})$		$^1J(\text{NH})$		$^1J(\text{OH})$	$^2J(\text{HH})$		$^3J(\text{HH})$	
	C_2H_6	FMA	FMA	CH_4	FMA	NH_3	FMA	H_2O	CH_4	FMA	FMA	C_2H_6
aug-pcJ-4	34.62	−14.03	28.96	134.32	201.68	−66.82	−97.72	−76.87	−13.33	7.51	15.57	18.25
pcJ-2	35.18	−13.86	28.91	135.07	199.53	−65.78	−96.71	−74.63	−13.73	7.47	15.42	18.01
aug-cc-pVTZ-J	34.58	−14.16	28.93	134.65	202.35	−66.75	−97.84	−76.15	−13.54	7.30	15.45	18.13
pcJ-2*	35.09	−13.86	29.11	134.99	199.44	−65.71	−96.64	−74.46	−13.79	7.36	15.39	17.98
pcJ-1	37.00	−15.35	28.10	133.88	196.67	−63.89	−96.19	−69.86	−13.50	7.02	14.67	17.58
pcJ-1*	36.92	−15.35	28.31	133.85	196.65	−63.87	−96.17	−69.75	−13.56	6.89	14.64	17.57
6-31G	46.71	−15.32	21.97	140.52	196.09	−62.36	−88.97	−53.66	−18.12	−0.64	11.84	14.77
6-31Guc	31.34	−11.58	39.13	111.34	165.71	−51.79	−80.70	−43.58	−12.13	3.33	10.71	13.14
6-31+G*	48.45	−18.99	7.46	138.45	197.31	−63.32	−88.89	−70.89	−15.19	2.34	11.50	14.01
6-31++G**	48.34	−19.61	7.52	138.98	200.20	−66.91	−92.77	−83.17	−14.27	2.69	11.34	14.08
6-31G-J	36.75	−14.15	44.35	137.19	204.39	−64.28	−99.81	−51.67	−16.72	3.16	13.40	16.75
6-31G-Juc	35.93	−13.49	43.67	136.12	202.66	−63.44	−98.70	−53.24	−15.60	4.69	14.52	17.60
6-31+G*-J	35.98	−15.18	29.34	136.05	204.43	−66.79	−99.13	−72.14	−15.72	4.62	13.91	16.79
6-31++G**-J	35.47	−14.92	29.43	134.97	204.10	−66.76	−98.69	−73.71	−14.73	5.19	14.02	17.08
6-311G	37.75	−14.40	42.88	129.15	187.45	−60.45	−92.49	−52.70	−15.30	0.81	11.25	14.60
6-311Guc	32.35	−11.86	39.55	117.36	174.50	−55.62	−85.40	−47.99	−13.06	3.55	11.29	14.21
6-311+G*	37.60	−15.35	26.55	125.86	181.64	−60.65	−89.32	−64.56	−13.44	3.71	11.91	14.55
6-311++G**	34.73	−14.46	27.42	119.85	180.07	−59.29	−87.84	−66.72	−11.84	4.55	11.88	14.53
6-311G-J	36.19	−13.82	42.15	136.96	203.08	−64.79	−99.37	−54.39	−15.81	4.30	13.59	17.05
6-311G-Juc	35.70	−13.39	42.69	136.16	202.71	−64.28	−98.80	−54.12	−15.58	4.83	14.14	17.53
6-311+G*-J	35.37	−14.60	29.38	135.81	203.06	−66.27	−98.33	−69.17	−15.08	5.48	14.70	17.54
6-311++G**-J	35.00	−14.26	29.48	135.51	203.42	−67.02	−98.60	−75.07	−14.05	6.11	14.78	17.63

obtained with Hartree–Fock calculations on the molecules. Nevertheless, we chose the atomic orbital coefficients as these coefficients are uniquely defined.

First we tried a contraction scheme for the 6-31G-Juc basis set, which would be equivalent to the original 6-31G contraction. However, contracting the s-type functions as in the 6-31G basis set gave unacceptably large errors. Jensen had also observed that the s-space cannot be contracted much, without loss of accuracy.¹⁴ Therefore we used the contraction scheme shown in Table 1. Unfortunately, the same contraction scheme could not be applied to the 6-311G-Juc basis set, and therefore the 6-311G-J basis sets are larger relative to the 6-311G basis sets than 6-31G-J is to 6-31G, as seen in Table 1. In both cases the new basis sets have twice the number of contracted s-type function as the original Pople basis sets but the same number of contracted p-type functions. The contracted basis sets can be found in the Supporting Information. The error introduced by the contraction is up to 2 Hz for 6-31G-J and only up to 1 Hz for 6-311G-J. Consequently, due to the contraction, the 6-311G-J basis set performs slightly better than the 6-31G-J basis set.

4. BENCHMARKING THE NEW BASIS SETS

4.1. DFT Calculations. The new basis sets were employed in calculations of the SSCCs of water, $^1J(\text{OH})$, methane, $^1J(\text{CH})$ and $^2J(\text{HH})$, ammonia, $^1J(\text{NH})$, ethane, $^1J(\text{CC})$ and $^3J(\text{HH})$, and formamide, (CH_3NO , FMA), $^1J(\text{CH})$, $^1J(\text{NH})$, $^1J(\text{CN})$, $^1J(\text{CO})$, $^2J(\text{HH})$, and $^3J(\text{HH})$; in total 12 one-, two-, and three-bond coupling constants. We compare the results obtained with the pcJ-2, aug-cc-pVTZ-J, pcJ-2*, pcJ-1, pcJ-1*, 6-31G, 6-31Guc,

Table 4. Mean (Absolute) Errors in Hz and % of the DFT/B3LYP Calculated Coupling Constants in the Test Set Relative to the Corresponding Results Obtained with the aug-pcJ-4 Basis Set

basis	size ^a CH_3NO	ME (Hz)	MAE (Hz)	ME (%)	MAE (%)
pcJ-2	225	−0.23	0.74	0.46	1.34
aug-cc-pVTZ-J	198	−0.07	0.23	0.19	0.73
pcJ-2*	165	−0.23	0.78	0.58	1.56
pcJ-1	111	−0.33	1.98	1.60	4.54
pcJ-1*	87	−0.33	1.99	1.71	4.69
6-31G	33	−1.72	7.40	11.63	25.75
6-31Guc	78	−0.23	12.96	19.49	25.34
6-31+G*	60	0.83	6.87	10.36	25.75
6-31++G**	72	2.14	6.03	7.98	24.36
6-31G-J	48	−3.10	5.37	2.12	17.33
6-31G-Juc	105	−3.21	4.51	1.09	13.50
6-31+G*-J	75	0.00	1.83	2.32	8.25
6-31++G**-J	87	0.06	1.33	2.32	6.26
6-311G	48	−1.37	7.44	9.97	22.40
6-311Guc	93	−0.56	10.34	15.24	21.33
6-311+G*	75	1.14	6.11	11.16	14.31
6-311++G**	87	1.61	6.46	12.72	13.28
6-311G-J	69	−2.75	4.50	1.90	14.08
6-311G-Juc	120	−2.95	4.32	1.37	13.11
6-311+G*-J	96	−0.48	1.57	2.00	5.88
6-311++G**-J	108	−0.07	0.87	1.38	3.54

^a Total number of basis functions for formamide in the given basis set. The aug-pcJ-4 basis set contains 789 basis functions for formamide.

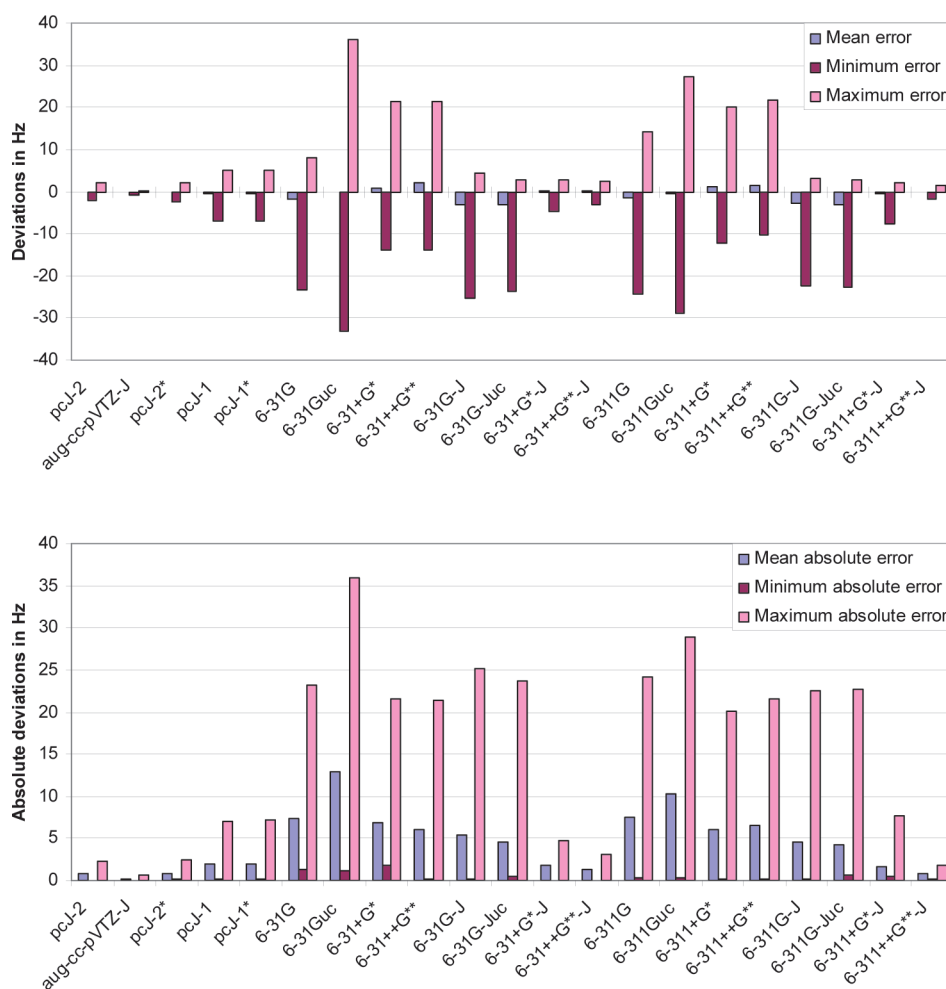


Figure 1. Mean, minimum, and maximum (top) and mean absolute, minimum absolute, and maximum absolute (bottom) errors in Hz of the SSCCs calculated with the given basis set relative to the aug-pcJ-4 result.

6-31+G*, 6-31++G**, 6-31G-J, 6-31G-Juc, 6-31+G*-J, 6-31++G**-J, 6-311G, 6-311Guc, 6-311+G*, 6-311++G**, 6-311G-J, 6-311G-Juc, 6-311+G*-J, and 6-311++G**-J basis sets with the corresponding results obtained with the aug-pcJ-4 basis set. We have chosen to use the aug-pcJ-4 results as reference, as this is the best possible basis set for DFT calculations of SSCCs that we are aware of. We include pcJ-2 in the comparison, as this is recommended for practical calculations,¹⁴ and aug-cc-pVTZ-J, as it is of approximately the same size as pcJ-2, but optimized for FC dominated couplings. We also include a pruned pcJ-2 basis set, pcJ-2*, where the tight p- and d-type functions are removed on hydrogen and the tight d- and f-type functions on non-hydrogen atoms, as these tight functions are not expected to be important for FC dominated couplings. We also include the pcJ-1 basis set, which is of approximately double- ζ quality, as well as its pruned counterpart pcJ-1*, which is of approximately the same size as our new Pople style basis sets.

Finally we include the new basis sets and their corresponding original Pople basis sets. Diffuse functions as well as polarization functions are expected to be important, and we added these functions to our basis sets, using the standard notation. The results are shown in Table 3, and the mean, maximum, and minimum deviations for each basis set are shown in Table 4 and in Figures 1 and 2.

The pcJ-2 and aug-cc-pVTZ-J basis sets are of approximately the same size, and both give excellent results for these couplings compared to the aug-pcJ-4 results. Nevertheless, the aug-cc-pVTZ-J basis set is slightly better for these couplings, which could be expected, as it is optimized for FC dominated couplings. For both pcJ-2* and pcJ-1* the results compare excellently with the results of their larger pcJ-2 and pcJ-1 counterparts, as expected for these couplings. The pcJ-1* performs slightly worse than the 6-311++G**-J basis set, which is also slightly larger. Compared to 6-31+G*-J, which contains fewer basis functions, the absolute deviations of the pcJ-1* results are slightly larger, while the relative deviations are smaller. The reason for this apparent discrepancy is that the relative deviations are dominated by the small $^2J(\text{HH})$ coupling constants, which are not as well described by the new Pople style basis sets.

For 6-31G we observe large errors, which are not reduced by uncontraction or addition of polarization and diffuse functions. The same trends are seen for 6-311G. For both 6-31G-J and 6-311G-J we see that the basis sets can systematically be improved by addition of polarization and diffuse functions. Especially diffuse and polarization functions on the second-row atoms are mandatory, while the polarization and diffuse functions are less important for hydrogen; the exception being the $^1J(\text{OH})$ coupling in combination with the 6-311++G**-J basis set, where

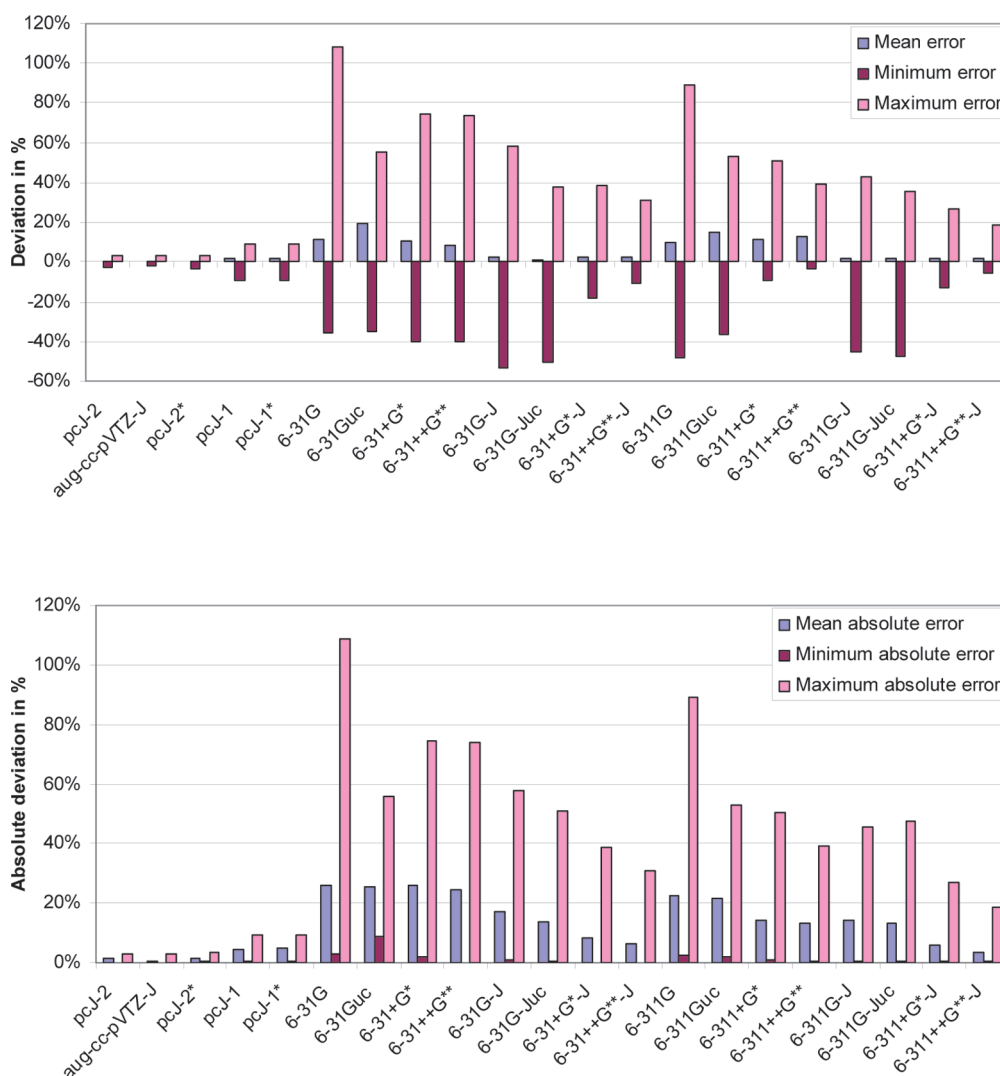


Figure 2. Mean, minimum, and maximum relative errors (top) and mean absolute, minimum absolute, and maximum absolute relative errors (bottom) in % of the SSCs calculated with the given basis set relative to the aug-pcJ-4 result.

we see a 6 Hz improvement relative to the 6-311+G*-J result. The 6-31+G*-J basis set gives results which deviate less than 5 Hz for all couplings, and 6-311++G**+J gives results which deviate less than 2 Hz for all couplings for the corresponding aug-pcJ-4 results. The largest error is observed for $^1J(\text{OH})$, even though $^1J(\text{CH})$ in formamide exhibits also a large error, however, this coupling is approximately 200 Hz. The relative errors are dominated by $^2J(\text{HH})$ in formamide, which is calculated to be 7.51 Hz by aug-pcJ-4. Here the errors with the new basis sets are between 1.4 and 4.4 Hz leading to the enormous relative errors in the figures. The $^2J(\text{HH})$, the $^3J(\text{HH})$, and the couplings involving oxygen are not completely dominated by the FC term. These couplings are thus not as well described by the new basis sets, even though the largest error produced by the 6-311++G**+J basis set is less than 2 Hz. Consequently these basis sets work well for FC dominated couplings but should be used with caution and only after careful benchmarking against better basis sets for couplings that have important contributions from the PSO, SD, and DSO terms. We have therefore not generated a corresponding basis set for fluorine, as fluorine couplings often

have very large contributions from especially the PSO term.^{10,12,14,44,52–54}

Furthermore we have only investigated the performance of the 6-31+G*-J basis set and not that of the 6-31+G-J and 6-31G*-J basis sets. For some couplings only the diffuse functions are important, as in $^1J(\text{NH})$ in ammonia, while for others the polarizations functions are important, as in $^1J(\text{CO})$ in formamide, and for others we need both contributions, as in $^1J(\text{OH})$ in water. Consequently one should always first test the effect of the different diffuse and polarization functions in order to see whether one could employ a smaller basis set.

Finally, we tested the performance of the new 6-31+G*-J basis set also for the $^1J(\text{NH})$ coupling constant of *N*-methylacetamide but did not include it in the test set, although it is also FC dominated. We find that the 6-31+G*-J result deviates by only 1.1 Hz from the corresponding aug-pcJ-4 result.

4.2. Correlated Wave Function Calculations. So far we have only investigated the performance of the new basis sets in DFT calculations and not in calculations with correlated wave function methods. However, the basis set dependence of correlated wave function methods differs from that of DFT. We have therefore

Table 5. Mean (Absolute) Errors in Hz and % of the SOPPA Calculated Coupling Constants in the Test Set Relative to the Corresponding Results Obtained with the aug-ccJ-pVQZ Basis Set

basis	ME (Hz)	MAE (Hz)	ME (%)	MAE (%)
ccJ-pVTZ	−0.12	0.81	0.43	1.67
aug-cc-pVTZ-J	−0.04	0.37	−0.35	1.37
6-31G	−1.08	8.03	13.25	41.44
6-31Guc	−0.24	8.94	15.55	24.59
6-31+G*	1.09	6.73	12.73	31.84
6-31++G**	2.41	6.76	10.56	29.88
6-31G-J	−2.40	7.24	0.39	29.79
6-31G-Juc	−2.64	6.34	−3.32	23.53
6-31+G*-J	0.06	3.12	2.82	14.59
6-31++G**-J	0.42	1.93	3.02	11.06
6-311G	−0.87	4.99	8.22	31.56
6-311Guc	−0.53	6.70	11.53	14.91
6-311+G*	1.10	4.36	10.51	18.62
6-311++G**	1.64	5.06	11.53	14.91
6-311G-J	−2.30	6.43	−1.60	24.63
6-311G-Juc	−2.48	6.22	−3.25	22.61
6-311+G*-J	−0.53	2.56	1.77	10.95
6-311++G**-J	0.01	1.38	1.03	6.70

also carried out the calculations of the previous section at the SOPPA level. The results are given in the Supporting Information. For these calculations we compared to the aug-ccJ-pVQZ basis set¹⁵ because the ccJ-pVXZ basis sets were optimized for correlated wave function calculations in contrast to the pcJ-*n* family of basis sets. The augmentation functions are taken from aug-cc-pVQZ. Due to the computational cost of the ccJ-pVSZ and aug-ccJ-pVSZ, we could not obtain the results of these basis sets for all the investigated molecules. For water and ammonia we could obtain both the aug-ccJ-pVSZ and the ccJ-pVSZ results, and in both cases the aug-ccJ-pVQZ results differed less than 0.1 Hz from the aug-ccJ-pVSZ results, and the aug-ccJ-pVQZ results were closer to the aug-ccJ-pVSZ results than the ccJ-pVSZ results. For methane and ethane where we could obtain the ccJ-pVSZ results, the aug-ccJ-pVQZ differed less than 0.3 Hz from the ccJ-pVSZ results. So it seems that the aug-ccJ-pVQZ results will be converged with respect to the aug-ccJ-pVSZ basis set, and therefore we will employ this in the benchmarking of the new Pople style basis sets. The statistics are shown in Table 5. We observe in general the same trends as for DFT, however, the errors relative to the reference calculations are slightly larger than in the DFT calculations. The 6-31+G*-J results deviate now less than 8 Hz from the aug-ccJ-pVQZ results, while 6-311++G**-J gives results which deviate less than 3 Hz from the aug-ccJ-pVQZ results. They are still superior to the original Pople basis sets, but they are not performing quite as well for SOPPA as they were in the DFT calculations, however, they will still be useful for SOPPA-calculations on large molecules.

5. SUMMARY

For the calculation of NMR indirect nuclear spin–spin coupling constants we present modified 6-31G and 6-311G Pople basis sets. The new basis sets, called 6-31G-J and 6-311G-J, have the same number of contracted p-type functions

and twice the number of contracted s-type functions as the original Pople basis sets. These basis sets can further be augmented with the polarization and diffuse functions of the standard Pople basis sets.

The performance of the new basis sets has been evaluated with DFT/B3LYP and SOPPA calculations on a test set of 12 one-, two- and three-bond coupling constants. We find that polarization and diffuse functions on the second-row atoms are mandatory, while the polarization and diffuse functions on hydrogen are less important, except in the case of ¹J(OH). The 6-31+G*-J basis set gives DFT results that deviate less than 5 Hz from the aug-ccJ-4 results for the 12 couplings investigated in this study, and 6-311++G**-J deviates less than 2 Hz from the aug-ccJ-4 results. At the SOPPA level, the maximum deviations from aug-ccJ-pVQZ results are 8 and 3 Hz, respectively.

These basis sets are only optimized for the calculation of FC dominated couplings and are not expected to give accurate results for couplings where the PSO, DSO or SD contributions will be important. Furthermore we have observed that the couplings involving oxygen and the ²J(HH) couplings are not as accurately described as the other couplings. Therefore these new basis sets are excellent for DFT calculations of FC dominated SSCCs, but they can also be employed in calculations with correlated wave functions. However, in the latter case the inclusion of polarization and diffuse functions on hydrogen is mandatory.

■ ASSOCIATED CONTENT

S Supporting Information. Final contracted 6-31G-J and 6-311G-J basis sets. In addition all SOPPA results for the SSCCs are given. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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■ ACKNOWLEDGMENT

The authors thank the Danish Center for Scientific Computing (DCSC) and the Danish Natural Science Research Council/The Danish Councils for Independent Research (grant number 272-08-0486) for financial support.

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