

## Optimized Basis Sets for the calculation of Indirect Nuclear Spin-Spin Coupling Constants Involving the Atoms B, Al, Si, P and Cl

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(Dated: 27 June 2010)

The aug-cc-pVTZ-J series of basis sets for indirect nuclear spin-spin coupling constants has been extended to the atoms B, Al, Si, P and Cl. The basis sets were obtained according to the scheme previously described by Provasi et al. [J. Chem. Phys 115, 1324-1334 (2001)]. First the completely uncontracted correlation consistent aug-cc-pVTZ basis sets were extended with four tight *s* and three tight *d* functions. Secondly the *s* and *p* basis functions were contracted with the molecular orbital coefficients of self-consistent-field calculations performed with the uncontracted basis sets on the simplest hydrides of each atom. As a first illustration we have calculated the one-bond indirect spin-spin coupling constants in  $\text{BH}_4^-$ , BF, AlH, AlF,  $\text{SiH}_4$ ,  $\text{SiF}_4$ ,  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{SF}_6$ , HCl and ClF at the level of density functional theory using the Becke three parameter Lee-Yang-Parr (B3LYP), and the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes - SOPPA(CCSD).

Keywords: Indirect nuclear spin-spin coupling constants, aug-cc-pVTZ-J basis set, B3LYP functional, SOPPA(CCSD)

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## I. INTRODUCTION

It is well known that the indirect nuclear spin spin coupling constant,  $J$ , is very sensitive to structural changes, which makes it a powerful tool for determining molecular structures as well as conformations. However, calculations of indirect nuclear coupling constants are also intrinsically difficult<sup>127-130</sup> because uncorrelated calculations at the self-consistent-field (SCF) level are often not even qualitatively correct due to triplet-instabilities<sup>131-136</sup>, a problem well known from semi-empirical calculations<sup>137-144</sup>. Furthermore, standard energy optimized basis sets are not flexible enough to represent the operators involved in the calculation of indirect nuclear spin-spin coupling constants correctly<sup>145-148</sup>. Accurate calculations of  $J$  require therefore correlated methods, such as the second order polarization propagator approximation (SOPPA)<sup>134,149-155</sup>, the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes - SOPPA(CCSD)<sup>134,156</sup>, the multiconfigurational self-consistent field linear response method<sup>157</sup>, various Coupled Cluster based methods such as EOM-CCSD<sup>158-160</sup>, CCSD<sup>161</sup> or CC3<sup>161</sup> or density functional theory (DFT)<sup>162-167</sup> with appropriate functionals and the use of large basis sets optimized for coupling constants.

The need for highly correlated methods makes it necessary to employ small basis sets optimized specially for indirect coupling constant, if one wants to study molecules with more than a couple of atoms. Furthermore it is desirable that such basis sets can be applied in calculations using at least some DFT functionals as well as correlated wave function methods.

Several groups have therefore recently developed slightly different approaches to modify standard basis sets in an easy-to-implement manner in order to produce such basis sets<sup>134,135,168-176</sup>. They are all based on the fact that the Fermi contact operator contains a delta function and thus measures the electron density at the position of the nucleus which is not well described by standard basis sets.

We had taken as the starting point of our development of such optimized basis sets<sup>134,135,170,177-179</sup> the correlation consistent aug-cc-pVTZ basis sets by Dunning and co-workers<sup>180-182</sup>. The calculations in the optimization steps were carried out at the SOPPA although the original study was performed at the level of self-consistent-field (SCF) linear response theory<sup>134</sup>. The final approach<sup>134,135,177</sup> consisted of total uncontraction of the original basis sets, addition of

four tight  $s$  functions for H, C, N, O and S as well as three additional sets of  $d$  functions for the elements of the third row, Si and S, and removal of the most diffuse second polarization function in the aug-cc-pVTZ basis sets. The addition of tight functions was done in an even-tempered manner with the ratio of the two largest exponents of the original basis set.

However, these basis sets, called aug-cc-pVTZ-Juc<sup>135</sup>, are rather large basis sets, which restricts their use to relatively small systems. One possibility for reducing the size of the basis set in calculations would be to use locally dense basis sets, *i.e.* to use basis sets adequate for coupling constant calculations only on the atoms in question<sup>136,170,172</sup>. Another possibility is reducing the size of the basis set by contracting the occupied atomic orbital functions in the basis set again. Earlier, Geertsen<sup>148</sup> or Guilleme and San Fabián<sup>169</sup> recontracted the basis sets with the SCF molecular orbital coefficients of the molecule in question following a segmented contraction scheme. However, this would require to generate a new basis set for each molecule studied, which is rather inconvenient. We had thus generalized this idea and employed the SCF molecular orbital coefficients of the simplest hydrides of each atom in question, which lead us to the aug-cc-pVTZ-J sets<sup>135</sup>. Recently, Jensen<sup>176</sup> presented also a contracted version of his pcJ-n series of basis sets employing a more general search strategy.

Peralta and co-workers could show that the aug-cc-pVTZ-J basis sets perform also very well in DFT calculations<sup>171,183</sup> and give results in close agreement with a much larger basis set based on the correlation consistent cc-pCV5Z basis set<sup>184</sup>. Deng *et al.*<sup>173</sup> recently wrote that it is unfortunate that the aug-cc-pVTZ-J basis sets are only available for H, C, N, O, F and S. Furthermore, very recently it was shown<sup>185</sup> that in DFT calculations of NMR shielding constants the aug-cc-pVTZ-J basis sets can even give results in close agreement with complete basis set estimates from the pcS-n<sup>62</sup> and pcJ-n basis sets<sup>174</sup> of Jensen. The purposes of this paper is therefore to fill this gap and to report aug-cc-pVTZ-J basis sets also for B, Al, P, Si and Cl.

In the papers, by Peralta *et al.* and Deng *et al.* as well as many other DFT calculations of spin-spin couplings<sup>163–167,171,186–190</sup> the Becke three parameter Lee-Yang-Parr (B3LYP) hybrid functional is employed<sup>191,192</sup>. Therefore, in this work we study the convergence of the basis sets at the SOPPA(CCSD) level and test them also with the DFT/B3LYP method.

## II. DETAILS OF THE CALCULATIONS

The theory of indirect nuclear spin-spin coupling constants and of the different response theory methods for calculating them has extensively been described in the literature<sup>127,134,165,193,194</sup>. Here we want to mention only that there are four contributions: the Fermi contact term (FC) and the spin-dipolar term (SD), which come from the interaction of the nuclear magnetic moments with the spin of the electrons as well as the orbital dia- (DSO) and paramagnetic (PSO) contributions which are due to the interaction of the nuclear spins with the orbital angular momentum of the electrons.

All calculations of the indirect spin spin coupling constants were performed with the 2.0 version of the Dalton program package<sup>195</sup>. Calculation were performed at the DFT/B3LYP<sup>165,191,192</sup> and SOPPA(CCSD)<sup>134,156</sup> level of theory.

The geometries employed in the current study are all equilibrium geometries, experimental or optimized and are taken from earlier publications:  $\text{BH}_4^-$  from ref.<sup>177</sup>, BF and AlF from ref.<sup>196</sup>, AlH from ref.<sup>134</sup>,  $\text{SiH}_4$ ,  $\text{SiF}_4$ ,  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{H}_2\text{S}$  and  $\text{SF}_6$  from ref.<sup>173</sup>, ClF from ref.<sup>197</sup> and finally HCl from ref.<sup>198</sup>.

## III. BASIS SET DEVELOPMENT

### A. Uncontracted Basis Sets

The main aim of this work was to extend the aug-cc-pVTZ-J series of basis sets with basis sets of the same quality and structure for the new atoms B, Al, P, Si and Cl. This implies decontraction of the original aug-cc-pVTZ basis set, addition of four tight *s*-type functions and three tight *d*-type functions for the third row atoms as well as removal of the most diffuse *f*-type function followed by contraction with the SCF molecular orbital coefficients. However, we have used the occasion to re-investigate the validity of this scheme by testing also other correlation consistent basis sets as well as the addition of tight *p*- and *f*-type functions. Results of this extended investigation are presented in Figures 1 and 2 for two representative molecules,  $\text{PH}_3$  and  $\text{SiH}_4$ , both at the SOPPA(CCSD) and DFT/B3LYP level. Tables with the corresponding results are given as supplementary material<sup>199</sup>. We have chosen two hydrides as test molecules in order to be able to carry out SOPPA(CCSD) calculations with basis sets as large as the aug-cc-pV6Z basis set. In addition we have tested

our scheme for the two fluorides SF<sub>2</sub> and ClF but only with the aug-cc-pVTZ. Results of this study are shown in Figures 3 and 4 and tabulated in the supplementary material<sup>199</sup>.

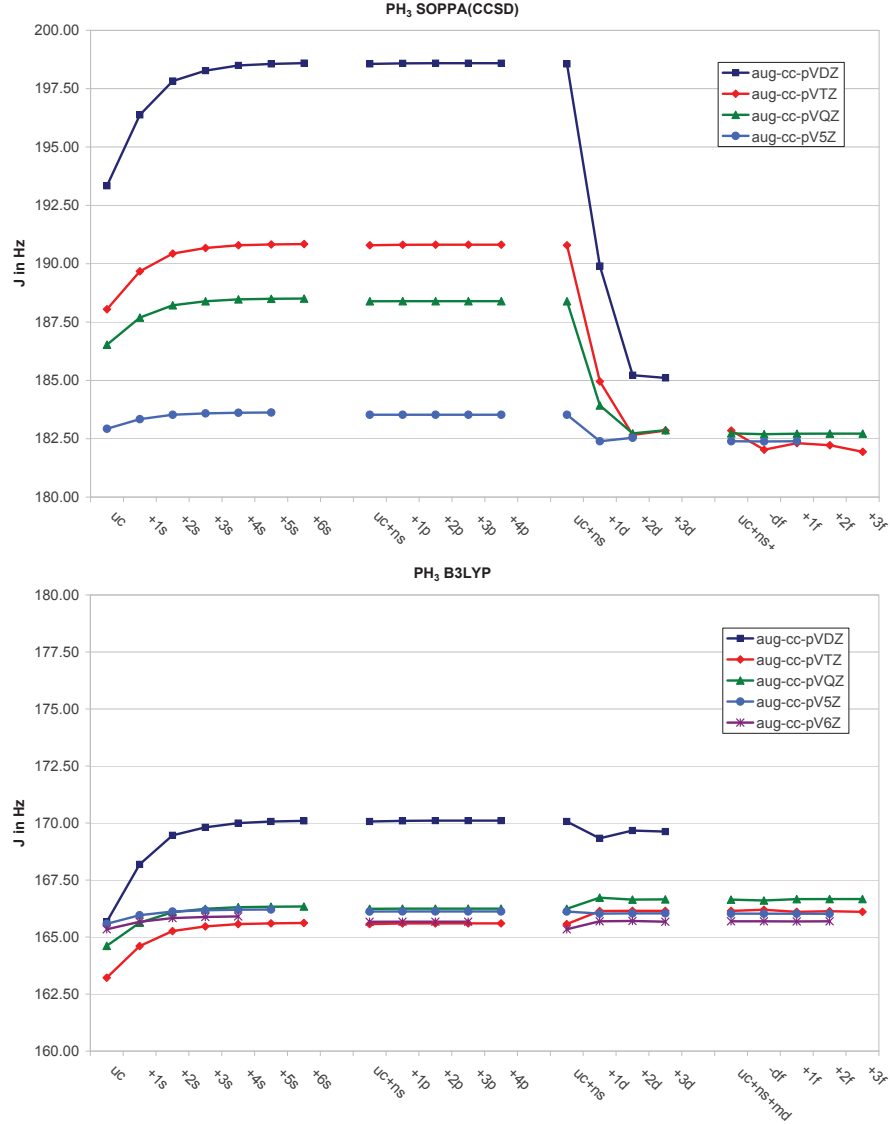


FIG. 1. Convergence of the one-bond spin spin coupling constant in PH<sub>3</sub> for aug-cc-pVXZ basis sets by Dunning *et al* at SOPPA(CCSD) and B3LYP levels.

We started from the original aug-cc-pVXZ (with X = D, T, Q, 5 and 6) basis sets by Dunning and co-workers<sup>180–182</sup> and uncontracted them. Tight *s*-type functions were added then until saturation was reached. The addition of the tight functions is done in an even-tempered manner using the ratio of the two largest exponents of the original basis set. Jensen<sup>174</sup> could recently show that this is not the most cost effective way. One can obtain results of same quality with a smaller number of extra tight functions, if one increases the

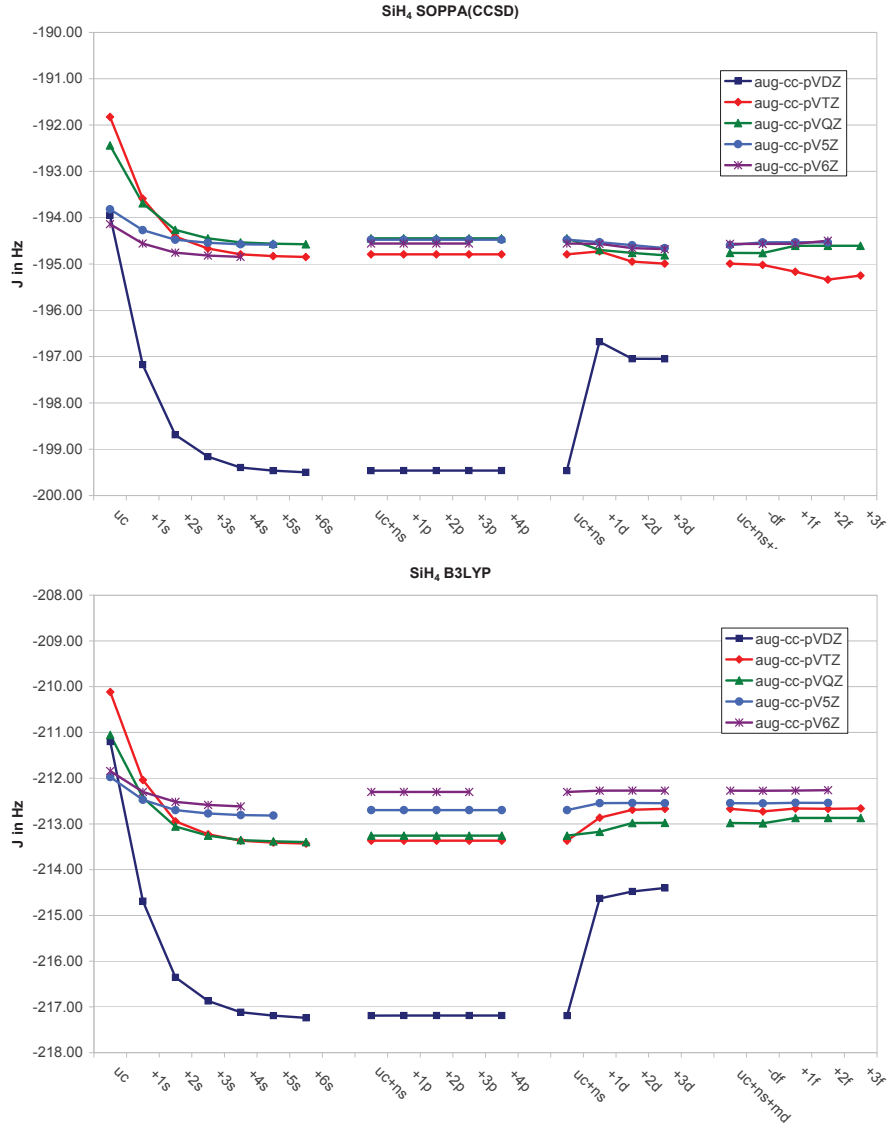


FIG. 2. Convergence of the one-bond spin spin coupling constant in  $\text{SiH}_4$  for aug-cc-pVXZ basis sets by Dunning *et al* at SOPPA(CCSD) and B3LYP levels.

ratio between them. However, in order to be consistent with the existing aug-cc-pVTZ-Juc basis sets we continue with an even-tempered series. Besides, the difference becomes irrelevant when the basis sets are contracted as in the aug-cc-pVTZ-J basis sets. Depending on the cardinal number  $X$  different numbers of tight  $s$ -type functions were necessary: 5 for  $X = D$ , 4 for  $X = T$ , 3 for  $X = Q$ , 2 for  $X = 5$  and 1 for  $X = 6$ . To these basis sets we added tight  $p$ -type functions. But for most of the systems studied in this work, with the exception of ClF, we found no significant effect of the extra tight  $p$ -type functions. For ClF the addition of an extra tight  $p$ -type function generates changes comparable to the

ones introduced but the addition of the four extra tight  $s$ -type functions. In both cases changes are within 1 Hz which is approximately 0.1% of the total. This fact does not imply that an extra  $p$ -type function has to be included but rather that the four extra tight  $s$ -type functions are not really necessary for this special molecule. Therefore these  $p$ -type functions were removed and  $d$ -type functions were added instead until saturation was reached. Finally the most diffuse  $f$ -type function was removed and tight  $f$ -type functions were added which did not give rise to any significant change in the coupling constants as can be seen in figures 1 and 2.

The most commonly observed behavior is the one shown in figures 1 and 2. In the case of  $\text{PH}_3$  we have not included the results of the SOPPA(CCSD) calculations with the modified aug-cc-pV6Z basis sets, because a triplet instability or quasi-instability appeared, when the basis set was uncontracted. The same happens also in the SOPPA(CCSD)/(aug-cc-pV5Z +3d) and SOPPA(CCSD)/(aug-cc-pV5Z +3f) calculations. In Figures 3 and 4 we illustrate the effect of adding additional tight functions to the aug-cc-pVTZ basis set for  $\text{SF}_2$  and  $\text{ClF}$ . We observe a small effect ( 1%) of the additional  $f$ -type functions but only at the SOPPA(CCSD) level.

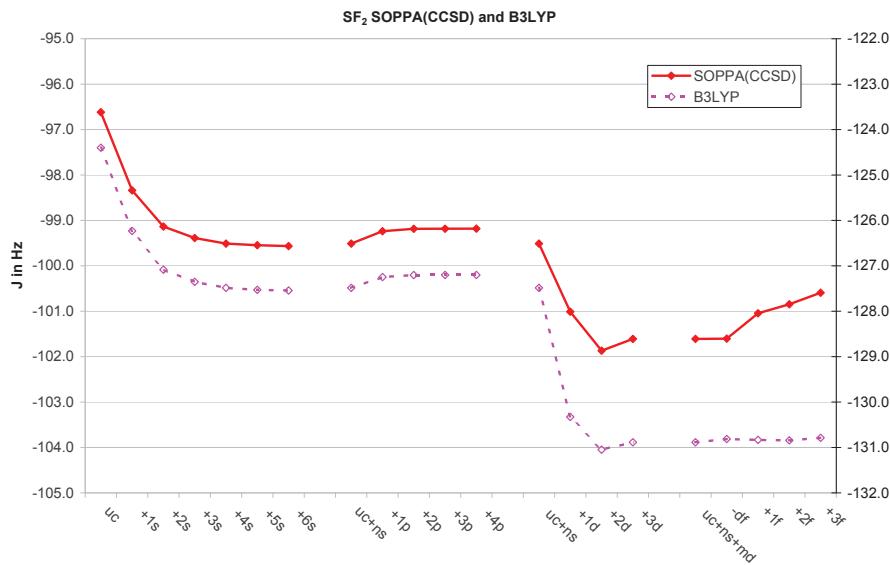


FIG. 3. Convergence of the one-bond spin spin coupling constant in  $\text{SF}_2$  for aug-cc-pVTZ basis sets by Dunning *et al* at SOPPA(CCSD) (left axis) and B3LYP levels (right axes).

We can see from the figures that the results obtained with the "aug-cc-pVTZ+4s+3d–diffuse f function" basis set differ by less than 1 Hz (or 1 % for the fluorides) from the results with

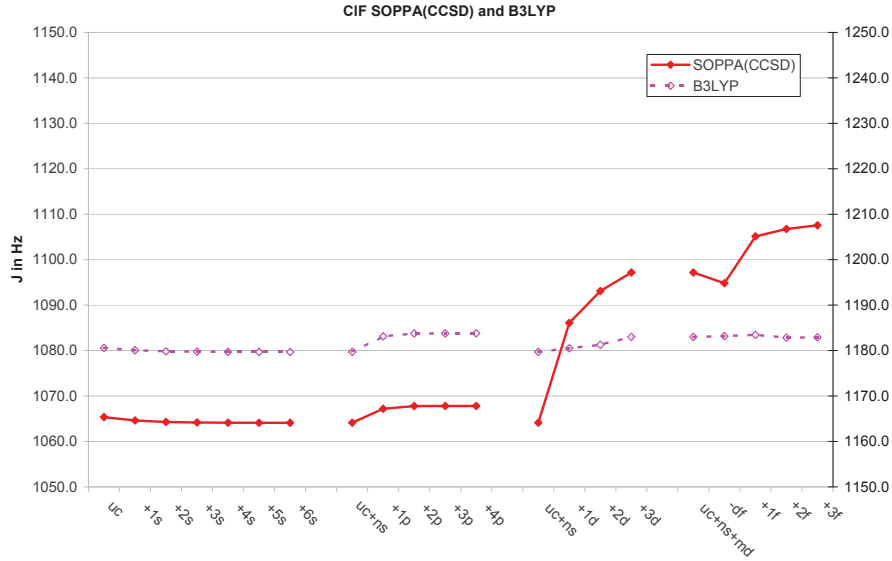


FIG. 4. Convergence of the one-bond spin spin coupling constant in CIF for aug-cc-pVTZ basis sets by Dunning *et al* at SOPPA(CCSD) (left axis) and B3LYP levels (right axes).

the largest basis sets at the SOPPA(CCSD) level and even less at the DFT/B3LYP level. We choose therefore this basis set as our aug-cc-pVTZ-Juc for P, Si, Al and Cl and the "aug-cc-pVTZ+4s–diffuse f function" basis set for B. The final aug-cc-pVTZ-Juc basis sets consist then of (15s6p3d1f) functions for B and (20s10p6d1f) functions for Al, Si, P and Cl. The details of the basis sets, i.e. the exponents of the additional functions, have already been reported for B (basis set II in<sup>134</sup>), and Si<sup>177,200</sup>, whereas the aug-cc-pVTZ-Juc basis set for Al is essentially basis set II from<sup>134</sup> but extended with three sets of tight  $d$  functions with exponents  $\zeta_d = 1.017, 3.108, 9.495$ . Finally, the exponents of the additional functions for P and Cl were newly generated: four tight  $s$  functions (P:  $\zeta_s = 2085336, 13920068, 92919431, 620257056$ , Cl:  $\zeta_s = 905429579, 135645698, 20321575, 3044449$ ) and three sets of tight  $d$ -functions (P:  $\zeta_d = 1.97, 5.94, 17.9$ ; Cl:  $\zeta_d = 29.407, 9.671, 3.180$ ) were added and the most diffuse set of  $f$  functions was removed. Details of the basis sets for H, S and F have been published previously<sup>134,135,170,201,202</sup>.

## B. Contraction of the Basis Sets

The converged uncontracted basis sets obtained in the previous section III A are still rather large and therefore mainly useful for calculations on small molecules. A convenient



TABLE I. One-bond spin-spin coupling constants (in Hz) obtained with the aug-cc-pVTZ-Juc and aug-cc-pVTZ-J basis sets at the B3LYP and SOPPA(CCSD) levels: Fermi contact contribution, total coupling constant as well as the absolute and per cent errors in the Fermi contact term and the total coupling due to the contraction in the aug-cc-pVTZ-J basis sets.

Molec.	Method	aug-cc-VTZ-Juc		aug-cc-VTZ-J		Error (Hz)		Error (%)	
		FC	Total	FC	Total	FC	Total	FC	Total
BH <sub>4</sub> <sup>-</sup>	B3LYP	87.57	88.31	87.94	88.65	0.37	0.34	0.43	0.39
	SOPPA(CCSD)	74.87	75.46	75.06	75.63	0.19	0.17	0.26	0.22
AlH	B3LYP	5.15	3.44	5.14	3.39	-0.01	-0.05	-0.22	-1.50
	SOPPA(CCSD)	9.14	6.75	9.09	6.64	-0.05	-0.11	-0.60	-1.60
SiH <sub>4</sub>	B3LYP	-212.85	-212.67	-214.36	-214.17	-1.51	-1.50	0.71	0.70
	SOPPA(CCSD)	-195.34	-194.98	-196.30	-195.94	-0.96	-0.96	0.49	0.49
PH <sub>3</sub>	B3LYP	160.45	165.89	162.96	168.39	2.51	2.50	1.57	1.51
	SOPPA(CCSD)	177.81	181.94	179.16	183.29	1.36	1.35	0.76	0.74
H <sub>2</sub> S	B3LYP	19.52	24.08	20.10	24.71	0.59	0.63	3.01	2.62
	SOPPA(CCSD)	26.70	30.74	26.99	31.08	0.29	0.33	1.08	1.08
HCl	B3LYP	8.34	24.53	9.17	25.46	0.83	0.94	9.89	3.82
	SOPPA(CCSD)	21.99	36.89	22.37	37.38	0.38	0.49	1.72	1.33
BF	B3LYP	-242.56	-347.07	-244.09	-348.80	-1.53	-1.72	0.63	0.50
	SOPPA(CCSD)	-206.74	-301.77	-206.09	-301.48	0.65	0.29	-0.32	-0.10
AlF	B3LYP	-502.45	-680.41	-507.25	-685.42	-4.80	-5.01	0.96	0.74
	SOPPA(CCSD)	-437.31	-595.81	-441.29	-600.45	-3.98	-4.64	0.91	0.78
SiF <sub>4</sub>	B3LYP	272.09	350.96	272.68	351.50	0.59	0.54	0.22	0.15
	SOPPA(CCSD)	124.23	192.54	123.32	191.38	-0.91	-1.16	-0.73	-0.60
PF <sub>3</sub>	B3LYP	-1329.96	-1607.82	-1337.71	-1615.30	-7.75	-7.48	0.58	0.47
	SOPPA(CCSD)	-1170.22	-1390.45	-1175.92	-1396.36	-5.70	-5.91	0.49	0.43
SF <sub>6</sub>	B3LYP	-299.83	-323.97	-301.41	-325.50	-1.58	-1.53	0.53	0.47
	SOPPA(CCSD)	-255.47	-270.08	-256.52	-271.12	-1.05	-1.04	0.41	0.39
ClF	B3LYP	-107.53	1013.90	-109.72	1012.71	-2.19	-1.19	2.04	-0.12
	SOPPA(CCSD)	-122.84	937.49	-124.29	938.42	-1.45	0.93	1.18	0.10

way of reducing their size is by contraction. The contraction scheme we use is a generalization of the idea of Geertsen<sup>148</sup> and Guilleme and San Fabián<sup>169</sup>, which consists of using the SCF molecular orbital coefficients of the simplest hydride one can form for the atom in question<sup>135</sup>, i.e. BH, AlH, SiH<sub>4</sub>, PH<sub>3</sub> and HCl. In preliminary calculations we have investigated how much the results will change on using *e.g.* the molecular orbital coefficients from the DFT/B3LYP calculation instead of the SCF calculation as contraction coefficients. However, we found that this changes the contraction coefficients by less than 10% and the most

sensitive coupling constant by only 0.2 Hz, which is in agreement with our earlier findings<sup>135</sup>. Also using the molecular orbital coefficients of other molecules than the smallest hydrides did not change the contraction coefficients significantly<sup>203</sup>. The aug-cc-pVTZ-J basis sets consist then of (15s6p3d1f) contracted to [9s5p3d1f] functions for B and (20s10p6d1f) contracted to [10s7p6d1f] functions for Al, Si, P and Cl. For the contraction we used a general contraction scheme where we included in the contraction all primitive Gaussian functions, whose molecular orbital coefficients are only slightly changed on going from one molecule to another. The remaining primitive basis functions were kept uncontracted. For B we generated one contracted *s*- and *p*-type function whereas for Al - Cl two. In addition we have successively added the most diffuse primitive functions from the contraction. The final contraction pattern became then for B 15s  $\rightarrow$ (13 1 1 1 1 1 1 1), 6p  $\rightarrow$ (5 1 1 1 1) and for Al - Cl 20s  $\rightarrow$ (17 17 1 1 1 1 1 1 1), 10p  $\rightarrow$ (7 7 1 1 1 1 1). Details of the basis sets are given in the **supplementary material**<sup>199</sup>.

In the following we will discuss the errors introduced by this contraction and which term is most affected by it. The Fermi contact contribution and the total coupling constants obtained with the aug-cc-pVTZ-Juc and aug-cc-pVTZ-J basis sets at the B3LYP and SOPPA(CCSD) level are shown in Table I. The absolute and percentage deviations of the results obtained with the contracted basis set from the results obtained with the aug-cc-pVTZ-Juc basis set are also included in the tables.

We can see that the errors in the SSCCs introduced by contraction of the aug-cc-pVTZ-Juc basis sets are at most 1.5 Hz at the SOPPA(CCSD) level or 2.5 Hz at the B3LYP level for the molecules studied here with the two exceptions AlH and PF<sub>3</sub>. In the latter two cases the absolute errors are larger due to much larger coupling constants, while in percent the errors amount to less than 1%. Comparing the SOPPA(CCSD) with the B3LYP results we observe that, in most cases, the contraction affects the B3LYP results more. We have mentioned earlier that employing the B3LYP Kohn-Sham orbital coefficients as contraction coefficients instead of the Hartree-Fock molecular orbitals has a minimal effect on the coupling constants. The explanation must therefore be sought in the intrinsic different basis set dependence of DFT and wave function methods. With the exception of the two silicon compounds the absolute errors are smaller for the hydride compounds, whereas in percent the errors are typically smaller for the fluorides and are always less than 1%.

Analyzing which term is most affected by the contraction, we can conclude that the FC

TABLE II. One-bond spin-spin coupling constants (in Hz) obtained with the aug-pcJ-n series<sup>174</sup>, the UGBS2P<sup>204,205</sup>, and the aug-cc-pVTZ-J basis sets and the Gaussian version of the B3LYP functional.

Molecule	SiH <sub>4</sub>		PH <sub>3</sub>		H <sub>2</sub> S		SiF <sub>4</sub>		PF <sub>3</sub>		SF <sub>6</sub>	
	FC	Total	FC	Total	FC	Total	FC	Total	FC	Total	FC	Total
aug-pcJ-0	-200.0	-199.8	91.4	95.7	-2.6	1.6	464.4	559.2	-1060.4	-1382.0	-272.2	-297.8
aug-pcJ-1	-209.2	-209.1	146.8	152.2	16.6	21.2	299.9	381.4	-1355.2	-1637.5	-294.1	-317.0
aug-pcJ-2	-214.4	-214.4	166.6	172.3	21.2	25.9	272.0	353.9	-1333.5	-1618.9	-301.2	-325.0
aug-pcJ-3	-211.6	-211.5	160.2	165.7	19.6	24.2	266.5	347.5	-1325.3	-1608.0	-299.5	-323.5
aug-pcJ-4	-211.7	-211.6	159.3	164.9	19.5	24.1	265.0	346.0	-1323.6	-1606.4	<i>c</i>	<i>c</i>
UGBS2P <sup>173</sup>	-210.0	-209.9	158.4	164.0	19.3	23.9	262.4	343.1	-1312.0	-1595.0	-296.1	-320.5
aug-cc-pVTZ-J	-214.5	-214.3	162.9	168.3	20.1	24.7	272.7	351.5	-1337.8	-1615.4	-301.4	-325.5
$\Delta(\text{UGBS2P})^a$	-4.5	-4.4	4.4	4.3	0.8	0.8	10.3	8.4	-25.8	-20.4	-5.3	-5.1
$\Delta\%(\text{UGBS2P})^a$	2%	2%	3%	3%	4%	4%	4%	3%	2%	1%	2%	2%
$\Delta(\text{aug-pcJ-4})^b$	-2.8	-2.7	3.5	3.4	0.6	0.6	7.7	5.5	-14.2	-9.0	-1.89	-1.98
$\Delta\%(\text{aug-pcJ-4})^b$	1%	1%	2%	2%	3%	2%	3%	2%	1%	1%	< 1% <sup>d</sup>	< 1% <sup>d</sup>

<sup>a)</sup> Deviation of the aug-cc-pVTZ-J results from UGBS2P results.

<sup>b)</sup> Deviation of the aug-cc-pVTZ-J results from aug-pcJ-4 results.

<sup>c)</sup> The calculation do not converge. <sup>d)</sup> Deviation of the aug-cc-pVTZ-J results from aug-pcJ-3 results.

term is the dominating source of the deviations with the exception of ClF. This molecule, however, is a special case and will be discussed in more detail in a later section IV B. For all but AlH and SiF<sub>4</sub> the absolute value of the FC term is slightly overestimated with the contracted basis set, as we have already observed in the first paper on the aug-cc-pVTZ-J basis sets<sup>135</sup>.

In order to be able to compare the performance of our new basis sets with the much larger UGBS2P basis sets (H: 20s20p20d; F: 24s40p40d16f; Si, P and S: 27s46p46d19f)<sup>204,205</sup> employed in the work of Deng *et al.*<sup>173</sup> we have also carried out calculations with the Gaussian version of the B3LYP functional. The results and deviations from the results obtained by Deng *et al.* with the UGBS2P basis sets are given in Table II. In all cases, the couplings

calculated with aug-cc-pVTZ-J basis set have larger absolute values than the UGBS2P results similar to the comparison with the uncontracted aug-cc-pVTZ-Juc basis set. The differences between the aug-cc-pVTZ-J and UGBS2P results of Deng *et al.*<sup>173</sup> are small and almost completely due to the Fermi contact term. The differences are between 1% and 2% with the exception of H<sub>2</sub>S, where the difference is as high as 4% but only 0.8 Hz in absolute values.

In addition we compare in Table II also with the aug-pcJ-n series of basis sets of Jensen<sup>174</sup>. We can see that the aug-cc-pVTZ-J basis sets give results lying somewhere between the results of the aug-pcJ-2 and aug-pcJ-3 basis sets, despite the fact that the aug-cc-pVTZ-J basis set is smaller than the aug-pcJ-2 basis set. This holds not only for the hydrides but also for the fluoride containing molecules. Compared to the largest basis set in this series, aug-pcJ-4, we observe even smaller differences as in the comparison with the UGBS2P basis set.

We conclude from both comparisons that the aug-cc-pVTZ-J basis sets are also for the third row atoms Si, P and S able to reproduce results of B3LYP calculations with much larger basis sets as it was shown previously for the first and second row atoms by Peralta and co-workers<sup>171</sup>.

#### IV. DISCUSSION OF THE CALCULATED COUPLINGS

During the development of the basis sets we have calculated couplings for a series of simple hydrides and fluorides of the atoms B, Al, P, Si, S and Cl. In the following we will discuss different trends exhibited by these coupling constants.

##### A. Comparison with Experiment

In Table III we present results for the one-bond coupling constants  $J$  (in Hz) and for the reduced one-bond coupling constants  $K$ , and all four contributions to  $K$ , obtained with the aug-cc-pVTZ-J basis set and the two methods used in this study, *i.e.* B3LYP and SOPPA(CCSD). The comparison of reduced coupling constants has the advantage that the differences in analogous couplings between different atoms are then solely due to the differences in electronic structure and not the possibly quite different nuclear g-factors.

We have also listed all the experimental, mostly liquid phase values (converted to reduced coupling constants), that we are aware of. One can see that the agreement between theory and experiment is very good in accordance with earlier studies<sup>134,135,177,179,188,189,200,206–226</sup>. The differences are under 12 % and therefore clearly within the range of what can be expected from vibrational correction<sup>147,148,157,177,186,188,189,200,206–213,218,219,227–237</sup> and solvent contributions<sup>190</sup>, which were not included in our calculations.

## B. Differences between hydrides and fluorides

Comparing now the one-bond couplings in the hydrides and fluorides only at SOPPA(CCSD) level, we observe firstly that the coupling in the majority of the hydrides is dominated by the FC term whereas the fluorides have also a significant PSO contribution. There are, however, three exceptions: the PSO term in AlH amounts to a significant fraction of the FC term; the ratio between the PSO and FC term is in H<sub>2</sub>S larger than in SF<sub>6</sub> and finally HCl, where the PSO term is 2/3 of the FC term. The interhalogen compound ClF stands apart from the other systems, because of its very large non-contact, *i.e.* PSO and SD, terms, which dominate the total coupling. This behavior is quite typical for couplings between atoms with more than one lone-pair<sup>135,160,172,215,216,244,245</sup>. The PSO term is thus the largest contribution in ClF and is more than six times as large as the FC term. The SD terms are less than 4% of the total couplings with the exception of AlH, where it amounts to 6%, SF<sub>2</sub> where it amounts 47% and ClF again, where it is a 32 % of the total coupling, *i. e.* the second largest contribution in the latter two cases. The DSO terms, finally, are negligible in all compounds.

Morover we can see that the FC contribution to the reduced coupling constants is positive for all hydrides studied here and negative for the corresponding fluorides. The decrease observed in the FC term is a well known effect of the lone pairs of fluorine (see Ref.<sup>246,247</sup> and therein cited references). As a consequence also the total reduced coupling constants of the hydrides are positive and negative for the fluorides with the exception of ClF, because it is dominated by the large and positive PSO and SD contributions.

Comparison of the results from the DFT/B3LYP and the correlated wave function method, SOPPA(CCSD), calculations (see Figure 5) corroborates the known fact that DFT/B3LYP underestimates the coupling constant which involve fluorine atoms, whereas

TABLE III. Reduced one-bond spin-spin coupling constants  ${}^1J$  (in Hz) and  ${}^1K$  (in  $10^7$  rad s $^{-1}$  T $^{-1}$ ) obtained with the aug-cc-pVTZ-J basis sets at SOPPA(CCSD) level.

Molec.	Method	K				J	
		DSO	PSO	SD	FC	Total	Total
BH $_4^-$	B3LYP	0.07	0.08	0.03	22.81	23.00	88.65
	SOPPA(CCSD)	0.08	0.06	0.01	19.47	19.62	75.63
	Exp. <sup>a</sup>					20.9 - 21.5	80.7 - 83
AlH	B3LYP	-0.03	-0.86	0.33	1.64	1.08	3.39
	SOPPA(CCSD)	-0.03	-0.88	0.13	2.90	2.12	6.64
SiH $_4$	B3LYP	0.01	-0.15	0.06	89.75	89.68	-214.17
	SOPPA(CCSD)	0.01	-0.17	0.01	82.19	82.04	-195.94
	Exp. <sup>b</sup>					84.29±0.17	-201.3±0.4
PH $_3$	B3LYP	0.00	1.28	-0.17	33.48	34.60	168.39
	SOPPA(CCSD)	0.00	1.09	-0.24	36.81	37.66	183.29
	Exp. <sup>c</sup>					38.77	188.7
	Exp. <sup>d</sup>					37.44±0.06	182.2±0.3
H $_2$ S	B3LYP	-0.01	5.05	-0.05	21.78	26.77	24.71
	SOPPA(CCSD)	-0.01	4.57	-0.14	29.24	33.67	31.08
HCl	B3LYP	-0.02	13.44	0.41	7.78	21.61	25.46
	SOPPA(CCSD)	-0.02	12.48	0.28	18.98	31.72	37.38
	Exp. <sup>e</sup>					32	38
BF	B3LYP	-0.11	-26.96	-1.80	-67.27	-96.13	-348.80
	SOPPA(CCSD)	-0.11	-24.92	-1.27	-56.80	-83.09	-301.48
AlF	B3LYP	-0.02	-59.53	-0.87	-172.04	-232.46	-685.42
	SOPPA(CCSD)	-0.03	-52.91	-1.05	-149.67	-203.65	-600.45
SiF $_4$	B3LYP	0.25	-37.17	1.86	-121.30	-156.36	351.50
	SOPPA(CCSD)	0.25	-32.38	1.85	-54.85	-85.13	191.38
	Exp. <sup>f</sup>					-79.2	178
PF $_3$	B3LYP	0.17	-68.75	7.98	-292.00	-352.59	-1615.30
	SOPPA(CCSD)	0.17	-56.41	8.12	-256.68	-304.80	-1396.36
	Exp. <sup>g</sup>					-314.5	-1441
SF $_2$	B3LYP	0.12	38.39	58.54	-248.40	-151.34	-131.49
	SOPPA(CCSD)	0.11	63.16	55.02	-235.87	-117.58	-102.16
ClF	B3LYP	0.07	692.67	319.28	-98.93	913.08	1012.71
	SOPPA(CCSD)	0.07	690.64	267.46	-112.07	846.10	938.42
	Exp. <sup>h</sup>					757±5	840±6

<sup>a</sup> depending on counterion and solvent<sup>238,239</sup>

<sup>b</sup> in pure liquid<sup>200</sup>

<sup>c</sup> in complex solution<sup>240</sup>

<sup>d</sup> in neat liquid<sup>241</sup>

<sup>e</sup> in liquid phase<sup>242</sup>

<sup>f</sup> in neat liquid<sup>243</sup>

<sup>g</sup> in neat liquid<sup>243</sup>

<sup>h</sup> in unknown phase<sup>197</sup>

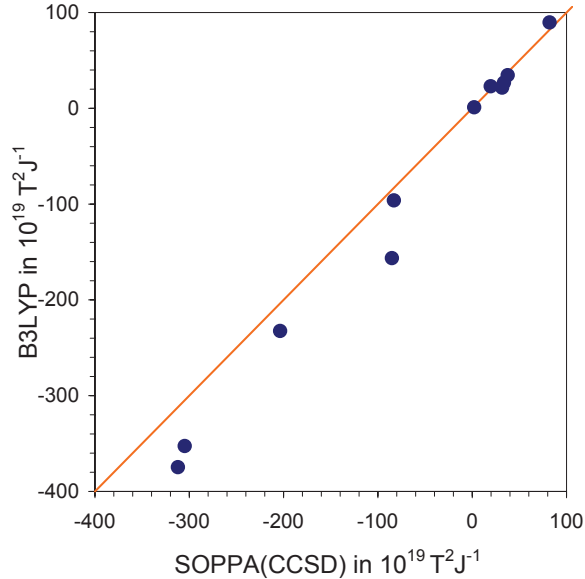


FIG. 5. Correlation plots for FC reduced coupling constants in  $10^7 \text{ rad s}^{-1} \text{ T}^{-1}$ : B3LYP versus SOPPA(CCSD).

the correlation is almost perfect for hydrides. And as explained above such a behavior is mainly due to the FC term. The exception in the present series of compounds is ClF which has an FC term that is overestimated by the DFT/B3LYP calculation.

## V. CONCLUDING REMARKS

We present aug-cc-pVTZ-Juc and aug-cc-pVTZ-J basis sets for the calculation of indirect nuclear spin-spin coupling constants for the atoms B, Al, Si, P and Cl. We show that the selection of functions in the aug-cc-pVTZ-Juc basis set is very well justified as it gives results in close agreement with the results obtained by extending the correlation consistent basis sets aug-cc-pVXZ, with  $X = \text{D, T, Q, 5}$  and  $6$ .

The contraction of aug-cc-pVTZ-Juc basis set to the aug-cc-pVTZ-J basis set using the Hartree-Fock molecular orbital coefficients obtained for the smallest hydrides allows a reduction in the basis set size without a significant loss in accuracy. Comparison at the DFT/B3LYP level with calculations carried out with the much larger UGBS2P and aug-pcJ-4 basis sets show that the aug-cc-pVTZ-J basis sets are also for the third row atoms able to reproduce the results of much larger basis sets.

As a first application of the new basis sets we have calculated the one-bond indirect

spin-spin coupling constants in the hydrides and fluorides of B, Al, Si, P, S and Cl with the aug-cc-pVTZ-J basis sets at the DFT/B3LYP level and employing SOPPA(CCSD) method. We find that, for the equilibrium geometry, the SOPPA(CCSD) results of the one-bond couplings are in good agreement with the available experimental values.

With respect to the four contributions to the coupling constants we observe that the one-bond couplings in the majority of the hydrides are dominated by the FC term whereas the fluorides have also significant PSO terms, which is also true for some of the hydrides because the importance of the PSO increase with the atomic number. The coupling in ClF, however, exhibits a completely different pattern of contributions and is dominated by very large PSO and SD terms.

## ACKNOWLEDGMENT

This research was made possible by grants from the Danish Center for Scientific Computing (DCSC) and the financial support from the Carlsberg Foundation and from the Danish Natural Science Research Council / The Danish Councils for Independent Research (SPAS grant number 272-08-0486 ). The authors acknowledge also support from CONICET and UNNE (PFP) and CU-DNRC (SPAS).



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