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Some Difficult Cases**

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On the Convergence of the ccJ-pVXZ and pcJ-n Basis Sets in CCSD Calculations of Nuclear Spin-Spin Coupling Constants: Some Difficult Cases

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Abstract The basis set convergence of nuclear spin-spin coupling constants (SSCC) calculated at the coupled cluster singles and doubles (CCSD) level has been investigated for ten difficult molecules. Eight of the molecules contain fluorine atoms and nine contain double or triple bonds. Results obtained using the ccJ-pVXZ, X=D,T,Q,5, hierarchy of basis sets of Benedikt et al. [J. Chem. Phys. **129**, 064111 (2008)], converge rather slowly towards the basis set limit, but fast convergence can be obtained by adding diffuse functions, in particular for couplings across several bonds. The pcJ-*n* basis sets of Jensen [J. Chem. Theory Comput. **2**, 1360 (2006)] exhibit large contraction errors for one-bond couplings, but in their uncontracted form they perform better than the ccJ-pVXZ basis sets. For multi-bond couplings, however, diffuse functions should be used, and when including these the two hierarchies show similar performance. The ccJ-pVXZ basis sets with diffuse functions included (aug-ccJ-pVXZ) show consistent performance across all types of SSCCs, with the triple zeta (X=T) basis set yielding sufficiently good results for most purposes.

Keywords NMR spin-spin coupling constants · Basis set · Coupled Cluster · CCSD · ccJ-pVXZ · pcJ-n

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1 Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a very commonly used analytical tool in chemistry. The widespread use of NMR-spectroscopy makes accurate calculations of the associated properties, the nuclear shielding and the indirect nuclear spin-spin coupling constant (SSCC), an important topic. While empirical "rules-of-thumb" are often sufficient for assigning spectra of some nuclei, like ^1H and ^{13}C , in common chemical environments, this will not be the case when investigating new types of systems, with little or no back catalogue of similar compounds to compare to. Furthermore, if conformational information is needed, empirical rules will often not be sufficient.

The theory required for the calculation of nuclear SSCCs is well developed [1–3]. However, the details of this theory, in particular the operators involved, imply that it is very challenging to calculate SSCCs with high accuracy. One of the main obstacles encountered is that the calculation of SSCCs involves triplet operators and thus reliable results cannot be obtained unless the electronic structure method used yields a ground state description that is stable towards such perturbations. In particular the response of the common Hartree-Fock (HF) method to such a perturbation is nearly singular in many cases [2, 4–8]. DFT has become a popular approach for the calculation of SSCCs, but inclusion of exact HF exchange in hybrid functionals may bring along the triplet instability problem again [9]. Correlation treatments that explicitly include the HF response, e.g. relaxed coupled cluster methods are also affected [10]. The other main challenge for accurate calculations of SSCCs is the choice of the one-electron basis. While this choice is without doubt critical for any electronic structure calculation, it is particularly crucial when calculating SSCCs as they are extremely sensitive to the description of the wavefunction close to the nuclei; a region not sufficiently well described using basis sets that are optimized for the calculation of electronic energies [11–13]. An often used approach is to take a normal, energy-optimized basis set and add additional tight s-functions in an even tempered series. Helgaker et al. [14, 15] have used various basis sets augmented in this manner with the s-functions uncontracted, and the convention of adding *-s n* to the name. The aug-cc-pVTZ-J set [8, 16–22] and the 6-31G-J and 6-311G-J basis sets [23] of Sauer et al. are similar, but with the s-functions recontracted.

While s-functions are the only ones which will directly contribute to the Fermi-Contact (FC) term, other types of functions may be needed for a good description of the remaining terms of the SSCCs. This is particularly important for SSCCs that are not dominated by the Fermi-Contact contribution. Jensen [24] has explored the importance of adding tight basis functions of higher angular momenta. In studies on improving the basis set convergence of DFT calculations he found that it was necessary to add also tight p-, d- and f-functions to the pc series of basis sets [25, 26] in order to uniformly improve the basis set convergence of all contributions to the SSCC. On the basis of this work the pcJ series of basis sets was proposed. A similar study for calculations using correlated wavefunctions was performed by Benedikt et al. [27]. They

performed CCSD calculations with Dunning’s correlation consistent basis sets and found once more that both p- and d-functions were required in order to evenly improve basis set convergence. Based on their findings Benedikt et al. proposed the ccJ-pVXZ series of basis sets, which are based on Dunning’s cc-pVXZ, X=D,T,Q,5, basis sets [28].

Although a number of basis sets have been proposed for the calculation of SSCCs, only a few of them have been extensively tested [29–32] for correlated methods outside the relatively small set of molecules used for fitting the exponents. Furthermore, the pcJ-n and ccJ-pVXZ hierarchies have been developed without diffuse functions. While this gives a consistent common baseline for optimization, the use of diffuse “augmentation” functions has become common and these are available for the closely related pc-n [26] and cc-pVXZ basis sets [33].

In the present work we will compare the performance of the pcJ-n and cc-pVXZ series of basis sets and their augmented and totally uncontracted versions in CCSD calculations of SSCCs. Contrary to earlier studies, our test set of molecules was chosen so each molecule has fluorine atoms and/or double or triple bonds, which are typically associated with large non-contact contributions [19, 32, 34–38]. This will allow us to test the importance of including optimized functions for these contributions and to test how well each series manages to give a balanced description of each. Furthermore, there has recently been a lot of interest in calculations of through-space couplings involving F atoms [39–41], which makes a better understanding of the basis set dependence of F-couplings an interesting goal to be achieved.

2 Theory

The indirect nuclear spin-spin coupling tensor can be defined as the second derivative of the electronic energy with respect to the spins of the two nuclei involved [2, 42]

$$J_{KL,\alpha\beta} = \frac{\partial^2 E}{\partial I_\alpha^K \partial I_\beta^L} \quad (1)$$

where I_α^K is the $\alpha \in \{x, y, z\}$ component of the nuclear spin of nuclei K . In gas or solvent phase experiments, the molecules rotate freely and only the trace of the coupling tensor is observable. In the present work we will therefore focus on the trace of the coupling tensor, which we will refer to as the spin-spin coupling constant (SSCC):

$$J_{KL} = \frac{1}{3} \sum_{\alpha \in \{x, y, z\}} J_{KL,\alpha\alpha} \quad (2)$$

Nuclear spins enter the electronic Hamiltonian through their magnetic moments, and what is obtained directly in theoretical calculations are thus the reduced coupling constants, K , defined in terms of the second derivative of the energy with respect to the nuclear fields. K thus represents the unscaled

result from the electronic structure calculation. However, the unit of K is different from the unit of J and it is therefore difficult to relate a K value to a J value. When we refer to reduced coupling constants in the present paper, we shall instead refer to \tilde{K} , which we define by simply scaling J using the nuclei specific unitless g-factors, g ,

$$J_{KL} = g_K g_L \tilde{K}_{KL}, \quad (3)$$

meaning that \tilde{K} will have the same unit (Hz) as J . When comparing the computational accuracy of SSCC calculations between different kinds of nuclei it is better to use the reduced couplings constants, as these represent the unscaled result from the electronic structure calculations and their differences reflect the changes in electronic structure and not just a different nuclear g-factor. When considering any particular SSCC, however, we will revert to the more familiar J coupling constants.

In non-relativistic theory the part of the perturbation which is linear in the nuclear magnetic moment splits into three distinct contributions, the Fermi-Contact (FC), spin-dipolar (SD) and paramagnetic spin-orbit (PSO) interactions. The associated perturbing operators can be written as

$${}^{FC}\hat{O}_\alpha^K \propto \sum_i \delta(\mathbf{r}_i - \mathbf{R}_K) \hat{s}_{i,\alpha} \quad (4)$$

$${}^{SD}\hat{O}_\alpha^K \propto \sum_i \left((r_{i,\alpha} - R_{K,\alpha}) \frac{\sum_\beta (r_{i,\beta} - R_{K,\beta}) \hat{s}_{i,\beta}}{|\mathbf{r}_i - \mathbf{R}_K|^5} - \frac{\hat{s}_{i,\alpha}}{|\mathbf{r}_i - \mathbf{R}_K|^3} \right) \quad (5)$$

$${}^{PSO}\hat{O}_\alpha^K \propto \sum_i \frac{\hat{l}_{i,\alpha}^K}{|\mathbf{r}_i - \mathbf{R}_K|^3}, \quad (6)$$

where $\hat{s}_{i,\alpha}$ is a component of the electron spin operator of electron i , \mathbf{r}_i and \mathbf{R}_K are the position vectors of the electron i and nucleus K and $\hat{l}_{i,\alpha}^K$ is a component of the orbital angular momentum of electron i around nucleus K . There is also a contribution, which is bi-linear in the nuclear magnetic moments of two nuclei,

$${}^{DSO}\hat{O}_{\alpha\beta}^{KL} \propto \sum_i \frac{(r_{i,\alpha} - R_{K,\alpha})(r_{i,\beta} - R_{L,\beta})}{|\mathbf{r}_i - \mathbf{R}_K|^3 |\mathbf{r}_i - \mathbf{R}_L|^3}. \quad (7)$$

When considering which basis set to use in the calculation of SSCCs, it should be realized that, in order to give good energies, a basis set needs to represent the wavefunction well enough near the nuclei to describe the nuclear-electron attraction well. That interaction behaves as the inverse of $|\mathbf{r}_i - \mathbf{R}_K|$. The operators in equations (4-7), however, fall off much faster and the FC term explicitly depends only on the wavefunction at the nucleus. Thus, the flexibility of the wavefunction at the position of the nuclei is critical in order to accurately describe perturbations of this kind. Hydrogenic atomic orbitals have a cusp at the nucleus, a behavior which cannot be exactly reproduced using Gaussian basis functions. Still, it is generally believed that the addition

of very tight s-type basis function is sufficient to give an accurate description of the FC interaction. Recent developments by McKemmish et al. [43,44] make it feasible to replace the Gaussians representing the inner s-type orbitals with "ramp" functions showing the correct cusp-behavior at the nuclei, which might allow for a good description of the FC contribution to the SSCCs with much fewer basis functions. However, to our knowledge, this has so far not yet been further investigated. While only s-functions can contribute directly to the FC interaction, other types of basis functions could be considered for improving the description of the remaining contributions. Indeed the operators defined above are much more sensitive to the behaviour near the nucleus than the potential energy operator. Acting with the SD operator of a nucleus on a s-type function centered on that same nucleus yields a function with d-symmetry. The PSO operator of a nucleus yield zero, when applied to a function, that has s-symmetry around that nucleus. As both of these operators fall off as the third power of the electron-nucleus distance, we would expect their contributions to require functions of non-zero angular momentum, which are tighter than those present in common energy optimized basis sets. Indeed, it has previously been demonstrated by Jensen et al. [24,27] that this is the case.

One should mention here that alternative forms of both the FC and DSO have been derived [45–47] which lead to different basis set requirements. However, they are not yet commonly employed and will therefore not be considered further here.

3 Computational Details

The geometries of all molecules were optimized using the CCSD(T) [48] method and the aug-cc-pCVQZ [49,33,50] basis set, except for difluoro-acetylene where a cc-pCVQZ geometry was used in order to give results that are directly comparable to previous work [32]. The SSCCs of all molecules were calculated using the unrelaxed CCSD method and the (aug-)ccJ-pVXZ, X=D,T,Q,5 [27] and (aug-)pcJ-n, n=1,2,3 [24] basis sets. The aug-ccJ-pVXZ basis sets were not proposed in the original work, but can easily be constructed by adding the diffuse functions of the aug-cc-pVXZ basis set [33] as additional uncontracted functions to the ccJ-pVXZ basis set. Both of these series of basis sets have been optimized for the calculation of the total nuclear spin-spin coupling constants. The aug-cc-pVTZ-J basis set of Sauer et al. [8,16–22] has been used for comparison, as an example of what can be obtained when the basis set is only augmented with s-type functions. Results obtained using the qzp basis set [51] are also presented, as this basis set has often been used in CCSD calculations of SSCCs [52–54]. All calculations have been performed using version 1.0 of the CFOUR program [55].

4 Results

In Table 1 we give the CCSD values obtained with the uncontracted aug-ccJ-pV5Z basis set for all molecules in the study. These are values that will be assumed to be converged to the basis set limit for the purpose of the comparisons in the following sections. One may of course wonder whether complete basis set extrapolated values would be more suitable for use in this comparison. However, in many cases we found uneven or oscillating convergence towards the basis set limit, and were thus not confident that any such extrapolated values would be reliable enough to use as a benchmark, as will be discussed in the final section.

These CCSD/aug-ccJ-pV5Z-unc results are compared to experimental results in Table 1. Perfect agreement with the experimental values should not be expected. This would require a proper treatment of both vibrational corrections [56–61] and solvent effects [62], which are not the topic of the present study.

In the following we will discuss only results for the total SSCC. While the different terms of the SSCC require different modifications to the basis set, the basis set series investigated here is designed to converge uniformly across all of them. Indeed they all seem to converge evenly to the point that a detailed discussion of each term would be of little use. Equivalents of figures 1-3 are given in the supplementary material (figures S1-S9).

The molecules discussed here have previously been investigated by Del Bene et al. [52,53], using the rather small qzp [51] basis and the "CI-like" EOM-CCSD method [63,64], which differs from the CCSD unrelaxed energy derivatives used in the present work. The results presented by Del Bene et al. are in general similar to ours, there is not a clear trend for which are closer to the experimental values. One example where the difference between the results are large is the $^1J_{\text{CN}}$ in HCN, where the results of Del Bene is -12.6 Hz, which is far from both our aug-ccJ-pV5Z result, -18.1 Hz and the experimental results, -19.1 Hz and -18.5 Hz. This may be a geometry issue, as our qzp value is -18.0 Hz, due to a favorable contraction error of 2.0 Hz. The results also differ significantly for the SSCCs of F_2CO , which again should be due to a difference in geometry as our qzp values are closer to our other results.

Jaszuński et al. [65] previously presented MCSCF results for *cis*- and *trans*-FNNF. They were able to obtain results in agreement with experiment for all but the symmetric couplings in *trans*-FNNF by changing the active space and basis set used, but they were not able to find one approach that consistently gave good results for all couplings.

4.1 One-bond Couplings

Figure 1 compares for each basis set the mean absolute deviation of the results for the reduced coupling constants (\hat{K} in Hz) obtained with the given basis set from the corresponding aug-ccJ-pV5Z-unc results. There are a few conclusions

Table 1 CCSD values of all SSCCs in the study (in Hz), as obtained in calculations using the largest basis set, aug-ccJ-pV5Z-unc. Some experimental results are given for comparison. All results are given in Hz for the ^1H , ^{13}C , ^{15}N , ^{17}O and ^{19}F isotopes.

	SSCC	FC	SD	PSO	DSO	Total	Experimental			
CO	$^1J_{\text{CO}}$	7.61	-5.17	13.30	0.10	15.84	16.4(1)	[66]		
	$^1J_{\text{CH}}$	256.63	0.48	-0.62	0.39	256.87	267.3(1)	[67]	261.7(4)	[68]
HCN	$^1J_{\text{CN}}$	-12.67	-5.28	-0.16	0.04	-18.08	-19.1	[69]	-18.5(1)	[67]
	$^2J_{\text{HN}}$	-4.07	-0.73	-3.55	0.62	-7.74	-8.7	[70]	-7.41	[68]
FCN	$^1J_{\text{CF}}$	-358.72	-10.50	-29.59	0.55	-398.26				
	$^1J_{\text{CN}}$	4.62	-5.80	-4.83	-0.03	-6.05				
OF ₂	$^2J_{\text{FN}}$	42.27	-10.21	17.08	0.41	49.55				
	$^1J_{\text{OF}}$	127.35	-157.41	-243.71	-0.40	-274.17	-300(30)	[71]		
FNO	$^2J_{\text{FF}}$	74.86	415.64	723.88	-1.01	1213.37				
	$^1J_{\text{NO}}$	-19.49	0.76	-16.60	-0.01	-35.34				
F ₂ CO	$^1J_{\text{NF}}$	136.69	-17.22	26.25	-0.27	145.46				
	$^2J_{\text{CO}}$	-33.07	-2.78	155.33	0.26	119.75				
F ₂ CO	$^1J_{\text{CO}}$	9.70	-3.67	7.15	-0.13	13.04				
	$^1J_{\text{CF}}$	-257.43	-0.05	-38.77	1.16	-295.08	-308	[72]		
FCCH	$^2J_{\text{OF}}$	-3.68	-4.74	47.30	0.32	39.19				
	$^2J_{\text{FF}}$	124.24	24.82	-256.55	-1.10	-108.59				
FCCH	$^1J_{\text{CC}}$	250.74	9.85	11.68	0.16	272.42				
	$^1J_{\text{CF}}$	-251.38	-10.36	-21.89	0.48	-283.15				
FCCH	$^1J_{\text{CH}}$	275.50	0.43	-0.82	0.43	275.54				
	$^2J_{\text{CF}}$	13.32	18.00	-4.26	-0.88	26.17				
FCCF	$^2J_{\text{CH}}$	61.84	1.01	5.77	-1.13	67.49				
	$^3J_{\text{FH}}$	-1.17	2.98	13.80	-2.62	12.98	21	[73]		
FCCF	$^1J_{\text{CC}}$	383.01	10.80	15.52	0.31	409.64				
	$^1J_{\text{CF}}$	-247.93	-8.02	-9.20	0.58	-264.58	287.3	[74]		
FCCF	$^2J_{\text{CF}}$	19.20	19.14	6.65	-0.69	44.30				
	$^3J_{\text{FF}}$	6.90	33.11	-32.94	-1.85	5.22	2.1	[74]		
<i>cis</i> -FNNF	$^1J_{\text{NN}}$	2.67	1.76	-4.54	0.03	-0.08	± 4.0	[75]		
	$^1J_{\text{NF}}$	244.42	-19.64	-12.13	-0.33	212.32	211.0	[75]		
<i>cis</i> -FNNF	$^2J_{\text{NF}}$	-47.57	-2.13	34.98	0.17	-14.54	-25.4	[75]		
	$^3J_{\text{FF}}$	150.18	42.03	-319.73	0.04	-127.48	-146.0	[75]		
<i>trans</i> -FNNF	$^1J_{\text{NN}}$	-10.33	1.43	-8.66	0.02	-17.53	-18.5	[75]		
	$^1J_{\text{NF}}$	220.41	-21.06	-21.47	-0.30	177.58	172.8	[75]		
<i>trans</i> -FNNF	$^2J_{\text{NF}}$	-62.10	-6.29	9.67	0.06	-58.66	-62.8	[75]		
	$^3J_{\text{FF}}$	21.26	52.05	-372.86	-2.29	-301.83	-316.4	[75]		

that are immediately apparent from Fig. 1. The contraction coefficients of the normal ccJ-pVXZ series of basis sets are nearly optimal for the calculation of this type of coupling constants, as completely uncontracting the basis sets (blue bars) changes neither the mean nor the maximum deviation significantly. However, this is no longer the case when diffuse functions are added. In terms of the maximum deviation, the aug-ccJ-pVXZ basis sets are a major improvement over the ccJ-pVXZ basis sets, at least at the triple and quadruple zeta level. For example, the deviation from the aug-ccJ-pV5Z-unc result for $^1\tilde{K}_{\text{NN}}$ in *cis*-FNNF is reduced from 3.5 Hz to 0.24 Hz, when diffuse functions are added to ccJ-pVTZ, and the deviation for $^1\tilde{K}_{\text{NO}}$ in FNO is reduced from 2.1 Hz to 1.2 Hz. However, the diffuse functions do not provide a similar improvement in the average performance unless the contraction is removed. Uncontracting

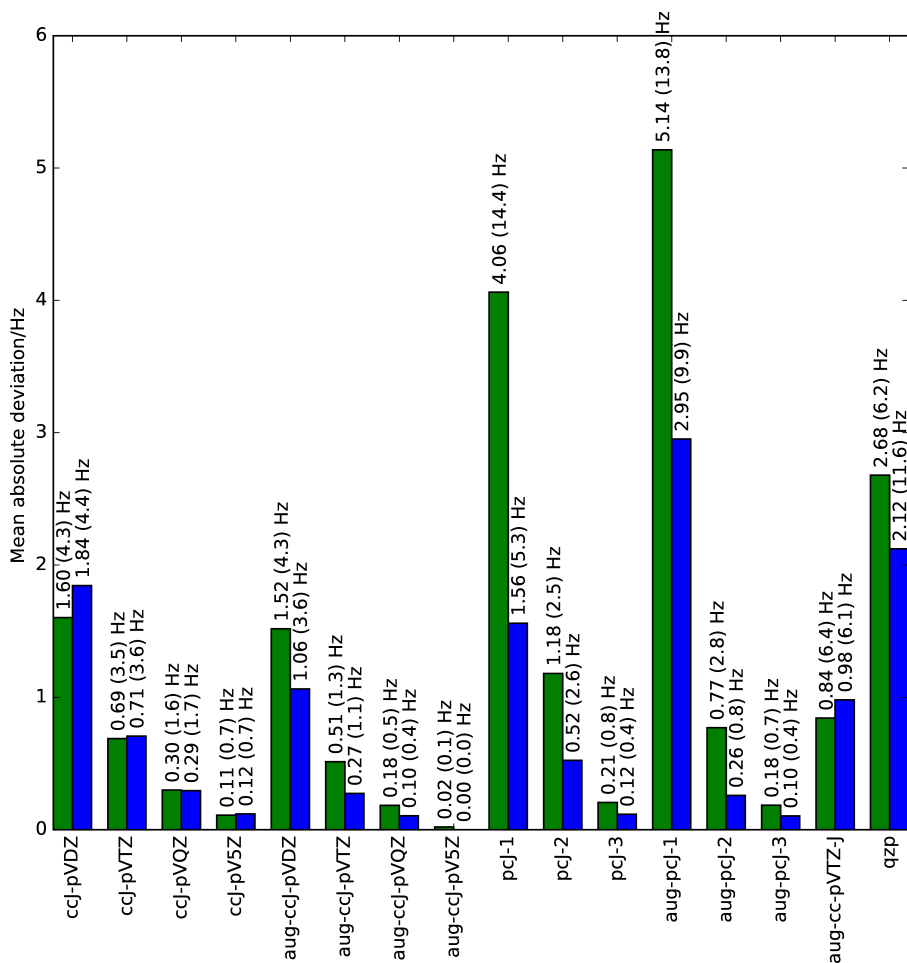


Fig. 1 One-bond reduced coupling constants (\bar{K} in Hz): The mean average deviation from the aug-ccJ-pV5Z-unc results obtained using the basis sets. Green bars represent the results obtained with contraction of the basis functions, blue bars represent the results obtained with all functions uncontracted. Values in brackets are the maximum deviation found amongst all the one-bond couplings. There are 19 total one-bond couplings in the set.

the aug-ccJ-pVTZ and aug-ccJ-pVQZ improves average performance of these basis sets by roughly a factor of two compared to the contracted versions and by almost a factor of three compared to basis sets without diffuse functions. On the other hand, the maximum deviation of the aug-ccJ-pVTZ and aug-ccJ-pVQZ basis sets change only slightly when contraction is removed. For the aug-ccJ-pVTZ, e.g., the largest deviation is found for ${}^1\bar{K}_{\text{OF}}$ in OF_2 , which is 1.3 Hz with contraction and 1.1 Hz without. We can thus conclude that the addition of diffuse functions is important for obtaining good results for the one-bond SSCs studied here, but also that the contraction scheme of the ccJ-pVXZ basis sets is no longer optimal for the augmented basis sets.

Turning our attention to Jensen’s pcJ basis sets, it is once again clear that contraction errors will be an important part of the discussion. Here it is important to note that the pcJ sets and thus also their contractions were optimized for DFT calculations rather than CCSD calculations. Nonetheless, it is surprising that there is a factor of two between the mean average deviation of the results obtained using the contracted and fully uncontracted version of the pcJ-2 basis set. The one outlier here is ${}^1\tilde{K}_{\text{NN}}$ of *cis*-FNNF, where the deviation from aug-ccJ-pV5Z-unc is slightly increased from 2.4 Hz to 2.6 Hz, when the contraction is removed from pcJ-2. However, that does not change the overall impression that while the functions included in the pcJ basis set are very well chosen, the contraction coefficients are suboptimal for the couplings or computational method studied here. When diffuse functions are added to the pcJ-1 basis set, the results obtained are even worse than those obtained without them. Considering the larger aug-pcJ basis sets the results are on the line with what is observed for the aug-ccJ sets, though the max absolute deviation is worse, unless contraction is removed. It should be mentioned that Jensen has published a second contraction scheme for the pcJ basis sets using a segmentet scheme, and were able to obtain a decreased contraction error in B3LYP [76]. However, even if that result is transferable to CCSD calculations, the contraction errors observed here are so large that reducing them, even by a factor of two, it would still be advantageous to avoid contractions for one-bond SSCCs.

The aug-cc-pVTZ-J basis set performs badly compared to the other triple-zeta basis sets for the couplings in the present study. In particular for one SSCC, the ${}^1\tilde{K}_{\text{OF}}$ coupling in OF_2 , the deviation is as much as 6.4 Hz! This particular SSCC has very large contributions from the SD and PSO contributions and it is therefore not surprising that a basis set, such as aug-cc-pVTZ-J, designed for the calculation of the FC contribution only, struggles to accurately describe it. Indeed the aug-cc-pVTZ-J basis set has errors of more than 3 Hz for both the SD and PSO contributions to this coupling. The errors in the other coupling constants are more in line with what is observed for the ccJ and pcJ basis set. Indeed the average error in the FC term is lower for the aug-cc-pVTZ-J than the other triple zeta basis sets if the contraction versions are used. In the case of aug-ccJ-pVTZ the contraction error furthermore partially cancels the basis set error, and so removing the contraction leads to larger average errors than all other uncontracted triples-zeta basis sets, even for the FC term alone. Still, the relatively unsatisfying results for aug-cc-pVTZ-J show that it is not always sufficient to add only tight s-type functions when modifying basis sets for the calculation of SSCCs, at least for the type of coupling constants and molecules considered in the present study.

4.2 Two-bond Couplings

Figure 2 shows the mean absolute deviation of the results for two-bond reduced SSCCs from the aug-ccJ-pV5Z-unc result for each basis set in the study.

Two-bond SSCCs are typically much smaller than one-bond SSCCs, and the absolute errors displayed in Fig. 2 are thus also smaller. Comparing relative errors in the two kind of SSCCs yields roughly similar results. One main difference from the one-bond SSCC results shown in Fig. 1 is immediately apparent: The contraction errors are no longer a primary concern. Only for the double zeta and the Jensen basis sets with diffuse functions included are there some noticeable differences between the contracted and totally uncontracted basis sets.

Looking at the ccJ-pVXZ basis sets, it is clear that diffuse functions are important. At the triple zeta level, for instance, the mean absolute deviation is 0.55 Hz with deviations of 1.72 Hz for ${}^2\tilde{K}_{\text{OF}}$ in FNO and 1.62 Hz for ${}^2\tilde{K}_{\text{NF}}$ in *trans*-FNNF, when diffuse functions are not included. With diffuse functions the mean deviation drops to only 0.08 Hz with the above mentioned outliers dropping to 0.14 Hz and 0.05 Hz respectively. In comparison ${}^2\tilde{K}_{\text{OF}}$ in FNO and ${}^2\tilde{K}_{\text{NF}}$ in *trans*-FNNF still have deviations of 0.62 Hz and 0.67 Hz, when calculated using the ccJ-pVQZ basis set. Thus for two-bond SSCCs the addition of diffuse functions improves the accuracy more than going to the next larger set in the same series.

The pcJ-n sets are less improved by the addition of diffuse functions. Only the results at the triple zeta level are improved, on average, when diffuse functions are added. Adding diffuse functions to the pcJ-n sets is therefore not necessarily a better strategy than going to the next larger basis set in the same series. In comparison to the ccJ-pVXZ basis sets of similar sizes, the pcJ-n are thus quite a lot better when comparison is made without diffuse functions, but fairly similar when diffuse functions are included.

The performance of the aug-cc-pVTZ-J basis is below that of all other optimized triple zeta basis sets and even that of the qzp basis set. On one hand the aug-cc-pVTZ-J performs well, if only the FC contribution is considered, with a mean average deviation of only 0.07 Hz, which is similar to aug-pcJ-2 and is below that of aug-cc-pVTZ (0.1 Hz). On the other hand aug-cc-pVTZ-J has quite high mean absolute deviations for the PSO term (0.42 Hz) and the highest mean absolute deviation of all the tested basis sets in the SD term (0.21 Hz). This underlines how important it is for the SSCCs studied here that the basis set is optimized for the calculation of all four contributions to the SSCC.

4.3 Three-bond couplings

In our set of molecules, there are only four three-bond SSCCs, so we will only quickly comment on basis set performance for calculating these, shown in Fig. 3. Broadly speaking the convergence is similar to that reported for the two-bond SSCCs. Two noticeable differences are the relative failure of the aug-pcJ-1 set and the surprisingly good performance of aug-pcJ-2. Due to the very low number of three-bond couplings, however, these results are likely coincidental.

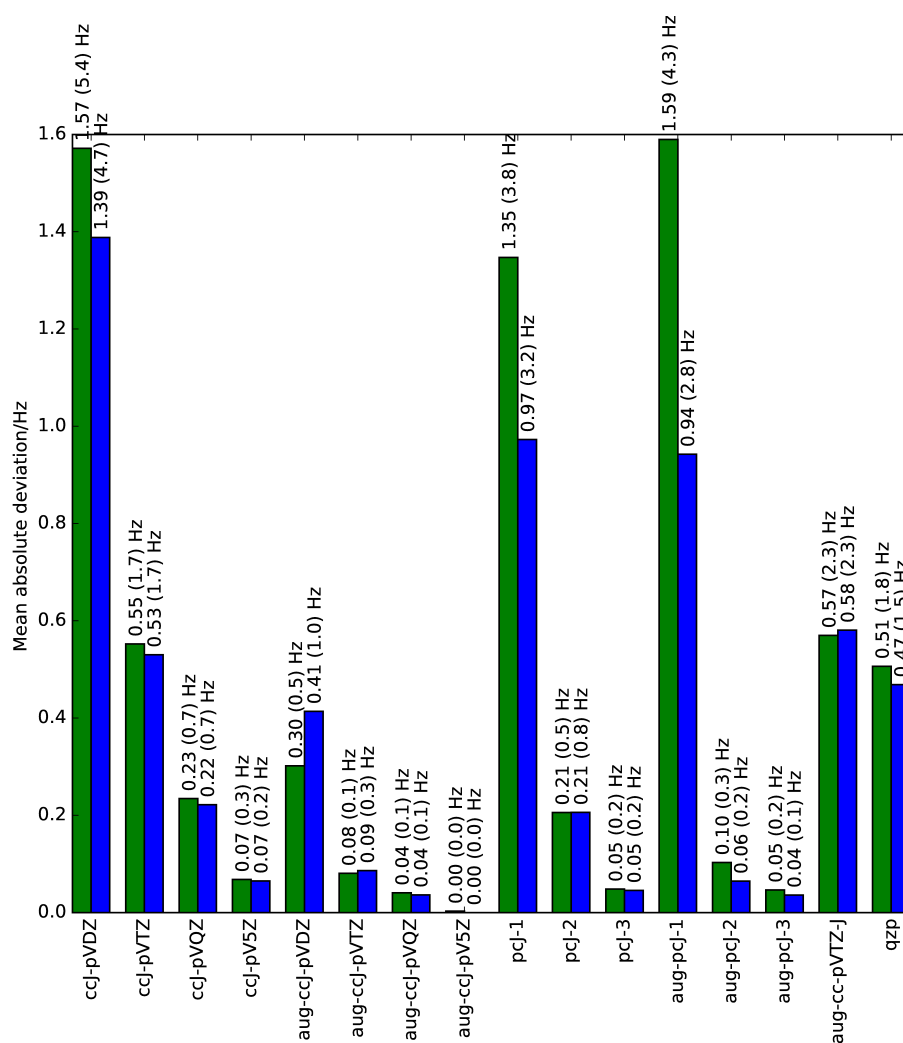


Fig. 2 Two-bond reduced coupling constants (\bar{K} in Hz): The mean average deviation from the aug-ccJ-pV5Z-unc results obtained using the basis sets. Green bars represent the results obtained with contraction of the basis functions, blue bars represent the results obtained with all functions uncontracted. Values in brackets are the maximum deviation found amongst all the two-bond couplings. There are 11 total two-bond couplings in the set.

4.4 Specific Examples

One issue that is somewhat blurred in the discussion above, when considering basis sets only by a general category, e.g. "triple zeta" or "triple zeta plus diffuse functions", is the actual size of the basis sets.

Having made some general comments based on the average performance of the difference basis sets, it is relevant to also consider a few specific examples.

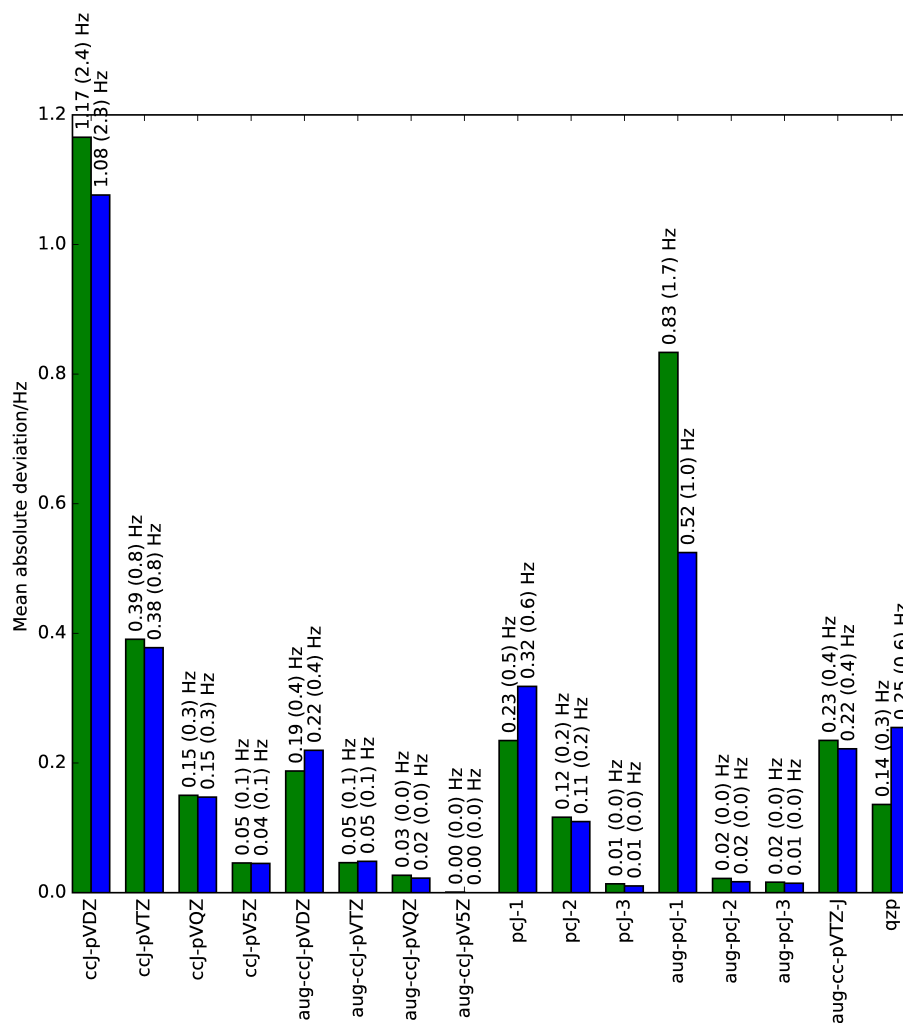


Fig. 3 Three-bond reduced coupling constants (\tilde{K} in Hz): The mean average deviation from the aug-ccJ-pV5Z-unc results obtained using the basis sets. Green bars represent the results obtained with contraction of the basis functions, blue bars represent the results obtained with all functions uncontracted. Values brackets are the maximum deviation found amongst all the three-bond couplings. There are 4 total two-bond couplings in the set.

In Fig. 4 the results for the ${}^1J_{\text{CF}}$ coupling in F_2CO calculated using each series, with and without contraction are plotted as a function of number of the basis functions. Following the curve for the ccJ-pVXZ basis set, the double zeta value is too low, but the remaining values converge from above. The aug-ccJ-pVXZ basis sets similarly converge from above, with the curve consistently above that of the ccJ basis sets without diffuse functions. When contraction is removed, convergence is significantly faster. The pcJ-n basis set yield too low values at the double and triple zeta levels and only appear to converge

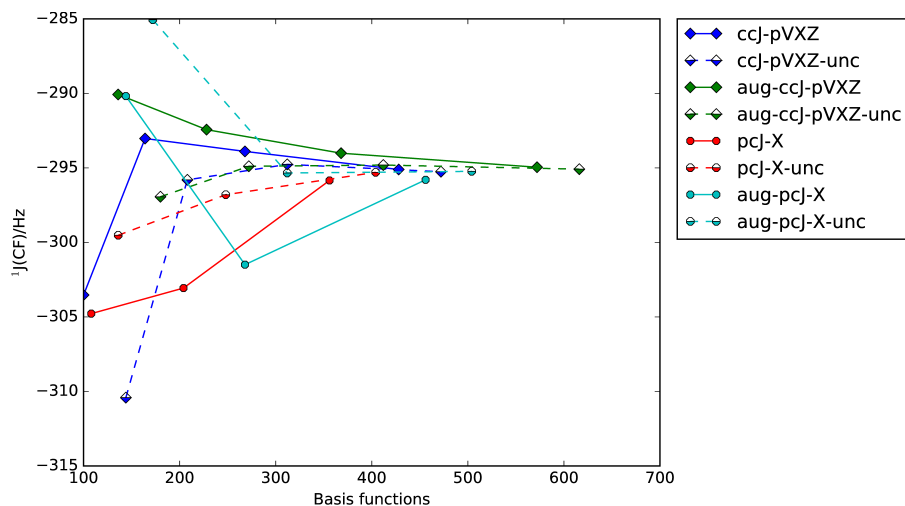


Fig. 4 The ${}^1J_{CF}$ coupling of F_2CO as calculated with various basis sets, plotted against the number of basis functions. $g_{13C}g_{19F}$ is about 7.4.

when used without contraction. The aug-pcJ-n basis set gives a too large value at the double zeta level and a too low one at the triple zeta level. Removal of the contraction shifts these points upwards, giving an impression of rapid convergence beyond the unreliable double zeta values. The smallest basis set that gives practically converged values, with a deviation of 0.2 Hz, is aug-ccJ-pVTZ-unc, which uses 272 functions for F_2CO .

As an example of a two-bond coupling we have plotted the ${}^2J_{NF}$ coupling in FCN in Fig. 5. Clearly the ccJ-pVXZ basis sets converge only very slowly. However, upon adding diffuse functions the convergence is quite rapid, though possibly in part due to favorable cancellation of the contraction error. The pcJ-n basis sets oscillate wildly with or without diffuse functions, though the removal of contraction does improve convergence. In this case the contracted aug-ccJ-pVTZ yields converged results, though the uncontracted version has an error of 0.4 Hz.

4.5 Basis set extrapolations

Basis set extrapolation has become a popular way of reducing the effort required in order to obtain highly accurate theoretical values for molecular energies [77] and properties [78]. The basic premise is that the functional form of the basis set incompleteness error as function of basis set size is known. If this is the case, that function can be fitted using results obtained with various finite basis sets. Various functional forms of the basis set incompleteness error have been proposed. The basis set error in HF and DFT energies are usually taken to decrease exponentially with basis set size [79,80]. On the other hand the error in the correlation energy decreases only polynomially. Considerations

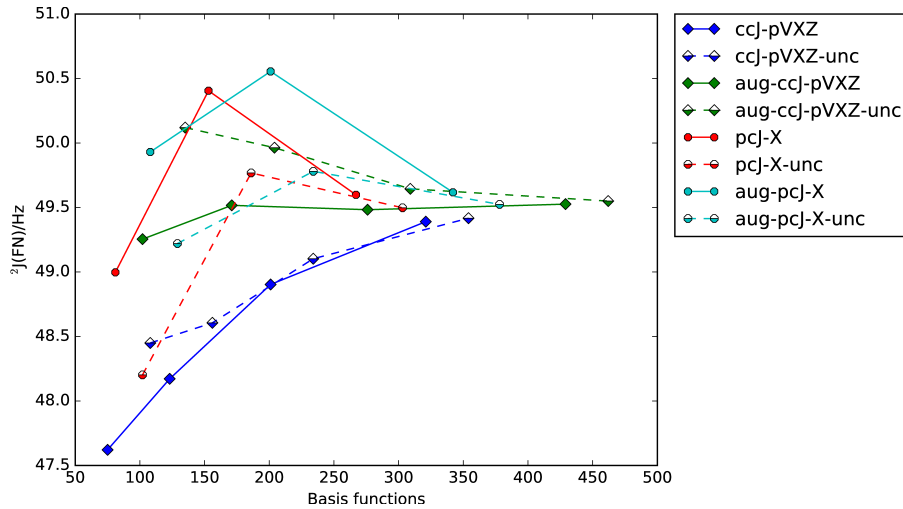


Fig. 5 The ${}^2J_{\text{NF}}$ coupling of FCN as calculated with various basis sets, plotted against the number of basis functions. $g_{15\text{N}}g_{19\text{F}}$ is about -3.0.

on helium suggests that the correct dependence should be as the inverse third power of basis set size [81, 82].

When trying to apply these considerations for property calculations, a number of issues must be addressed. For energy calculations it is reasonable to expect that the energy decreases monotonously towards the basis set limit, even for non-variational methods. However, there is no variational theorem for molecular properties and so the addition of any one basis function could both raise or lower the calculated result. While much effort has been put in to constructing both the ccJ-pVXZ and pcJ-n basis sets and we have shown that they converged nicely *on average*, it would nonetheless be desirable with at least visual confirmation that even convergence is obtained for any particular coupling constant. An additional concern when calculating SSCCs is that it is not possible to separate the calculated value in HF and correlation contributions. Two approaches thus seem viable. Either we can empirically try out various extrapolation schemes and find one that fits reasonably. Or we can assume that exponential decay of the HF incompleteness is so rapid that the total basis set error, at least from the triple zeta level and onwards, is practically identical to the error in the correlation contribution. In the following, we shall take the second approach. That is, we will try to fit our result on the assumption that the coupling constant calculated with a basis set of maximum angular momentum l is related to that in the basis set limit as

$$J(l) = J(\infty) + \frac{a}{l^3}, \quad (8)$$

where a is an unknown constant.

We believe that in practice the most useful type of basis set extrapolation will be two point extrapolations using two consecutive basis sets in the

same hierarchy of basis sets. Performing such extrapolations for all the one-bond SSCCs and calculating their mean average deviation from the result of the aug-ccJ-pVQZ-unc to aug-ccJ-pV5Z-unc extrapolation leads to the results displayed in Fig. 6. The pcJ-n style basis sets perform quite a lot worse when extrapolations are attempted than when we compared the results from single calculations. Actually, the error is roughly twice as large when using the two-point extrapolated values. That is not surprising given the non-monotonic convergence pattern that we observed for these basis sets in Fig. 4. Analyzing the individual contributions, we find that this is due to the FC contribution, while the SD or PSO terms alone would lead to better results on extrapolation.

For the ccJ-pVXZ basis sets, the results are closer. The result obtained with the ccJ-pVQZ and aug-ccJ-pVQZ basis set can be improved by an extrapolation using also the (aug-)ccJ-pVTZ results. On the other hand the triple zeta results are not in general improved by the extrapolation, probably due to the low quality of the results obtained with double zeta basis sets.

Similar results are shown for the two bond SSCCs in Fig. 7. The results for the ccJ basis set are favourable for extrapolations using both ccJ-pVTZ and ccJ-pVQZ, leading to better results than those of the non-extrapolated values, particularly when diffuse functions are not used. However, for the CBS(ccJ-pV5Z) extrapolations the average deviations are actually larger than for CBS(ccJ-pVQZ). Thus one still needs to be a bit careful about making extrapolations and conclusions based on them. The pcJ basis sets do not appear to be to be suitable for extrapolations of two-bond SSCCs either.

5 Conclusion

We have compared the accuracy of various basis sets for the calculation of indirect nuclear spin-spin coupling constants using the CCSD method. For one-bond couplings we found relatively large contraction errors for both Jensen’s pcJ-n basis sets and also the ccJ-pVXZ basis sets when diffuse functions are added to them. When not using basis set contraction, the pcJ-2 and pcJ-3 outperformed the similar ccJ-pVTZ and ccJ-pVQZ, however on adding diffuse functions the results are fairly similar. Without contraction, the aug-ccJ-pVTZ basis set leave errors in the reduced couplings constants of about 0.27 Hz corresponding to about 2.0 Hz for $^1J_{CF}$ type coupling constants. This should be seen in the light that these types of coupling typically exceed 200 Hz. The error can be improved to about 0.10 Hz in the reduced coupling if instead the aug-ccJ-pVQZ basis set is used.

When calculating two- and three-bond couplings, it is quite important to add diffuse functions. On the other hand, contraction errors are no longer a concern. With diffuse functions added the ccJ-pVXZ and pcJ-n basis sets yield similar results. The aug-ccJ-pVTZ basis set gives good results, with an error in the reduced coupling constant of about 0.08 Hz, although this still corresponds to about 0.6 Hz for $^2J_{CF}$ type coupling constants. If higher accuracy is needed,

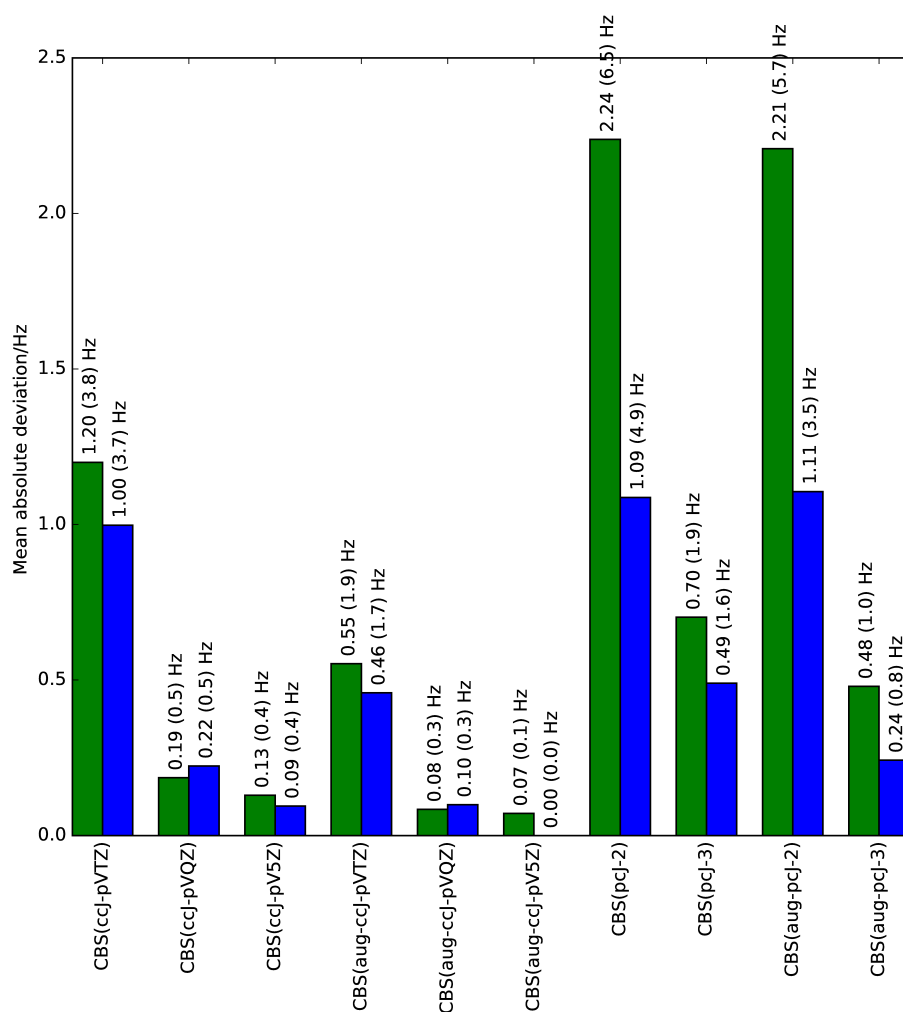


Fig. 6 Extrapolated one-bond reduced coupling constants (\tilde{K} in Hz): Mean average deviations of the extrapolated values from the CBS(aug-ccJ-pV5Z-unc) results. Numbers in brackets are the max deviations. CBS(b) should be understood as the extrapolated value obtained using b and the next smaller basis set in the same series, eg. CBS(ccJ-pVTZ) is obtained from extrapolating using the ccJ-pVDZ and ccJ-pVTZ results.

the basis set error can be reduced by roughly a factor of two by going to the quadruple zeta basis set.

We found that basis set extrapolations can improve the results obtained with medium size basis sets of the ccJ type, but not those of the pcJ type. However, it was not clear that the two-point extrapolations used do in fact converge as the size of the basis sets used in the extrapolations increases. While it thus appears that these extrapolation can be a useful way of improving results calculated using medium sized basis sets, at this time we do not believe

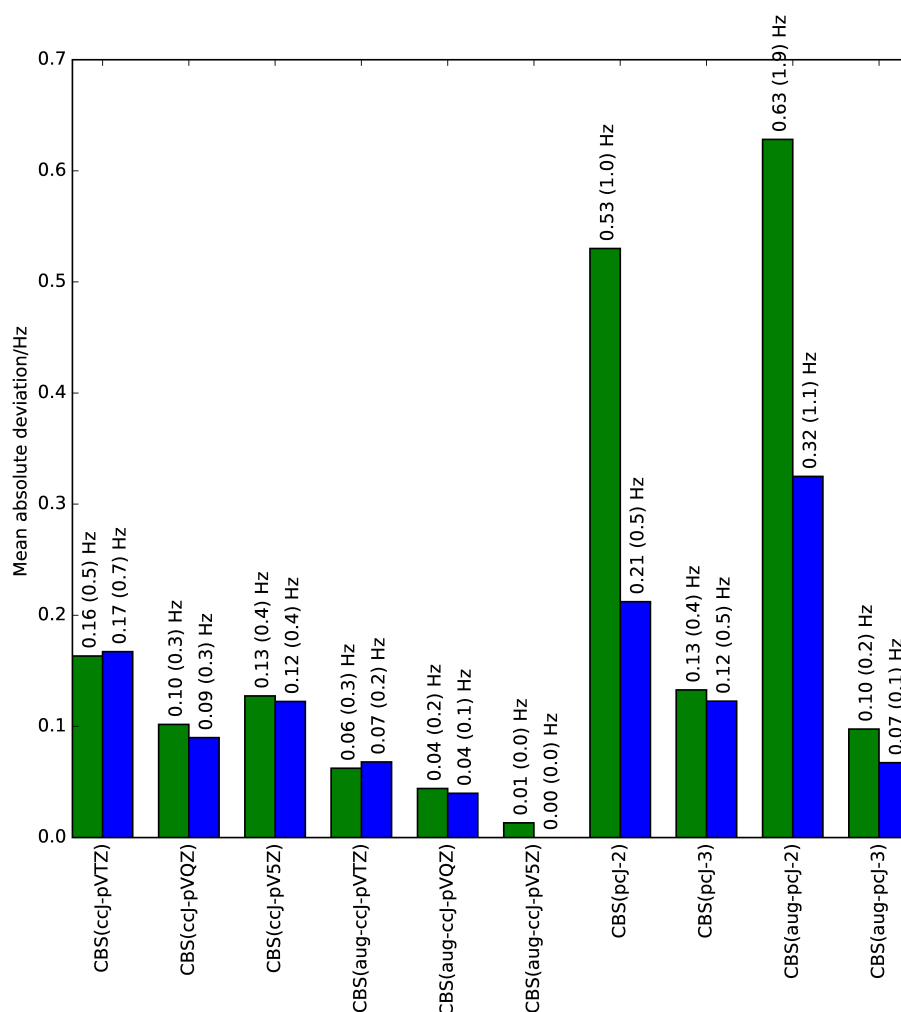


Fig. 7 Extrapolated two-bond reduced coupling constants (\tilde{K} in Hz): Mean average deviations of the extrapolated values from the CBS(aug-ccJ-pV5Z-unc) results. Numbers in brackets are the max deviations. CBS(b) should be understood as the extrapolated value obtained using b and the next smaller basis set in the same series, eg. CBS(ccJ-pVTZ) is obtained from extrapolating using the ccJ-pVDZ and ccJ-pVTZ results.

that they can replace calculations with very large basis sets if highly accurate results are desired.

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