Theor Chem Acc (1998) 99:175–182

Theoretical
Chemistry Accounts

Regular article

Basis-set dependence of nuclear spin-spin coupling constants

Trygve Helgaker[1], **Michał Jaszuński**[2], **Kenneth Ruud**[3,*], **Anna Górska**[4]

[1] Department of Chemistry, University of Oslo, Box 1033, Blindern, N-0315 Oslo, Norway
[2] Institute of Organic Chemistry, Polish Academy of Sciences, PL-01 224 Warsaw, Kasprzaka 44, Poland
[3] Institute of Physics and Measurement Technology, Linköping University, S-58 183 Linköping, Sweden
[4] The College of Sciences, PL-01 224 Warsaw, Kasprzaka 44, Poland

Received: 22 September 1997 / Accepted: 30 December 1997

Abstract. The convergence of NMR indirect spin-spin coupling constants with the extension of the basis set is analyzed, based on calculations carried out at the multiconfigurational self-consistent-field level for the HF and H_2O systems. For the dominant and difficult Fermi-contact contribution, the standard correlation-consistent basis sets of electronic-structure theory are not suitable, lacking flexibility in the core region. Improved but not satisfactory convergence of the couplings is observed when decontracting the s functions of the correlation-consistent cc-pVXZ basis sets for $2 \leq X \leq 6$. Next, by systematically extending these basis sets with tight s functions, new sets are obtained that are sufficiently flexible for accurate calculations of indirect nuclear spin-spin couplings, without sacrificing the smooth convergence behavior of the correlation-consistent basis sets.

Key words: Basis sets – Basis-set convergence – NMR parameters – Spin-spin coupling constants

1 Introduction

In this paper, we analyze the basis-set requirements for the accurate description of indirect NMR spin-spin coupling constants in ab initio theory. The standard basis sets of quantum chemistry have been developed for a flexible description of the valence region of the electronic system. However, to describe spin-spin couplings accurately, other regions are relevant since NMR experiments probe the electron density close to the nuclei, making the standard basis sets of ab initio theory ill-suited for the calculation of spin-spin coupling constants [1,2]. Another complication is that, for indirect spin-spin couplings, restricted Hartree-Fock (RHF) results are often meaningless – giving, for instance, results of the wrong order of magnitude or with the wrong sign (see Ref. [3]). A reliable analysis of basis-set dependence is therefore not possible at the RHF level. In short, for calculating accurate spin-spin couplings, one needs basis sets flexible enough to describe the electron density at the nuclei as well as the main effects of electron correlation in the molecule.

For our analysis of the basis-set dependence, we have selected two simple molecules, HF and H_2O, for which we can satisfactorily describe the correlation effects and at the same time apply large basis sets in the calculations. For both molecules, we use complete active space self-consistent field (CAS SCF) wave functions with a large active space. To illustrate the transferability of our results, we apply the best-behaved basis sets to calculate the spin-spin couplings of HCN, using a restricted active space (RAS SCF) function. Similar multiconfigurational (MC) SCF functions have been successfully used in previous studies of NMR parameters [4, 5].

There have been many other studies of the spin-spin coupling constants of these molecules – see, for example, the recent work by Perera et al. [6], which includes a comparison with previous studies of HF and H_2O, and the earlier work by Geertsen et al. [7] on HF. Although fairly large basis sets were used in these studies, their aim was primarily to investigate the correlation treatment of these systems rather than the basis-set convergence as such.

2 Theory and computational aspects

The expressions needed to evaluate indirect nuclear spin-spin coupling constants using perturbation theory were derived by Ramsey [8] in the 1950s. The presence of r_{iK}^{-n} and $\delta(r_{iK})$ terms in the perturbing operators, where r_{iK} is the electron-nucleus distance, indicates the importance of an accurate description of the electron density close to and at the nuclei. An accurate description of this part of the electron density requires the use of tighter s orbitals

---

[*] *Permanent address*: Department of Chemistry, University of Oslo, Oslo, Norway

Correspondence to: T. Helgaker

than those normally included in energy-optimized basis sets [1, 2].

A formulation of perturbation theory for the calculation of spin-spin couplings for MC-SCF wave functions has been presented by Vahtras et al. [9]. The paramagnetic spin-orbit (PSO), spin-dipole (SD) and Fermi-contact (FC) contributions are expressed as linear response properties, whereas the diamagnetic spin-orbit (DSO) term is an expectation value. In this work, we have calculated systematically – for each molecule, wave function and basis set – all contributions to the spin-spin couplings. We discuss the convergence of the individual contributions with extension of the basis set but do not analyze the large number of individual tensor components of any contribution.

We shall discuss primarily the results obtained for different sequences of the correlation-consistent basis sets developed by Dunning and coworkers [10]. These basis sets were chosen as they provide a convenient framework for the systematic treatment of dynamic correlation effects. However, since these sets are optimized with respect to the total energy, they must be augmented by auxiliary functions to provide sufficient flexibility for the calculation of the indirect spin-spin coupling constants. Although it would be possible to pursue a different strategy for the design of the basis sets – namely, building the basis sets from scratch and introducing primarily those functions needed for spin-spin couplings – we believe that, for high precision and flexibility and especially for accurate calculations at the correlated level, the basis sets should contain the correlating functions present in the correlation-consistent basis sets. This approach has the additional advantage that the basis sets may be augmented with diffuse functions and core functions in a well-established, standard manner.

First, we analyze the correlation-consistent cc-pVXZ sets (with $2 \leq X \leq 6$). To these basis sets, one can add functions needed to describe the core-valence correlation [11] and functions needed to describe the outer regions of the molecule [12]. We have computed the spin-spin coupling using these cc-pCVXZ and aug-cc-pVXZ series, as well as the basis sets derived by simultaneously adding both types of functions – the aug-cc-pCVXZ basis sets.

In correlation-consistent basis sets, correlating orbitals are added in full shells since all orbitals belonging to the same shell provide similar contributions to the correlation energy. The resulting sets therefore quickly become very large (see Table 1). For computational reasons, in this work we have restricted ourselves to basis sets containing fewer than 256 orbitals. Even for the small molecules studied here, some of the $X = 5$ basis sets were far beyond this limit (Table 1). We have therefore considered modified series of smaller basis sets that may be useful in calculations of spin-spin and hyperfine couplings.

In the cc-pVXZ-su0 series, we decontract the *s* functions of the cc-pVXZ basis completely. Next, we investigated a simple method to improve upon the description of the cc-pVXZ-su0 sets, adding a sequence of *n* tight *s* functions with the exponents forming a geometric progression. The resulting sets are denoted cc-pVXZ-su*n*. In another series, called cc-pVXZ-Cs, we take the cc-pVXZ basis set and add as extra functions only the *s*-type orbitals of the corresponding cc-pCVXZ basis, omitting the extra core-valence functions of higher angular momentum. Both the cc-pVXZ-su0 and the cc-pVXZ-Cs sets are much smaller than the full cc-pCVXZ sets, as can be seen in Table 1. Our modifications should not affect the smooth convergence of the correlation energy characteristic of the underlying cc-pVXZ and cc-pCVXZ sets.

In previous studies of NMR properties, we have successfully used the basis sets of Huzinaga [13, 14] (also called IGLO basis sets [15]). They are less systematically constructed and are not designed for use in correlated calculations, their main advantage being that they are much smaller than the correlation-consistent sets, at the same time having sufficient flexibility in the *s* functions. We used these HII, HIII and HIV basis sets as another series for comparison of the convergence.

In all the calculations, we used C_{2v} symmetry and, except for one calculation, kept the core orbital inactive. For the HF and H_2O molecules, we correlated the eight valence electrons in six orbitals of A_1 symmetry, three of B_1, three of B_2, and one orbital of A_2 symmetry. This CAS (6331) wave function has previously been used successfully to study the nuclear shieldings of HF and H_2O [5].

All our calculations were performed using the DALTON program [16]. The results reported are for the ^{1}H, ^{19}F, ^{17}O, ^{13}C and ^{15}N isotopes. The molecular geometries have been taken from other studies of NMR properties [4–6, 17]: For HF, we use a bond length of 0.917 Å, for H_2O a bond length of 0.972 Å and a bond angle of 104.5°. The bond lengths of the HCN molecule are $r_{\mathrm{HC}} = 1.064$ Å and $r_{\mathrm{CN}} = 1.156$ Å.

Table 1. Basis-set size, number of CGTO functions for second row atom/H atom

X	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ	aug-cc-pCVXZ	cc-pVXZ-Cs	cc-pVXZ-su0
D	14/5	23/9	18/5	27/9	15/5	20/7
T	30/14	46/23	43/14	59/23	32/14	36/16
Q	55/30	80/46	84/30	109/46	58/30	62/32
5	91/55	127/80	145/55	181/80[a]	95/55	99/58
6	140/91					149/95

For Huzinaga's basis sets HII, HIII and HIV: 22/6, 35/10 and 51/19 respectively

[a] Not used in any calculation

3 Results

3.1 HF

The results for the HF molecule are shown in Tables 2 and 3 and Fig. 1 and 2. The spin-spin coupling constant in HF is dominated by the FC and PSO contributions (see Table 3). Since convergence is harder to achieve for the FC term, we will discuss this contribution first.

The convergence of the cc-pVXZ and aug-cc-pVXZ series is very poor – they are neither systematic nor finally converged. The two series have minima, at $X = T$ and $X = Q$, respectively. Although, when compared with the other basis-set sequences in Table 3, the final values obtained for the quintuple or sextuple-zeta basis appear to be satisfactory, there is no indication of convergence within the series itself. Similarly poor convergence has recently been observed for spin densities [18]. In contrast, the three series of basis sets that include core-valence *s*-type orbitals (cc-pCVXZ, aug-cc-pCVXZ and cc-pVXZ-Cs) converge to approximately the same value. The double-zeta results are far too small, the triple-zeta values significantly better, and the values obtained for the quadruple- and quintuple-zeta sets all converge to within 5%. Smooth convergence is also observed for the cc-pVXZ-su0 series and the final $X = 6$ result (355.81 Hz) appears to be the most accurate (see below).

As shown in Table 3, the convergence of the PSO contribution is significantly better than for the FC term. Apart from some DZ results, all values are reasonable. The HIV result, 181.53 Hz, appears to be somewhat too small. Furthermore, the differences among the correlation-consistent basis sets are very small – the last results vary from 183.08 to 185.53 Hz. It thus appears to be easier to describe the r_{iK}^{-n} dependence than the $\delta(r_{iK})$ function. The effect of the *s* orbitals in the cc-pVXZ-Cs series is small. In fact, for the PSO, SD and DSO contributions, the cc-pVXZ-Cs basis sets yield results similar to the cc-pVXZ sets, in contrast to what was observed for the FC term.

For the small SD and DSO contributions, it is difficult to make a definite statement about the results. The double-zeta sets are undoubtedly too small; the differences between the $X = T, Q$, and 5 results decrease systematically in the cc-pCVXZ series, which appears to yield the best results for these contributions.

The final total spin-spin coupling constants for all the series (including Huzinaga's basis sets) are in the range 510–540 Hz, the differences being approximately 5%. Since our aim was to establish the basis-set limit (within

Table 2. HF molecule, total ^{1}J(HF) in Hz

X	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ	aug-cc-pCVXZ	cc-pVXZ-Cs	cc-pVXZ-su0
D	447.47	698.34	270.19	383.70	264.79	392.18
T	325.98	514.22	448.90	497.56	459.22	479.34
Q	433.39	439.42	518.62	526.53	514.33	505.92
5	478.21	518.58	515.43		515.59	529.35
6	531.89					538.02

Other results: Huzinaga's basis sets HII, HIII and HIV: 481.11, 517.72 and 510.22, respectively; Exp. 529 ± 23 [20]

Table 3. HF molecule, individual contributions to ^{1}J(HF) in Hz

X	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ	aug-cc-pCVXZ	cc-pVXZ-Cs	cc-pVXZ-su0
FC						
D	273.67	539.31	92.29	220.65	91.11	218.39
T	140.00	334.22	264.76	319.00	273.38	292.75
Q	252.44	261.83	334.99	345.86	333.34	325.13
5	295.89	336.89	333.11		333.26	346.52
6	349.56					355.81
PSO						
D	181.91	162.68	185.95	166.36	181.82	183.03
T	189.99	180.93	189.02	180.50	189.86	190.39
Q	185.27	181.05	187.07	183.08	185.29	185.24
5	184.81	183.94	185.32		184.81	185.01
6	185.53					185.49
SD						
D	−9.45	−4.56	−8.95	−3.83	−9.48	−10.52
T	−4.34	−1.18	−4.95	−1.91	−4.37	−4.12
Q	−4.26	−3.36	−3.27	−2.21	−4.24	−4.39
5	−2.26	−2.01	−2.76		−2.25	−1.95
6	−2.93					−3.00
DSO						
D	1.35	0.91	0.90	0.51	1.35	1.29
T	0.34	0.25	0.07	−0.03	0.35	0.33
Q	−0.06	−0.11	−0.17	−0.21	−0.06	−0.06
5	−0.23	−0.23	−0.25		−0.23	−0.23
6	−0.27					−0.27

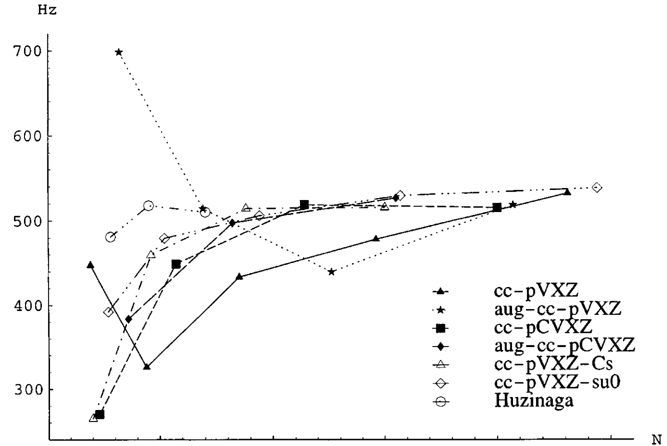

Fig. 1. Total spin-spin coupling, ^{1}J(HF) in Hz, as a function of the number of orbitals in the basis set, for the HF molecule, CAS (6331) wave function

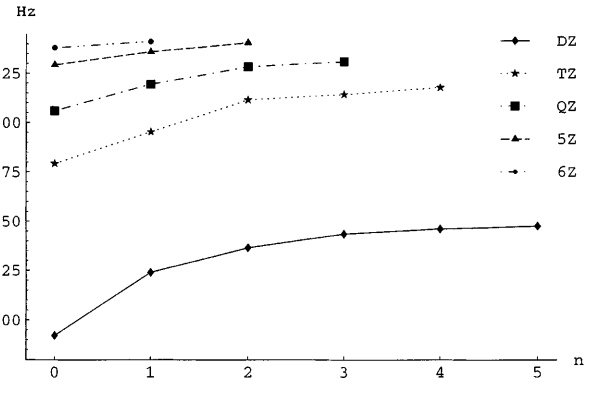

Fig. 2. Total spin-spin coupling, ^{1}J(HF) in Hz, as a function of n for the cc-pVXZ-su*n* series, for the HF molecule, CAS (6331) wave function

a given choice of MCSCF active space), this result is not encouraging; it illustrates well the difficulties faced when very accurate calculations of spin-spin couplings are attempted. On the other hand, it is satisfying that, as can be seen in Fig. 1, smooth convergence is observed within the cc-pVXZ-su0 series. We also note that the cc-pVXZ-Cs results provide a good approximation to the cc-pCVXZ series.

As HF is our smallest molecule, we performed a series of additional calculations to estimate the basis-set limit for the CAS (6331) approximation. We uncontracted all the *s* functions in cc-pV5Z-Cs, all the *s* functions in cc-pCV5Z, and all the functions in the cc-pCV5Z basis. The results were 529.37, 528.80 and 528.89 Hz respectively, confirming the important role of the *s* orbitals (caused by the poor convergence of the FC term and its large contribution to the spin-spin coupling constant). The FC, PSO, SD and DSO contributions in the fully uncontracted cc-pCV5Z basis set were 346.50, 185.46, −2.81 and −0.25 Hz, respectively.

Next, in a series of calculations, we added to the fully uncontracted cc-pCV5Z basis a number of tight *s*, *p* and *d* functions. Adding up to a total of $(8s2p1d/8s1p1d)$ functions on fluorine and hydrogen, respectively, we arrived at our largest basis containing $(26s14p8d5f3g1h/16s5p4d2f1g)$ uncontracted functions. The first two added *s* functions on the F atom and the first *s* function on the H atom were inserted between the functions of the primary cc-pCV5Z set, with exponents chosen as the geometric mean of the largest cc-pCV5Z exponents. The exponents of the remaining added functions form a geometric progression, with the ratio of exponents approximately equal to 2.58 for each atom. Based on the eigenvalues of the molecular orbital (MO) overlap matrix, two σ orbitals (out of 255 functions) were deleted in the calculation because of linear dependence. For this basis set, the results for the individual contributions are 359.84 Hz for FC, 185.93 Hz for PSO, −2.90 Hz for SD and −0.27 Hz for DSO, with the total value being 542.60 Hz. As expected, the largest change with respect to the uncontracted cc-pCV5Z calculation occurred in the FC term because of the addition of tight *s* functions. The changes in the FC term arising from the last s_F and s_H functions were less than 1 Hz, but the convergence was slow. For example, having added to the uncontracted cc-pCV5Z basis a set of $(3s2p1d/2s1p1d)$ functions, we obtained $J^{\mathrm{FC}} = 350.89$ Hz – still 9 Hz off our final value. The other contributions appeared to be converged at this stage (although we did not attempt later to add more *p*, *d*, or *f* orbitals). The extra *s* functions have large exponents, the last *s* functions added having exponents $\xi_{s,F} \approx 6.3 \cdot 10^7$ and $\xi_{s,H} \approx 3.1 \cdot 10^5$ (such functions are not included in any standard basis sets). Similar large exponents have also been shown to be needed in order to obtain convergence in the calculation of ^{1}J(HD) in the HD molecule [1].

The accurate basis sets discussed so far are too large to be useful in calculations on larger molecules. In order to arrive at smaller sets for accurate calculations of spin-spin coupling constants, a practical starting point is the cc-pVXZ-su0 sets, which represent a significant improvement on cc-pVXZ at little extra cost. Based on our experience with the larger sets, a useful systematic sequence of basis sets would be obtained by adding tight *s*-type functions. Thus, to each of the cc-pVXZ-su0 sets, we added a sequence of *s* functions with the exponents forming a geometric series, each exponent five times larger than the previous one; the corresponding sets are denoted cc-pVXZ-su*n*. The results in Table 4 and in Fig. 2 demonstrate that the dominant corrections to the FC term are accounted for in this manner. Beginning with $X = T$, the best result for each X series is similar to or better than the value for the $(X + 1)$ set *without* the tight functions. In addition, the value for cc-pV6Z-su1, 541.20 Hz is very close to our estimate of the basis-set limit, 542.60 Hz, confirming the accuracy of our estimate and indicating that the final value is not sensitive to the ratio of exponents in the geometric series of added *s* functions. We will not discuss the results obtained within the cc-pVXZ-su*n* sequence for the PSO, SD and DSO terms, since in every case they are practically identical to the cc-pVXZ-su0 values.

A number of other commonly used basis sets were also considered. For the 6-31G** and 6-311G** sets, we obtain a total coupling constant of 606.5 and 485.3 Hz, respectively; a better result (525.0 Hz) is obtained using the 6-311G++(2*d*2*p*) set. For this basis set, the FC term is relatively accurate (348.7 Hz), but the corresponding PSO contribution is 176.7 Hz, in disagreement with the final values in Table 3 and our best results. We also considered the use of ANO basis sets [19]. The results depend strongly on the contraction pattern, the best value we obtained being 541.5 Hz for a (5*s*4*p*3*d*/4*s*3*p*) basis. However, the addition of extra contracted ANO orbitals does not lead to a convergent series and a primitive set of *s* functions is needed for convergence. For a [14*s*9*p*4*d*/14*s*5*p*4*d*] fluorine basis and an uncontracted [8*s*4*p*] hydrogen basis, a calculation of this type yields a reasonable result, 523.6 Hz.

For comparison, we also performed some calculations using a CAS (4220) wave function. The results differ from CAS (6331) and from experimental values, the FC contribution being very similar to that obtained in MBPT(2) calculations using similar basis sets [17] – approximately 50 Hz too large relative to the CAS (6331) result. However, the basis-set variations that we observe for CAS (4220) are very similar to those for the more accurate CAS (6331) wave function. We have also, in a test calculation, included all ten electrons in the active space. The FC contributions obtained with the cc-pVQZ-su0 basis set and the CAS (4220) and CAS (5220) wave functions differ by less than 0.2% (i.e. less than 1 Hz). In the remaining investigations, therefore, we excluded the core electrons from the active space.

Even though it is not our main purpose here to reproduce the experimental results, we conclude this section with a brief comparison with the measured ^{1}J(HF) coupling constant. The experimental result for the ^{1}J(HF) coupling is 529 ± 23 Hz [20]. In a recent study of the HF molecule, it was found that, at 300 K, rovibrational corrections reduce the spin-spin coupling constant by approximately 25 Hz [21]. Applying the same correction to our best calculated result using the chosen geometry, we obtain a final nuclear spin-spin coupling of 518 Hz, in good agreement with experimental results.

3.2 H_2O

For the water molecule, we have restricted our analysis to the correlation-consistent basis sets, including the cc-pVQZ-su*n* series. For comparison, we have included the results at the cc-pVXZ-Cs and at the HII, HIII, and HIV levels, but we have not attempted to establish the basis-set limit in the same manner as for HF since, for H_2O, the largest *standard* set (cc-pCV5Z) already contains 255 functions.

The results obtained for ^{1}J(OH) are similar to those for ^{1}J(HF) – see Table 5. The double-zeta sets are too small and the results obtained in the cc-pVXZ series are unreliable. The cc-pCVXZ, aug-cc-pCVXZ, cc-pVXZ-Cs and cc-pVXZ-su0 series converge, the differences between the final values of these series being less than 3% of the total coupling constant. Also, the HIV value is similar to these results. As for the ^{1}J(HF) coupling, the convergence pattern reflects the dependence of the FC term on the basis set (see Table 6). Moreover, the DSO, PSO and SD contributions to ^{1}J(OH) vary with the basis set in the same manner as for ^{1}J(HF). Adding the tight *s* functions in the cc-pVQZ-su*n* series, we obtain −75.90, −77.58 and −78.08 Hz for $n = 1, 2$ and 3, respectively. As for ^{1}J(FH), the last numbers are close to the corresponding cc-pV5Z-su0 result.

For ^{2}J(HH), the convergence pattern is rather different. As expected, the addition of core orbitals to oxygen has little effect, whereas augmentation with diffuse functions leads to larger changes (see Table 7). Analyzing the individual contributions in Table 8, we note that the slow convergence in this case also reflects the behavior of the FC contribution. For ^{2}J(HH), the total spin-spin couplings in Table VII depend on three large contributions: negative FC and DSO terms and a positive PSO term. The DSO and PSO terms converge well and almost cancel each other out. However, as shown by Table VIII, there is, for all basis sets, a small positive remainder and a small positive SD term to be added to the negative FC term. When added, these terms increase the oscillations observed for the FC

Table 4. HF molecule, cc-pVXZ-su*n* series, ^{1}J(HF) in Hz

n	cc-pVDZ-su*n*	cc-pVTZ-su*n*	cc-pVQZ-su*n*	cc-pV5Z-su*n*	cc-pV6Z-su*n*
0	392.18	479.34	505.92	529.35	538.02
1	423.94	495.26	519.32	535.87	541.20
2	436.54	511.38	528.31	540.57	
3	443.56	514.15	530.87		
4	446.15	517.78			
5	447.62				

Table 5. H_2O molecule, total ^{1}J(OH) in Hz

X	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ	aug-cc-pCVXZ	cc-pVXZ-Cs	cc-pVXZ-su0
D	−72.31	−94.11	−49.73	−61.23	−49.24	−57.85
T	−56.07	−75.55	−66.77	−72.40	−67.94	−68.90
Q	−65.81	−66.50	−73.76	−75.42	−73.29	−73.33
5	−71.31		−75.20		−75.33	−77.23

Other results: Huzinaga's basis sets HII, HIII and HIV: −72.20, −74.52 and −73.81, respectively; cc-pVQZ-su*n*: −75.90, −77.58 and −78.08 for n = 1, 2, and 3; Exp. −79 ± 2 [22], −73.5 ± 2.1 [23]

Table 6. H_2O molecule, individual contributions to $^1J(OH)$ in Hz

X	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ	aug-cc-pCVXZ	cc-pVXZ-Cs	cc-pVXZ-su0
FC						
D	−61.97	−84.17	−39.05	−50.97	−38.91	−47.54
T	−44.23	−64.03	−55.13	−61.01	−56.12	−57.01
Q	−54.37	−55.21	−62.09	−63.89	−61.86	−61.91
5	−59.69		−63.57		−63.71	−65.58
PSO						
D	−10.51	−9.80	−10.83	−10.07	−10.51	−10.61
T	−11.63	−11.10	−11.50	−11.00	−11.63	−11.68
Q	−11.29	−11.02	−11.41	−11.16	−11.29	−11.28
5	−11.28		−11.32		−11.28	−11.29
SD						
D	0.33	−0.03	0.27	−0.12	0.33	0.45
T	−0.13	−0.37	−0.09	−0.34	−0.12	−0.14
Q	−0.11	−0.24	−0.23	−0.35	−0.11	−0.10
5	−0.33		−0.28		−0.33	−0.34
DSO						
D	−0.16	−0.11	−0.12	−0.08	−0.16	−0.16
T	−0.08	−0.06	−0.05	−0.04	−0.08	−0.07
Q	−0.04	−0.03	−0.03	−0.02	−0.04	−0.04
5	−0.02		−0.02		−0.02	−0.02

Table 7. H_2O molecule, total $^2J(HH)$ in Hz

X	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ	aug-cc-pCVXZ	cc-pVXZ-Cs	cc-pVXZ-su0
D	−5.72	−12.78	−4.97	−11.95	−5.64	−7.73
T	−10.69	−8.98	−10.05	−8.24	−10.66	−8.08
Q	−8.42	−8.77	−8.12	−8.36	−8.32	−8.39
5	−9.32		−9.41		−9.25	−9.01

Other results: Huzinaga's basis sets HII, HIII and HIV: −10.83, −9.55 and −8.04, respectively; cc-pVQZ-su*n*: −9.07, −9.58 and −9.70 for n = 1, 2, and 3; Exp. −7.2 ± 0.7 [24]

Table 8. H_2O molecule, individual contributions to $^2J(HH)$ in Hz

X	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ	aug-cc-pCVXZ	cc-pVXZ-Cs	cc-pVXZ-su0
FC						
D	−6.40	−13.45	−6.37	−13.35	−6.35	−8.52
T	−12.93	−11.19	−12.91	−11.06	−12.90	−10.32
Q	−11.16	−11.51	−11.12	−11.35	−11.06	−11.14
5	−12.28		−12.50		−12.21	−11.97
PSO						
D	6.64	6.49	7.35	7.21	6.67	6.72
T	8.18	8.12	8.80	8.73	8.18	8.18
Q	8.68	8.65	8.93	8.89	8.68	8.68
5	8.82		8.95		8.82	8.82
SD						
D	0.75	0.92	0.75	0.93	0.75	0.78
T	0.87	0.90	0.86	0.90	0.86	0.86
Q	0.91	0.95	0.91	0.95	0.91	0.91
5	1.00		1.00		1.00	1.00
DSO						
D	−6.71	−6.74	−6.71	−6.74	−6.71	−6.71
T	−6.80	−6.81	−6.80	−6.81	−6.80	−6.80
Q	−6.85	−6.85	−6.85	−6.85	−6.85	−6.85
5	−6.86		−6.86		−6.86	−6.86

contribution, making the total $^2J(HH)$ appear so poorly convergent.

Smooth behavior of the FC term, and in consequence of the total coupling constant, is observed only for the cc-pVXZ-su0 series. The addition of the tight *s* functions leads to quite large changes – in the cc-pVQZ-su*n* sequence we obtain −9.07, −9.58 and −9.70 Hz, respectively. The last results appear to be our best estimate of this coupling constant.

3.3 HCN

For HCN, an RASSCF function from a previous investigation [4] was used. In the notation (inactive/RAS1/RAS2/RAS3), this function is described as (2000/0000/5220/3111) with a maximum of two electrons in the RAS3 subspace. We also used a smaller full-valence CASSCF function and observe that, although the calculated coupling constants differ, the basis-set depen-

Table 9. HCN molecule, total J in Hz

X/n	^{1}J(CN)		^{1}J(CH)		^{2}J(HN)	
	cc-pVXZ-Cs	cc-pVXZ-su*n*	cc-pVXZ-Cs	cc-pVXZ-su*n*	cc-pVXZ-Cs	cc-pVXZ-su*n*
D/0	−13.17	−16.60	239.75	217.42	−5.14	−5.07
T/0	−22.64	−18.29	247.16	236.49	−7.90	−6.27
Q/0	−19.54	−18.91	243.08	250.51	−6.47	−6.58
Q/1		−19.08		261.11		−6.70
Q/2		−19.31		267.85		−6.74
Q/3		−19.66		269.86		−6.85
5	−19.75		258.93		−6.80	

Other results, for ^{1}J(CN), ^{1}J(CH) and ^{2}J(HN) respectively. Huzinaga's HIV basis: −19.83, 249.27, and −6.44; Exp. −18.5, 267.3, and −8.7 [25]

dence is similar to that for the RASSCF function. We shall discuss here only the more accurate RASSCF results.

Since, for a given basis set, the total number of basis functions is larger for HCN than for HF and H_2O, we selected the sets that we found to be optimal for the couplings in the smaller molecules. In Table 9, we display the results of the cc-pVXZ-Cs and cc-pVXZ-su0 calculations and, as for the H_2O molecule, we have analyzed the n-sequence for cc-pVQZ-su*n*. The cc-pVXZ-Cs results are close to cc-pCVXZ for X = D, T and Q (the cc-pCV5Z being too large for HCN). For example, the cc-pCVQZ results are −20.00, 243.86 and −6.64 Hz for ^{1}J(CN), ^{1}J(CH) and ^{2}J(HN), respectively. However, the convergence of the cc-pVXZ-Cs series is not smooth. Again, the best behavior is observed for the cc-pVXZ-su0 series and for the subsequent cc-pVQZ-su*n* series. As shown in Table 9, the final cc-pVQZ-su3 results are in very good agreement with the cc-pV5Z-Cs values for ^{1}J(CN) and ^{2}J(HN), whereas for ^{1}J(CH) a 5% difference remains. Considering the good convergence of the cc-pVQZ-su*n* sequence, it appears that all the other results in this case are less accurate.

4 Conclusions

It appears difficult to construct a systematic series of small basis sets that would be suitable for the calculation of spin-spin couplings. The requirements for a systematic description of correlation effects and for the description of the $\delta(r_{iK})$ perturbation are very different – the standard correlation-consistent basis sets are inadequate for the description of spin-spin coupling constants because of lack of flexibility in the *s*-function space. Similar conclusions concerning energy-optimized basis sets have been reached in other studies – see, for example, the work by Oddershede and coworkers [1, 2].

In the present paper, we propose systematic extensions to the energy-optimized correlation-consistent basis sets, obtained by decontracting the *s* space and adding sequences of tight *s* functions to the original set. Such basis sets provide an improved description of the FC contribution to the coupling constants. The decontraction yields basis sets (cc-pVQZ-su0) that provide qualitatively accurate values. For higher accuracy, one needs to add a number of very tight *s*-type functions, as in the cc-pVQZ-su*n* series, to improve the convergence of the FC term. In any case, the cc-pVDZ-based sets are too small and, to ensure sufficient accuracy, the triple-zeta or larger correlation-consistent sets must be used as the starting point, indicating that small basis sets such as those of Huzinaga – which are not systematic with respect to treatment of electron correlation – may still sometimes be useful.

The MCSCF wave functions used here give a reasonable approximation to the spin-spin couplings of the molecules analyzed. It is beyond the scope of the present study to systematically investigate remaining errors, due to the deficiencies of the MCSCF wave function. In this work, test calculations using smaller active spaces gave a similar basis-set convergence to that for the final MCSCF functions we have described. Presumably, the basis sets that we found to be satisfactory would also perform well for other approximate wave functions, better than CAS (6331) – for example, functions that explicitly take into account the core and dynamic correlation effects. In addition, our best results are close to the known experimental values, and our description of the correlation effects thus appears to be sufficiently accurate for a study of the basis-set dependence of spin-spin couplings.

Finally, let us note that both the wave-function approximation and the basis sets used in the present paper are more elaborate than those presently used for studies of spin-spin coupling in larger molecules. However, considering the development of various correlated integral-direct response methods, systematically constructed basis sets of this size may soon become useful for ab initio studies of larger systems. Thus, for future applications, we advocate the use of cc-pVQZ-su*n* or similar basis sets.

Acknowledgements. This work was supported by The Research Council of Norway through a travel grant to M.J. (Grant No.111182/410), and the Programme for Supercomputing through a grant of computing time. M.J. also acknowledges financial support within Grant 3 T09A 133 09 from the Polish Committee for Scientific Research.

References

1. Oddershede J, Geertsen J, Scuseria GE (1988) J. Phys Chem 92:3056
2. Geertsen J, Oddershede J, Raynes WT, Scuseria GE (1991) J Magn Reson 93:458

3. Barszczewicz A, Helgaker T, Jaszuński M, Jørgensen P, Ruud K (1994) J Chem Phys 101:6822
4. Barszczewicz A, Helgaker T, Jaszuński M, Jørgensen P, Ruud K (1995) J Magn Reson A 114:212
5. Ruud K, Helgaker T, Kobayashi R, Jørgensen P, Bak KL, Jensen HJA (1994) J Chem Phys 100:8178
6. Perera SA, Sekino H, Bartlett RJ (1994) J Chem Phys 101:2186
7. Geertsen J, Oddershede J, Scuseria GE (1987) Int J Quantum Chem Symp 21:475
8. Ramsey NF (1953) Phys Rev 91:303
9. Vahtras O, Ågren H, Jørgensen P, Jensen HJA, Padkjær SB, Helgaker T (1992) J Chem Phys 96:6120
10. Dunning TH Jr (1989) J Chem Phys 90:1007
11. Woon DE, Dunning TH Jr (1995) J Chem Phys 103:4572
12. Woon DE, Dunning TH Jr (1994) J Chem Phys 100:2975
13. Huzinaga S (1971) Approximate atomic functions. Technical report, University of Alberta, Edmonton
14. Huzinaga S (1965) J Chem Phys 42:1293
15. Schindler M, Kutzelnigg W (1982) J Chem Phys 76:1919
16. Helgaker T, Jensen HJA, Jørgensen P, Olsen J, Ruud K, Ågren H, Andersen T, Bak KL, Bakken V, Christiansen O, Dahle P, Dalskov EK, Enevoldsen T, Heiberg H, Hettema H, Jonsson D, Kirpekar S, Kobayashi R, Koch H, Mikkelsen KV, Norman P, Packer MJ, Saue T, Taylor PR, Vahtras O (1997) Dalton, an ab initio electronic structure program, release 1.0. See http://www.kjemi.uio.no/software/dalton/dalton.html.
17. Fukui H, Miura K, Matsuda H, Baba T (1992) J Chem Phys 97:2299
18. Carmichael I (1997) J Phys Chem A 101:4633
19. Widmark PO, Malmqvist PÅ, Roos BO (1990) Theor Chim Acta 77:291
20. Muenter JS, Klemperer W (1970) J Chem Phys 52:6033
21. Åstrand PO, Ruud K, Mikkelsen KV, Helgaker T (submitted to Journal of Chemical Physics)
22. Florin AE, Alei M Jr (1967) J Chem Phys 47:4268
23. Jenkins WB, McFarlane W (1977) J Chem Soc Chem Commun, 922
24. Holmes JR, Kivelson D, Drinkard WC (1962) J Chem Phys 37:150
25. Dombi G, Diehl P, Lounila J, Wasser R (1984) Org Magn Reson 22:573