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Basis Set Convergence of Indirect Spin–Spin Coupling Constants in the Kohn–Sham Limit for Several Small Molecules

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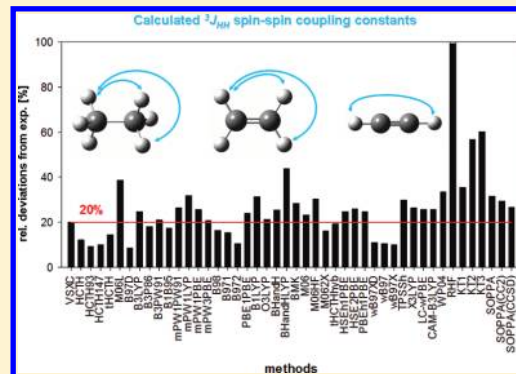
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S Supporting Information

ABSTRACT: The performance of more than 40 density functionals in predicting indirect spin–spin coupling constants (SSCCs) in the Kohn–Sham basis set limit was tested. For comparison, similar calculations were performed using the RHF, SOPPA, SOPPA(CC2), and SOPPA(CCSD) methods, and the results were estimated toward the complete basis set (CBS) limit. The SSCCs of nine small molecules (N_2 , CO, CO_2 , NH_3 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , and C_6H_6) were calculated using the dedicated Jensen pcJ- n polarization-consistent basis sets and used for the CBS limit estimations within the Kohn–Sham limit. These CBS results were compared with calculations using the aug-cc-pVTZ-J basis set. Among the 41 studied DFT methods, the thCTHhyb, HSEh1PBE, HSE2PBE, wB97XD, wB97, and wB97X functionals reproduced accurately the experimental $^1J(XH)$ SSCCs and $^3J(HH60)$ and $^2J(HH_{gem})$ in ethane. Similarly, the functionals HSEh1PBE, HSE2PBE, wB97XD, wB97, and wB97X predicted accurately $^1J(CC)$, and B98, B97-1, B97-2, PBE1PBE, B1LYP, and O3LYP provided accurate $^1J(CO)$ results in the CO molecule. A very good performance for the calculation of the SSCCs based on the use of the relatively small basis set aug-cc-pVTZ-J was observed.



1. INTRODUCTION

Indirect nuclear spin–spin coupling constants (SSCCs) and chemical shifts are the two most important spectral parameters in nuclear magnetic resonance (NMR) spectroscopy. Experimental NMR studies are often supported by calculations at several theoretical levels. It is well recognized that both high-level theoretical methods and very large and flexible basis sets are necessary to obtain accurate and quantitative ^{13}C , ^{19}F , or ^{17}O isotropic nuclear shieldings^{1–3} or indirect nuclear spin–spin coupling constants.^{4–6}

In analogy to accurate thermochemical studies,⁷ the complete basis set (CBS) limit approach has been applied to estimate reliable isotropic shielding constants and SSCCs.^{8–12} In these studies, a series of specially constructed basis sets were applied and the results were fitted with simple two- or three-parameter formulas to obtain estimations toward the complete basis set limit.^{8–12} Initially, augmented Dunning correlation-consistent basis sets (aug-cc-pVxZ, where $x = D, T, Q, 5, 6$, and sometimes 7), often used to estimate accurate energies and other molecular and spectroscopic properties, were applied.^{13–15} Later, Jensen's general-purpose polarization-consistent basis sets pc- n , where $n = 0, 1, 2, 3$, and 4 (refs 16–21), were

introduced in CBS studies of dihydrogen and water nuclear shielding constants (as well as structural parameters) at the B3LYP, MP2, and CCSD(T) levels of theory.²² Subsequently, Jensen's pcS- n ²³ and pcJ- n ²⁴ basis set families, designed for accurate calculations of nuclear shielding constants and spin–spin coupling parameters, and Jorge's XZP basis sets were tested^{8–12} in CBS estimation of NMR parameters. Recently, the performance of over 40 density functionals for predicting isotropic nuclear shielding constants of 9 molecules was studied.²⁵ The corresponding CBS values were estimated and compared with experimental values, when augmented by vibrational corrections, as well as compared to the results of calculations with the use of the smaller basis set aug-cc-pVTZ-J.^{26–31} The aug-cc-pVTZ-J basis set is designed to provide reliable SSCC parameters of larger molecules on the basis of the use of a moderate basis set. Prediction of SSCC parameters is very challenging, and special basis sets are necessary to correctly describe the electron density close to

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nuclei.^{4–6} According to nonrelativistic theory, initially presented by Ramsey,³² the total J coupling is the sum of four components, the Fermi contact (FC), the spin dipole (SD), and diamagnetic spin–orbit (DSO) and paramagnetic spin–orbit (PSO) coupling. In most cases the FC term is dominating. On the other hand, different types of coupling constants (e.g., for nuclei of two heavy atoms, X and Y, or heavy atoms and hydrogen) over one, two, or three bonds are governed by various mixing of FC and other Ramsey terms.³² However, the FC component is very sensitive to the flexibility of the basis set and method of calculations.^{4–6,9} Thus, due to singlet–triplet instability,³³ the RHF method generally provides inaccurate SSCC parameters^{4–6,9,10} and other methods, including multi-configurational self-consistent field (MCSCF) or density functional theory (DFT), were advocated.³⁴ Contrary to many other applications, including quantitative predictions of nuclear shielding constants, CCSD(T) also suffers from singlet–triplet instability and therefore is not a good choice for calculating SSCC parameters.³⁵ DFT shows in many practical applications the best compromise between accuracy and computational cost.³⁶ The B3LYP functional is the most tested density functional and is therefore the most predominantly used functional for prediction of both nuclear shieldings (and chemical shifts) and J couplings.

On the other hand, Maximoff³⁷ showed that the PBE density functional significantly outperforms B3LYP in calculations of $^1J(\text{CH})$ and also the $^1J(\text{OH})$ of water was more accurately predicted by the BHandH density functional. Thus, due to the “semiempirical” nature of DFT,³⁸ it is important to search for the best density functional (if it exists), capable of calculating accurate SSCC parameters. There has been much research in testing the performance of different density functionals, including B3LYP, PBE, KT1, KT2, and KT3, and various basis sets for predicting indirect spin–spin coupling constants.^{24,37,39–41} Since accurate predictions of SSCCs generally require use of very large and flexible basis sets, impractical for larger molecular systems, the locally dense basis set approach⁴² was also used for prediction of reliable J couplings in molecules of practical size.^{43,44} In addition, only very few density functionals were used¹² to estimate the Kohn–Sham limit values of coupling constants in several model molecules, including H_2O , CH_3OH , HF, H_2 , F_2 , and F_2O .

The current study extends our previous test of the performance of DFT for estimating isotropic nuclear shielding constants in the basis set limit and proposes a systematic search for a density functional (or a set of functionals) suitable for calculations of indirect spin–spin coupling constants using the pcJ- n basis set family.²⁵ The aug-cc-pVTZ-J basis set^{26–31} was also tested as a promising compromise of calculation cost and accuracy. Over 40 density functionals and 9 model molecules (N_2 , CO, CO_2 , NH_3 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , and C_6H_6), previously used for studies of isotropic nuclear shielding constants, were selected, and the CBS results were compared with RHF-, MP2-, SOPPA-, SOPPA(CC2)-, and SOPPA(CCSD)-predicted couplings and available experimental gas-phase measurements. Additionally, separately calculated vibrational corrections were included in assessing the performance of the individual methods (the corresponding temperature corrections, being an order of magnitude smaller, were not considered).

2. COMPUTATIONAL DETAILS

Most of the DFT calculations (39 density functionals) as well as the RHF-based calculations were performed using the Gaussian 09 program.⁴⁵ Among them, 7 “pure” and 31 “hybrid” density functionals were selected. In addition, calculations using the three exchange–correlation density functionals $\text{KT}n$, where $n = 1, 2$, and 3 (refs 40 and 46–48), recommended for isotropic nuclear shielding calculations, as well as SOPPA,^{49–52} SOPPA(CC2),⁵³ and SOPPA(CCSD)^{54,55} methods, suitable for calculations of SSCC parameters, were performed with the Dalton 2.0 code.⁵⁶ The SOPPA(CC2)⁵³ implementation was very recently developed as an efficient method, computationally less demanding than SOPPA(CCSD). The SOPPA(CC2) calculations were done with a local development version of Dalton 2.0. For some molecules, due to the computational requirements of SOPPA, SOPPA(CC2), and SOPPA(CCSD) calculations, the results obtained with the largest affordable basis set were used for comparison with CBS values obtained at the DFT and RHF levels of theory. For comparison with earlier studies, in most cases the experimental geometries from the compilation by Bak and co-workers⁵⁷ were used in the calculations (NN distance of 1.09768 Å in N_2 , CO distances of 1.1283203 and 1.15995 Å in CO and CO_2 , NH distance of 1.011 Å and HNH angle of 106.7° in NH_3 , CH distance of 1.0858 Å in CH_4). The experimental geometries of acetylene (CC distance of 1.2026 Å and CH distance of 1.0621 Å), ethane (CH distances of 1.5351 and 1.094 Å, HCC angle of 111.17°), and benzene (CC distance of 1.3914 Å and CH distance of 1.0802 Å) were used from Baldacci,⁵⁶ Hirota,⁵⁸ and Gauss and Stanton,⁵⁹ respectively.

Similarly to our recent study, the 46 selected computational methods will appear in the following order: VXSC (1), HCTH (2), HCTH97 (3), HCTH147 (4), THCTH (5), M06L (6), B97D (7), B3LYP (8), B3P86 (9), B3PW91 (10), B1B95 (11), MPW1PW91 (12), MPW1LYP (13), MPW1PBE (14), MPW3PBE (15), B98 (16), B971 (17), (B972 (18), PBE1PBE (19), B1LYP (20), O3LYP (21), BHandH (22), BHandHLYP (23), BMK (24), M06 (25), M06HF (26), M062X (27), tHCTHhyb (28), HSEh1PBE (29), HSE2PBE (30), PBEh1PBE (31), wB97XD (32), wB97 (33), wB97X (34), TPSSH (35), X3LYP (36), LC-wPBE (37), CAM-B3LYP (38), WP04 (39), RHF (40), KT1 (41), KT2 (42), KT3 (43), SOPPA (44), SOPPA(CC2) (45), and SOPPA(CCSD) (46). Methods 1–7 refer to pure and 8–38 to hybrid density functionals and as such will be applied to all results in the subsequent tables and figures. The WP04 density functional was recently designed^{60,61} for better prediction of proton shieldings and executed in the Gaussian 09 program as a modification of BLYP with IOp entries. Methods 40 (RHF), 41–43 ($\text{KT}n$), and 44–46 (SOPPA, SOPPA(CC2), and SOPPA(CCSD)) close the list, being reference tools. Note that we have had some problems running SOPPA(CCSD) for some of the larger compounds, and this would be even more problematic if the calibration were performed on more standard CCSD.

All calculations were performed on a single molecule in the gas phase with an absence of intermolecular interactions (at zero gas density and without solvent present).

The Jensen polarization-consistent basis set family pcJ- n ²⁴ was selected for subsequent estimation of the results of the individual calculations toward the complete basis set limit. This basis set hierarchy was designed for accurate calculations of spin–spin coupling constants. Initially, in the case of the N_2

molecule, calculations for $n = 0, 1, 2, 3$, and 4 were tested. Due to the reduced flexibility in the smaller basis sets, the results obtained with the smallest basis sets ($n = 0$, and sometimes 0 and 1) were far away from the results obtained with larger basis sets, and thus, the convergence of the results obtained for $n = 2, 3$, and 4 , and sometimes only for $n = 3$ and 4 , was evaluated in the Kohn–Sham basis set limit using a simple two-parameter fit. The CBS values for SOPPA, SOPPA(CC2), and SOPPA(CCSD) were extrapolated from pcJ-2 and pcJ-3 calculations only for ammonia, methane, ethane, and benzene due to a too high computational requirement with the large pcJ-4 basis set. In the case of ammonia with SOPPA, the results were odd due to a triplet instability.³³

For comparison, additional single-point (SP) calculations employing the aug-cc-pVTZ-J basis set^{26,27} were performed (abbreviated in the text as “aVTZJ”). All the nonstandard basis sets were downloaded from the EMSL basis set library.^{62,63} The convention used in earlier works,^{22,25} for graphical purposes only, was applied in the current study: pcJ- n , where $n = 0, 1, 2, 3$, and 4 were set equivalent to Dunning’s $x = 2, 3, 4, 5$, and 6 . Individual plots of the SSCC convergence and fittings toward the complete basis set limit are similar to those observed in our earlier works^{22,25} and therefore are not shown in this work.

Theoretical NMR values obtained at the equilibrium or experimental geometry should be compared with experiment after inclusion of zero-point vibrational (ZPVC) and thermal (TC) corrections. The latter term, being an order of magnitude smaller, has sometimes been neglected. Ruden et al.⁶⁴ subtracted the correction term from the total observed coupling, $J_{\text{tot}}^{\text{exptl}}$, arriving at the so-called “empirical equilibrium” coupling constant, $J_{\text{eq}}^{\text{emp}} = J_{\text{tot}}^{\text{exptl}} - J_{\text{vib}}^{\text{B3LYP}}$. In our study the empirical “experimental” value of the J couplings was compared directly with the theoretical equilibrium coupling, $J_{\text{eq}}^{\text{theor}}$, obtained from our ab initio calculations using the different theoretical methods. Thus, we want to underline that, in this work, the CBS-predicted theoretical indirect nuclear SSCCs, calculated at the experimental equilibrium geometry, are compared with empirical equilibrium values, which include vibrational correction terms, obtained from separate calculations.

Vibrational averaging of SSCCs in semirigid molecules can be based on the expansion of the nuclear potential V and the coupling constant J in a Taylor series of coordinates. In this study, the potential was expanded up to the fourth power of the normal mode coordinates Q_i as described elsewhere.^{25,65,66} All cubic and semidiagonal quartic constants were considered. Similarly, the SSCCs were expanded to the second-order Taylor series with both the first and second normal mode coupling constant derivatives. The vibrationally averaged SSCCs were obtained from a vibrational function Ψ as

$$J_{\text{av}} = \langle \Psi | J | \Psi \rangle \quad (1)$$

The function Ψ was obtained using the second-order degeneracy-corrected perturbational formula from harmonic-oscillator functions or using limited vibrational configuration interaction (VCI).

We numerically obtained the cubic and quartic force constants from geometrical Hessians calculated analytically by the Gaussian program, for geometries displaced in normal modes, as well as the first and diagonal second coupling constant derivatives. The program S4 interfaced to Gaussian was used for the anharmonic vibrational averaging.^{67,68} The

vibrational contributions were assessed at the BHandH/pcJ-2 and BHandH/pcJ-3 levels.

3. RESULTS AND DISCUSSION

In the first step of our study the pcJ- n polarization-consistent basis sets with $n = 0, 1, 2, 3$, and 4 were tested for dinitrogen. It was apparent that, due to inherent errors in the basis set design, the coupling constants calculated with basis sets for which $n = 0$, and sometimes 0 and 1 , were often very scattered and did not show any regular convergence consistent with results obtained using basis sets with higher n (results not shown for brevity). Therefore, it was possible to omit calculations for $n = 0$ and 1 and decrease the number of calculations while saving the main information obtained from the study. The couplings based on basis sets for which $n = 2, 3$, and 4 were fitted using a two-parameter formula. In several cases the couplings for $n = 2$ were slightly off the trend of the two last points ($n = 3$ and 4), and therefore, for consistency, all the results were uniformly fitted with the two last points only. Obviously, the two largest basis sets should be the most complete and flexible ones, and the obtained indirect SSCCs, being the second derivatives of the total energy of the molecular system, should be the least corrupted ones by any accidental error cancellation. It was also noticed that the Kohn–Sham CBS limit results for $^1J(^{14}\text{N}^{15}\text{N})$ in N_2 , based on the use of the basis set hierarchy pcJ- n , were close to results obtained with the relatively small aug-cc-pVTZ-J basis set (compare 92 vs 236 and 274 basis functions for aug-cc-pVTZ-J, pcS-4, and pcJ-4, respectively). To inspect the performance of the individual density functionals for the prediction of the SSCC parameters in the complete basis set limit versus less demanding calculations (e.g., using the aug-cc-pVTZ-J basis set and RHF, SOPPA, SOPPA(CC2), and SOPPA(CCSD) methods), the deviation between theoretical parameters and experimental values will be plotted against the method number (assigned in the Computational Details). Results obtained with a few selected methods will be explicitly marked on the plots (B3LYP, BHandH, RHF, SOPPA(CCSD), and some others producing the least accurate J couplings).

3.1. Vibrational Corrections to Spin–Spin Coupling Constants. Molecular response to the electromagnetic field also includes the nuclear contribution. We estimated the vibrational parts of the coupling constants at the BHandH/pcJ-2 and BHandH/pcJ-3 levels of theory. Table 1 summarizes the calculated vibrational corrections to the SSCCs of the title compounds.

The use of larger basis sets resulted in most cases only in small changes in the vibrational contribution (lower than $\sim 6\%$). Only the NH_3 , CH_4 , and C_2H_4 homonuclear couplings $^2J(\text{HH})$ (for NH_3 and CH_4) and $^3J(\text{HH})$ (for C_2H_6) were significantly changed if pcJ-3 was used. However, the usage of a higher (pcJ-4) basis set is practically impossible because of the long CPU time needed for the calculation. Nevertheless, the ZPV corrections obtained with the pcJ-3 basis set are assumed sufficiently accurate considering the error caused by different theoretical levels and are used in our study to obtain empirical SSCCs. In general, the vibrational corrections in Table 1 are reasonably similar to earlier reported values. However, in some cases there are some discrepancies due to the use of different electronic and vibrational theoretical approaches. For example, Wigglesworth et al.⁶⁹ referenced their vibrational contributions for acetylene at the CCSD level instead of DFT, which was utilized in this work. Some authors also only accounted for a selected number of magnetic terms in the Hamiltonians, like

Table 1. BHandH-Calculated Vibrational Corrections (Hz) to Indirect Spin–Spin Coupling Constants for N₂, CO, CO₂, NH₃, CH₄, C₂H₂, C₂H₄, C₂H₆, and C₆H₆^a

coupling	pcJ-2	pcJ-3	lit.		J^{exptl}	J^{emp}	$J^{\text{emp } b}$
				N ₂			
$1J(^{14}\text{N}^{15}\text{N})$	−0.02	−0.02	0.1 ^c		$1.8 \pm 0.6^{c-e}$	1.7 ^c	1.77
				CO			
$1J(^{13}\text{C}^{17}\text{O})$	0.72	0.71	0.76 ^c		16.4 ^e	15.6, ^f 15.7 ^c	15.69
				CO ₂			
$1J(^{13}\text{C}^{17}\text{O})$	2.64	2.63	2.8 ^f		16.1 ^e	13.3 ^f	13.47
				NH ₃			
$1J(^{14}\text{N}^1\text{H})$	1.32	1.33	−0.3 ^d		43.8 ^g	44.1 ^d	42.47
$2J(^1\text{H}^1\text{H})$	1.02	1.29	0.7 ^d		−9.6 ^g	−10.3 ^d	−10.89
				CH ₄			
$1J(^{13}\text{C}^1\text{H})$	6.00	5.70	5.3, ^d 4.43 ^c		125.31 ^h	120.87, ^f 120.0 ^d	119.61
$2J(^1\text{H}^1\text{H})$	−1.51	−0.85	−0.7, ^d −0.58 ⁱ		−12.57, ^j −12.8 ^k	−12.1, ^d −11.99 ^f	−11.72
				C ₂ H ₂			
$1J(^{13}\text{C}^{13}\text{C})$	−2.79	−2.83	−8.67, ^c −10.26, ^m −10 ^d		174.78 ^l	185.04 ^f	177.61
$1J(^{13}\text{C}^1\text{H})$	7.42	7.23	5.16, ^c 4.86, ^m 4.6 ^d		247.56 ^l	242.70 ^f	240.33
$2J(^{13}\text{C}^1\text{H})$	−1.05	−1.04	−2.87, ^c −3.68, ^m −3 ^d		50.14 ^l	53.82 ^f	51.18
$3J(^1\text{H}^1\text{H})$	0.53	0.56	−0.062, ^c −1.27, ^m −0.1 ^d		9.62 ^l	10.89 ^f	9.06
				C ₂ H ₄			
$1J(^{13}\text{C}^{13}\text{C})$	2.15	2.06	0.9 ^d		67.457 ⁿ	66.6 ^f	65.397
$1J(^{13}\text{C}^1\text{H})$	5.98	5.86	5.1 ^d		156.302 ⁿ	151.2 ^f	150.442
$2J(^{13}\text{C}^1\text{H})$	−1.71	−1.69	−1.2 ^d		−2.403 ⁿ	−1.2 ^f	−0.713
$2J(^1\text{H}^1\text{H})$	−0.13	−0.14	0.3 ^d		2.394 ⁿ	2.1 ^f	2.534
$3J(^1\text{H}^1\text{H})_{\text{trans}}$	2.36	2.38	2.3 ^d		19.015 ⁿ	16.7 ^f	16.635
$3J(^1\text{H}^1\text{H})_{\text{cis}}$	1.42	1.40	1.2 ^d		11.657 ⁿ	10.5 ^f	10.257
				C ₂ H ₆			
$1J(^{13}\text{C}^{13}\text{C})$	1.81	1.78	na		34.521 ⁿ	na	32.741
$1J(^{13}\text{C}^1\text{H})$	5.31	5.26	na		125.206 ⁿ	na	119.946
$2J(^{13}\text{C}^1\text{H})$	−0.84	−0.84	na		−4.657 ⁿ	na	−3.817
$2J(^1\text{H}^1\text{H})$	−1.07	−1.05	na		−13.12 ^p	na	−12.07
$3J(^1\text{H}^1\text{H})_{180}$	1.06	1.07	na		16.92 ^o	na	16.36
$3J(^1\text{H}^1\text{H})_{60}$	0.55	0.56	na		3.92 ^o	na	
				C ₆ H ₆			
$1J(^{13}\text{C}^{13}\text{C})$	0.73	0.69	−0.1 ^d		56.0 ^q	56.1 ^d	55.31
$1J(^{13}\text{C}^1\text{H})$	5.47	5.43	4.8 ^d		158.6 ^q	153.8 ^d	153.17
$2J(^{13}\text{C}^{13}\text{C})$	−1.24	−1.20	−0.8 ^d		−2.5 ^q	−1.7 ^d	−1.3
$2J(^{13}\text{C}^1\text{H})$	−0.75	−0.74	−0.4 ^d		1.0 ^q	1.4 ^d	1.74
$3J(^{13}\text{C}^{13}\text{C})$	1.12	1.09	0.7 ^d		10.1 ^q	9.4 ^d	9.01
$3J(^{13}\text{C}^1\text{H})$	0.68	0.68	0.5 ^d		7.5 ^q	7.0 ^d	6.82
$3J(^1\text{H}^1\text{H})$	0.63	0.61	0.5 ^d		7.5 ^q	7.0 ^d	6.89
$4J(^{13}\text{C}^1\text{H})$	−0.44	−0.42	−0.3 ^d		−1.3 ^q	−1.0 ^d	−0.88
$4J(^1\text{H}^1\text{H})$	0.03	0.03	0.2 ^d		1.4 ^q	1.2 ^d	1.37
$5J(^1\text{H}^1\text{H})$	0.18	0.17	0.1 ^d		0.7 ^q	0.6 ^d	0.53

^aLiterature data including experimental and empirical couplings are shown for comparison. na stands for not available data. ^bThis work. For empirical values the ZPV corrections calculated with the pcJ-3 basis set were used. ^cFrom ref 72. ^dFrom ref 64. ^eFrom ref 62. ^fFrom ref 74. ^gFrom ref 75. ^hFrom ref 76. ⁱFrom ref 77. ^jFrom ref 78. ^kFrom ref 79. ^lFrom ref 80. ^mFrom ref 69. ⁿFrom ref 81. ^oFrom ref 84. ^pFrom ref 85. ^qFrom ref 82.

Lutneas et al.,⁷⁰ who used only the FC term in calculations of SSCCs of benzene. However, we found the other terms (SD, DSO, PSO) to be significant in benzene, and neglecting them caused large errors (see Table 1). We only found corrections to $2J(\text{CH})$ in C₂H₄ problematic, where the resulting empirical value of −0.713 is probably too low (see section 3.6).

Table 2 summarizes the vibrational contributions to the SSCC of all the studied compounds caused by the first and second property derivatives and calculated at the BHandH/pcJ-3 level. Contributions of the first and second derivatives are in most cases within a range of a few percent of the SSCCs and

follow similar observations reported before.^{65,66,71} The relative contribution of the second derivatives to the equilibrium value of $2J(\text{CH})$ in benzene is huge; however, the absolute change is small and within the method precision. Thus, the percent value can run high. The vibrational corrections thus seem important, but their contribution might be smaller than the error related to the equilibrium values. Further improvement could be expected with higher electronic methods (such as coupled cluster) as well as the use of larger and flexible basis sets (e.g., pcJ-4), which, unfortunately, is beyond our computational possibilities.

Table 2. Spin–Spin Coupling Constants (Hz) for the Nine Studied Systems Calculated with the Zeroth-, First-, and Second-Derivative Corrections^a

coupling	J_0	J_i	J_{ii}	$\Delta J_i/J_0$ (%)	$\Delta J_{ii}/J_0$ (%)
N₂					
$^1J(^{14}\text{N}^{15}\text{N})$	1.01	0.89	0.98	−12	9
CO					
$^1J(^{13}\text{C}^{17}\text{O})$	9.31	10.36	10.03	11	−4
CO₂					
$^1J(^{13}\text{C}^{17}\text{O})$	5.39	6.90	8.02	28	21
NH₃					
$^1J(^{14}\text{N}^1\text{H})$	49.29	50.51	50.62	2	0
$^2J(^1\text{H}^1\text{H})$	−9.26	−8.21	−7.98	11	2
CH₄					
$^1J(^{13}\text{C}^1\text{H})$	126.40	128.90	132.12	2	3
$^2J(^1\text{H}^1\text{H})$	−13.40	−13.36	−14.21	0	−6
C₂H₂					
$^1J(^{13}\text{C}^{13}\text{C})$	204.80	204.85	201.95	0	−1
$^1J(^{13}\text{C}^1\text{H})$	257.80	259.31	265.03	1	2
$^2J(^{13}\text{C}^1\text{H})$	54.40	54.19	53.32	0	−2
$^3J(^1\text{H}^1\text{H})$	11.20	11.40	11.71	2	3
C₂H₄					
$^1J(^{13}\text{C}^{13}\text{C})$	75.90	76.25	77.91	0	2
$^1J(^{13}\text{C}^1\text{H})$	158.40	160.32	164.26	1	2
$^2J(^{13}\text{C}^1\text{H})$	−3.40	−3.46	−5.09	−2	−48
$^2J(^1\text{H}^1\text{H})$	1.30	1.48	1.14	14	−26
$^3J(^1\text{H}^1\text{H}_{\text{trans}})$	20.50	20.81	22.85	2	10
$^3J(^1\text{H}^1\text{H}_{\text{cis}})$	14.40	14.33	15.80	0	10
C₂H₆					
$^1J(^{13}\text{C}^{13}\text{C})$	36.57	36.90	38.34	1	4
$^1J(^{13}\text{C}^1\text{H})$	124.80	126.06	130.06	1	3
$^2J(^{13}\text{C}^1\text{H})$	−4.49	−4.43	−5.33	1	−20
$^2J(^1\text{H}^1\text{H})$	−13.93	−14.06	−14.98	−1	−7
$^3J(^1\text{H}^1\text{H}_{180})$	4.60	4.49	5.16	−2	15
$^3J(^1\text{H}^1\text{H}_{60})$					
C₆H₆					
$^1J(^{13}\text{C}^{13}\text{C})$	61.96	62.02	62.69	0	1
$^1J(^{13}\text{C}^1\text{H})$	158.27	159.70	163.74	1	3
$^2J(^{13}\text{C}^{13}\text{C})$	−3.85	−4.05	−5.02	−5	−25
$^2J(^{13}\text{C}^1\text{H})$	0.24	0.30	−0.44	25	−308
$^3J(^{13}\text{C}^{13}\text{C})$	12.88	12.92	13.95	0	8
$^3J(^{13}\text{C}^1\text{H})$	8.39	8.45	9.07	1	7
$^3J(^1\text{H}^1\text{H})$	9.45	9.31	10.07	−1	8
$^4J(^{13}\text{C}^1\text{H})$	−1.74	−1.81	−2.18	−4	−21
$^4J(^1\text{H}^1\text{H})$	0.85	0.86	0.89	1	4
$^5J(^1\text{H}^1\text{H})$	1.04	1.07	1.20	3	13

^aZeroth, J_0 , first, J_i , and second, J_{ii} , diagonal derivatives of the indirect spin–spin coupling constants are included, using the perturbational formula by default. Relative contributions of the first and second diagonal derivatives related to the equilibrium values J_0 are gathered in the last two columns.

3.2. Basis Set Convergence of Indirect Spin–Spin Coupling Constants in N₂, CO, CO₂, and NH₃. Absolute calculated CBS $^1J(^{14}\text{N}^{15}\text{N})$ values estimated using the pcJ-*n* series of basis sets, as well as aug-cc-pVTZ-J results, for all the studied functionals are summarized in Table S1 in the Supporting Information. Data were assigned as Supporting Information to make the main text as short as possible. Included also in this table are the deviations from empirical values^{64,72}

(derived from experimental values^{62,64}). In most cases, the CBS results are closely reproduced by the less expensive calculations using the aug-cc-pVTZ-J basis set. Only a few DFT methods (M06L, BMK, and M06HF) show larger discrepancies. The deviations produced by the RHF method are significantly larger than those observed for the remaining DFT methods. Clearly, this illustrates the inability of RHF to properly handle singlet–triplet instabilities as earlier reported by Auer and Gauss.³³ The largest deviations of density functional calculations are observed for M06L, BMK, and M06HF (CBS deviations of −0.5, −2.2, and −2.4 and aug-cc-pVTZ-J-calculated deviations of −2.8, −7.1, and −7.5 Hz), and the B3LYP result is closer than the corresponding BHandH value (CBS deviation of −0.6 vs −2.4 Hz). Most functionals provide the 1J coupling in the nitrogen molecule within 1–2 Hz accuracy. As assumed, SOPPA(CCSD) gives very accurate results with a deviation of only 0.38 Hz.

A significantly larger scattering of $^1J(\text{CO})$ deviations from the empirical value (derived from experimental data from ref 73 and similar to the value reported by San Fabian⁷⁴), centered at 5 Hz, is observed for the CO molecule (Table S2, Supporting Information). In this case the least accurate methods are also RHF and M06HF, while B3LYP, BHandH, and SOPPA-(CCSD) produce fairly accurate results. Similarly to N₂, less demanding calculations based on the use of the aug-cc-pVTZ-J basis set are of comparable accuracy to those obtained using pcJ-3 and pcJ-4 basis sets and fitted toward the complete basis set limit.

In the case of the CO₂ molecule (Table S3, Supporting Information), the deviations of $^1J(\text{CO})$ from the empirical value⁶² are centered around 10 Hz. Surprisingly, also the SOPPA(CCSD) method seems to overestimate the empirical value by about 6.9 Hz (compare with the result used in ref 74).

Several density functionals are capable of an accurate prediction of $^1J(^{14}\text{N}^1\text{H})$ in ammonia.⁷⁵ The worst results are found when using the M06HF, RHF, M06, and M06L functionals (aVTZJ deviations of −12.5, 13.3, 13.9, and 10.6 Hz; see Table S4A, Supporting Information). It is obvious that the M06HF density functional has problems in predicting SSCC parameters, and contrary to other density functionals, this functional is also very sensitive to the incompleteness and size of the basis set (compare the corresponding CBS and aVTZJ deviations of −1.2 and −12.5 Hz). Also both B3LYP and BHandH fail to provide a reasonable agreement with empirical values for $^1J(\text{NH})$ and have CBS deviations of 3.3 and 3.4 Hz. On the other hand, the geminal coupling constant $^2J(\text{HH})$ from ref 75 is predicted within 2 Hz by most of the functionals, and only M06HF, RHF, M06, and M06L produce larger CBS deviations from the empirical value (22.5, −13.3, −9.0, and −7.2 Hz; see Table S4B).

3.3. Basis Set Convergence of Indirect Spin–Spin Coupling Constants in CH₄, C₂H₂, C₂H₄, and C₂H₆. Similarly to the one-bond coupling in ammonia, the deviation of $^1J(\text{CH})$ from the recent experimental gas-phase value in methane,⁷⁶ calculated using various density functionals, shows a very scattered pattern (from −15 to +30 Hz; see Table S5A, Supporting Information). The least accurate methods from the test set were found to be M06HF, RHF, and BMK (CBS deviations of −47.8, 36.6, and 35.5 Hz). Our results are close to earlier reported empirical values with inclusion of rovibrational corrections.^{64,77} Note that the BHandH density functional is significantly more accurate than the popular B3LYP functional (CBS deviations of 5.3 and 12.5 Hz). $^2J(\text{HH})$ for the geminal interaction in methane deviates from the experimental value⁷⁸

Table 3. Deviations of Coupling Constants in C₆H₆ Calculated with Selected Methods from Empirical Values^a

	CBS deviation (Hz)											
	VSXC	B3LYP	BHandH	wB97	wB97X	RHF	KT1	KT2	KT3	SOPPA ^b	SOPPA(CC2) ^b	SOPPA(CCSD) ^b
¹ J(¹³ C ¹³ C)	−7.15	4.02	5.54	−1.04	−1.67	−27.11	−13.04	−10.31	−2.11	4.88	4.75	5.01
¹ J(¹³ C ¹ H)	−12.36	13.15	6.93	−11.55	−8.75	15.48	−0.46	15.29	24.03	11.03	8.53	4.95
² J(¹³ C ¹³ C)	−1.73	−0.48	−3.03	−2.53	−1.19	48.88	1.42	−0.16	−0.89	−2.29	−1.88	−2.30
² J(¹³ C ¹ H)	−1.95	0.33	−1.18	−0.64	−0.13	16.76	2.39	0.94	0.40	−1.69	−1.55	−1.65
³ J(¹³ C ¹³ C)	1.90	2.22	3.88	4.41	2.85	−51.81	0.27	0.96	1.70	2.15	1.51	2.12
³ J(¹³ C ¹ H)	0.68	1.15	1.50	1.06	0.68	−20.89	1.05	1.87	2.38	1.12	0.87	0.98
³ J(¹ H ¹ H)	1.14	1.91	1.97	0.96	0.96	−9.31	1.78	2.84	3.06	1.13	0.99	0.83
⁴ J(¹³ C ¹ H)	−0.62	−0.32	−0.97	−1.01	−0.51	21.81	0.24	−0.27	−0.74	−0.82	−0.70	−0.90
⁴ J(¹ H ¹ H)	−0.59	−0.07	−0.57	−0.85	−0.64	11.99	0.58	0.48	0.47	−0.46	−0.43	−0.57
⁵ J(¹ H ¹ H)	0.52	0.24	0.60	0.68	0.48	−12.62	−0.04	0.47	0.56	0.58	0.50	0.66
	aug-cc-pVTZ-J deviation (Hz)											
	VSXC	B3LYP	BHandH	wB97	wB97X	RHF	KT1	KT2	KT3	SOPPA	SOPPA(CC2)	SOPPA(CCSD)
¹ J(¹³ C ¹³ C)	−3.17	4.68	6.16	3.06	1.95	−26.71	−9.50	−6.28	0.20	4.46	4.36	4.45
¹ J(¹³ C ¹ H)	−7.74	13.95	7.56	−7.38	−5.30	15.73	3.43	19.89	26.77	9.86	7.67	3.92
² J(¹³ C ¹³ C)	−1.84	−0.36	−2.92	−3.16	−1.69	49.46	1.34	−0.39	−0.95	−2.14	−1.80	−2.14
² J(¹³ C ¹ H)	−1.94	0.41	−1.15	−0.90	−0.35	17.31	2.37	0.80	0.41	−1.66	−1.53	−1.60
³ J(¹³ C ¹³ C)	2.12	2.02	3.68	5.10	3.36	−52.50	0.25	1.00	1.69	1.85	1.27	1.79
³ J(¹³ C ¹ H)	1.00	1.19	1.53	1.42	0.94	−21.40	1.26	2.16	2.59	1.17	0.93	1.01
³ J(¹ H ¹ H)	1.15	1.86	1.90	0.93	0.90	−9.55	1.72	2.79	3.08	1.30	1.17	0.98
⁴ J(¹³ C ¹ H)	−0.78	−0.35	−1.00	−1.30	−0.77	22.32	0.11	−0.49	−0.86	−0.82	−0.71	−0.89
⁴ J(¹ H ¹ H)	−0.63	−0.13	−0.64	−0.94	−0.72	12.13	0.51	0.40	0.40	−0.47	−0.45	−0.58
⁵ J(¹ H ¹ H)	0.48	0.18	0.53	0.66	0.43	−12.90	−0.10	0.42	0.53	0.51	0.45	0.60

^aBoth CBS (when available) and aug-cc-pVTZ-J results are shown. The best results are shown in bold. ^bFrom pcJ-2 results only.

by +1 to −5 Hz (Table S5B). HF and the DFT functionals M06HF, M06, and M06L are the least accurate methods (deviations of −15.1, 4.4, −6.2, and −7.3 Hz, respectively) for the geminal coupling in methane, while B3LYP and BHandH again produce small ²J(HH) deviations (−1.4 and −1.5; see Table S5B). The corresponding calculated rovibrational corrections and estimated empirical couplings are similar to earlier reported values.^{78,79}

The acetylene molecule is the first example of a compound with both carbon–carbon and several carbon–proton coupling constants.⁸⁰ Several studies of ZPV corrections^{64,69,72} and empirical experimental coupling constants⁷⁴ of acetylene have been published, and some of these data are gathered in Table 1. The corresponding ¹J(CH), ¹J(CC), ²J(CH), and ³J(HH) CBS and aVTZJ values and their comparison with experiment measured in the gas phase⁸⁰ are presented in Table S6, Supporting Information. Similarly to previously discussed coupling constants for the N₂, CO, CO₂, and CH₄ molecules, RHF, M06HF, and M06L are the least accurate methods in predicting coupling constants over one, two, or three bonds, respectively. The BHandH density functional, analogous to methane, provides more accurate ¹J(CH), ¹J(CC), and ²J(CH) parameters in comparison to B3LYP.

Selected experimentally observed ethylene coupling constants,⁸¹ previously calculated ZPV corrections,⁶⁴ and the corresponding empirical values⁷⁴ are compared with our calculated results in Table 1. Table S7 in the Supporting Information gathers deviations of six theoretically predicted coupling constants in ethylene for the studied methods. As before, the results obtained with the aVTZJ basis set are very close to the corresponding CBS estimates and RHF, M06HF, M06, and BMK are the least accurate methods. Most density functionals give ¹J(CH) within −10 to +20 Hz (Table S7A), ¹J(CC) within 0–20 Hz range (Table S7B), ³J(HH_{cis}) within

0–4 Hz (Table S7D), and ³J(HH_{trans}) within 0–5 Hz (Table S7E) of the corresponding empirical values, respectively. In contrast, ²J(HH_{gem}) is underestimated and the majority of deviations are in the range from −2 to 0 Hz (Table S7F). A relatively small two-bond proton–carbon coupling (²J(CH)_{emp} = −0.713 Hz) is underestimated by 1–2 Hz by the majority of studied density functionals (Table S7C). The BHandH functional performs better than B3LYP in predicting ¹J(CH), ¹J(CC), and ³J(HH_{trans}) and is less accurate in the case of the ³J(HH_{cis}), ²J(CH), and ²J(HH_{gem}) parameters.

The CBS-estimated ethane coupling constants deviate from the empirical values (Table S8, Supporting Information) in a manner very similar to that of the previously presented values for methane, acetylene, and ethylene. The least accurate methods used to predict ethane couplings are RHF, M06HF, and M06L, and most density functionals show deviations from empirical values from −10 to +20 Hz for ¹J(CH) and from −10 to +10 Hz for ¹J(CC). BHandH performs better than B3LYP in predicting ethane J couplings too.

3.4. Basis Set Convergence of Indirect Spin–Spin Coupling Constants in C₆H₆. The benzene molecule is the largest and most challenging system considered in this study, and therefore, only a few selected methods were used to calculate the indirect spin–spin coupling constants. Kaski et al.⁸² reported experimental coupling constants of benzene, and Ruden et al.⁶⁴ calculated the corresponding ZPV corrections at the B3LYP level of theory and published the empirical SSCC values. Our calculated benzene J coupling deviations from empirical values and some literature data are gathered in Table 3. As observed before, deviations from empirical values for 10 benzene coupling constants, calculated with 5 selected density functionals and RHF with the compact aug-cc-pVTZ-J basis set, are fairly close to results obtained with very demanding calculations in the complete basis set limit.

Not surprisingly, the RHF results possess very large deviations. The wB97X and B3LYP functionals outperform all other methods. In particular, the CBS-extrapolated $^1J(\text{CC})$ calculated with the wB97 density functional is underestimated by only 1.07 Hz ($\sim 2\%$ of the empirical value) compared to experiment and overestimated by 3.06 Hz ($\sim 6\%$ of the empirical value) when calculated using the aug-cc-pVTZ-J basis set. The VSXC functional provides $^1J(\text{CC})$ with the highest error and thereby underestimates this coupling constant by 7.15 Hz in the complete basis set limit (the corresponding deviation for the aug-cc-pVTZ-J basis set is 3.17 Hz). Recently, Del Bene and co-workers⁸³ calculated the same parameter using advanced SOPPA and EOM-CCSD methods with smaller basis sets. They obtained values 63.1 and 60.3 Hz, and the corresponding recalculated deviations from our empirical value are 7.8 and 5.0 Hz. On the contrary, BHandH outperforms other methods in predicting $^1J(\text{CH})$ coupling (deviation of 6.93 Hz, $\sim 5\%$ of the empirical value).

3.5. Coupling Constant Component Analysis. Although all coupling constants in this study are dominated by the Fermi contact contribution (FC term $\geq 95\%$ of overall J coupling), for some systems and coupling constants (mainly over multiple bonds) also other terms are negligible. Figure 1 shows the

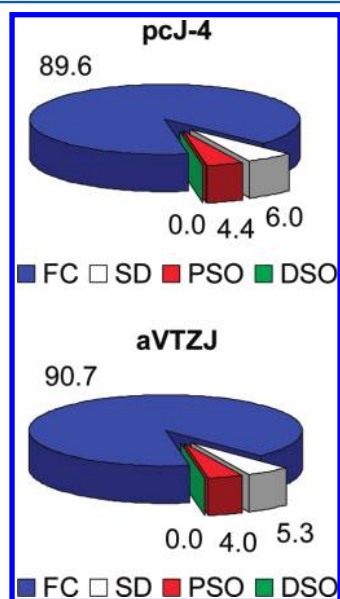


Figure 1. Contributions of particular terms (%) to the overall value of the $^1J(\text{CC})$ coupling constant in C_2H_2 . FC stands for Fermi contact, SD is the spin-dipole term, DSO is diamagnetic spin–orbit coupling, and PSO is the paramagnetic spin–orbit coupling term. Data were averaged over all theoretical methods. The pcJ-4 (top) and aug-cc-pVTZJ (bottom) basis sets were used.

percent contribution of particular terms to the $^1J(\text{CC})$ coupling constant of acetylene obtained with the pcJ-4 basis set. The figure represents the average value obtained by all studied methods. However, changes among functionals are within 1%. Only the M06HF functional provides slightly different percent contributions (difference from the average value up to 9%; see Figure S1, Supporting Information). Note that for the $^1J(\text{CC})$ coupling constant of acetylene FC represents only about 90% of the overall value and the rest is created mainly by the SD and PSO terms. The DSO term is in all cases under 0.01% of the overall J coupling value. It is also important to note that ratios of the particular terms are similar if the pcJ-4 or

aug-cc-pVTZJ basis set is used (cf. Figure 1). This is kept for all studied theoretical methods. Thus, we conclude that, for J couplings, where terms other than FC play a negligible role, the aug-cc-pVTZJ basis set provides well-converged values if compared to the pcJ-4 data. The pcJ-4 basis is known to provide results very close to the CBS limit. However, once more, we must emphasize that these conclusions are valid mainly for coupling constants with a dominating FC term.

3.6. Accuracy Related to Different Types of Calculated Indirect Spin–Spin Coupling Constants. Analysis of the SSCC calculations for the different methods described above indicates a very similar performance of the aug-cc-pVTZ-J compared to the use of very large and flexible basis sets. The SSCC magnitudes for $^1J(\text{XX})$, $^1J(\text{XH})$, $^2J(\text{XH})$, $^2J(\text{HH})$, and $^3J(\text{XH})$ sometimes differ by several orders of magnitude for various types of couplings. Therefore, a better picture is obtained by showing not only the absolute deviations of the calculated J values from the empirical values but also their corresponding relative deviations (%). Such a way of presenting the data would also stress the inaccuracy in predicting small couplings, operating via several bonds. Generally, it can be concluded that in most cases the highest errors are produced by RHF and the DFT functionals M06 and M06HF (methods 6, 7, 26, and 40).

Figure 2A contains the averaged CBS relative deviations of $^1J(^{14}\text{N}^{15}\text{N})$ and $^1J(\text{CO})$ for the N_2 , CO, and CO_2 molecules in

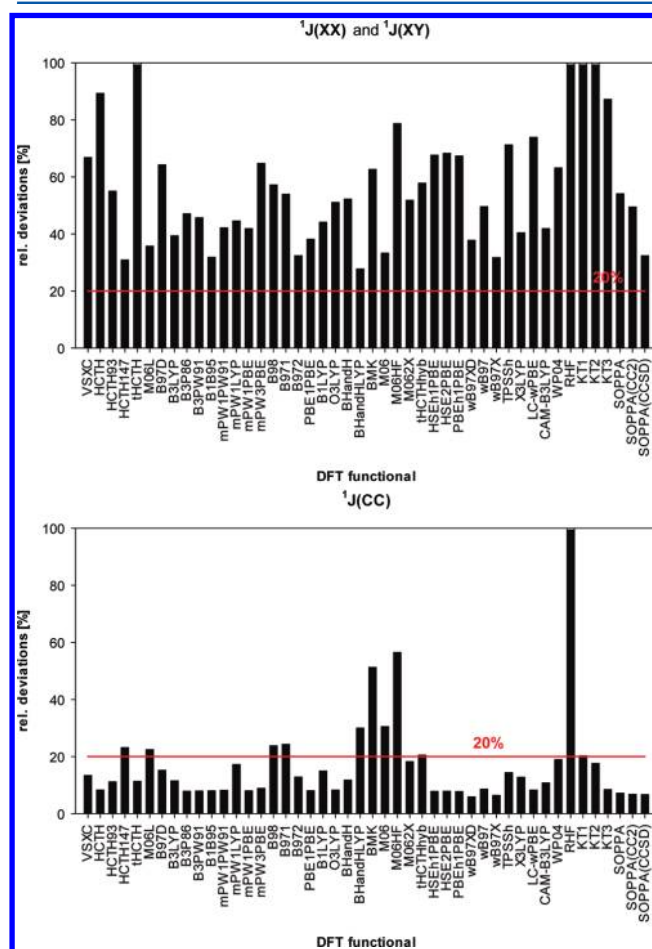


Figure 2. CBS-estimated (pcJ- n) ratio of SSCC deviations from empirical values (%) calculated with several methods for (A, top) $^1J(^{14}\text{N}^{15}\text{N})$ in N_2 and $^1J(\text{CO})$ in CO and in CO_2 and (B, bottom) $^1J(\text{CC})$ in acetylene, ethylene, and ethane.

the gas phase. RHF and the KT_n and tHCTH density functionals give rise to the largest errors. It should be noted, however, that the accuracy related to the predictions is in this case very low for all the studied methods. If we set up an internal accuracy threshold of 20% (relative deviation), which separates good performers from bad, all methods provide $^1J(\text{XX})$ or $^1J(\text{XY})$ with a higher relative deviation. Only some functionals come close to the relative deviation threshold of 30% (HCTH147, 31%; B1B95, 32%; B972, 32%; BHandHLYP, ~28%; wB97X, ~32%). Average relative deviations over all methods (excluding the too high HF) for all three systems were relatively high: ~57% for N_2 , ~33% for CO , and ~77% for CO_2 .

On the contrary, as shown in Figure 2B, the averaged accuracy related to the prediction of $^1J(\text{CC})$ in acetylene, ethylene, and ethane is significantly better and the deviations for most functionals fulfill the accuracy given by the threshold of 20%. The smallest relative deviations are provided by the wB97X and wB97XD (all 6%) functionals as well as by the SOPPA methods (SOPPA, SOPPA(CCSD), SOPPA(CC2), all ~7%). RHF and the Minnesota functionals M06, M06HF, and BMK do not perform satisfactorily (>30% relative deviation). Note that hybridizations on carbon atoms have only a negligible effect on the deviation of $^1J(\text{CC})$. Average relative deviations over all methods (excluding HF) were for acetylene, ethylene, and ethane approximately 15%.

As shown in Figure 3, the heteronuclear one-bond $^1J(\text{XH})$ coupling constants are predicted relatively well, with most

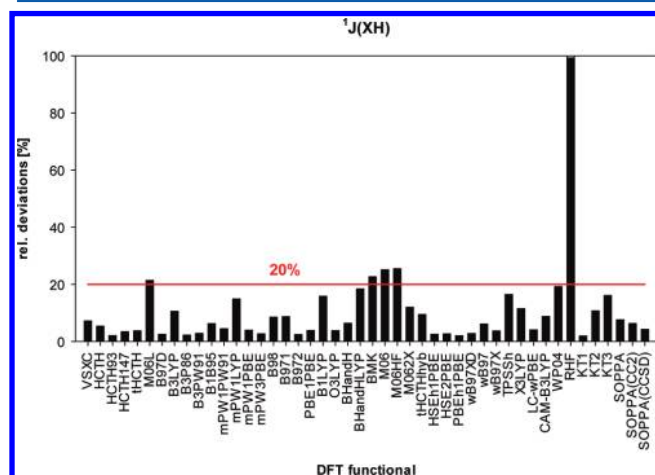


Figure 3. CBS-estimated (pcJ- n) ratio of SSCC deviations from empirical values (%) calculated with several methods for $^1J(\text{XH})$ in ammonia, methane, acetylene, ethylene, and ethane.

methods producing relative deviations below 20%. As found for the $^1J(\text{CC})$ couplings above, the M06 family of functionals and RHF provided coupling constants with substantially higher relative deviation (>25%). On the other end of a quality scale stand the KT1, PNEh1PBE, HCTH93, B3P86, B972, and B97D functionals with relative deviations lower than 3%. Note that among the two popular functionals, BHandH performs better than B3LYP (relative deviation ~6% vs 11%). The average deviations were found similar (~9%) for all related systems (NH_3 , CH_4 , C_2H_2 , C_2H_4 , and C_2H_6).

The $^3J(\text{HH})$ relative deviations in all relevant systems given by all methods are summarized in Figure 4. Only some functionals are able to fulfill the 20% relative deviation criterion. Above all stand the B97D and HCTH93 functionals, which

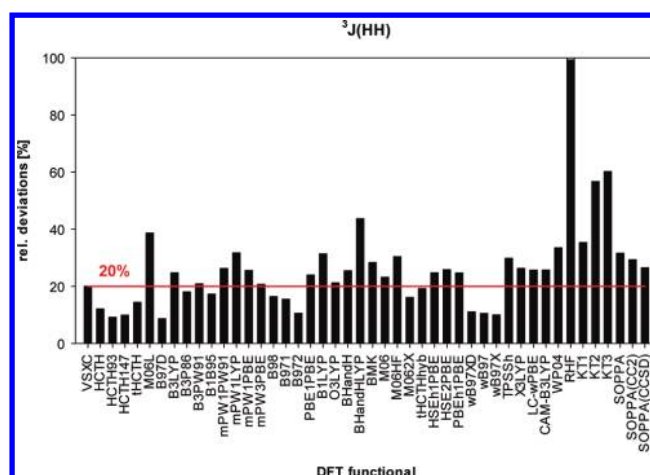


Figure 4. CBS-estimated (pcJ- n) ratio of SSCC deviations from empirical values (%) calculated with several methods for $^3J(\text{HH})$ in acetylene, ethylene, and ethane.

provide results with a deviation lower than 10%. The highest errors relative to the empirical values are provided by the KT2, KT3, and RHF methods (>50%). Note that the $^3J(\text{HH}_{\text{trans}})$ coupling constant in C_2H_4 is in general predicted slightly better than the $^3J(\text{HH}_{\text{cis}})$ coupling by most of the methods (average relative deviation ~23% vs ~26%; HF results were excluded). On the other hand, in the case of C_2H_6 , the $^3J(\text{HH}_{60})$ constants are obtained with lower relative deviation than $^3J(\text{HH}_{180})$ (18% vs 22%). It is also interesting that the accuracy of predicting $^3J(\text{HH})$ increases in the sequence acetylene (average relative deviation 32%) < ethylene (~25%) < ethane (~20%).

The relative deviations for $^2J(\text{HH})$ in the relevant systems are gathered in Figure 5. Several functionals produced very high

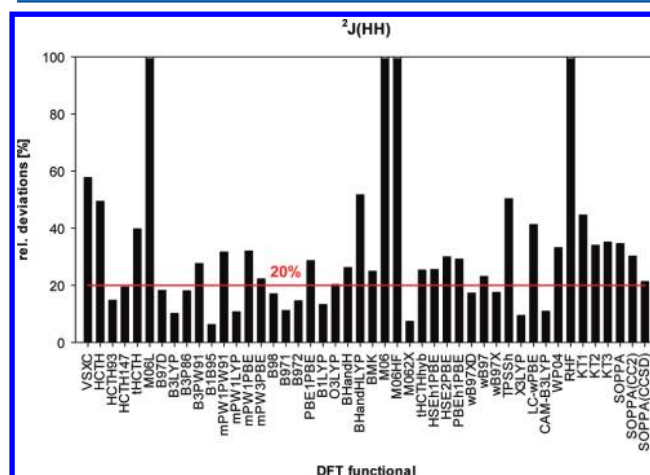


Figure 5. CBS-estimated (pcJ- n) ratio of SSCC deviations from empirical values (%) calculated with several methods for $^2J(\text{HH})$ in ammonia, methane, ethylene, and ethane.

differences from the empirical values. The worst were the M06, M06HF, and M06L functionals and RHF. Eleven of the studied methods provided a deviation higher than 40%, and only 16 methods gave a deviation lower than the desired 20% and only 3 of them lower than 10% (B1B95, M062X, and X3LYP). Interestingly, C_2H_4 is predicted with an average relative deviation (averaged over all methods except HF and M06-type functionals) significantly higher (~64%) than that for other related molecules (~15%).

In the end, Figure 6 summarizes relative deviations for ${}^2J(\text{CH})$ coupling constants for all methods. The figure averages

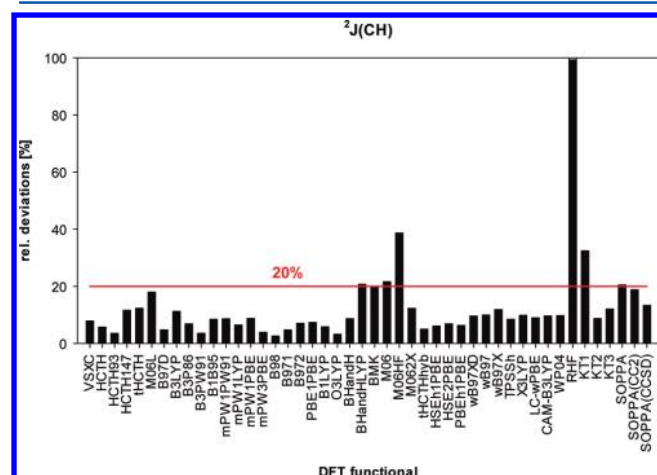


Figure 6. CBS-estimated (pcj-*n*) ratio of SSCC deviations from empirical values (%) calculated with several methods for ${}^2J(\text{CH})$ in C_2H_2 and C_2H_6 . Deviations for C_2H_4 were observed to be too high and are not included.

only relative deviations for C_2H_2 and C_2H_6 because the deviations for C_2H_4 were observed to be suspiciously high (see Table S17, Supporting Information). It is probably because the empirical value is wrong; thus, values for C_2H_4 were excluded from the average. Nevertheless, it can be seen that almost all functionals reproduce empirical coupling constants with relative deviations lower than 20%. Only M06, KT1, M06HF, and RHF methods produce higher errors. Among the most efficient functionals for ${}^2J(\text{CH})$ belong B98, O3LYP, HCTH93, and B97D, which reproduce the empirical value with an error lower than 5%.

All specific deviations can be found in the Supporting Information in Tables S13–S17. According to the observations discussed above, we conclude that most studied methods predict all couplings but the homonuclear ${}^1J(\text{XX})$ with reasonable accuracy. Note that especially CO is a special case and the methods do not work that well for this coupling. However, exceptionally good performers are found to be the B97-family functionals (also the long-range-corrected version of B97). Especially wB97X and B972 provide all the studied coupling constants with an average deviation lower than 14% relative to the empirical values. Also Handy's GGA functionals (HCTH93 and HCTH147), SOPPA(CCSD), and the popular hybrid functionals B3P86 and B3LYP yield very good results (average relative deviation lower than 19%). On the other hand, the M06-type functionals, as well as the KT_n functionals, provide all coupling constants with a relative deviation from empirical values higher than 40%. Therefore, it is not possible to make any general statement that hybrid functionals provide better results than GGA or vice versa. As could be expected, the worst agreement with experiment is obtained with the RHF method. Therefore, it is not surprising that the M06HF functional performs poorly, as it contains 100% HF exchange.

3.7. Analysis of the Efficiency of the Popular B3LYP Functional in Coupling Constant Calculations. As stated above, the popular B3LYP functional is able to provide ${}^1J(\text{CC})$, ${}^1J(\text{XH})$, ${}^3J(\text{HH})$, ${}^2J(\text{HH})$, and ${}^2J(\text{CH})$ coupling constants with a relatively low error when compared to experiment. In this section we briefly analyze possible changes available for this

functional. Thus, the effect of using different correlation parts of the functional with the same exchange part (and vice versa) was tested. Also the modification of B3LYP correcting the too rapid die-off of the non-Coulomb part of the exchange functional (CAM-B3LYP) as well as the effect of an amount of exact exchange (BLYP vs B3LYP vs BHandH) will be discussed.

Table 4 (and Table S18, Supporting Information) shows the effect of using different correlation functionals (P86 vs LYP vs

Table 4. Effect of Correlation Functionals^a

	1J		2J	3J
	single bond	multiple bond		
B3P86	6.18	8.86	1.65	2.07
B3LYP	17.04	13.38	2.31	2.72
B3PW91	7.23	9.13	2.14	2.39

^aThe table shows rms deviations from empirical values.

PW91) with the same B3 exchange part. We conclude that for all 1J , 2J , and 3J coupling constants the use of P86 gives rise to a better agreement than that of PW91 and LYP.

The effect of different exchanges (O3 vs B3 vs X3), with the same correlation LYP functional, can be seen from Table 5

Table 5. Effect of Exchange Functionals^a

	1J		2J	3J
	single bond	multiple bond		
O3LYP	9.24	10.98	1.27	2.34
B3LYP	17.04	13.38	2.31	2.72
X3LYP	18.23	13.94	2.36	2.88

^aThe table shows rms deviations from empirical values.

(and Table S19, Supporting Information). According to the rms deviations from the table, it is obvious that O3 possesses better accuracy than B3 and X3 for all couplings. A simple combination of P86 and O3 made according to the conclusions above could give good results for the SSCCs. However, one needs to determine the exact amount of the correlation and exchange parts, and this means a fitting procedure which goes beyond the scope of this work.

If the range-separated correction is added to B3LYP in the way of CAM-B3LYP, we can see from Table 6 (and Table S20,

Table 6. Effect of Long-Range-Corrected Functionals^a

	1J		2J	3J
	single bond	multiple bond		
B3LYP	17.04	13.38	2.31	2.72
CAM-B3LYP	14.20	12.69	2.67	2.81

^aThe table shows rms deviations from empirical values.

Supporting Information) that this makes only negligible changes. It is interesting that CAM-B3LYP gives better results (lower rms when compared to experiment) than B3LYP especially for short-distance 1J coupling and worse for couplings over more bonds. Note that negligible changes were noticed if the B97 and wB97X or wB97XD functionals were considered. This is obvious, because the dispersion term is only an empirical energy correction that does not affect the electronic wave function. Thus, B97 with or without dispersion correction must give the same SSCC.

The amount of exact HF exchange in hybrid functionals plays an important role in their capability to predict NMR coupling constants as can be seen from Table 7 (and Table S21,

Table 7. Effect of HF Exchange^a

	¹ J		² J	³ J
	single bond	multiple bond		
BLYP	19.63	6.33	3.75	2.30
B3LYP	17.86	11.43	2.04	2.39
BHandH	10.55	11.61	1.92	2.68

^aThe table shows rms deviations from empirical values.

Supporting Information). Three different functionals with different amounts of HF exchange were considered. The GGA functional BLYP has 0% HF exchange, standard B3LYP contains 20% HF exchange, and another hybrid functional, BHandH, has 50% HF exchange. The rms deviations (Table S21) reveal that the sequence of accuracy is (from the best to the worst) BHandH, B3LYP, and BLYP. This could lead to the simple conclusion that including a higher amount of HF in the functional is better for calculating coupling constants. However, deeper analysis according to the type of particular coupling constant shows that a higher amount of HF is better for predicting only ¹J(single bond) and ²J coupling constants. On the other hand, for ¹J(multiple bond) and ³J constants a higher amount of HF causes a negligible effect or even a worsening of the agreement with experiment. Furthermore, functionals with 100% HF exchange (e.g., M06HF) fail completely; thus, an amount of HF exchange from 20% to 50% is a good compromise for predicting SSCCs.

4. CONCLUSIONS

The performance of over 40 density functionals were tested for their ability to predict indirect spin–spin coupling constants in 9 small molecules (N₂, CO, CO₂, NH₃, CH₄, C₂H₂, C₂H₄, C₂H₆, and C₆H₆) using the pcJ-*n* basis set hierarchy. The calculated SSCCs based on the use of DFT and further extrapolated to the complete basis set limit were compared with empirical couplings obtained from experimental values (and calculated ZPV corrections) and RHF-, SOPPA-, SOPPA(CC2)-, and SOPPA-(CCSD)-based results. For the ¹J(CC), ^γJ(XH), and ^αJ(HH) ($\gamma = 1, 2$, and 3 and $\alpha = 1$ and 2) coupling constants good performance is found to be provided by the B97 family of functionals, including the long-range-corrected version of B97. For example, the ¹J(XH) coupling constants are predicted within 5% accuracy using wB97XD. For ¹J(NN) use of wB97XD also results in reasonable results despite the small size of this coupling in N₂. ¹J(CO) on the other hand represents a more complicated case in relation to the use of the above recommended functionals. This clearly shows that no single functional can be recommended for calculation of general SSCCs and that benchmarking of functionals in relation to their ability for calculation of specific types of SSCCs is an important subject.

Finally, we note that use of the less expensive aug-cc-pVTZ-J basis set resulted in SSCCs that compare very well with the CBS estimates, and calculations using the aug-cc-pVTZ-J basis set can therefore be seen as a cheaper alternative than performing explicit basis set extrapolation to estimate SSCCs in the CBS limit.

■ ASSOCIATED CONTENT

■ Supporting Information

Tables listing coupling constants and their deviations from empirical values, relative deviations of coupling constants in several molecules, effect of the use of different correlation functionals, different exchange functionals, and long-range-corrected functionals and different amounts of HF exchange on the coupling constants and a figure showing the contributions of particular terms to the overall value of ¹J(CC) in C₂H₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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