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Basis set dependence of NMR spin–spin couplings in density functional theory calculations: first row and hydrogen atoms

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Abstract

We analyze the basis set dependence of NMR spin–spin coupling constants calculated using density functional theory in a set of benchmark molecules containing first row and hydrogen atoms. We find that similarly to calculations based on wavefunction theory, the flexibility of core gaussian basis functions plays a key role. For the set of molecules under consideration, we have analyzed the basis set limit and studied basis set of triple- ζ quality, which may be useful for practical applications.

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1. Introduction

NMR spin–spin coupling constants (SSCC) are, among all response properties, one of the most difficult to reproduce quantitatively. Predictions from state-of-the-art wavefunction-based methods are generally in good agreement with experimental values even in the most difficult cases [1,2]. Unfortunately, the high computational cost required by these methods limits their applicability to systems involving just a few atoms. As shown in re-

cent work [3,4], methods based on density functional theory provide an interesting alternative to deal with large compounds. The performance of hybrid density functionals, particularly B3LYP [5], combined with analytical linear response techniques has been shown to be a powerful tool for reproducing experimental values in a wide variety of molecules [3,4,6,7].

It is well known that calculated SSCC strongly depend on the quality of the gaussian basis set employed. The Fermi contact (FC) term is usually the largest contribution and the main source of inaccuracy. This contribution is originated by the FC operator whose spatial representation contains a Dirac delta function placed at the coupled

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nuclear sites. Therefore, a good description of the core electrons in the presence of the FC operator is needed to achieve reliable results. For this reason, the election of the basis set is a critical point when undertaking SSCC calculations. An extensive analysis of the basis set dependence of SSCC in the wavefunction framework has been performed by Helgaker et al. [8], who provided a systematic way to extend correlation-consistent gaussian basis set by decontracting and augmenting the *s*-type functions at the tight end. Although their study is transferable to other wavefunction-based methods, DFT based methods may have different basis set requirements and deserve to be tested.

In this work, we present a systematic study of the basis set dependence of NMR SSCC within the DFT framework. We have chosen the hybrid B3LYP functional for benchmark purposes, which yields accurate predictions for DFT calculated SSCC [3,4]. The FC, spin–dipolar (SD), and paramagnetic spin–orbit (PSO) terms were evaluated using the coupled perturbed Kohn–Sham (CPKS) methodology. Details on the theory of SSCC calculated within the CPKS framework are given in [3,4]. For each perturbed nucleus a total of 10 linear response equations must be solved; 7 of them are real and triplet (1 for the FC operator and 6 for the SD operator), and 3 imaginary and singlet (PSO operator). The DSO contribution was evaluated using fully numerical quadrature [9].

The implementation of SSCC calculation was performed within the *Gaussian* development version program [10]. A set of five small molecules containing first row and hydrogen atoms was selected to perform this analysis in such a way that very large basis set can be employed: HF, H₂O, CH₄, C₂H₄, and FCH₃. Although this set contains challenging molecules for SSCC calculations [11,12], the aim of this work is to establish the basis set dependence of the results instead of the quality of the finally converged results. All geometrical structures were taken from experimental data in [13]. For each compound, all SSCC were calculated employing different gaussian basis sets, but we focus the analysis in one- and two-bond couplings. As expected, the relative importance of each contribution to the total isotropic SSCC presents large variations for the different molecules. For this reason and to limit space, we only report individual contributions for the largest basis set employed. In all cases quoted, SSCC are referred to ¹H, ¹³C, ¹⁴N, ¹⁷O, and ¹⁹F isotopes.

We start our study using the correlation-consistent polarized valence Xtuple- ζ basis set of Dunning and coworkers [14–17], cc-pVXZ, ranging from double- ζ to sextuple- ζ (X = D, T, Q, 5, and 6). As seen from Table 1, the convergence of this series is unsatisfactory, showing in most cases not only a change in the trend along the series, but a large difference between the cc-pV5Z and the

Table 1
Basis set dependence of total spin–spin couplings in the cc-pVXZ series (X = D, T, Q, 5, and 6)

| | | D | T | Q | 5 | 6 |
|-------------------------------|---------------------|--------|--------|--------|--------|--------|
| HF | ¹ J(F,H) | 360.0 | 230.1 | 325.7 | 370.1 | 488.5 |
| H ₂ O | ¹ J(O,H) | −69.5 | −48.7 | −61.7 | −65.7 | −82.4 |
| | ² J(H,H) | −2.8 | −8.5 | −6.1 | −7.2 | −8.0 |
| NH ₃ | ¹ J(N,H) | 42.6 | 36.0 | 39.5 | 41.4 | 48.0 |
| | ² J(H,H) | −7.1 | −9.4 | −8.7 | −9.7 | −10.6 |
| CH ₄ | ¹ J(C,H) | 124.3 | 115.8 | 120.8 | 126.2 | 138.4 |
| | ² J(H,H) | −9.9 | −10.9 | −11.5 | −12.9 | −13.3 |
| C ₂ H ₄ | ¹ J(C,C) | 85.3 | 79.6 | 66.3 | 74.8 | 72.4 |
| | ¹ J(C,H) | 156.2 | 150.0 | 153.8 | 159.3 | 176.5 |
| | ² J(C,H) | −2.4 | −1.0 | −0.8 | −0.9 | −1.3 |
| | ² J(H,H) | 1.8 | 4.0 | 4.7 | 3.3 | 3.8 |
| FCH ₃ | ¹ J(F,C) | −172.6 | −219.9 | −243.9 | −243.3 | −234.2 |
| | ¹ J(C,H) | 139.7 | 136.0 | 141.3 | 148.6 | 161.8 |
| | ² J(F,H) | 48.5 | 38.0 | 46.3 | 50.3 | 52.1 |
| | ² J(H,H) | −6.4 | −7.3 | −7.9 | −9.4 | −9.7 |

All values in Hz.

cc-pV6Z, with the only exceptions of $^2J(\text{H,H})$ in CH_4 and FCH_3 . These results are not surprising since a similar trend was found for these basis sets in HF and H_2O [8] employing the complete active space self-consistent field (CAS SCF) method.

We next analyze the dependence of calculated SSCC using the cc-pCVXZ series of basis set ($X = \text{D, T, Q, and 5}$), which consists of the previous cc-pVXZ augmented with extra functions to describe core–core and core–valence correlation [18]. These results are presented in Table 2. We find that the overall trend in this series exhibits less oscillations than those in Table 1 (cc-pVXZ), although the final results, corresponding to the cc-pCV5Z basis set, are clearly not fully converged and more basis functions need to be added.

As commented above, the correct evaluation of the FC term requires a good description of the electronic density near the the nuclear positions. For this reason, we have fully decontracted the s -type functions of the cc-pCVXZ basis set, yielding the cc-pCVXZ-sd ($X = \text{D, T, Q, and 5}$) series. Results obtained with this basis set (Table 3), show a smoother trend than the former cc-pVXZ and cc-pCVXZ sets. SSCC in Table 3 present a monotonic behavior, except for $^1J(\text{C,C})$ in C_2H_4 and $^1J(\text{F,C})$ in FCH_3 . This suggests that most values in the last column, i.e., cc-pCV5Z-sd, are not far from being converged.

We next add tight functions to our cc-pCVXZ-sd basis set to improve the description of the core region. We included four tight s -type primitives to the cc-pCVXZ-sd basis set following the procedure suggested in [8]. These functions were extended at the tight end in an even-tempered way with a constant ratio of 6, yielding what we here call the cc-pCVXZ-sd+t ($X = \text{D, T, Q, and 5}$) basis set series. SSCC calculated using this basis set are presented in Table 4. As expected, the addition of tight s -type functions improves the convergence of calculated SSCC, mainly due to its effect on the FC contribution. The non-contact terms vary much less than the FC with the addition of tight functions. For instance, the PSO contribution to $^1J(\text{O,H})$ ranges from -12.7 to -13.2 Hz in our cc-pCVXZ-sd and cc-pCVXZ-sd+t series, while the FC ranges from -42.0 to -61.3 Hz in the former, and from -52.3 to -65.9 Hz in the latter. The non-contact contributions to $^1J(\text{F,C})$ in FCH_3 present a variation of less than 0.1 Hz when ranging from the cc-pCVXZ-sd to the cc-pCVXZ-sd+t series (for the same X) whereas the difference between total couplings in both series (Tables 4 and 5), is mainly accounted for the FC term. This fact can be used to save significant CPU time by computing the FC contribution using a large basis set supplemented with tight functions, while the remaining terms may be evaluated with a smaller

Table 2

Basis set dependence of total spin–spin couplings in the cc-pCVXZ series ($X = \text{D, T, Q, and 5}$)

| | | D | T | Q | 5 |
|------------------------|-------------------|--------|--------|--------|--------|
| HF | $^1J(\text{F,H})$ | 172.5 | 346.9 | 426.0 | 419.0 |
| H_2O | $^1J(\text{O,H})$ | −45.7 | −61.1 | −70.7 | −72.3 |
| | $^2J(\text{H,H})$ | −2.0 | −7.7 | −5.9 | −7.4 |
| NH_3 | $^1J(\text{N,H})$ | 33.6 | 37.9 | 41.2 | 43.4 |
| | $^2J(\text{H,H})$ | −6.4 | −8.9 | −8.6 | −9.8 |
| CH_4 | $^1J(\text{C,H})$ | 108.1 | 115.5 | 119.3 | 126.2 |
| | $^2J(\text{H,H})$ | −9.4 | −10.4 | −11.5 | −12.9 |
| C_2H_4 | $^1J(\text{C,C})$ | 67.1 | 73.0 | 70.5 | 71.3 |
| | $^1J(\text{C,H})$ | 139.9 | 148.3 | 151.5 | 160.2 |
| | $^2J(\text{C,H})$ | −1.2 | −1.2 | −1.5 | −1.4 |
| | $^2J(\text{H,H})$ | 2.5 | 4.5 | 4.5 | 3.2 |
| FCH_3 | $^1J(\text{F,C})$ | −234.2 | −214.6 | −221.6 | −224.1 |
| | $^1J(\text{C,H})$ | 126.0 | 135.0 | 140.0 | 148.4 |
| | $^2J(\text{F,H})$ | 43.1 | 45.7 | 50.0 | 51.7 |
| | $^2J(\text{H,H})$ | −5.9 | −6.9 | −8.0 | −9.5 |

All values in Hz.

Table 3

Basis set dependence of total spin–spin couplings in the cc-pCVXZ-sd series (X = D, T, Q, and 5)

| | | D | T | Q | 5 |
|-------------------------------|-------------------|--------|--------|--------|--------|
| HF | $^1J(\text{F,H})$ | 301.1 | 391.9 | 420.6 | 436.7 |
| H ₂ O | $^1J(\text{O,H})$ | −54.9 | −66.1 | −71.2 | −74.9 |
| | $^2J(\text{H,H})$ | −5.0 | −5.3 | −6.0 | −6.6 |
| NH ₃ | $^1J(\text{N,H})$ | 34.9 | 39.1 | 41.9 | 44.1 |
| | $^2J(\text{H,H})$ | −7.2 | −8.0 | −8.7 | −9.4 |
| CH ₄ | $^1J(\text{C,H})$ | 107.9 | 115.7 | 122.6 | 128.1 |
| | $^2J(\text{H,H})$ | −9.5 | −10.7 | −11.5 | −12.4 |
| C ₂ H ₄ | $^1J(\text{C,C})$ | 68.4 | 67.0 | 69.7 | 70.7 |
| | $^1J(\text{C,H})$ | 136.5 | 146.5 | 155.4 | 162.6 |
| | $^2J(\text{C,H})$ | −1.8 | −1.5 | −1.4 | −1.4 |
| | $^2J(\text{H,H})$ | 2.6 | 3.5 | 3.9 | 4.2 |
| FCH ₃ | $^1J(\text{F,C})$ | −227.6 | −211.0 | −219.9 | −223.4 |
| | $^1J(\text{C,H})$ | 124.9 | 134.8 | 143.3 | 150.0 |
| | $^2J(\text{F,H})$ | 45.6 | 47.2 | 50.0 | 51.7 |
| | $^2J(\text{H,H})$ | −6.2 | −7.4 | −8.1 | −8.8 |

See text for details on the construction of this basis set. All values in Hz.

Table 4

Basis set dependence of total spin–spin couplings in the cc-pCVXZ-sd+t series (X = D, T, Q, and 5)

| | | D | T | Q | 5 |
|-------------------------------|-------------------|--------|--------|--------|--------|
| HF | $^1J(\text{F,H})$ | 326.3 | 415.6 | 439.0 | 445.8 |
| H ₂ O | $^1J(\text{O,H})$ | −65.0 | −73.6 | −76.0 | −77.3 |
| | $^2J(\text{H,H})$ | −8.1 | −7.2 | −7.2 | −7.2 |
| NH ₃ | $^1J(\text{N,H})$ | 42.7 | 44.5 | 45.3 | 45.8 |
| | $^2J(\text{H,H})$ | −10.5 | −10.1 | −10.1 | −10.0 |
| CH ₄ | $^1J(\text{C,H})$ | 133.0 | 132.6 | 132.9 | 133.1 |
| | $^2J(\text{H,H})$ | −13.3 | −13.2 | −13.2 | −13.2 |
| C ₂ H ₄ | $^1J(\text{C,C})$ | 74.9 | 72.4 | 72.5 | 72.4 |
| | $^1J(\text{C,H})$ | 168.4 | 167.8 | 168.6 | 168.9 |
| | $^2J(\text{C,H})$ | −1.8 | −1.4 | −1.4 | −1.4 |
| | $^2J(\text{H,H})$ | 3.7 | 4.2 | 4.3 | 4.3 |
| FCH ₃ | $^1J(\text{F,C})$ | −252.2 | −232.0 | −230.0 | −229.8 |
| | $^1J(\text{C,H})$ | 154.3 | 154.7 | 155.9 | 156.0 |
| | $^2J(\text{F,H})$ | 54.2 | 53.6 | 53.8 | 54.5 |
| | $^2J(\text{H,H})$ | −8.7 | −9.1 | −9.3 | −9.4 |

See text for details on the construction of this basis set. All values in Hz.

basis set. It is worth noting that the variation of total SSCC calculated with the cc-pCVXZ-sd+t basis set with X ranging from triple- ζ to quintuple- ζ is less than 8% for all spin–spin couplings, and in most cases less than 3%. This indicates that SSCC calculated using DFT are almost converged with the triple- ζ basis set, in opposition to multi-reference methods where higher angular momentum functions are needed for correlation purposes [8].

In order to determine if SSCC calculated with our cc-pCV5Z-sd+t basis set are already con-

verged in the core and in the valence regions we proceeded as follows. First, we performed calculations including an extra tight *s*-type orbital with an even-tempered ratio of 6 as commented above. We found that the largest variation with respect to our cc-pCV5Z-sd+t corresponds to the $^1J(\text{F,H})$ coupling, which changes only 1 Hz. This suggest that the core region is already well described with our cc-pCV5Z-sd+t basis set. We next use our cc-pCV5Z-sd+t basis set and augmented with the diffuse functions taken from the aug-cc-pV5Z set

Table 5

Individual contributions to the basis set converged SSCC couplings. Wavefunction-based contributions taken from the literature are shown in parenthesis^a

| | | FC | SD | PSO | DSO | Total |
|-------------------------------|---------------------|-----------------|-------------|---------------|-------------|-----------------|
| HF | ¹ J(F,H) | 244.4 (338.2) | −0.3 (−1.0) | 205.2 (176.2) | −0.2 (0.0) | 448.7 (513.4) |
| H ₂ O | ¹ J(O,H) | −64.2 (−65.5) | −0.7 (−0.2) | −12.8 (−9.1) | −0.2 (−0.1) | −77.7 (−74.9) |
| | ² J(H,H) | −10.7 (−11.1) | 1.0 (0.8) | 9.6 (6.5) | −7.2 (−7.1) | −7.2 (−10.8) |
| NH ₃ | ¹ J(N,H) | 43.3 (40.2) | 0.2 (0.1) | 2.3 (1.5) | 0.0 (0.1) | 45.9 (41.8) |
| | ² J(H,H) | −11.8 (−11.7) | 0.7 (0.6) | 6.4 (4.2) | −5.3 (−5.1) | −10.0 (−12.1) |
| CH ₄ | ¹ J(C,H) | 131.0 (118.8) | 0.2 (0.0) | 1.8 (1.5) | 0.2 (0.3) | 133.2 (120.6) |
| | ² J(H,H) | −13.9 (−13.9) | 0.4 (0.4) | 3.9 (3.8) | −3.5 (−3.5) | −13.2 (−13.2) |
| C ₂ H ₄ | ¹ J(C,C) | 78.3 (75.7) | 4.2 (3.1) | −10.3 (−8.7) | 0.1 (0.1) | 72.3 (70.2) |
| | ¹ J(C,H) | 167.6 (151.4) | 0.3 (0.1) | 0.6 (0.4) | 0.4 (0.5) | 168.8 (153.2) |
| | ² J(C,H) | 0.3 (−0.9) | 0.1 (0.0) | −1.2 (−1.0) | −0.7 (−0.7) | −1.5 (−3.0) |
| | ² J(H,H) | 3.6 (0.3) | 0.3 (0.3) | 4.2 (4.0) | −3.8 (−3.9) | 4.3 (0.4) |
| FCH ₃ | ¹ J(F,C) | −287.7 (−226.2) | 23.8 (23.6) | 33.3 (34.2) | 0.4 (0.4) | −230.3 (−169.6) |
| | ¹ J(C,H) | 155.3 (136.4) | 0.2 (0.0) | 0.0 (0.0) | 0.6 (0.7) | 156.1 (137.2) |
| | ² J(F,H) | 47.5 (41.7) | −3.3 (−2.8) | 13.3 (11.9) | −1.9 (−1.8) | 55.7 (49.0) |
| | ² J(H,H) | −10.0 (−9.8) | 0.5 (0.4) | 3.1 (2.7) | −3.0 (−3.0) | −9.4 (−9.8) |

All values in Hz.

^a Wavefunction-based values for HF and NH₃ were taken from [11], for CH₄ from [21], for C₂H₄ from [12,22], and for FCH₃ from [12].

[19]. Values thus obtained closely match those calculated with the cc-pCV5Z-sd+t basis set. The largest relative variation corresponds to the ¹J(O,H) coupling, 1.4%, suggesting that even though the cc-pCV5Z-sd+t does not explicitly incorporate diffuse functions it is flexible enough to achieve an acceptable convergence. This is not necessarily the case when evaluating, for instance, through-space couplings [6], or couplings across a hydrogen bond [20]. We adopt SSCC calculated with this basis set as the converged values. Individual contributions to the basis set converged SSCC are displayed in Table 5. For the sake of comparison, SSCC obtained from wavefunction methods taken from the literature [11,12,21,22] are also shown in Table 5. As can be seen from this table, the main differences between DFT and wavefunction calculated SSCC arise from the FC contribution. We stress that our analysis is valid only for molecules containing first row and hydrogen atoms.

From a practical viewpoint, it is frequently useful to employ small-size basis sets, especially when dealing with large compounds. Among several basis sets commonly used in the literature for calculating SSCC, we have chosen four triple- ζ

basis sets to test their performance: the aug-cc-pVTZ-J [14–18,23] and the Sadlej-J [23,24] basis set (both specially designed for the calculation of NMR properties), the EPR-III [25] (developed for the calculation of hyperfine couplings), and the Huzinaga-III [26], also dubbed IGLO-III [27]. Results obtained with all these bases are compared in Table 6 with experimental [28–35] and wavefunction calculations [11,12,21,22]. It should be noted that the geometrical structures of C₂H₄ and FCH₃ employed in our analysis differ from those used by other authors in wavefunction-based SSCC calculations. From the results shown in Table 6 we can conclude that although all the triple- ζ basis set tested perform reasonably well, the aug-cc-pVTZ-J yields the SSCC closest to the converged values. This feature is worth considering when computational time is important. For instance our basis set limit calculations were performed with a total number of 647 functions for FCH₃, while the aug-cc-pVTZ-J has only 152 functions for the same molecule. This implies a dramatic reduction of the total CPU time by a factor of ≈ 400 .

The agreement between DFT-calculated couplings with experimental values is generally good,

Table 6

Total NMR spin–spin couplings using selected triple- ζ basis set

| | | TZ-J ^a | Sad-J ^a | EPR-III ^b | H-III ^c | Conv | WF | Exp. |
|-------------------------------|---------------------|-------------------|--------------------|----------------------|--------------------|--------|---------------------|------------------------------|
| HF | ¹ J(F,H) | 437.4 | 449.3 | 427.6 | 419.2 | 448.7 | 513.4 ^d | 500 ± 20 ^e |
| H ₂ O | ¹ J(O,H) | −76.9 | −77.4 | −74.6 | −71.6 | −77.7 | −74.9 ^d | −79 ± 2 ^f |
| | ² J(H,H) | −7.7 | −8.5 | −7.5 | −7.1 | −7.2 | −10.8 ^d | −7.2 ± 0.7 ^g |
| NH ₃ | ¹ J(N,H) | 45.8 | 45.6 | 44.5 | 42.3 | 45.9 | 41.8 ^d | 43.6 ± 0.7 ^h |
| | ² J(H,H) | −10.4 | −10.8 | −10.1 | −8.9 | −10.0 | −12.1 ^d | −10.0 ± 0.8 ^h |
| CH ₄ | ¹ J(C,H) | 133.2 | 132.3 | 129.2 | 122.5 | 133.2 | 120.6 ⁱ | 120.78 ± 0.05 ^j |
| | ² J(H,H) | −13.4 | −13.7 | −13.3 | −11.2 | −13.2 | −13.2 ⁱ | −12.564 ± 0.004 ^j |
| C ₂ H ₄ | ¹ J(C,C) | 72.7 | 72.3 | 69.7 | 69.9 | 72.3 | 70.2 ^k | 67.6 ± 0.1 ^l |
| | ¹ J(C,H) | 169.1 | 168.2 | 164.0 | 155.4 | 168.8 | 153.2 ^m | 156.4 ± 0.3 ^l |
| | ² J(C,H) | −1.3 | −1.5 | −1.4 | −1.3 | −1.5 | −3.0 ^m | −2.4 ± 0.2 ^l |
| | ² J(H,H) | 4.2 | 3.9 | 3.7 | 3.4 | 4.3 | 0.4 ^m | 2.5 ± 0.2 ^l |
| FCH ₃ | ¹ J(F,C) | −234.9 | −233.9 | −225.6 | −227.8 | −230.3 | −169.2 ^m | −157.5 ± 0.2 ⁿ |
| | ¹ J(C,H) | 156.2 | 155.2 | 151.5 | 143.6 | 156.1 | 137.2 ^m | 149.1 ± 0.2 ⁿ |
| | ² J(F,H) | 53.2 | 53.3 | 51.3 | 50.7 | 55.7 | 49.9 ^m | 46.4 ± 0.1 ⁿ |
| | ² J(H,H) | −9.6 | −9.8 | −9.5 | −7.7 | −9.4 | −9.8 ^m | −9.5 ± 0.4 ^o |

Converged B3LYP SSCC (Conv) and results based on wavefunction methods (WF) taken from the literature are also shown. See text for details on the calculation of converged B3LYP values. All couplings in Hz.

^a aug-cc-pVTZ-J and Sadlej-J, Ref. [23].

^b Ref. [25].

^c Huzinaga-III, Ref. [26].

^d Ref. [11].

^e Ref. [28].

^f Ref. [29].

^g Ref. [30].

^h Ref. [31].

ⁱ Ref. [21].

^j Ref. [32].

^k Ref. [22].

^l Ref. [33].

^m Ref. [12].

ⁿ Ref. [34].

^o Ref. [35].

excluding ¹J(C,H) in CH₄ and C₂H₄, and ¹J(F,C) in FCH₃, where the agreement is rather poor. The larger SSCC corresponds to the HF molecule, where the discrepancy between calculated and experimental values is approximately 50 Hz, which represents 10% of the total coupling. In the set of benchmark molecules studied in this work, geminal ²J(H,H) couplings exhibit better agreement with experimental values than the rest of the couplings. The ability of DFT to reproduce different types of SSCC deserves further investigation.

SSCC calculated using density functional theory are very sensitive to the election of the basis set. In this work, we have analyzed this depen-

dence in a set of trial molecules containing first row and hydrogen atoms using very large basis sets furnished with appropriate flexibility in the core region and tight functions. Although in some cases basis set converged values differ substantially from experimental results, the aug-cc-pVTZ-J basis set yields the SSCC closest to converged values. This makes the combination of B3LYP with the aug-cc-pVTZ-J basis set an excellent alternative for calculating SSCC in large molecules. Non-contact terms are reasonably well reproduced with B3LYP and are less sensitive to the basis set than the FC contribution. This suggests that any attempt to improve DFT calculated SSCC should be focused on the proper evaluation of the FC term.

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