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Convergence of Nuclear Magnetic Shieldings in the Kohn−Sham Limit for Several Small Molecules

Teobald Kupka,*,[†] Michał Stachów,[†] Marzena Nieradka,[†] Jakub Kaminsky,*,[‡] and
Tadeusz Pluta[§]

*University of Opole, Faculty of Chemistry, Poland, Department of Molecular
Spectroscopy, Institute of Organic Chemistry and Biochemistry, Prague, Czech
Republic, and University of Silesia, Institute of Chemistry, Katowice, Poland*

Abstract: Convergence patterns and limiting values of isotropic nuclear magnetic shieldings were studied for several small molecules (N_2, CO, CO_2, NH_3, CH_4, C_2H_2, C_2H_4, C_2H_6, and C_6H_6) in the Kohn−Sham limit. Individual results of calculations using dedicated families of Jensen's basis sets (pcS-n and pcJ-n) were fitted toward the complete basis set limit (CBS) using a simple two-parameter formula. Several density functionals were used; calculated vibrational corrections (ZPV) applied; and, for comparison purposes, similar calculations performed using RHF, MP2, SOPPA, SOPPA(CCSD), and CCSD(T) methods and additionally, the aug-cc-pVTZ-J basis set. Finally, the CBS estimated results were critically compared with earlier reported literature data and experimental results. Among 42 studied DFT methods, the KTn and "pure" functionals produced the most accurate heavy atom isotropic nuclear shieldings.

I. Introduction

Nuclear shieldings belong to the most important spectral features and are often nowadays predicted at several levels of theory (Hartree−Fock, HF; Density Functional Theory, DFT; Möller-Plesset second-order perturbation theory, MP2; or Coupled Cluster with singles, doubles, and perturbative treatment of triple excitations, CCSD(T)).[1−6] However, very sophisticated and expensive coupled-cluster methods and large basis sets appeared to be necessary to obtain quantitative ^{13}C, ^{19}F, or ^{17}O NMR parameters.[3,7,8]

Recently, the complete basis set limit (CBS) approach, typical for estimation of accurate energy,[9] has been adopted for NMR calculations, too.[10−13] Initially, Dunning's correlation-consistent basis sets (aug-cc-pVxZ, where x = D, T, Q, 5, 6, and sometimes 7) have been applied for accurate evaluations of energy and other molecular and spectroscopic properties.[14−16] Very recently, a detailed overview of esti-

mating CCSD(T) structural parameters in the complete basis set limit was reported by Puzzarini.[17] Jensen proposed general purpose polarization-consistent basis sets,[18−24] pc-n (where n = 0, 1, 2, 3 and 4), capable of regular convergence. Later, he published modified versions of polarized-consistent basis sets, pcS-n,[24] designed for nuclear shieldings. The energy, and other parameters, including nuclear shieldings obtained with polarization-consistent basis sets, were estimated in the CBS limit with accuracy similar to those obtained with correlation-consistent basis sets.[11] Another family of regularly converging basis sets was proposed by Jorge et al.[25−27]

The electron correlation methods, MP2 and even more coupled-cluster methods, are computationally very expensive, and therefore density functional theory including some amount of electron correlation is very promising in studies of larger molecular systems.[28] For example, the BHandH hybrid density functional, capable of correctly reproducing π-stacking geometry and interactions,[29,30] was recently reported as superior to B3LYP and seemed to be the most accurate DFT functional among over 20 others for predicting water's CBS estimated isotropic shieldings.[31] On the other hand, theoretical methods are verified by comparison with reliable gas-phase experimental data.[32] However, it is not

* Corresponding author tel.: +48 665 921 475; fax: +48 77 452 7101; e-mail: teobaldk@yahoo.com (T.K.), kaminskj@gmail.com (J.K.).

† University of Opole.

‡ Institute of Organic Chemistry and Biochemistry.

§ University of Silesia.

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easy to find accurate values of experimental nuclear shieldings in the gas phase.[32] For example, the experimental value of water oxygen shielding was recently significantly revised—from 344 ± 17.2[33] to 323.6[34] and 323.5 ± 6 ppm.[35] The latter value has been currently modified to 325.3 ± 3 ppm.[36]

Unfortunately, currently available density functionals are usually semiempirical, calibrated mainly on energy of selected molecular systems.[28] Thus, there is an open question in the literature of which density functional provides the most accurate nuclear shieldings.[12,31,37,38] And, is there a unique density functional, or a group of well performing ones, in predicting NMR properties in the Kohn–Sham limit? Therefore, a selection of high-quality DFT functional(s) for prediction of nuclear shieldings is of vital importance for a wide community, currently using predominantly B3LYP as the method of choice.

This study addresses the problem of standardization of DFT for predicting nuclear shieldings of several small and common inorganic and organic molecules (N_2, CO, CO_2, NH_3, CH_4, C_2H_2, C_2H_4, C_2H_6, and C_6H_6). Over 40 pure and hybrid density functionals were selected somewhat arbitrarily from the recent Gaussian 09 program edition.[39] The HF and MP2 as well as KT1, KT2, and KT3 density functionals, claiming to be the best in predicting oxygen nuclear shieldings, were studied (see also, refs 31, 37, 40–42). In addition, SOPPA and SOPPA(CCSD) methods, which produce accurate spin–spin coupling parameters, were tested. Additionally, for verification purposes, CCSD(T) calculations were used as a gold standard. In addition, for meaningful comparison of theory with experimental data in the gas phase, the vibrational corrections to the nuclear shieldings were applied. Among selected molecules, N_2 and CO are fairly challenging for computations, and they have been described previously using a multiconfigurational approach (MC-SCF[43]). However, to avoid extending the current work, this method was not considered in our studies.

Apart from the theoretical method, the selection of a regularly converging basis set family is important for the current studies. As a continuation of our recent works,[11,31] Jensen's basis set hierarchy pcS-n,[24] designed for accurate reproduction of nuclear shieldings, was chosen. Jensen's pcJ-n[44] series and aug-cc-pVTZ-J,[45,46] typically used in calculations of SSCC parameters, were additionally studied to check whether basis sets, solely designed for accurate calculations of spin–spin couplings, would correctly reproduce nuclear shieldings too. The latter basis set is relatively small, though efficient for calculating spin–spin couplings.[31,47]

II. Computational Details

Most DFT calculations (approximately 40 density functionals), as well as computations at the HF or MP2 levels, were performed using the Gaussian 09 program.[39] To be concrete, 7 "pure" and 31 "hybrid" density functionals were selected. In addition, three exchange-correlation density functionals KTn (where $n = 1$, 2, and 3),[37,40–42] recommended for isotropic nuclear shielding calculations, and the SOPPA and SOPPA(CCSD) methods were performed with the Dalton 2.0 code.[38] The CCSD(T) results were obtained with the

Acess 2.0 program.[48] For some molecules, due to the demands of CCSD(T), SOPPA, and SOPPA(CCSD) calculations, the results obtained with the largest affordable basis set were used for comparison with CBS values obtained at DFT, RHF, and MP2 levels of theory. Both MP2 and CCSD(T) calculations were performed using the "Frozen-Core, FC" option (see reference 11 for a comparison of NMR accuracy for a water molecule calculated with "all-electrons" and "FC" schemes). In the subsequent parts of this paper, all 47 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), MP2 (41), KT1 (42), KT2 (43), KT3 (44), SOPPA (45), SOPPA(CCSD) (46), and CCSD(T) (47).

For comparison with earlier studies, the experimental geometries from Bak and co-workers'[49] compilation were used in all NMR calculations. Nuclear shieldings were obtained using the Gauge Including Atomic Orbitals (GIAO) approach.[50–52] All NMR calculations were performed at the single level, and with no interacting (free) molecule, resembling the gas phase in the absence of intermolecular interactions (at zero gas density and without solvent present).

Two sets of Jensen's polarization-consistent basis set families, pcS-n[24] and pcJ-n,[44] were selected. These basis set hierarchies are dedicated to accurate calculations of nuclear shieldings and spin–spin coupling constants, respectively. The former are significantly smaller and somehow "pruned" from the latter ones, developed solely for accurate prediction of J-couplings. In case of the N_2 molecule, the calculations for $n = 0$, 1, 2, 3, and 4 were tested. Due to inaccuracies in smaller basis set designs, the initial results ($n = 0$ and sometimes 0 and 1) were considered meaningless, and the convergence of results obtained for $n = 2$, 3, and 4, and sometimes only for $n = 3$ and 4, were evaluated in the Kohn–Sham basis set limit using a simple two-parameter fit.[53] For comparison, additional single-point calculations employing the aug-cc-pVTZ-J basis set[45,46] were performed. All the nonstandard basis sets were downloaded from the EMSL basis set library.[54] The convention used in earlier works,[10,11,55] for graphical purposes, was applied also in the current study: pcS-n and pcJ-n, where n = 0, 1, 2, 3, and 4, were set equivalent to Dunning's $X = 2$, 3, 4, 5, and 6 and plotted at $X = 4$, 5, and 6. Individual plots of shielding convergence and fittings toward the complete basis set limit are similar to those observed in our earlier works[10,11,55] and therefore are not shown in this work.

Theoretical NMR values obtained at equilibrium or experimental geometry should be compared with experimental results[32,56,57] after inclusion of zero-point vibrational (ZPVC) and thermal corrections (TC). The latter term, being an order of magnitude smaller, has been neglected. Ruden

et al.[58] subtracted the correction term from the total observed coupling, J_{tot}^{exp}, arriving at the so-called "empirical equilibrium" coupling constant, J_{eq}^{emp}: $J_{eq}^{emp} = J_{tot}^{exp} - J_{vib}^{B3LYP}$. In our study, the empirical "experimental" value of nuclear isotropic shielding σ was compared directly with theoretical equilibrium coupling, σ_{eq}^{theor}, obtained from our ab initio calculations using different methods. Thus, we want to underline that, in this work, the CBS predicted theoretical nuclear shieldings calculated at experimental equilibrium geometry are compared with empirical equilibrium values, which include vibrational correction terms, obtained from separate calculations.

Vibrational averaging of NMR chemical shieldings in semirigid molecules can be based on the expansion of the nuclear potential V and the chemical shielding δ in Taylor series of the coordinates. In this study, the potential was expanded up to fourth powers of the normal mode coordinates Q_i as[59,60]

$$V = \frac{1}{2} \sum_{i=1} \omega_i^2 Q_i^2 + \frac{1}{6} \sum_{i=1} \sum_{j=1} \sum_{k=1} c_{ijk} Q_i Q_j Q_k + \frac{1}{24} \sum_{i=1} \sum_{j=1} \sum_{k=1} \sum_{l=1} d_{ijkl} Q_i Q_j Q_k Q_l \quad (1)$$

where the summations run over all modes i with harmonic frequencies ω_i. All cubic (c_{ijk}) and the semidiagonal (d_{iijk}) quartic constants were considered.

Similarly, the shieldings were expanded as

$$\delta = \delta_0 + \sum_i \delta_{1,i} Q_i + \frac{1}{2} \sum_{i,j} \delta_{2,ij} Q_i Q_j \quad (2)$$

where δ_1 and δ_2 are the first and second normal mode shielding derivatives, respectively. The vibrationally averaged rotations were obtained from a vibrational function Ψ as

$$\delta_{ave} = \langle \Psi | \delta | \Psi \rangle \quad (3)$$

The function ψ was obtained using the second-order degeneracy-corrected perturbational formula[59,60] from harmonic-oscillator functions, or using limited vibrational configuration interaction (VCI). As observed before,[59] these two wave function approximations gave almost the same results for the NMR shielding corrections.

The cubic and quartic force constants we obtained numerically from Hessians calculated analytically by Gaussian program,[39] for geometries displaced in normal modes. Likewise, the first and diagonal ($\delta_{2,ii}$) second shielding derivatives were calculated numerically by Gaussian. Program S4[61] interfaced to Gaussian was used for the anharmonic vibrational averaging. The vibrational contributions were assessed at the BHandH/pcS-2, BHandH/pcS-3, and MP2/pcS-3 levels.

III. Results and Discussion

In the first step of our studies, Jensen's basis sets without and with additionally augmented polarization functions (significantly larger) were used: pcS-n and aug-pcS-n and pcJ-n and aug-pcJ-n. The basis sets with all possible values of n were tested (0, 1, 2, 3, and 4) for dinitrogen, carbon

oxide, and carbon dioxide. Executing all calculations poses a considerable computational effort, and therefore, it was possible to decrease the number of calculations while saving the main information obtained from the study. The shieldings obtained with pcS-n and pcJ-n basis sets, and n = 2, 3, and 4 were fitted using a two-parameter formula.[49] In several cases, the shieldings 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 nuclear shieldings, being the second derivatives of total energy of the atomic system, should be the least corrupted ones by the accidental error cancellation.

The nitrogen shieldings in the Kohn–Sham basis set limit for extended, larger basis set hierarchies (aug-pcS-n and aug-pcJ-n) were practically identical with those obtained with the corresponding parent basis sets (pcS-n and pcJ-n). Thus, this extensive study was limited to the calculations with pcS-n and pcJ-n basis sets only, and for n = 2, 3 and 4, and with the relatively small aug-cc-pVTZ-J basis set, resulting in considerable time savings.

III.1. Vibrational Corrections to Nuclear Isotropic Shielding. Molecular response to the electromagnetic field also includes the nuclear contribution. We estimated the vibrational parts of chemical shielding at the BHandH/pcS-2 and pcS-3, as well as at the MP2/pcS-3 levels of theory. For benzene the MP2/pcS-3 level was too computationally demanding, and the "cheaper" basis set pcS-2 was used. The calculated vibrational corrections to the nuclear magnetic shieldings of the title compounds are summarized in Table S1 in the Supporting Information.

In most cases, MP2 provided larger absolute corrections than those obtained at the DFT level. The difference is most significant in systems with multiple bonds. The corrections calculated at the BHandH level for N_2, CO, CO_2, and NH_3, respectively, seem to be well converged, while the difference in pcS-2 and pcS-3 values for hydrocarbons indicates an incomplete convergence. However, the usage of a higher (pcS-4) basis set is practically impossible because of the long CPU time needed for the calculation. Nevertheless, the ZPV results obtained with the pcS-3 basis set are assumed sufficiently accurate considering the error caused by different theoretical levels and are used in our study to obtain empirical shieldings. In general, the vibrational corrections in Table S1 are similar to earlier reported values.[3,8,67,73,77,78] In some cases there are some discrepancies due to different electronic and vibrational theoretical approaches.

Figure 1 summarizes the vibrational changes of NMR shielding tensors of all studied compounds caused by the first and second property derivatives, calculated at the BHandH/pcS-3 and MP2/pcS-3 levels. In all cases, the inclusion of the vibrational corrections leads to smaller shielding tensor values. The contribution of the first shielding derivatives is approximately half (∼1.4 ppm for BHandH and 1.5 ppm for MP2) of that caused by the second derivatives (2.5 ppm for BHandH and 3.0 ppm for MP2). However, the vibrational corrections do not improve the overall agreement with experimental results: the mean average deviation changes
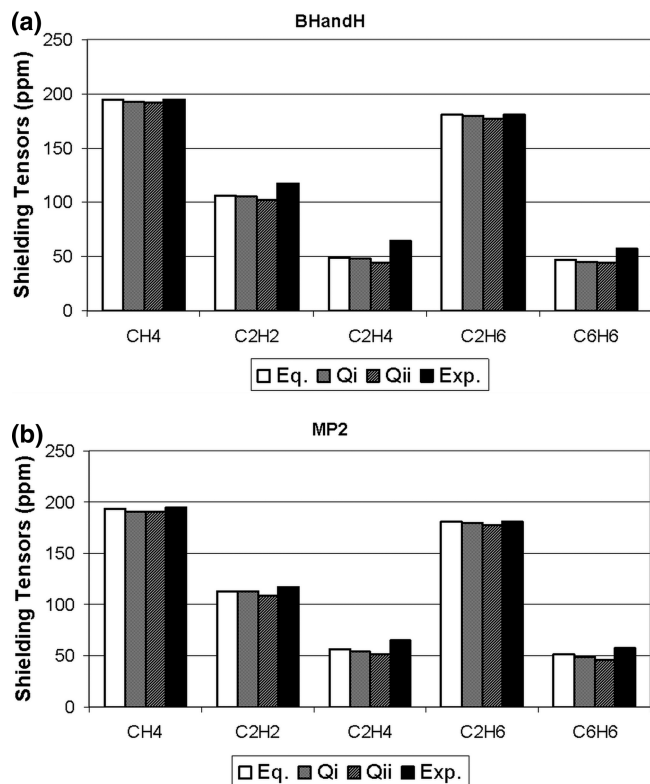
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(a)

(b)

Figure 1. NMR shielding tensors (in ppm) calculated with the zero (Eq.), first (Qi), and second (Qii) shielding derivative corrections as compared to the experiment. NMR features were calculated at the (a) BHandH/pcS-3 and (b) MP2/pcS-3 (right) levels. Only in case of benzene was the MP2/pcS-3 level not available; thus the basis set used was pcS-2.

from 7.3 ppm (*Equilibrium*; BHandH) to 8.5 ppm (Q_i) or 11.0 ppm (Q_{ii}). For the MP2 method, the trend is the same, but the errors are lower than for DFT (4.1 ppm for *Equilibrium*, 5.4 ppm for Q_i, and 8.4 ppm for Q_{ii}). Similar observations have been already reported for NMR properties by Dračínský et al.,[59] and for the optical rotation, similar observations have been pointed out by Mort and Autschbach[62] and Kaminský et al.[60] The vibrational corrections thus seems important, but their contribution might be smaller than the error of the equilibrium values. Further improvement could be expected with higher electronic methods (such as coupled-cluster) and larger basis sets (e.g., pcS-4), which is, unfortunately, beyond our computational possibilities.

In order to better understand the role of individual vibrations in the averaging, in Figure 2, we plot the approximate contributions of individual modes defined as $\delta_{1,i}\langle Q_i \rangle + 1/2\delta_{2,ii}\langle Q_i^2 \rangle$ (cf. eq 2) for methane. A similar analysis for acetylene, ethane, and benzene is shown in the Supporting Information (Figures S1A–S1D). As apparent from Figures 2 and S1A–S1D, most of the harmonic normal modes significantly contribute to the nuclear magnetic shielding.

The contributions of the lowest-energy mode in C_2H_6 cannot be considered reliable, as this mode (methyl rotation) exhibits a strongly anharmonic potential, for which the limited Taylor expansion (eq 1) is probably inappropriate.
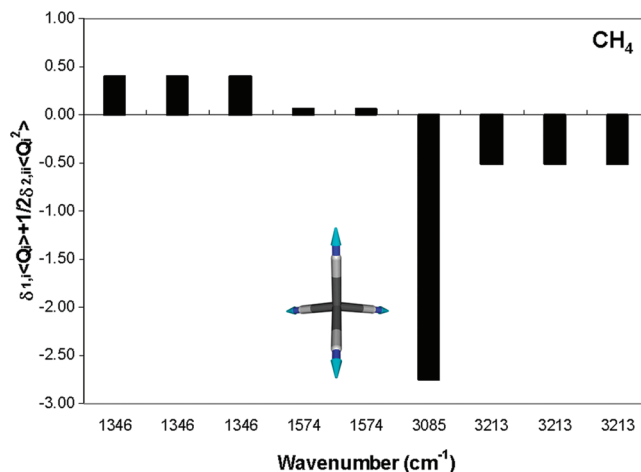

Figure 2. Contribution of individual normal modes to the magnetic shielding vibrational correction in methane. Picture represents the most contributive vibration.

The largest contributions come from the C−H stretch (for CH_4 and C_2H_6 at 3085 cm^{-1} and 3096 cm^{-1}, respectively), the CH bending (C_2H_2, 803 cm^{-1}), C≡C stretching (C_2H_4, 1754 cm^{-1}), and benzene symmetric ring breathing (C−C stretch, 1063 cm^{-1}). Note that the four lowest modes in C_2H_2 are double-degenerated. The potential energy of such a linear symmetric molecule thus could be given, for example, as[63]

$$2V = k_1 Q_{23}^2 + k_2(Q_{12}^2 + Q_{34}^2) + k_\delta(\delta_{13}^2 + \delta_{24}^2) \quad (4)$$

where δ_{13} is the deviation of the angle between atoms H1, C2, and C3 from 180° and δ_{13} is the corresponding deviation for C2−C3−H4. However, no simple judgment to predict the biggest contributions comes to our mind, and a complete estimation of the corrections for all the modes seems the only option.

III.2. Convergence of Nuclear Isotropic Shielding in N_2, CO, CO_2, and NH_3. N_2 nuclear isotropic shielding predicted in the CBS limit using pcS-n and pcJ-n basis set families and the single point aug-cc-pVTZ-J results were calculated at several theoretical levels and are gathered in Table S2 in the Supporting Information. The method numbers 1−7 refer to "pure" and 8−38 to "hybrid" density functionals and as such will be applied to all calculated results in the subsequent tables and figures. Analogous shielding data in the CBS limit for all studied compounds are contained in the Supporting Information (Tables S3−S8). The WP04 density functional (method No. 39 in Table S2) was recently designed[64,65] for better prediction of proton shieldings and executed in the Gaussian 09 program as a modification of the BLYP functional with IOp entries (see refs 64 and 65). Method numbers 40 and 41 (RHF and MP2), 42−44 (KT*n*), and 45−47 (SOPPA, SOPPA(CCSD), and CCSD(T)) close the list, being a kind of reference tool.

Obtained data are compared with experimental nitrogen shielding[2,66] and the estimated "empirical shielding", containing the BHandH/pcS-3 calculated ZPV correction from Table S1. To distinguish the performance of the individual method, the deviations of calculated results from the empirical nitrogen shielding are plotted in Figure 3 (the methods
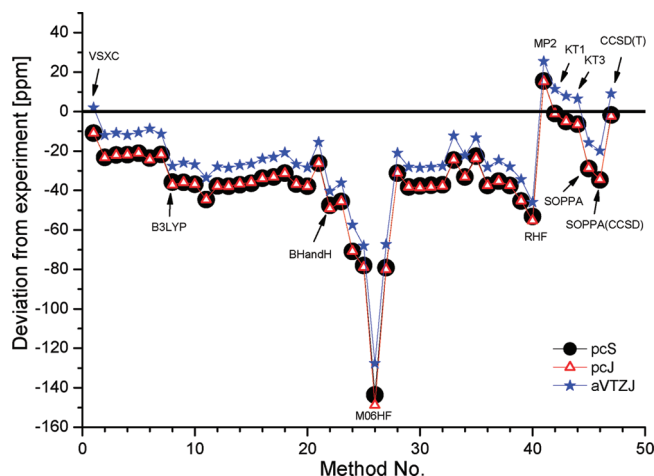
Figure 3. CBS estimated (pcS-n and pcJ-n) and SP aug-cc-pVTZ-J deviations of nitrogen isotropic shieldings from empirical values in N_2 (method numbers are listed in Table S2).

given on the horizontal axis are selected according to their order of appearance in Table S2).

Some methods, producing very poor (deviation of about −150 ppm for M06HF) or very good results (VSXC, KT1, KT2, and KT3 with deviations −11, −1, −5, and −6 ppm) as well as the popular B3LYP functional (deviation of about −37 ppm) are directly indicated in the plot. It is apparent from Figure 3 that both pcS-n and pcJ-n basis set hierarchies perform practically identically, and the corresponding results obtained with a significantly smaller basis set, aug-cc-pVTZ-J, are slightly closer (by about 10 ppm) to experimental results. Nitrogen shieldings predicted with RHF and BHandH methods (dev. −55 and −50 ppm) are worse than the B3LYP value. Moreover, the corresponding MP2 and CCSD(T) calculations produce smaller deviations from experimental results (+15 and −2 ppm). In general, the majority of density functionals underestimate N_2 isotropic nuclear shielding by −20 to −40 ppm. SOPPA and SOPPA(CCSD) results significantly deviate from experimental results (−30 to −35 ppm). The excellent predicting power of the CCSD(T) benchmark method is not surprising. In addition, the very good performance of KTn density functionals is encouraging, and fairly good results obtained with "pure" density functionals (method numbers 1−7) are remarkable.

In the Supporting Information (Figures S2A,B) are shown carbon and oxygen nuclear magnetic shielding deviations of CO from experimental results obtained with pcS-n, pcJ-n, and aug-cc-pVTZ-J basis sets. It is obvious that general trends, reflecting the performance of different density functionals and basis sets, are very similar to those observed for N_2 (Figure 3). Thus, the results produced with both of Jensen's basis sets are practically identical, and shieldings obtained with the compact aug-cc-pVTZ-J basis set are about 10 ppm closer to experimental values.[3,8,67,68] The majority of density functionals underestimate experimental carbon shieldings by 15 to 25 ppm (Figure S2A) and oxygen shieldings by 10 to 30 ppm (Figure S2B). The B3LYP and BHandH performance is similar to the majority of density functionals, and VSXC, KTn's, and MP2 reproduce experi-

mental results significantly better than the remaining methods. The M06HF produces the worst result (carbon and oxygen deviations are about −80 and −185 ppm).

In the case of CO_2, very similar deviations to those of carbon monoxide patterns of shielding from the experiment[3,8,68] are observed. The corresponding graphs are placed in the Supporting Information (Figure S3A,B). The worst results are again observed for the M06HF density functional with carbon and oxygen shielding deviations of −23 and −44 ppm, respectively.

The general pattern of the studied method's performance is similar to the case of ammonia nitrogen shielding deviations from the experiment[2,69,70] (Figure S4A); the tHCTH, M06L, M06, and WP04 density functionals show the worst results (−15, −17, −27, −23 ppm), and the best performance is observed for VSXC, BHandH, BMK, and wB97 density functionals (−4, −4, −3, −5 ppm). As expected, proton shieldings of ammonia deviate from experimental results[70] less than the nitrogen ones (compare Figure S4A and B). Surprisingly, a very large deviation of the ammonia proton shielding from the empirical value is predicted with the BHandH and CCSD(T) methods (−0.6 and −0.4 ppm). The last result is difficult to explain taking into account the excellent performance of the CCSD(T) method in predicting nuclear shieldings of small molecules. On the other hand, we notice that accurate CCSD(T)/pz3d2f calculations reported by Gauss et al.[2] resulted in a similar value of this deviation (0.3 ppm) compared to the empirical value.

III.3. Convergence of Nuclear Isotropic Shielding in CH_4, C_2H_2, C_2H_4, C_2H_6, and C_6H_6. The carbon and proton nuclear isotropic shielding deviations from experimental values of methane[2,3,70] are shown in Figure 4.

Both the pcS-n and pcJ-n basis set hierarchies perform practically identically, and the corresponding results obtained using a significantly smaller aug-cc-pVTZ-J basis set give slightly better values.

In general, the majority of density functional methods underestimate the carbon shielding in CH_4 by −5 to −10 ppm. Some methods, producing very poor or good results in comparison to the popular B3LYP density functional, are again directly indicated in the plot. Carbon nuclear shieldings in methane predicted by the VSXC, BHandH, wB97, and MP2 methods are better than using the B3LYP. Corresponding deviations from the experiment are −4, −2.5, −2, 2.5, and −10 ppm, respectively. The worst methods (M06 and WP04) predict methane carbon shieldings significantly deviating from experimental results (−18 and −20 ppm).

In general, the pcS-n and pcJ-n families of basis sets overestimate the experimental proton nuclear shieldings of methane by 0.2−0.35 ppm. With the VSXC, BHandH, and MP2 methods, these basis sets provide the lowest deviations of about 0.15, −0.04, and 0.02. In addition, a compact aug-cc-pVTZ-J basis set predicts proton shieldings worse by about 0.10−0.15 ppm than those obtained in the complete basis set limit. Similarly to the previous compounds, the largest deviations (0.55 and 0.45 ppm) are observed for M06HF and WP04.
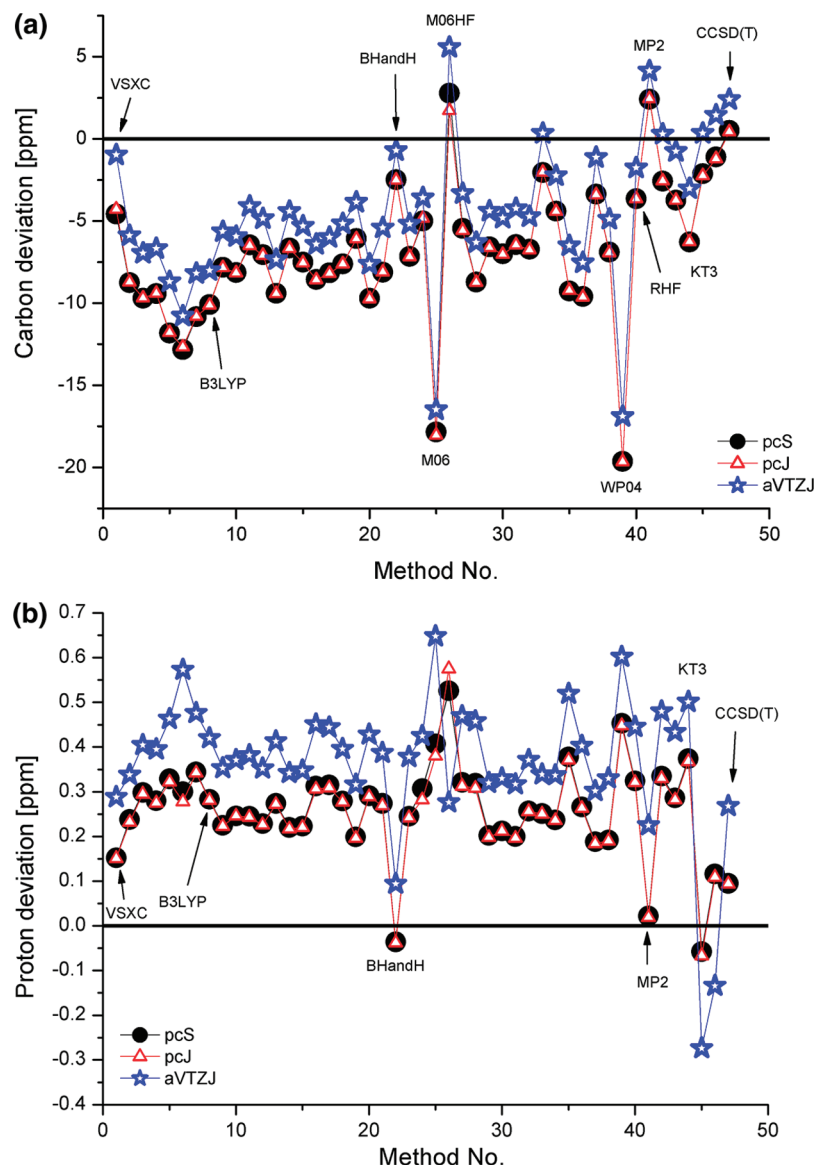
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Figure 4. CBS estimated (pcS-n and pcJ-n) and SP aug-cc-pVTZ-J deviations of (a) carbon and (b) proton isotropic shieldings from empirical values in CH_4 (method numbers are listed in Table S2).

The majority of methods underestimate carbon shielding[71] in acetylene by −10 to −15 ppm (Figure S5A, Supporting Information), and the best performing methods are VSXC and MP2, deviating −5 and 2 ppm. On the other hand, the largest deviation is observed for M06HF (−33 ppm).

Acetylene proton shieldings[71,72] (Figure S5B) are overestimated by 0.1 to 0.2 ppm, and the best results are observed for VSXC, LC-wPBE, and RHF (dev. −0.09, 0.03, and 0.01 ppm). The worst performances are observed for BHandH and MP2 (dev. −0.27 and −0.26 ppm) and WP04 and M06 (dev. 0.48 and 0.57 ppm).

Carbon nuclear shieldings in ethylene (Figure S6A, Supporting Information) deviate from the experimental value (64.4 ppm reported by Auer and co-workers[3] and augmented with calculated ZPV correction) by about −15 to −25 ppm, and the best methods are VSXC, RHF, and MP2 (dev. −12, −11, and −2 ppm). The performance of B3LYP and BHandH (dev. −25 and −23 ppm) is similar to the majority of density functionals, and the worst case is observed for

M06HF (dev. −58 ppm). The KTn methods underestimate the experiment by about 8 ppm.

Proton shieldings in ethylene (25.43 ppm,[72] see Figure S6B) are underestimated by −0.1 to −0.4 ppm, while the best method reproduces experimental results very well (−0.01 ppm deviation for TPSSh). M06HF, BHandH, VSXC, B3LYP, MP2, and RHF deviate from experimental results by −0.9, −0.7, −0.5, −0.2, −0.16, and 0.12 ppm.

Carbon nuclear shieldings in ethane (Figure S7A, Supporting Information) deviate from the experimental value (180.8 ppm by Auer and co-workers[3] and augmented with calculated ZPV correction) by about −5 to −15 ppm, and the best results are for MP2, RHF, wB97, M06HF, and BHandH (dev. 1, −3, −3, −3, and −5 ppm). B3LYP deviates by −14 ppm, and the M06, WP04, and BHandH density functionals are significantly worse (dev. −19, −22, and −25 ppm).

Experimental proton shieldings in ethane (experimental value (29.86 ppm) reported by Chesnut[73] and corrected with

Table 1. C_6H_6 Isotropic Shieldings Calculated Using a Few Selected Methods and Basis Sets Compared with Experimental Results before and after Inclusion of ZPV Correction

basis	method			
C shielding	RHF	B3LYP	BHandH	CCSD(T)
6-311G**	**59.930**	**51.330**	**52.604**	**71.559**
pcS-0	51.747	50.485	50.734	74.144
pcS-1	57.431	47.320	50.043	68.759
PcS-2	53.023	42.071	43.975	62.866
PcS-3	53.196	41.732	43.983	
PcS-4	53.222	41.673	44.002	
CBS	**53.258**	**41.591**	**44.028**	
pcJ-0	59.028	50.873	52.905	
pcJ-1	57.157	45.521	48.487	
PcJ-2	53.834	42.043	44.604	
PcJ-3	53.207	41.754	43.990	
PcJ-4	53.228	41.681	44.008	
CBS	**53.258**	**41.580**	**44.032**	
aVTZJ	57.929	47.020	48.800	
exp.		**57.105 ± 0.009**[a]		
emp.		**59.905**[b]		

H shielding	RHF	B3LYP	BHandH	CCSD(T)
6-311G**	24.675	24.568	23.994	24.765
pcS-0	25.502	25.487	24.899	26.002
pcS-1	24.364	24.244	23.707	24.481
PcS-2	24.222	24.020	23.468	24.105
PcS-3	24.196	23.984	23.434	
PcS-4	24.194	23.982	23.428	
CBS	**24.191**	**23.980**	**23.419**	
pcJ-0	25.672	25.703	25.080	
pcJ-1	24.379	24.271	23.706	
PcJ-2	24.236	24.046	23.494	
PcJ-3	24.198	23.989	23.435	
PcJ-4	24.193	23.983	23.427	
CBS	**24.186**	**23.975**	**23.415**	
aVTZJ	24.344	24.146	23.581	
exp.		**23.60**[c]		
emp.		**23.90**[b]		

[a] From ref 74. [b] Including ZPV corrections for C and H of −2.8 and −0.3 ppm (see Table S1). [c] From refs 75 and 76.

calculated ZPV contribution, see Figure S7B) are very well reproduced (dev. −0.1 to 0.1 ppm for most cases), and the least accurate results produce BHandH, MP2, RHF, WP04, and M06HF (dev. −0.25, −0.13, 0.33, 0.33, and 0.42 ppm).

Benzene is the largest molecule in the set of studied hydrocarbons, and DFT calculations of its shieldings using the pcS-4 basis set are very lengthy. Carbon isotropic shielding (57.105 ± 0.009 ppm) of the isolated benzene molecule in xenon gas was reported by Jackowski and co-workers.[74] Thus, it is a real challenge to get accurate shieldings of C_6H_6 at the level of CCSD(T) or to dream about estimating such results in the basis set limit. Therefore, we limited our CBS studies to a few methods only—RHF and BHandH with pcS-n and pcJ-n basis sets. In addition, we compared the CBS values obtained with pcS-n and pcJ-n basis sets using the popular B3LYP hybrid functional (Table 1). The corresponding results obtained with aug-pcS-n and aug-pcJ-n basis sets were almost identical (not shown in Table 1).

The RHF and DFT CBS fitted shieldings we compare directly with the CCSD(T) results with smaller basis sets

pcS-n (n = 0, 1, and 2 only) and a relatively small Pople type basis set 6-311G**.

At first, we notice that RHF and CCSD(T) carbon and proton shieldings of benzene obtained with smaller basis sets (6-311**, pcS-0 and pcJ-0, pcS-1 and pcJ-1) deviate significantly from results obtained using larger basis sets (n = 2, and in some cases n = 3 and 4). Another important observation from Table 1 is that the CBS estimated B3LYP shieldings are practically identical for pcS-n and pcJ-n basis set families. It is also apparent from Table 1 that, by using a small basis set (6-311G**) and hoping for accidental error cancellation, we may obtain a perfect agreement of the theoretical result with experimental results (compare RHF and CCSD(T) carbon shielding of 59.930 and 71.559 ppm with an empirical value of 59.905 ppm). In such a drastic case, one could wrongly conclude that in practice it is enough to use a fast RHF calculation with a small basis set to confirm experimental data. On the other hand, this also shows that using a much elaborated method (for example, the coupled cluster wave function) with a deficient basis set may produce poor results.

The limited results from Table 1 confirm earlier reports that RHF is somehow more reliable in predicting carbon shieldings than DFT. The latter one tends to predict significantly lower heavy atom shieldings due to overestimation of their paramagnetic terms. The CBS predicted carbon shieldings of benzene calculated with RHF, BHandH, and B3LYP are 53.26, 44.03, and 41.6 ppm and are poor estimates of an empirical value (59.91 ppm). To the contrary, the corresponding CBS proton shieldings (24.2, 23.4, and 24.0 ppm for RHF, BHandH, and B3LYP) are significantly closer to experimental results (23.60 ppm[75,76] augmented with ZPV).

In spite of a limited number of studied systems, we would like to show some statistical data showing the general trends in performance of individual methods (due to very limited available calculation results, benzene is excluded from this analysis). Averaged nuclear shielding deviations from experimental results somehow mask the real performance of the methods (see Figures S8A and S8B). Hence, in Figure 5, the root-mean square (RMS) deviations of nuclear shieldings from experimental results are presented. In general, RMS deviations of 10 heavy atoms (Figure 5A) are between 10 and 20 ppm, and only a few advanced methods (MP2, KTn and CCSD(T)) produce better results. On the other hand, due to the large deviations of nuclear shieldings calculated using the Minnesota density functionals from experimental results, these methods are not recommended for NMR calculations in the studied molecules and in similar atomic systems. The performance of the pcS-n basis set is similar to pcJ-n hierarchy, and therefore, the first ones are computationally more accessible. Furthermore, the inexpensive aug-cc-pVTZ-J basis set generally produces slightly more accurate results at the DFT level of calculations (exceptions are observed for MP2, KTn, and CCSD(T)). RMS deviations of proton nuclear shieldings in the studied systems are about 0.2 ppm, and the aug-cc-pVTZ-J basis set produces slightly worse results (see Figure 5B).
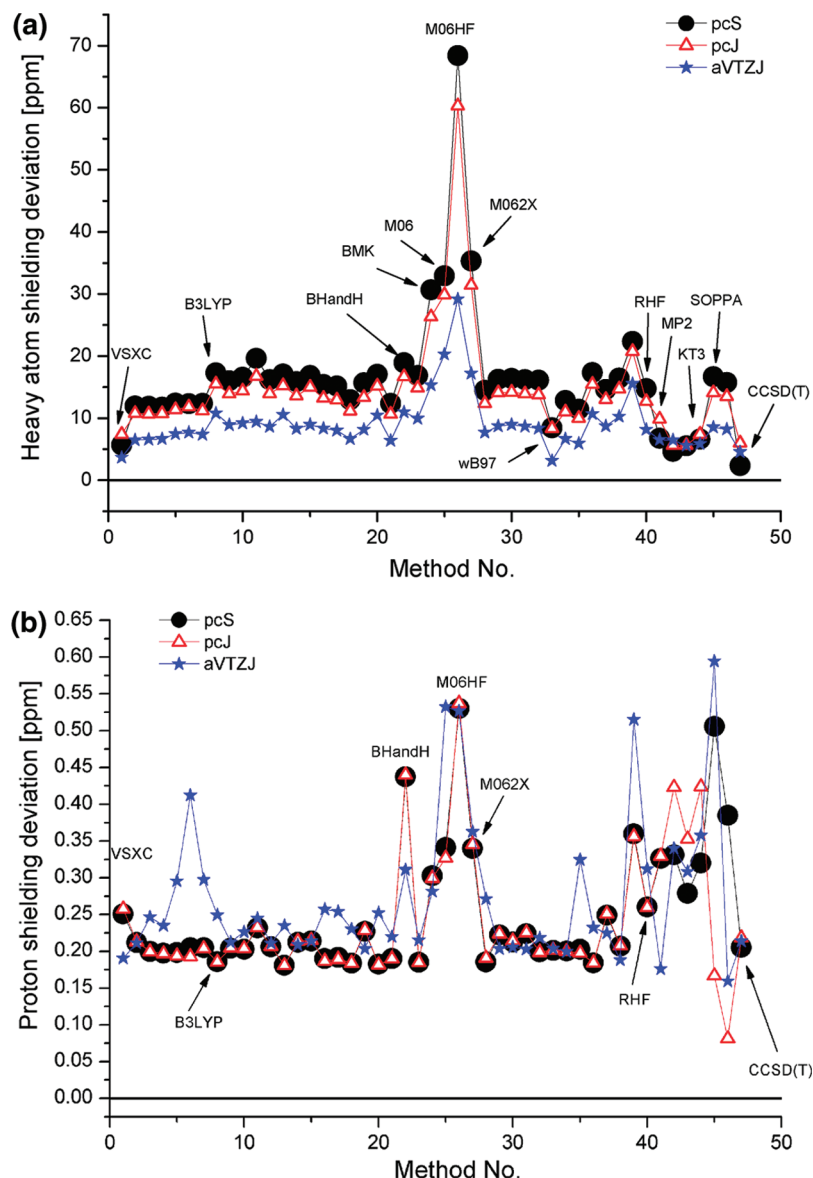
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Figure 5. CBS estimated (pcS-n and pcJ-n) and SP aug-cc-pVTZ-J RMS deviations of (a) heavy atoms and (b) proton isotropic shieldings from empirical values in the studied systems. Results for benzene are excluded due to incompleteness of theoretical data, and method numbers are listed in Table S2.

IV. Conclusions

The performances of several density functionals were tested for predicting isotropic nuclear shieldings 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) using pcS-n and pcJ-n basis set hierarchies. The DFT nuclear shieldings estimated in the complete basis set limit were compared with empirical shieldings obtained from experimental values and calculated ZPV corrections and RHF, MP2, SOPPA, SOPPA(CCSD), and CCSD(T) results. RMS deviations of 10 heavy atoms reproduce experimental results by about $\pm 10-20$ ppm. Better results are obtained using MP2, KTn, and CCSD(T) methods. Jensen's pcS-n and pcJ-n basis sets work similarly; thus, the first ones are recommended. The inexpensive aug-cc-pVTZ-J basis set produces very accurate results. The studied DFT methods calculate proton isotropic shieldings with RMS deviations of about 0.2 ppm, and the aug-cc-pVTZ-J basis set gives

slightly worse results. Surprisingly, the "pure" density functionals produce fairly accurate NMR shieldings, better than the popular B3LYP. The Minnesota density functionals are not suitable for shielding calculations of the selected molecules (and probably for similar molecules). However, it should be noted that our series of compounds is limited in structural diversity, and the general applicability of conclusions made in this work need to be verified in the future.

Supporting Information Available: Detailed information about CBS estimated nuclear shieldings for all studied molecules using the pcS-n, pcJ-n, and aug-cc-pVTZ-J basis sets, as well as calculated vibrational corrections at BHandH and MP2 levels. This information is available free of charge via the Internet at http://pubs.acs.org/.

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