Toward Hartree−Fock- and Density Functional Complete Basis-Set-Predicted NMR Parameters

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The molecular and spectroscopic parameters calculated using the hybrid density functional B3PW91 are reported for a model set of compounds composed of H_2, N_2, NH_3, CH_4, C_2H_4, HCN, CH_3CN, and H_2O. An estimation of the DFT and Hartree−Fock complete basis-set limit (CBS) energy and NMR parameters from the 2- (3-) point exact fit versus least-squares fit (NLLSQ) was obtained with the cc-pVxZ and aug-cc-pVxZ basis sets ($x = D, T, Q, 5, 6$). A marginally faster convergence of the fitted parameters obtained with core-valence basis sets cc-pCVxZ and aug-cc-pCVxZ was noticed. The Hartree−Fock-predicted CBS heavy-atom isotropic shieldings of the model molecules, as compared with those of DFT, were closer to experiment. It was also shown that GIAO MP2-predicted NMR parameters yield the best agreement with those obtained from experiment and benchmark calculations. As support for experimental studies, the CBS approach of calculating accurate nuclear shieldings of larger molecules is proposed.

Introduction

Current experimental chemistry quite often seeks support from accurate theoretical model predictions as provided by ab initio and density functional theory (DFT) calculations.[1−3] Chemical accuracy (±1−2 kcal/mol) of theoretical predictions that relate to the computed total electronic energy (such as thermochemical properties) can be achieved for small molecules typically by using high-level methods that include electron correlation and employ very large basis sets (for example, MP2, composite approaches such as the Gaussian family of methods,[4−8] or coupled-cluster methods[9,10]). However, the unfavorable scaling of time with respect to the number of basis-set functions, in conjunction with practical limitations of available computer resources, makes these methods inaccessible for routine applications to larger-sized molecules. However, DFT methods, though significantly more approximate in their nature, have been shown to provide acceptable results using a fraction of the time and storage space required by high-level calculations.[2,3]

In general, there are two distinct features limiting the accuracy of computed molecular and spectroscopic parameters: one relates to the inherent approximations encapsulated in the chosen method (Hartree−Fock, MP2, CCSD(T), DFT, etc.), and the other relates to errors arising from basis-set truncation and incompleteness.[1−7,9] Whereas the assessment of the accuracy of various theoretical approaches for NMR parameters lags behind similar assessments for more common molecular properties such as energy or equilibrium geometry, the general strategy is similar: if affordable, higher-level methods with large basis sets are obviously the most desirable approach.[11] However, there are indications in the literature that for NMR properties of larger molecules it may be sufficient to carry out calculations at a DFT or even a HF level.[12−19] In fact, one can find occasional examples of good agreement between experiment and HF and DFT calculations of NMR parameters even when small basis sets are used.[12−24]

The use of large but affordable basis sets that regularly converge to the desired property can in practice address the problem of basis-set incompleteness. For example, the cc-pVxZ correlation-consistent family of polarized valence basis sets developed by Dunning and co-workers[25−30] provides regular and smooth convergence of the computed total electronic energy with the increased x value. The cardinal number of the basis sets $x = D, T, Q, 5, 6$ corresponding to double-ζ, triple-ζ, et cetera indicates the number of contractions used to represent Slater-type orbitals and in this family of basis sets also happens to correspond to the highest “angular momentum” of the basis functions employed in the set. In general, the use of correlation-consistent basis sets with additional augmented diffuse (aug-cc-pVxZ) or core functions (cc-pCVxZ) leads to additional improvement and even better agreement with experiment. One approach typically used with selected higher-level methods[9,25−38] is to perform a series of calculations with increasing basis-set zeta and extrapolate the result to the complete basis-set limit (CBS) (i.e., to infinite zeta).

The correlation-consisted basis sets were initially developed for high-level calculations using methods that recover the correlation energy. This approach has enabled the calculation of very accurate energies of molecular systems and provided valuable support for experimental thermochemistry over the past decade.[9,25−40] However, the exponential decrease in energy and its convergence upon increasing the basis-set size was also reported by Dunning’s group[27,28,32,33,37] for Hartree−Fock methods, although, not surprisingly, the estimated thermochemical properties from CBS-fitted HF energies showed somewhat larger deviations from the experimental values than higher-level methods (e.g., MP2 and CCSD). In addition, Wheller et al.[41] recently suggested that extrapolation to the CBS limit could minimize the errors due to basis-set incompleteness in B3LYP-DFT calculations.

In principle, only the total energy (as opposed to its derivatives) is guaranteed to keep improving with better basis sets. Furthermore, because the total energy is averaged over the entire molecular ensemble, its dependence on the quality

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of the basis set is less sensitive to basis-set deficiencies than the dependence of derivatives of energy describing local molecular properties. This implies that, at least in principle, the convergence of other molecular properties, as a function of basis-set size, might be less regular. However, one suspects that even these properties will show monotonic improvements as a function of basis-set size. Indeed, in a series of papers, Dunning,[27,28,36] Feller,[32,33,35,37] Xantheas,[39] and Helgaker[38] demonstrated the regular convergence of bond lengths, dipole moments, polarizabilities, and harmonic frequencies.

The Hartree−Fock and DFT methods, including the hybrid density functional B3PW91, have enabled the prediction of adequately accurate molecular and spectroscopic parameters, including nuclear shieldings of several medium-sized and larger molecules.[12−24,42−46] Moreover, regular trends in restricted Hartree−Fock (RHF)- and DFT-predicted NMR parameters were observed with the enlargement of the correlation-consistent basis sets.[22]

Several benchmark calculations of NMR parameters for small molecules have been performed using highly accurate methods and large basis sets and have been compared with experiment (for example, see selected reviews[46−48] and references therein). Gauss[11] reported excellent agreement between experimental and MP2- and CCSD(T)-calculated values of nuclear shieldings of molecular hydrogen, nitrogen, methane, ammonia, water, and hydrogen cyanide. MCSCF calculations performed by Helgaker and Ruud[49−51] provided results with a slightly lower accuracy. Unfortunately, the computation of larger molecular systems has not been possible using these methods because of the severe expense of the calculation time.

DFT calculations of NMR parameters have produced results comparable to Hartree−Fock and even to MP2 for some molecules with large correlation effects.[16−19,52−54] Malkin et al.[19] has shown that scaling the excitation energies leads to an additional improvement in the accuracy of DFT methods for predicting NMR parameters. Helgaker and Handy[52] further improved the DFT-calculated NMR parameters by optimizing the B3LYP functional.

Some time ago, the convergence of nuclear isotropic shieldings and shielding anisotropies of formaldehyde were reported.[22] More recently, Sadlej[55] reported on regular changes of ^{17}O and ^{1}H isotropic shieldings calculated for water monomers, but no attempt was made to fit the data toward the CBS limit.

Whereas higher-level methods certainly would provide the most accurate results, they often cannot be applied to larger molecules. However, although Hartree−Fock and DFT methods have been used in calculations of NMR parameters, no systematic studies have been performed on the influence of the results on the size of the basis set in the limits of the CBS approximation, nor has any comparison been made of the extrapolated CBS results with experiment.

The aim of this work is to explore the CBS approach for predicting nuclear isotropic shieldings by DFT and Hartree−Fock methods. The study provides practical guidelines on how best to obtain optimal results for NMR parameters of larger molecules, and it compares the accuracy and intrinsic errors of the theoretical approaches. Calculated NMR shielding parameters obtained by fitting double-, triple-, and quadruple- or even double- and triple-ζ basis sets to the CBS limit are compared with values from experiment or from benchmark calculations.

The molecules chosen for this study were related structurally to tetracyanoethylene (TCNE),[56,57] which is known to form charge-transfer complexes readily with a wide variety of aromatic systems. Calculations of the shielding parameters will give support to our experimental NMR studies of TCNE and its complexes, allowing an analysis of the electronic redistribution occurring in TCNE upon complexation. The set of molecules chosen has structural and spectroscopic properties that are well known from previous NMR studies (see, for example, refs 11−19 and 42−55): dihydrogen, dinitrogen, ammonia, methane, ethene, hydrogen cyanide, acetonitrile, and water.

As we shall show, systematic RHF and DFT calculations using cc-pVxZ and aug-cc-pVxZ valence basis sets for ammonia, methane, and HCN allow an assessment of the sensitivity of the obtained parameters to the basis-set quality and size and the method of fitting (choice of fitting function and number of fitted points) as well as the deviation of the method from experiment. These results are shown to compare favorably with higher-level methods, including calculations using MP2 methods for which results obtained with the smallest basis sets have been performed.

Computational Aspects

The calculated NMR isotropic shielding tensor $\sigma^{(n)}{}_{ij}$ of a nucleus (n) is defined by the following well-known relation:[13,15,58]

$$\sigma^{(n)}{}_{ij} = \partial^2 E/(\partial\mu^{(n)}{}_i\, \partial B_j) \qquad (1)$$

where E is the total molecular energy of the system, $\mu^{(n)}$ is the nuclear magnetic moment, and B is the magnetic field ($i, j = x, y, z$). The isotropic shielding $\sigma^{(n)}$ and shielding anisotropy $\Delta\sigma^{(n)}$ are calculated from the tensor components as

$$\sigma^{(n)} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3 \qquad (2)$$

$$\Delta\sigma^{(n)} = \sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2 \qquad (3)$$

for $\sigma_{zz} > \sigma_{yy} > \sigma_{xx}$. The chemical shift is obtained by using a reference compound:

$$\delta^{(n)} = \sigma^{(\mathrm{ref})} - \sigma^{(n)} \qquad (4)$$

In general, the nuclear shielding can be decomposed into two parts—diamagnetic and paramagnetic:

$$\sigma^{(n)} = \sigma^{(n)}{}_{\mathrm{d}} + \sigma^{(n)}{}_{\mathrm{p}} \qquad (5)$$

In the case of hydrogen, the diamagnetic part is dominant, whereas for heavy atoms, the paramagnetic component prevails.[12,13,15,58]

Geometry, dipole moments, harmonic frequencies, and NMR parameters were calculated for H_2, N_2, NH_3, CH_4, C_2H_4, HCN, H_2O, and CH_3CN using the Hartree−Fock and density functional methods. All calculations were performed using Gaussian98W[59] on medium-to-high-end desktop PC computers, which represent the computational power most likely to be available to experimental NMR spectroscopists. The hybrid density functional B3PW91 was used in all DFT calculations. This functional has proven fairly accurate and flexible in earlier calculations of geometry, harmonic vibrational frequencies, and even NMR parameters.[20−24] Geometry optimizations were performed with both methods using the popular 6-31G* and 6-311++G** basis sets. The optimized structural parameters, energies, dipole moments, and nuclear isotropic shieldings of the model compounds are given as Supporting Information.[60]

A literature survey appears to indicate that using an optimized (as opposed to experimental) geometry is generally preferred for NMR calculations.[14,20−24,49−51] Of course, in practice, one has a range of possibilities regarding the selection of the basis set that can be used for optimization and further calculations of NMR parameters. It has been noticed that the basis-set effects for heavy (non-hydrogen) atoms are very large and that the differences in the calculated absolute carbon, nitrogen, and oxygen isotropic shielding and shielding anisotropy parameters of small molecules using the two popular 6-31G* and 6-311++G** basis sets are of the order of 15−30 ppm.[20−24] The latter basis set is usually selected as a tradeoff between accuracy and speed for medium-sized and larger molecules. In contrast to the large dependence of the calculated parameters on the selected basis set, the dependence on geometry optimized with the same method alone appears to be much milder. For example, the carbon chemical shifts from GIAO DFT calculations using the 6-311++G** basis set, at geometries optimized using 6-311++G** or 6-31G* basis sets, differed by less than 1 ppm.[20−24] A very similar result has been observed for restricted Hartree−Fock (RHF).[20−24]

Single-point GIAO NMR calculations,[12,58,59] using various basis sets of interest (cc-pVxZ, cc-pCVxZ, aug-cc-pVxZ, and aug-cc-pCVxZ, $x = D$, T, Q, 5 and, in some cases, 6), were carried out on the 6-311++G** (and in some cases 6-31G*) optimized geometries. The most demanding calculations of the NMR parameters, those using the aug-cc-pV6Z basis set and involving more than about 800 basis-set functions, were impossible to complete in some cases, mostly because of limited computer storage resources.

The majority of experimental NMR data is obtained on molecules in condensed phases (see, for example, refs 61 and 62). To adequately compare computed values with experiment, the NMR parameters calculated for isolated molecules should be compared with gas-phase data.[50−64] In the present study, rovibrational corrections reported in the literature for H_2, N_2, NH_3, CH_4, C_2H_4, and H_2O are taken into account.[50,51,63] Such corrections are not currently available for larger molecules.

In addition, several GIAO MP2 calculations were performed on MP2/6-311++G** optimized geometries using smaller basis sets. Unfortunately, GIAO MP2 calculations failed to produce results with the largest aug-cc-pV6Z basis set even for H_2 because of computer memory limitations. Hence, most of the GIAO MP2 results were obtained with double-, triple-, and in several cases quadruple-ζ basis sets. As we shall demonstrate below, each method allowed excellent exponential fitting of the aug-cc-pVxZ-calculated dihydrogen energy with a correlation coefficient of $r > 0.999$. In the case of ammonia and hydrogen cyanide, similar patterns of decreasing energy were observed with increasing basis-set size. The MP2 fitting for larger molecules was limited to the initial points (vide infra).

The extrapolation of the calculated energy to the CBS limit, $Y(x)$, is typically achieved by fitting the calculated results with relatively simple three- or even two-parameter exponential-like decaying functions.[9, 31,34,38,39] For example,

$$Y(x) = Y(\infty) + A^* \exp(-x/B) \tag{6}$$

$$Y(x) = Y(\infty) + A/x^3 \tag{7}$$

The extrapolated value $Y(\infty)$ corresponds to the best estimate of the predicted energy for infinite zeta. Other molecular properties, particularly those that are closely related to energy, display similar convergence (see, for example, refs 9, 27, 28, 32, 33, 35, 36, 38, and 39).

As an approximate measure of the sensitivity of the calculated molecular and spectroscopic parameters to the basis-set effect, an additional parameter ΔY_i is introduced in this work:

$$\Delta Y_i = |Y_i\,(X = 2) - Y_i(\mathrm{CBS})\,| \tag{8}$$

This parameter shows a range of changes of the calculated parameters when going from double-ζ basis sets to the evaluated CBS limit.

Equations 6 and 7 were used to extrapolate the values of molecular energy, dipole moments, and isotropic shielding in the CBS limit. It should be noted that there is no general consensus on the “proper” or “best” fitting function to be used. Rather, we have tried two representative functions, eqs 6 and 7, and have found that they produce similar results. The notation CBS($x_i - x_j$) designates the range of points used for fitting using the specified equation. For example, CBS(2−6) stands for the $Y(\infty)$ value estimated from fitting all available points ($x = 2$, 3, 4, 5, and 6), and CBS(2−3) corresponds to an exact fit (with, in this case, a two-parameter function (eq 7)) to the results of calculations using double-ζ and triple-ζ basis sets.

Results And Discussion

I. Basis-Set Effect on NMR Parameters. The NMR parameters are calculated indirectly as fairly complex values derived from molecular energy (eq 1). Whereas the variational theorem guarantees that only the energy will improve as the wave function improves, and not necessarily the various derivatives of the energy, one intuitively expects that the nuclear-shielding tensor also will show improvement as the basis set improves. This expectation is based on the fact that gradual improvement of the basis set should reflect increased accuracy with which the second derivative of energy is calculated with respect to the magnetic field and the magnetic moment (eq 1). In fact, one could expect that each component of the complex shielding-tensor equation might show a different sensitivity toward the basis-set change. In particular, of interest here is determining whether the NMR parameters calculated using a DFT method display a dependence on the basis set that is similar to the dependence observed for energy.

Figure 1 presents the basis-set dependence of nitrogen and carbon isotropic shieldings calculated for the compounds studied using the B3PW91 method and without the inclusion of rovibrational effects. The 6-31G* result was obtained at a geometry optimized using the same basis set. All other calculations presented in this Figure were performed at the 6-311++G** geometry.

In general, a similar pattern is observed for all compounds:

(1) The aug-cc-pVxZ correlation-consistent basis set appears to predict smoothly converging (decaying) carbon and nitrogen isotropic shieldings.

(2) There is a significant gap between the values of the NMR parameters calculated with the 6-31G* and 6-311++G** basis sets. Not surprisingly, the values (and the gap) are similar to those obtained with the significantly larger aug-cc-pVDZ and aug-cc-pVTZ basis sets.

The corresponding shielding anisotropies (not shown) display similar behavior but are found to increase gradually with increasing zeta. These data will be reported elsewhere.

II. Selection of the Fitting Functions and the Number of Points Used for Extrapolation. Unless the total energy is used to obtain some relative energy such as the energy of atomization or bond dissociation, this quantity cannot be compared to experiment. In addition, the energy obtained from various DFT methods cannot be compared to each other or to the HF (or

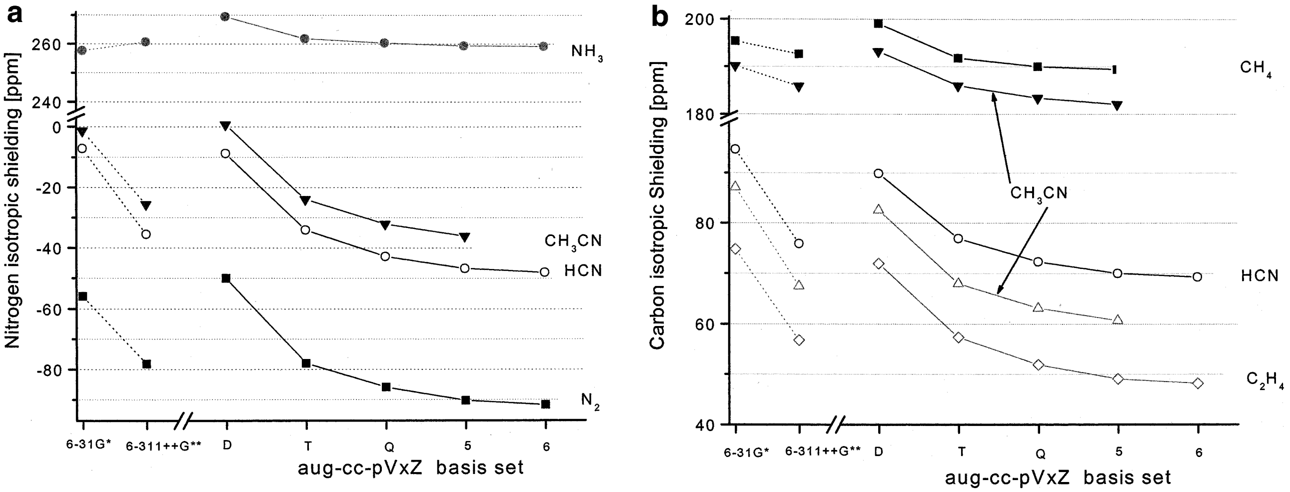

Figure 1. DFT/aug-cc-pVxZ-predicted absolute values of isotropic shieldings of small molecules as function of basis-set size: (a) nitrogen shielding, (b) carbon shielding.

TABLE 1: CBS Fitting of DFT/aug-cc-pVxZ Calculated Ammonia Energy (au)[a]

parameter	CBS(2−6)	CBS(3−6)	CBS(4−6)	CBS(5−6)	CBS(2−5)	CBS(3−5)	CBS(4−5)	CBS(2−4)	CBS(3−4)	CBS(2−3)
eq 6[b]	−56.57193	−56.57196	−56.57185		−56.57195	−56.57209		−56.57183		
deviation[c]	**0.000**	−0.019	0.050		−0.013	**−0.100**		0.063		
deviation[d]	−0.050	−0.069	**0.000**		−0.063	**−0.151**		0.013		
eq 7[e]	−56.57309	−56.57292	−56.57252	−56.57208	−56.57327	−56.57322	−56.57286	−56.57338	−56.57349	−56.5733
deviation[c]	**0.000**	0.107	0.358	**0.634**	−0.113	−0.082	0.144	−0.182	−0.251	−0.132
deviation[f]	−0.634	−0.527	−0.276	**0.000**	−0.747	−0.715	−0.490	−0.816	**−0.885**	−0.766

[a] Deviations are given in kcal/mol; 1 au = 627.5 kcal/mol. [b] $Y(x) = Y(\infty) + A^* \exp(-x/B)$. [c] $Y_i - Y_{2-6}$. [d] $Y_i - Y_{4-6}$. [e] $Y(x) = Y(\infty) + A/x^3$. [f] $Y_i - Y_{5-6}$.

higher) methods. However, in the present context, we are interested only in briefly demonstrating the general behavior of the total DFT energy rather than its absolute value.

In particular, the goal is to check in a cursory manner the consistency of the two different fitting approaches used here, as illustrated by using the results of B3PW91/aug-cc-pVxZ calculations on ammonia as an example. Functions 6 and 7 are meant to represent examples of three- and two-parameter functions, respectively. They were used here to fit via least squares all of the available data points as well as smaller data sets consisting of five, four, et cetera data points. Of course, two-point fits using eq 7 and three-point fits using eq 6 are exact (not least-squares) fits. When the selected points represent the highest-zeta calculations, the approach corresponds to the extrapolation of energy using correlation-consistent basis sets generally favored in the literature.

The reasoning behind exact fits (as opposed to least-squares fits using all available points) is based on the simple qualitative argument that the two highest-zeta calculations are always the closest to asymptotic behavior and that inclusion of lower-zeta calculations may “contaminate” the asymptotic behavior. Hence, in Table 1, we give for each function two measures of the deviation of the extrapolated result: one measure adopts the exact two- (three-) point solution as the benchmark, and the other uses the least-squares fit to all available points as a reference.

In general, the spread between various fits is not large, and there seems to be reasonably good agreement between the results across all of the explored fitting schemes. Deviations that occur between various fits using eq 7 appear to be somewhat larger than those using eq 6. This is perhaps not entirely surprising: Helgaker[38] has shown recently that the SCF energy is best fitted with a three-parameter function, whereas the correlated energy is best fitted with a two-parameter function. Indeed, the largest difference in Table 1, ∼0.9 kcal/mol, occurs between the CBS(5−6) and CBS(3−4) exact fits using eq 7. This is a direct consequence of the fact that the former extrapolates to the highest (least negative) value, whereas the latter produces the other extreme. As a result, all deviations that use the CBS(5−6) fit with eq 7 as a benchmark are of the same sign, and many have a magnitude similar to that of the maximum deviation. In contrast to this, the CBS(2−6) least-squares fit with eq 7 extrapolates to a value that is closer to the median and hence produces deviations that are more uniformly scattered between positive and negative values. The extrapolated energies obtained from the exponential function (6) appear to be generally less sensitive to the number of points used for fitting, leading to deviations on the order of 0.1−0.2 kcal/mol or less. Albeit on a smaller scale, the least-squares fits of all of the available points here also produce extrapolated values that are closer to bisecting the spread. However, not only are the differences between the explored fitting schemes not particularly dramatic, but they also tend to change from one molecule to the next, and hence there is no clear preference for any of the tested extrapolation approaches.

For the rest of this paper, we will arbitrarily choose the three-parameter function (6) fit to as many points as possible to extrapolate the CBS values of various calculated properties.

III. Basis-Set Effect Using Ammonia and Hydrogen Cyanide Energies and Dipole Moments as Examples. The energy and dipole moment of NH_3 and HCN calculated at the RHF and B3PW91 levels using basis sets without and with the inclusion of diffuse functions are presented in Figure 2. In addition, calculations on ammonia performed using core-valence basis sets are also shown. All of the obtained results were fitted with eq 6. The quality of these fits appears quite good, judging from the small values for standard deviations and very high correlation coefficients (all greater than 0.99).

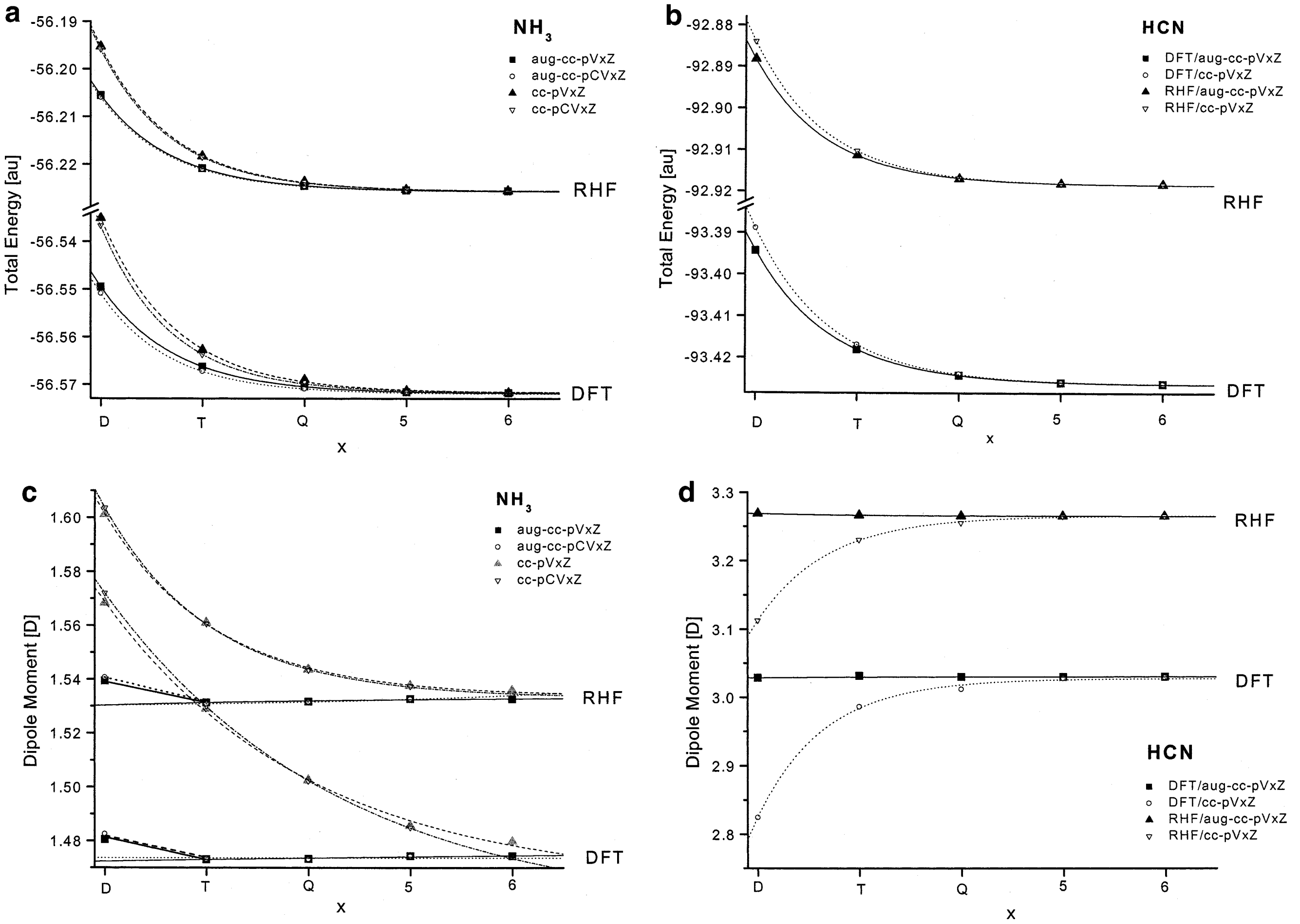

Figure 2. DFT- and RHF-calculated parameters of ammonia as a function of basis-set size and quality: (a) ammonia total energy, (b) ammonia dipole moment, (c) HCN total energy, (d) HCN dipole moment.

As expected, the energies obtained with the aug-cc-pVxZ basis-set family are lower than those obtained with the cc-pVxZ basis set (see Figure 2a and c). Whereas the differences in the energy calculated with these two types of basis sets are large for double-ζ, they become almost negligible at pentuple- and sextuple-ζ levels. The core-valence basis sets cc-pCVxZ and aug-cc-pCVxZ yield only slightly lower energies than the corresponding valence basis sets (as seen in case of ammonia, Figure 2a).

Inclusion of the diffuse function may be quite important for calculating the dipole moment.[38] Here, the augmented basis sets seem to achieve convergence at much lower zeta values than the nonaugmented basis sets (Figure 2b and d). Whereas markedly similar behavior is observed in both cases, the size of the effect is larger for ammonia than for hydrogen cyanide, probably because the augmented basis sets are able to describe the nitrogen lone electron pair better. In the case of ammonia, aug-cc-p[C]VDZ deviates markedly from the higher-zeta calculations (a behavior not observed in HCN), probably for a similar reason: double-ζ basis sets may be insufficient to describe the nitrogen lone pair properly.

Although the NH_3 dipole moment calculated using the cc-pVxZ basis set converges much slower than those calculated with the aug-cc-pVxZ basis set, the results become similar at $x = 5$ or 6. HCN shows qualitatively similar behavior, and the two basis sets start producing similar results earlier ($x = 4$). Also, the dipole moment appears to be practically insensitive (at least for ammonia) to the presence of core-valence basis-set functions.

The basis-set dependence of both the energy and the dipole moment appears to be more pronounced for DFT than it is for RHF (Figure 2 and Tables 2−10). However, at any given zeta level of the employed basis set, the DFT dipole moments are much closer to the experiment than the RHF values are. In fact, the DFT dipole moments (CBS estimates) of ammonia, HCN, and acetonitrile (Tables 2, 3, 8, and 9) appear to be remarkably accurate.

IV. Basis-Set Effect on Ammonia and HCN Nuclear Isotropic Shieldings. Nuclear isotropic shieldings of ammonia and HCN using the RHF and B3PW91 methods and correlation-consistent basis sets (on geometries optimized using 6-311++G**) are shown in Figure 3. The basis-set dependence and the CBS values were obtained from fits with eq 6. The shieldings appear to converge monotonically to the CBS value(s). The calculations using augmented basis sets converge more rapidly than their nonaugmented counterparts. This effect is slightly more pronounced for ammonia (Figure 3a and b) than it is for hydrogen cyanide (Figure 3c, d, and e). In addition, the core-valence basis sets (used here for NH_3 but not for HCN) produce further enhancement of the convergence for the heavy (non-hydrogen) nuclei. It is also interesting that in the case of HCN the result obtained by using the augmented double-ζ seems to produce a surprisingly low value (see Figure 3e) and was hence excluded from the fits. In all cases, the DFT results are lower than the corresponding RHF values.

Table 11 shows the CBS results for nitrogen isotropic shielding in ammonia using various fitting approaches, similar to what was shown in Table 1 for energy. The conclusion is

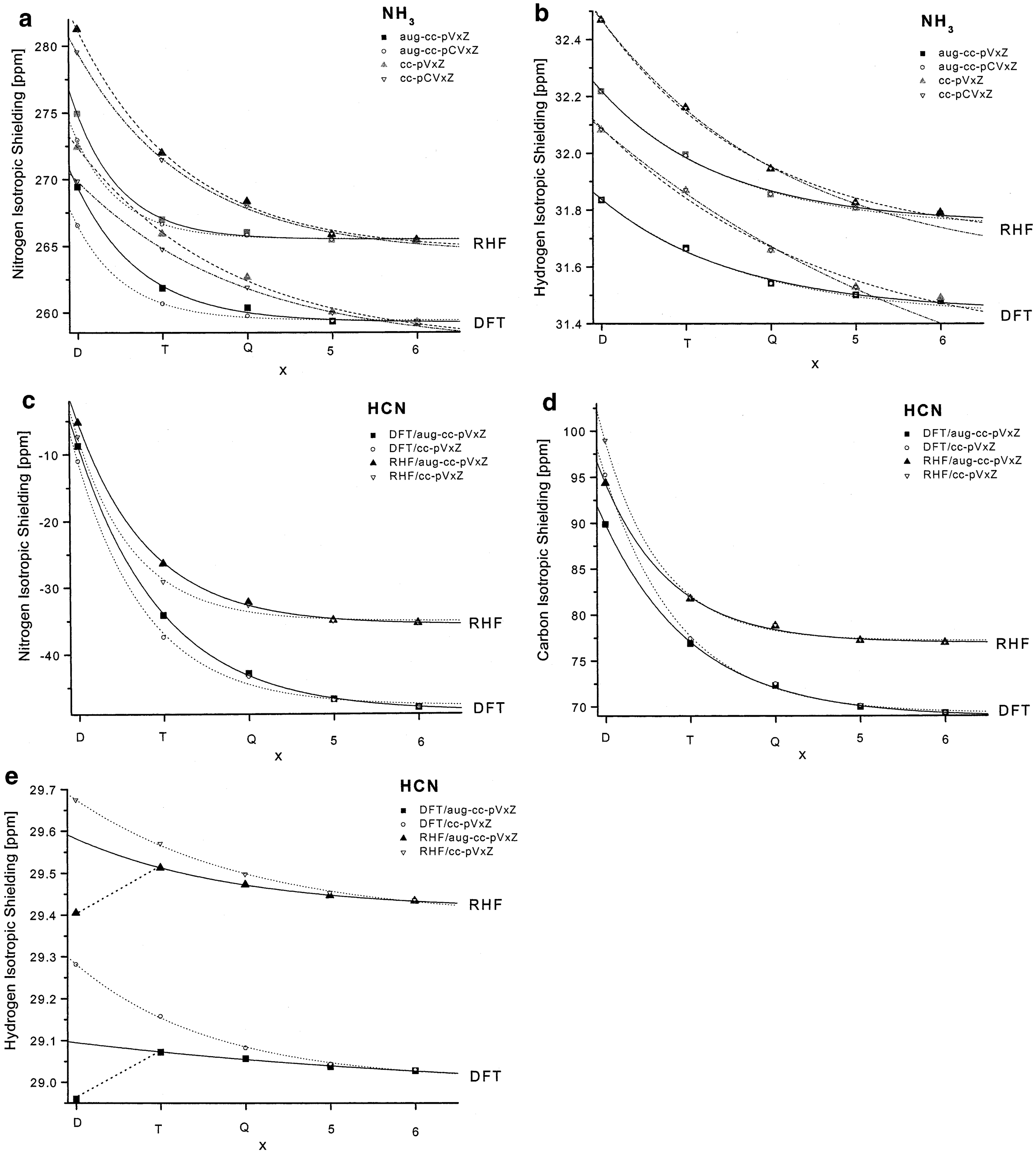

Figure 3. DFT- and RHF-calculated NMR parameters of ammonia and HCN as a function of basis-set size and quality: (a) nitrogen isotropic shielding in ammonia, (b) hydrogen isotropic shielding in ammonia, (c) nitrogen isotropic shielding in hydrogen cyanide, (d) carbon isotropic shielding in hydrogen cyanide, (e) hydrogen isotropic shielding in hydrogen cyanide.

still the same: all fitting approaches produce similar results, although perhaps eq 6 now shows slightly larger deviations than eq 7. In any case, the differences between various fitting schemes are usually a fraction of 1 ppm, and even the largest difference (2.4 ppm) is less than 1% of the calculated value. In particular, fits including only lower-zeta results (*D*, *T*, *Q* and *D*, *T*) differ from those utilizing the highest-zeta results by less than 1 ppm. This may be of relevance to the treatment of larger molecules because the higher-zeta-level calculations may be difficult to apply.

V. Comparison with Experiment and Benchmark Calculations. The predicted CBS values for the nuclear shieldings and dipole moments (when appropriate) for H_2, N_2, CH_4, C_2H_4, NH_3, HCN, CH_3CN, and H_2O are gathered in Tables 2−10. Tables 4−10 list the CBS values before and after the inclusion of rovibrational corrections[50,51,63] as well as representative benchmark calculations and available gas-phase experimental data. The Tables also include the ΔY_i values (which are a measure of the basis-set dependence, see eq 8). In almost all cases, the ΔY_i values for the DFT calculations are larger than those for the RHF calculations, clearly showing that DFT is more sensitive to the basis-set quality.

In all cases, there is a good agreement between the CBS results and those reported in the literature using Hartree−Fock and higher-level calculations or those obtained experimentally. In particular, rovibrationally corrected proton shieldings produce very close agreement with experiment, irrespective of the method used (DFT or RHF). For the heavy (C and N) nuclei,

TABLE 2: Comparison of Ammonia CBS Parameters Obtained Using Different Methods (DFT or RHF) and Basis Sets

parameter	DFT				RHF				expt
	aug-cc-pVxZ	aug-cc-pCVxZ	cc-pVxZ	cc-pCVxZ	aug-cc-pVxZ	aug-cc-pCVxZ	cc-pVxZ	cc-pCVxZ	
isotropic shielding (ppm)									
N	259.27	259.42	257.55	257.31	265.53	265.57	264.67	264.41	
N(rovibr[a])	252.47	**252.69**	250.75	250.51	258.73	**258.77**	257.87	257.61	264.54 ± 0.05[b]
H	31.44	31.42	31.29	30.89	31.75	31.74	31.69	31.59	
H(rovibr[a])	30.83	**30.81**	30.68	30.28	31.14	**31.13**	31.08	30.98	31.2 ± 1.0[b]; 30.68 ± 0.6[c]
dipole moment	1.477	**1.473**	1.464	1.453	1.534	**1.529**	1.534	1.533	1.472[d]
energy	−56.57193	**−56.57202**	−56.57175	−56.57173	−56.2256	**−56.22564**	−56.22555	−56.22554	
ΔE (kcal/mol)	0.056	0.0	0.169	0.182	0.025	0.0	0.056	0.063	

[a] After adding MCSCF rovibrational corrections (N = −6.80 ppm, H = −0.61 ppm, respectively) from reference 50. [b] Reference 64. [c] Reference 65. [d] Reference 66.

TABLE 3: Comparison of CBS Isotropic Shielding Values (ppm) with Experiment and Earlier Results for NH_3

method	geometry	σ(N)	σ^{rov}(N)	σ(H)	σ^{rov}(H)	dipole moment	comment
RHF/aug-cc-pVxZ (CBS)[a]	RHF/6-311++G**[b]	265.53	258.73[c]	31.75	31.14[c]	1.534	this work
B3PW91/ aug-cc-pVxZ (CBS)[a]	B3PW91/6-311++G**[d]	259.27	252.47[c]	31.44	30.83[c]	1.477	this work
MP2/ aug-cc-pVxZ (CBS)[a]	MP2/6-311++G**[e]	273.50	266.70[c]	31.26	30.65[c]	1.581	this work
literature							
RHF/12s8p4d2f	expt	261.61		31.57			Cybulski[f]
RHF/ANO	RHF/ANO	262.03	254.82	31.55	30.95		Ruud[g]
RHF/pz3d2f-pz3p	expt	262.3		31.7			Gauss[h]
MP2	expt	276.5		31.4			Gauss[h]
MP2/12s8p4d2f	expt	275.04		31.56			Cybulski[f]
PW91-SOS-DFPT/IGLO-II	expt	245.5		31.1			Malkin[i]
PW91-SOS-DFPT/IGLO-III	expt	257.2		31.1			Malkin[i]
PW91-SOS-DFPT/IGLO-II	expt	248.0		31.2			Malkin[j]
L-CCD/12s8p4d2f	expt	268.82		31.72			Cybulski[f]
MCSCF/ANO	MCSCF/ANO	273.79	266.99	31.39	30.78		Ruud[k]
CCSD(T)/ pz3d2f-pz3p	expt	270.7		31.6			Gauss[h]
expt		273.3 ± 0.1	264.54 ± 0.05		30.68 ± 0.6	1.472[l]	Gauss[h]

[a] Exponential fitting of GIAO results. [b] NH = 1.0003, HNH = 108.35. [c] Rovibration corrections from reference 50 (N = −6.80 ppm, H = −0.61 ppm). [d] NH = 1.0137, HNH = 107.66. [e] NH = 1.0137, HNH = 107.29. [f] NH = 1.01244, HNH = 106.67, reference 43. [g] Reference 50, NH_e = 0.997812, HNH_e = 108.158, NH_{eff} = 1.008564, HNH_{eff} = 108.595. [h] Both experimental values and isotropic shielding are from reference 19. [i] From reference 19. [j] With Loc. 1 correction, reference 19. [k] Reference 19, NH_e = 1.013446, HNH_e = 106.926, NH_{eff} = 1.025886, HNH_{eff} = 107.200. [l] Reference 66.

TABLE 4: Comparison of CBS Isotropic Shielding Values (ppm) with Experiment and Earlier Results for H_2

method	geometry	σ(H)	σ^{rov}(H)[a]	deviation[b]	ΔY[c]	comment
RHF/aug-cc-pVxZ (CBS)[d]	RHF/6-311++G** [e]	26.598	26.229	−0.059	0.002	this work
B3PW91/aug-cc-pVxZ (CBS)[d]	B3PW91/6-311++G** [f]	26.637	26.268	−0.020	0.058	this work
MP2/aug-cc-pVxZ (CBS)[d]	MP2/6-311++G** [g]	26.681	26.312	0.024	0.045	this work
literature						
RHF/11s9p6d2f	h	26.493	26.127	−0.161		Cybulski[h]
MP2/11s9p6d2f	h	26.646	26.277	−0.011		Cybulski[h]
L-CCD/11s9p6d2f	h	26.680	26.311	0.023		Cybulski[h]
CCSD(T)/8s4p3d2f	CCSD(T)/8s4p3d2f	26.667	26.298	0.010		Gauss[i]
expt		26.689 ± 0.003	26.288 ± 0.002			Gauss[a]

[a] Experimental and theoretical values and rovibrational correction (−0.3691 ppm) of isotropic shielding from reference 67. [b] Deviation = σ^{rov}(calcd) − σ (expt). [c] $\Delta Y = Y(\mathrm{CBS}) - Y(x = 2)$. [d] Exponential fitting of GIAO results in which points for $x = D$ and T were excluded from fits; both experimental values and rovibrational correction (−0.3691 ppm) of isotropic shielding are from reference 67. [e] HH = 0.7354. [f] HH = 0.7454. [g] HH = 0.7383. [h] Approximate equilibrium value, HH = 0.74088, is from reference 43. [i] HH = 0.741536 is from reference 67.

RHF appears to produce results that are significantly closer than DFT to experimental values (vide infra). All MP2 results reported here, although they are based on a very limited number of points, show the best agreement with the results from the highest-level calculations and from experiment.

Chesnut[44] pointed out that deviations between calculated versus experimental shieldings relative to the typical chemical-shielding range are significantly higher for protons than for heavy nuclei (15−20 vs 3−4%). However, rovibrational effects for proton shieldings were considered to be more important than correlation effects.[15,44] Cybulski[43] reported on fairly large deviations of SCF shieldings for molecular hydrogen (−0.161 ppm) with experiment. Higher-level CCSD(T) and MP2 calculations showed excellent agreement between experimental and rovibrationally corrected theoretical shieldings for molecular hydrogen (Table 4). Absolute deviations of the CCSD(T) shieldings from the experimental values reported by Gauss et al.[67] were only 0.01 ppm.

In the case of the hydrogen molecule, the MP2 shieldings were calculated using double- through fifth-ζ basis sets. The

TABLE 5: Comparison of CBS Isotropic Shielding Values (ppm) with Experiment and Earlier Results for N_2

method	geometry	σ(N)	σ^{rov}(N)[a]	ΔY	comment
RHF/aug-cc-pVxZ (CBS)[b]	RHF/6-311++G**[c]	−83.35	−87.62	32.47	this work
B3PW91/aug-cc-pVxZ (CBS)[b]	B3PW91/6-311++G**[d]	−91.97	−96.23	42.02	this work
MP2/aug-cc-pVxZ (CBS)[b]	MP2/6-311++G**[e]	−49.89	−54.16	44.64	this work
literature					
RHF/12s9p5d3f	expt	−111.40			Cybulski[f]
RHF/pz3d2f-pz3p	expt	−112.4			Gauss[g]
MP2/pz3d2f-pz3p	expt	−41.6			Gauss[g]
MP2/12s9p5d3f	expt	−39.70			Cybulski[f]
PW91-SOS-DFPT/IGLO-II	expt	−71.9			Malkin[h]
PW91-SOS-DFPT/IGLO-III	expt	−55.5			Malkin[h]
PW91-SOS-DFPT /IGLO-II	expt	−54.4			Malkin[i]
L-CCD/12s9p5d3f	expt	−55.73			Cybulski[f]
CCSD(T)/pz3d2f-pz3p	expt	−58.1			Gauss[g]
expt		−59.6 ± 1.5	−61.6 ± 0.5		Gauss[g]
expt		−101.3 ± 25[j]; −61.6[j,k]			Gauss[g]

[a] Rovibrational correction (−4.27 ppm) from reference 67. [b] Exponential fitting of GIAO results. For MP2, only the results at $x = D$, T, and Q were fitted. [c] NN = 1.0706. [d] NN = 1.0951. [e] NN = 1.1203. [f] NN = 1.09773 from reference 43. [g] Both calculated and experimental values are from reference 11. [h] From reference 18. [i] With Loc. 1 correction from reference 18. [j] From reference 68. [k] From reference 67.

TABLE 6: Comparison of CBS Isotropic Shielding Values (ppm) with Experiment and Earlier Results for CH_4

method	geometry	σ(C)	σ^{rov}(C)[a]	ΔY	σ(H)	σ^{rov}(H)[a]	ΔY	comment
RHF/aug-cc-pVxZ (CBS)[b]	RHF/6-311++G**[c]	194.91	191.71	9.54	31.57	30.97	0.21	this work
B3PW91/ aug-cc-pVxZ CBS)[b]	B3PW91/6-311++G**[d]	189.25	186.05	9.82	31.21	30.61	0.25	this work
MP2/ aug-cc-pVxZ (CBS)[b]	MP2/6-311++G**[e]	200.36	197.16	8.66	31.10	30.49	0.17	this work
literature								
RHF/12s8p4d2f	expt	194.78			31.57			Cybulski[f]
RHF/ANO	RHF/ANO	194.66	191.59		31.59	30.99		Ruud[g]
RHF/pz3d2f-pz3p	expt	194.8			31.7			Gauss[h]
MP2/pz3d2f-pz3p	expt	201.0			31.4			Gauss[h]
MP2/12s8p4d2f	expt	200.77			31.50			Cybulski[f]
PW91-SOS-DFPT/IGLO-II	expt	193.9						Malkin[i]
PW91-SOS-DFPT/IGLO-III	expt	191.9						Malkin[i]
PW91-SOS-DFPT/IGLO-II	expt	195.4						Malkin[j]
L-CCD/12s8p4d2f	expt	198.61			31.54			Cybulski[f]
MCSCF/ANO	RHF/ANO	201.69	198.49		31.40	30.80		Ruud[k]
CCSD(T)/pz3d2f-pz3p	expt	198.9			31.6			Gauss[f]
expt		194.8 ± 0.9[l]	198.4 ± 0.9[l]; 198.7[l]			30.611 ± 0.024[l]		Gauss[f]

[a] MCSCF rovibrational correction (C = −3.20 ppm, H = −0.60 ppm) from reference 50. [b] Exponential fitting of GIAO results; for MP2, only $x = D$ and T were used. [c] CH = 1.0843. [d] CH = 1.0911. [e] CH = 1.903. [f] CH = 1.085844 from reference 43. [g] CH_e = 1.081447, CH_{eff} = 1.09360 from reference 50. [h] From reference 11. [i] From reference 18. [j] With Loc. 1 correction from reference 18. [k] CH_e = 1.092281, CH_{eff} =1.105756 from reference 50. [l] From reference 66.

TABLE 7: Comparison of CBS Isotropic Shielding Values (ppm) with Experiment and Earlier Results for C_2H_4

method	geometry	σ(C)	σ^{rov}(C)[a]	ΔY	σ(H)	σ^{rov}(H)[a]	ΔY	comment
RHF/aug-cc-pVxZ (CBS)[b]	RHF/6-311++G**	61.45	56.66	17.89	26.37	25.85	0.098	this work
B3PW91/aug-cc-pVxZ (CBS)[b]	B3PW91/6-311++G**	47.54	42.75	24.41	25.65	25.13	0.23	this work
literature								
RHF/6-311G*	RHF/6-311G*	67.9						Chesnut[c]
RHF/pz3p	MP2/6-311G**				26.16			Chesnut[d]
RHF/vtz	RHF/vtz	65.68	60.89		26.80	26.28		Ruud[e]
MP2/ pz3p	MP2/6-311G**				26.06			Chesnut[d]
PW91-SOS-DFPT/IGLO-II	expt	60.3			25.6			Malkin[f]
PW91-SOS-DFPT/IGLO-III	expt	56.5			25.7			Malkin[f]
PW91-SOS-DFPT/IGLO-II	expt	64.5			25.7			Malkin[g]
expt			64.5[h]; 57.5[h]			25.43 [i]		

[a] With rovibrational correction (C = −4.79 ppm; H = − 0.52 ppm) from reference 51 (supplement). [b] Exponential fitting of GIAO results; [c] From reference 14. [d] From reference 44. [e] From reference 51 (supplement). [f] From reference 18. [g] With Loc. 1 correction from reference 18. [h] Both values are from references 45 and 16. [i] From reference 15.

RHF, DFT, and MP2 proton-shielding values were fitted using the CBS approximation to eq 7 (see Table 4). Systematic changes in the proton shieldings were found for basis sets larger than triple-ζ. The deviations obtained from the corresponding CBS value with aug-cc-pVDZ were very small (about 0.05 and 0.06 ppm); however, the rovibrational correction significantly improved the agreement of calculations with experiment.

The usual assumption that small basis sets (here, double-ζ) result in the saturation of proton shielding[12,49−51,77−79] seems to be valid in the case of H_2 also. However, a close inspection of the plotted shieldings versus the basis-set size reveals that regular and smooth changes of σ(H) begin only for the larger basis sets (results not shown). Thus, we conclude that the smallest basis sets give results close to the CBS limit because

TABLE 8: Comparison of HCN Predicted CBS[a] Isotropic Shielding Values (ppm) with Experiment and Earlier Results

method	geometry	σ(N)	σ(C)	σ(H)	ΔY(N)	ΔY(C)	ΔY(H)	dipole moment, μ	comment
RHF/aug-cc-pVxZ (CBS)[a]	RHF/6-311++G**	−35.52	77.12	29.40	30.31	17.25	0.17	3.266	this work
B3PW91/aug-cc-pVxZ (CBS)[a]	B3PW91/6-311++G**	−48.69	68.84	28.96	39.94	21.03	0.11	3.031	this work
MP2/aug-cc-pVxZ (CBS)[a]	MP2/6-311++G**	−6.03	84.06		41.76	22.32		3.308	this work
literature									
RHF/12s8p4d2f	expt	−50.031	71.071	29.206					Cybulski[b]
RHF/pz3d2f-pz3p	expt	−50.7	70.9	29.2					Gauss[c]
MP2/pz3d2f-pz3p	expt	−0.3	87.6	28.9					Gauss[c]
MP2/12s8p4d2f	expt	1.478	88.209	29.236					Cybulski[b]
SOPPA/8s5p1d	equilibrium[d]	−15.95	84.77	37.86					Paidarova[d]
BLYP/tz2p2d	expt	8.4	91.5						Ziegler[e]
L-CCD/12s8p4d2f	expt	−14.436	86.390	29.362					Cybulski[b]
CCSD(T)/pz3d2f-pz3p	expt	−13.6	86.3	29.0					Gauss[c]
expt		−20.4	82.1	28.3				2.98519[f]	Gauss[c]

[a] Exponential fitting of GIAO results. [b] From reference 43. [c] Both theoretical and experimental values are from reference 11. [d] CN = 1.156048, HC = 1.0640466 from reference 69. [e] From reference 18. [f] Reference 70.

TABLE 9: Comparison of CBS Isotropic Shielding Values (ppm) with Experiment and Earlier Results for CH_3CN

method	geometry	σ(N)	$\sigma(C_M)$	$\sigma(C_N)$	σ(H)	ΔY(N)	$\Delta Y(C_M)$	$\Delta Y(C_N)$	ΔY(H)	dipole moment, μ	comment
RHF/aug-cc-pVxZ (CBS)[a]	RHF/6-311++G**	−26.46	191.96	69.27	30.24	29.98	9.62	18.39	0.24	4.209	this work
B3PW91/aug-cc-pVxZ (CBS)[a]	B3PW91/6-311++G**	−37.72	181.41	59.73	29.62	38.46	11.78	22.82	0.22	4.042	this work
literature											
RHF/6-31G**	RHF/6-31G**	−33.04	192.20	70.03	29.77						Jackowski[b]
CSGT/6-311+(2d,p)	CSGT/6-31G*	−22.16	193.00	71.47	30.40						Cammi[c]
expt		−2.1[d]; −9.1[e]	187.7[d]	73.8[d]; 67.5[e]	29.06[f]					3.92[g]; 3.9252[g]	

[a] Exponential fitting of GIAO results. [b] From reference 71. [c] From reference 72. [d] From reference 16. [e] From references 54 and 73. [f] From reference 74. [g] From reference 75.

of accidental error cancellations. Deviations of DFT- and MP2-derived CBS results from experiment are very small (about 0.02 ppm) and only slightly exceed the best CCSD(T) value reported by Gauss.[67] The corresponding RHF deviations are somewhat larger (Table 4).

In numerous earlier studies (see, for example, refs 18, 24, 42, and 53), the DFT NMR results for heavy nuclei were often reported as superior to the corresponding RHF values. This was attributed to the inclusion of a correlation effect in DFT calculations. However, these studies primarily utilized smaller basis sets. The current study clearly indicates that the calculated NMR parameters display a significant basis-set dependence and that calculations with smaller basis sets produce results that are far from the CBS limit, although they may accidentally be close to the experimental values. Clearly, if a computational method ultimately converges to a CBS value that is significantly lower than the experimental values, stopping at a low zeta will by necessity produce a result that appears to be better. This coincidence, however, arises entirely because of a fortuitous cancellation of errors: the use of an inferior basis set, coupled to the high sensitivity to basis-set selection, compensates for the tendency of the method to overestimate the paramagnetic contribution.

In the set of molecules explored here, there is little difference in the RHF and DFT methods as far as the proton-shielding parameters are concerned. Perhaps not surprisingly, the two methods produce considerably different results in the case of heavy nuclei. However, the surprising behavior is that the RHF method systematically leads to CBS values that are moderately- (nitrogen nuclei) to-significantly (carbon nuclei) closer to the experiment than the corresponding DFT result is. This is a consequence of the interplay of two factors: the RHF results appear to be systematically higher than the corresponding DFT values, and the DFT values (after rovibrational corrections) tend to be lower than the experimental values. The fact that both methods predict hydrogen shielding (differing mutually /or from the experiment by ∼0.1−0.3 ppm) nearly equally well but that the RHF method ultimately leads to values for heavy nuclei that are closer to experiment (by ∼6−14 ppm) strongly supports the notion that the DFT method overestimates the paramagnetic component of the nuclear shielding.[12,13,18,19]

Again, it is worth mentioning that the DFT method has a higher sensitivity to the basis-set size. This alone would suggest that it is better to use RHF calculations when computational resources severely limit the highest-quality basis set that can be employed. However, because of the partial cancellation of errors, DFT produces low zeta values that appear to be close to the experiment. What is not quite clear, though, is whether counting on such a cancellation of errors is a sound theoretical approach to estimating NMR parameters.

In retrospect, the fact that DFT overestimates the paramagnetic component of the nuclear shielding has been well established.[12,13,18,19] Most of the currently available density functionals were developed, optimized, and calibrated to predict atomization energies rather than NMR properties (see, for example, refs 2 and 3). Consequently, one would expect that modifications of existing density functionals might improve the accuracy of NMR predictions (see ref 52). Alternatively, the correction introduced by Malkin[19] may be used to improve upon the results obtained by CBS DFT calculations.

VI. Guidelines for Using CBS Estimates Derived from CPU Time. Figure 4 illustrates the dependence of the computational effort of the DFT NMR calculations as a function of the number of used basis-set functions, approximately measured by the reported CPU time at the end of the Gaussian output file for the case of hydrogen cyanide.

Although performing calculations at the six-ζ level is very costly and possible only for very small systems, an approach

TABLE 10: aug-cc-pVxZ-Calculated CBS[a] Values of GIAO-Predicted H_2O NMR Parameters (ppm)

method	geometry	σ(O)	σ^{rov}(O)[a]	σ(H)	σ^{rov}(H)[a]	dipole moment, μ	energy	comment
RHF/aug-cc-pVxZ (CBS)[b]	RHF/6-311++G**[c]	336.16	325.23	31.00	30.51	1.939	−76.06862	this work
RHF/aug-cc-pVxZ (CBS)[b]	rovibrational averaged[d]	320.44		29.88		1.989	−76.06649	this work
B3PW91/aug-cc-pVxZ (CBS)[b]	B3PW91/6-311++G** [e]	326.55	315.62	30.87	30.38	1.847	−76.44434	this work
MP2/aug-cc-pVxZ (CBS)[b]	MP2/6-311++G** [f]	345.56	334.63	30.05	29.56	1.999	−76.41808	this work
literature								
RHF/pz3d2f-pz3p	expt	328.1		30.7				Gauss[g]
RHF/12s8p4d2f	expt	327.96		30.701				Cybulski[h]
RHF/ANO	RHF/ANO	328.15	317.10	30.58	30.08			Ruud[i]
RHF/aug-cc-pV5Z	rovibrational averaged[d]	320.15		29.92				Sadlej[j]
MP2/12s8p4d2f	expt	344.87		30.968				Cybulski[h]
MP2/pz3d2f-pz3p	expt	346.1		30.7				Gauss[g]
MP2/aug-cc-pVQZ	rovibrational averaged[d]	340.37		29.91				Sadlej[j]
PW91-SOS-DFPT/IGLO-II	expt	304.0		31.1				Malkin[k]
PW91-SOS-DFPT/IGLO-III	expt	325.6		31.2				Malkin[k]
PW91-SOS-DFPT/IGLO-II	expt	307.3		31.1				Malkin[l]
RHF-GIAO/H IV	expt	320.5						Helgaker[m]
B3LYP/H IV	expt	319.1						Helgaker[m]
$B3LYP^{0.05}$/H IV	expt	326.7						Helgaker[n]
MCSCF/ANO	MCSCF/ANO	341.76	330.83	30.62	30.13			Ruud[o]
L-CCD/12s8p4d2f	expt	335.88		31.247				Cybulski[h]
CCSD(T)/pz3d2f-pz3p	expt	337.9		30.9				Gauss[g]
expt σ_o			344.0 ± 17.2		30.052 ± 0.015	1.855 [p]		Gauss[g]
expt σ_e		357.6 ± 17.2						Gauss[g]

[a] Rovibrational corrections for O and H: SCF = −11.05 and −0.50 and MCSCF = −10.93 and −0.49 from reference 50. [b] Exponential fitting of GIAO results. Values of $x = 2, 3, 4$ were used for MP2 fitting. [c] HO = 0.9412, HOH = 106.22. [d] Experimental geometry estimated by Szalewicz[76] (HO = 0.9716257, HOH = 104.69) and used by Sadlej[55]. [e] HO = 0.9601, HOH = 104.86. [f] HO = 0.9595, HOH = 103.47. [g] Theoretical and experimental values were taken from reference 11. [h] HO = 0.95724, HOH = 104.52 from reference 43. [i] Reference 50: OH_e = 0.939747, HOH_e = 106.324, OH_{eff} = 0.952782, HOH_{eff} = 106.365. [j] Reference 55. [k] From reference 18. [l] Loc. 1 correction is from reference 18. [m] From reference 52. [n] Optimized density functional (5% exact exchange) from reference 52. [o] Reference 50: OH_{eff} = 0.972523, HOH_{eff} = 104.719. [p] Reference 66.

TABLE 11: CBS Fitting of DFT/aug-cc-pVxZ Calculated Nitrogen Isotropic Shielding of Ammonia (ppm)

parameter	CBS(2−6)	CBS(3−6)	CBS(4−6)	CBS(5−6)	CBS(2−5)	CBS(3−5)	CBS(4−5)	CBS(2−4)	CBS(3−4)	CBS(2−3)
eq 6[a]	259.2691	258.7823	259.2041		259.3914	256.8418		260.0350		
deviation[b]	0	−0.4868	−0.0650		0.1223	**−2.4273**		0.7659		
eq 7[c]	258.8248	258.8504	258.6055	259.0463	258.8225	258.8634	258.2595	258.9405	259.3167	258.6739
deviation[b]	0	0.0256	−0.2193	0.2215	0.00 23	0.0386	**−0.5653**	0.1157	0.4919	−0.1509

[a] $Y(x) = Y(\infty) + A^* \exp(-x/B)$. [b] $Y_i - Y_{2-6}$. [c] $Y(x) = Y(\infty) + A/x^3$.

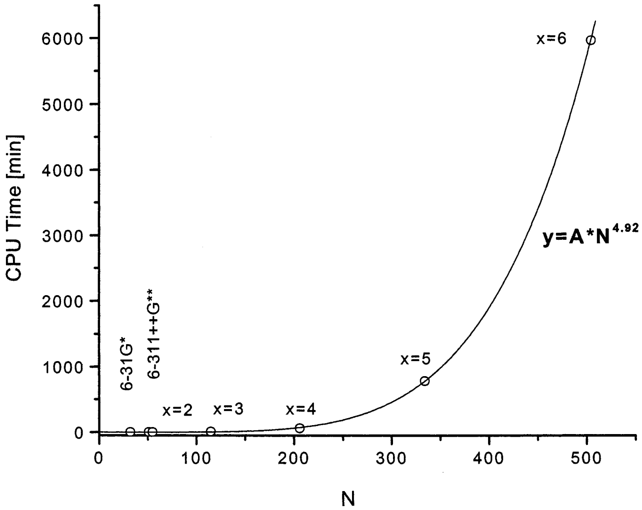

Figure 4. Time of SP GIAO NMR calculations on HCN molecule vs the number of basis-set functions (DFT/aug-cc-pVxZ, solid line corresponds to fitting with $y = A^*N^{4.92}$).

using CBS extrapolation from smaller basis sets (*D*, *T*, *Q* or even *D*, *T*, preferably containing diffuse functions aug-cc-pVxZ) produces a similar result with a significantly smaller computational effort. As demonstrated in the present paper, CBS extrapolations using only *D*, *T*, *Q*, and even *D*, *T* appear to produce NMR shielding parameters that are within ~1% of the value obtained by extrapolating the full available complement of calculations.

As far as the choice of the method is concerned, the CBS values based on GIAO RHF calculations seem to be in better agreement with experiment than DFT results. This CBS behavior is opposite to what has been reported thus far for any smaller basis sets. MP2 results show the best agreement with experiment and benchmark calculations but are computationally too expensive at present to be applied to larger molecular systems. However, regardless of the method of choice, the prerequisite to a good CBS extrapolation is a careful (graphical) inspection of the behavior at low zeta: in several cases, the double-ζ result deviates from monotonic behavior, and the corresponding point should be removed from fittings.

Conclusions

The convergence of the DFT and RHF GIAO NMR predicted parameters with cc-pVxZ and aug-cc-pVxZ basis sets was studied for H_2, N_2, NH_3, CH_4, C_2H_4, HCN, CH_3CN, and H_2O. The first detailed CBS approach tested the accuracy of fitting the NMR parameters using two- and three-parameter functions.

NMR shieldings converge monotonically to the CBS value(s). The calculations using augmented basis sets converge more rapidly than their nonaugmented counterparts. In addition, the core-valence basis sets produce further enhancement of the convergence for the heavy (non-hydrogen) nuclei. The Hartree–Fock-predicted CBS isotropic shieldings of heavy atoms were closer to experiment than the B3PW91-DFT results were. The MP2-derived CBS values, limited to the smallest basis sets, show the best agreement with experiment and benchmark theoretical studies. A CBS approach for calculating accurate nuclear shieldings of larger molecules was proposed, resulting in significant savings in computational time.

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Supporting Information Available: Tables with DFT- and RHF-optimized structures, dipole moments, energies, harmonic frequencies, and nuclear isotropic shieldings of the studied molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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