JCTC Journal of Chemical Theory and Computation

Accuracy of Computed ^{15}N Nuclear Magnetic Resonance Chemical Shifts

Adriana Gregušová, S. Ajith Perera, and Rodney J. Bartlett*

*Quantum Theory Project, Department of Chemistry and Physics,
P.O. Box 118435, Gainesville, Florida 32611*

Received October 29, 2009

Abstract: Benchmark CCSD(T) ^{15}N NMR calculations are performed for 35 experimentally known ^{15}N shifts of 29 molecules. For the eight known gas phase experimental values of N_2, HCN, CH_3CN, $N\underline{N}O$, NH_3, $\underline{N}NO$, $(CH_3)_3N$, and CH_3NH_2, CCSD(T) with a basis set previously calibrated for ^{13}C shifts is accurate to 0.2−3 ppm except for the $\underline{N}NO$ shift, which shows a deviation of 6 ppm. However, the differences between the computed and experimental values in solution due to solvent and finite temperature effects can be as large as ~25 ppm and must be estimated to relate gas phase 0 K computed values to experiment. An empirical correction is obtained by studying the variations between the estimated solvent effects and the absolute shielding constant. It is shown that the average deviation of computed shifts falls to 3.6 ppm from 12.6 ppm when the correction is applied.

Introduction

Gauge origin independent NMR shielding calculations[1−15] with electron correlation effects reported at the second order many body perturbation theory (MBPT(2))[16−18] have been extended to the predictive infinite order coupled cluster (CC) methods[18] including some triple excitation effects at various levels (CC single doubles and triples, CCSDT) and CCSD(T).[18−22] Also, multiconfiguration self-consistent field (MCSCF) methods have been applied for special cases with large nondynamic correlation effects.[23,24] Density functional theory (DFT) methods,[25−30] which are applicable for large molecules,[10−14] still suffer from accuracy and reliability issues which prohibit offering a truly predictive tool.

The accuracy of computed values, a prerequisite for validating experimental assignments or making new assignments, or in some cases supplanting the experiments, are customarily assessed by comparing the computed results either to experiment or to the full configuration interaction results. The latter gives an unambiguous measure of the errors associated with the theoretical approximations for *a given basis set* and geometry. However, the full CI NMR shielding calculations are only available for the H_2 molecule.[31] Comparisons with reliable experimental data are far more important to gauge the accuracy of the computed data.

However, these are complicated by the fact that the theory cannot account for the solution and the other conditions of most experiments.

In practice, a judicious choice has to be made for what experimental data is best used for the property under consideration, since the experiments are done in conditions that are far from ideal (noninteracting isolated molecules at 0 K) as assumed in calculations. For example, shielding constants are known to be highly influenced by the nature of the solvent effects.[32−35]

Another matter of concern in comparisons with experiment is the inability to choose the geometry and the basis sets. For example, which geometry, optimized, experimental, or in solution, is the most appropriate. Since there are no clear-cut choices, this step is best done by using a series of basis sets and geometries to establish the accuracy of the method compared to experiment for a given geometry and basis set.

Gauss and co-workers presented a systematic study of the accuracy of the ^{13}C NMR shielding constants computed by CC methods.[36] The results from this paper and from a series of papers published earlier by Gauss, Stanton, and co-workers[4,10−12,14,16−22] form the basis for the current knowledge of the accuracy of computed NMR shielding constants for the widely used NMR isotopes by CC and MBPT methods. In this paper our focus is on the accuracy of the computed ^{15}N NMR shielding constants in solutions.

---

* Corresponding author e-mail: bartlett@qtp.ufl.edu.

Accuracy of Computed NMR Shifts

J. Chem. Theory Comput., Vol. 6, No. 4, 2010 **1229**

In the context of the accuracy of computed ^{15}N chemical shifts in the present work, two recent papers are of great interest. One of them is the widely publicized work on the synthesis and the identification of the N_5^+ molecule,[37] the only other homoleptic polynitrogen species that is known beside N_2 and the azide anion (N_3^-). Among the spectroscopic techniques used, the ^{15}N NMR is regarded as the most definitive, and the agreement between the computed chemical shifts for the N_5^+ molecule at its optimized geometry and the measured shifts is quoted as the strongest evidence to support the presence of N_5^+. The computed values are obtained at the CCSD(T) level by Stanton[38] and are expected to be within $1-2$ ppm from the gas phase measurements analogous to the accuracy of the computed values of ^1H and ^{13}C NMR chemical shifts. However, the experiments are done in highly polar solvents, and only after an empirical correction is applied to account for the condensed phase effects can the agreement between scaled and measured values be considered adequate to support the conclusion that the observed NMR corresponds to N_5^+. While this is a successful application of computational methodology, we note that the correction for the condensed phase effects is chosen with severely inadequate numerical support and the accuracy of the CCSD(T) ^{15}N shifts for the geometry and basis set used needs further assessment.

The recent report of the potential isolation of the long predicted[39-41] pentazole anion (N_5^-) in solution by Butler et al.[42] is another example that employs the computed ^{15}N NMR chemical shifts to assign the measured spectra. In this case, the computations use DFT levels of theory. Despite large error bars (± 20 ppm), a match between the computed and measured shifts is one of the two pieces of evidence quoted as indicating the presence of N_5^-. However, Schroer et al.[43] who attempted to independently verify these findings by replicating the experiments of Butler et al.[42] argue that the ^{15}N NMR signal that Butler et al.[42] assigned to the nitrogen atoms in N_5^- is actually due to the nitrogen atom in NO_3^- which is abundant in the reaction mixture. Hence, Schroer et al.[43] question the validity of the claim that the N_5^- had been observed. Since the accuracy of the DFT level NMR chemical shifts are known to vary from case to case, a match between the DFT values with the measured ones may not be used as prima facie evidence to establish the presence of N_5^-. We also recognize that Schroer et al.'s arguments are exclusively based on the published NMR shifts of the primary species present in the experiment and are not further supported by computations. Part of the resolution of these conflicting experiments rests upon having reliable and also highly accurate ^{15}N NMR calculations of all the primary species involved in the experiment, in solution. We have pursued such a study, and the details are presented in a separate paper[44] devoted to the theoretical evaluation of the experimental findings of the Butler et al. and Schroer et al.[42,43] experiments and the findings in another follow up paper by Butler et al.[67] In that paper we also address the scalar spin-spin coupling constants.

In this study our focus is on the accuracy of the computed ^{15}N NMR shielding constants. When reliable gas phase experimental ^{15}N shielding data are available, analysis similar to the ^{13}C work of Gauss and co-workers for ^{13}C NMR can be performed to augment the computed data set to include the ^{15}N results. However, practical problems such as those involving N_5^+ and N_5^- described above raise additional concerns that need to be addressed. First and foremost experiments are done in solution (most cases highly polar), and a practically viable, justifiable scheme to obtain a measure of the solvent effects must be established. Moreover, since it has been noted that the solvent effects are more pronounced for ^{15}N shielding than those for ^{13}C, correcting for the solvent effects is even more relevant in the case of ^{15}N NMR chemical shielding calculations.[45] It is impractical to assume that we can incorporate the solvent effects on a first principle basis in the reasonable future for complicated solutions, though certainly electrostatic cavity models could be used,[46,47] as well as classical water force fields[48,49] for some cases. Lacking this capability, we advocate looking at the differences between the measured shifts in any solution and the very accurately computed gas phase values for a series of molecules to possibly identify systematic variations.

Another issue that needs attention is the molecular size, since it is not always possible to do a large basis set CCSD(T) calculation for the individual molecules that are of interest in experiments. For example, in the case of the above experiments, the precursors and the decomposition products in the synthesis are also ^{15}N NMR active, and they are larger molecules than the N_5^- itself; a full resolution of the measured spectra might require knowledge of their NMR as well. It is now generally accepted that electron correlation effects must be included, preferably at least at the CCSD(T) level with large basis sets, but when such high level calculations are impractical, at a minimum a small basis MBPT(2) (or DFT) result at the best possible geometry (preferably experimental) must be obtained (minimum threshold). The difference between the minimum threshold and the best possible calculations (CCSD(T) with large basis sets) must be known with some certainty.

While mindful of these special requirements for the problem we plan to address, the following concerns are significant: (1) We consider the accuracy of the ^{15}N CCSD(T)/pz3d2f shielding constants when gas phase experimental data is available and the corresponding CCSD(T) calculations that can be performed. The geometries are optimized at the CCSD(T) level using cc-pVQZ or aug-cc-pVQZ basis sets. (2) We assess the variation of the difference between the MBPT(2) and CCSD(T) ^{15}N shieldings for a given geometry with respect to basis set choice. We want to explore the possibility of estimating CCSD(T)/pz3d2f values for larger systems for which such calculations are impractical by first computing the MBPT(2)/pz3d2f results followed by adding the difference between CCSD(T) and MBPT(2) shieldings computed using a much smaller basis set such as cc-pVTZ. In order to be successful the difference between the CCSD(T) and MBPT(2) shielding must be insensitive to basis set. If successful, this will expand the range of molecules that we can access since there are many cases where the MBPT(2)/pz3d2f calculations are practical but not those for CCSD(T)/pz3d2f. We use cc-pVTZ or cc-pVDZ optimized geometries for larger molecules. (3) We consider
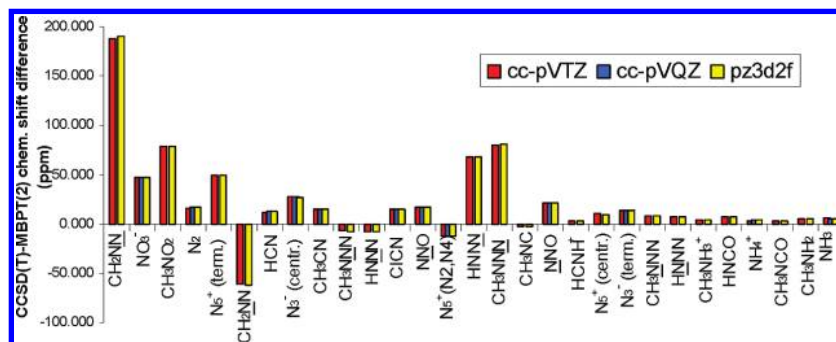
Figure 1. Differences between CCSD(T) and MBPT(2) calculated ^{15}N NMR chemical shifts (ppm). Different colors represent various basis set results for the molecules from set-A.

the difference between the computed or estimated CCSD(T)/pz3d2f and the condensed phase experimental results to quantify our averaged condensed phase effects and possibly identify correlations.

The details of all the NMR calculations and geometry optimizations, including a description of various basis sets used, the calculation level, and the molecules considered, are presented in the Theoretical Calculations section. It is followed by sections devoted to results, their analysis, and conclusions.

Theoretical Calculations

Both the ACES II UF[50] and ACES II MAB[51] versions of the ACES II program system are used for the calculations. The geometries are optimized at the CCSD(T) level employing Dunning et al.[52] correlation consistent polarized valence and augmented basis sets: CCSD(T)/aug-cc-pVQZ level optimizations for N_5^- and N_2O; CCSD(T)/cc-pVQZ level for N_3^-, N_5^+ NO_3^-, NH_3, NH_4^+, N_2, HCN, $HCNH^+$, CH_2NN, and CH_3CN, and ClCN; CCSD(T)/cc-pVTZ level for CH_3NO_2, CH_3NC, HNCO, CH_3NCO, CH_3CNH^+, CH_3NH_2, $CH_3NH_3^+$, CH_3NNN, HN_3, and N_5H; and CCSD(T)/cc-pVDZ level for the others. All the CCSD(T)/cc-pVQZ and CCSD(T)/aug-cc-pVQZ optimized geometries are confirmed to be minima by computing the harmonic frequencies. The ^{15}N NMR chemical shielding constants are computed at the MBPT(2) and CCSD(T) levels by employing gauge-including atomic orbitals (GIAOs). The basis sets, pz3d2f (pz3p2d for hydrogen), cc-pVTZ, and cc-pVQZ, are selected. As discussed earlier, the pz3d2f and pz3p2d (H) basis sets are shown to provide ^{13}C NMR chemical shielding in close agreement with experimental results for a set of 16 molecules (standard deviation of CCSD(T)/pz3d2f shielding from experiment is 1.3 ppm)[36] and are chosen as our benchmark basis sets. The pz3d2f and pz3p2d (H) basis sets are derived from the original basis set of Ahlrichs and co-workers[53] using polarization function exponents from ref 54. The two other sets, cc-pVTZ and cc-pVQZ, are used whenever the pz3d2f and pz3p2d (H) series are beyond the level of available computer resources. Nitromethane is used as the external reference (experimental absolute shielding) to obtain the ^{15}N NMR chemical shifts. We have also used NH_3 as an internal standard (absolute shielding at CCSD(T)/pz3d2f level) for

those molecules for which the gas phase experimental results are available.

Results and Discussions

Before proceeding to present our results, let us briefly summarize the points discussed previously about the nature of various calculations and their purpose and the organization of the results. Our primary target is to compute CCSD(T)/pz3d2f quality ^{15}N chemicals shifts for a series of nitrogen containing molecules. For the cases where such direct calculations are impractical, they are obtained indirectly. The molecules whose results can be obtained directly at the CCSD(T)/pz3d2f level are labeled as set-A. Similarly, set-B consists of molecules for which the highest level NMR calculations currently possible are the CCSD(T)/cc-pVTZ and MBPT(2)/pz3d2f, and set-C consists of molecules for which the highest level NMR calculations currently possible are the MBPT(2)/cc-pVDZ, MBPT(2)/cc-pVTZ, and CCSD(T)/cc-pVDZ. As a consequence, for those molecules in both set-B and set-C, the CCSD(T)/pz3d2f quality values must be estimated. The individual molecules in each category follow: set-A, CH_2NN, NO_3^-, CH_3NO_2, N_2, N_5^+, HCN, N_3^-, CH_3CN, CH_3NNN, HNNN, ClCN, NNO, CH_3NC, $HCNH^+$, $CH_3NH_3^+$, HNCO, NH_4^+, CH_3NCO, CH_3NH_2, NH_3, N_5^-, and N_5H; set-B, $C_3H_4N_2$ (12-diazole), C_4H_4NH (pyrrole), CH_3CNH^+, $(CH_3)_3N$, and $CH_3CH_2NH_2$; set-C, $MeOC_6H_4N_5$ and $MeOC_6H_4N_3$.

The first series of data presented is to establish the proposed scheme to estimate the CCSD(T)/pz3d2f quality results for the systems that are not directly amenable to the CCSD(T)/pz3d2f calculations, i.e., molecules in set-B and set-C. Then, a comparison of our calculated values with the gas phase experimental values will be presented. Finally, the computed results are compared with the available experimental data irrespective of the nature of the medium of the experiments. The purpose of this comparison is to see whether a justifiable empirical correction can be established that in general can apply to the computed values to account for the medium effects which are absent in the theoretical models that we have used to make valid comparisons with the condensed phase experiments.

Variation of the Difference between CCSD(T) and MBPT(2) Shielding Constants with Basis Sets. Figure 1 shows the difference of the CCSD(T) and the MBPT(2) ^{15}N shielding constants for nitrogen atoms in 28 molecules

Accuracy of Computed NMR Shifts

J. Chem. Theory Comput., Vol. 6, No. 4, 2010 **1231**

Table 1. Comparison of the Gas and Liquid Phase Experimental ^{15}N NMR Chemical Shifts (ppm) with Those Calculated at CCSD(T)/pz3d2f Level

nitrogen position	N$_2$	HCN	CH$_3$CN	N$\underline{N}$O	$\underline{N}$NO	(CH$_3$)$_3$N	CH$_3$NH$_2$	NH$_3$
gas phase expt chem shift (ppm)	−75.3[a]	−115.4[b]	−126.7[a]	−148.0[a]	−232.3[a]	−372.8[c]	−385.4[c]	−400.1[a]
liquid phase expt chem shift (ppm)	−70.2[a]	−127.5	−137.1[d]	−140.0[c]	−225.0[d]	−363.1[d]	−377.3[d]	−380.2[d]
CCSD(T)/pz3d2f chem shift (ppm)	−77.5	−123.0	−132.3	−149.9	−244.9	−370.0[e]	−392.8	−407.2
CCSD(T)/pz3d2f chem shift (ppm) with NH$_3$ as internal standard	−70.7	−116.1	−125.4	−143.1	−238.1	−363.1	−385.9	−400.3

[a] Reference 57. [b] Reference 58. [c] Reference 60. [d] Reference 59. [e] CCSD(T)/pz3d2f chem shift for (CH$_3$)$_3$N was estimated using MBPT(2)/pz3d2f, CCSD(T)/cc-pVTZ, and MBPT(2)/cc-pVTZ results, and the constant basis set correction (see detailed explanation in the text for set-B molecules).

obtained with the cc-pVTZ, cc-pVQZ, and pz3d2f basis sets. Note that most of the molecules in this set have multiple nitrogen atoms and hence the corresponding multiple shielding constants. For convenience, unless it becomes necessary within the context of the discussion, no reference to individual nitrogen atoms in a given molecule is made.

As we can see, the difference between CCSD(T) and MBPT(2) shielding constants is nearly invariant with respect to basis sets for a given nitrogen atom. Also, we note that this difference can be as large as 200 ppm (CH$_2$NN) or as small as 1−2 ppm while the average is 18 ppm (the average is computed using CCSD(T)/cc-pVTZ results[36]). Another observation is that the difference is largest for NN−X, where X = C, N, O, etc., systems. Further analysis of the results for the NN−X type systems included in this selection of molecules shows that the largest difference occurs for the terminal nitrogen atom, and it is positive while for the central nitrogen the error is smaller (compared to that of the terminal nitrogen) and often negative. The association of the relative change in the density to the shielding constant is the basis for all the empirical rules which have been used very successfully in relating the structures to the corresponding NMR spectra.[55,56] While it is an interesting point to further investigate the nature of the larger difference between CCSD(T) and MBPT(2) for certain bonding situations, that is left for a future study.

The pertinent observation here is that the MBPT(2) and CCSD(T) shielding constant differences are insensitive to basis set, since that provides a mechanism to reliably estimate the CCSD(T)/pz3d2f results for the molecules in set-B and set-C (for molecules in set-A, the CCSD(T)/pz3d2f level shielding constants can be computed directly). For the molecules in set-B, we first compute the MBPT(2) and CCSD(T) shielding constants with the cc-pVTZ basis set and the MBPT(2) shielding constants with the pz3d2f basis set. The difference between MBPT(2) and CCSD(T) computed with the cc-pVTZ basis set is used to correct the computed MBPT(2)/pz3d2f basis set results to obtain an estimate for the CCSD(T)/pz3d2f results using the fact that the difference is relatively insensitive to the basis sets. For the molecules in set-C, we can directly compute shielding constants at the CCSD(T)/cc-pVDZ, MBPT(2)/cc-pVDZ, and MBPT(2)/cc-pVTZ levels. The basis set independence of the shielding constant difference between the CCSD(T)/cc-pVDZ and MBPT(2)/cc-pVDZ results is used to scale the MBPT(2)/cc-pVTZ values to obtain an estimate for the CCSD(T)/cc-pVTZ shielding constants.

Comparison of the CCSD(T)/pz3d2f Results with Gas Phase Experimental Results. As we have pointed out earlier, it is best to compare computed shielding constants (or shifts) to gas phase experimental shielding constants (or shifts). To the best of our knowledge there are only eight gas phase experimental ^{15}N NMR chemical shifts reported in the literature. They are shown in Table 1 along with the computed values at the CCSD(T)/pz3d2f level and the corresponding liquid phase experimental results. The CCSD-(T)/pz3d2f chemical shifts using NH$_3$ as an internal standard are also included in Table 1 for comparison. It can be seen that, with respect to NH$_3$, internal standard computed shifts for polar N atoms are in closer agreement with the gas phase experiment than with respect to the CH$_3$NO$_2$ external standard. However, for less polar or nonpolar N atoms, the gas phase experimental and theoretical chemical shift differences is larger. Therefore, while discussing the results in Table 1, we use chemical shifts with NH$_3$ as an internal standard for polar molecules and CH$_3$NO$_2$ as an external standard for N atoms in less polar or nonpolar molecules. The absolute deviations of such defined CCSD(T)/pz3d2f computed values are within 0.2−3 ppm of the gas phase experimental results, which is slightly higher than the Gauss and co-workers findings for the ^{13}C NMR shielding constants using the same level of theory.[36] The biggest deviation (6 ppm) occurs for the terminal nitrogen atom of NNO. This may be an indication that the terminal nitrogen in NN−X type systems may need correlation effects that go beyond the CCSD(T) level. We note that the CCSDT/qz2p calculations of NMR chemical shifts for NNO reported by Gauss[61] are in very good agreement with our CCSD(T)/pz3d2f results (they are within 0.2 and 0.6 ppm for terminal and central nitrogen atom in NNO, respectively).

As discussed previously, we have also noted that the terminal nitrogen in other NN−X systems shows the largest difference between CCSD(T) and MBPT(2) results irrespective of the basis set size. It would be interesting to further evaluate the special nature of the terminal nitrogen in the NN−X type systems.

Note that the gas phase experiments are conducted at finite temperatures and the molecules can vibrate and rotate freely. In this work, we have not considered the ro-vibrational effects or the relativistic effects. The prior work done with the ^{13}C NMR shielding constants reported that on the average ro-vibrational effects amount to 1−2 ppm.

Comparison of the CCSD(T)/pz3d2f Results with Experimental Results: Set-A and Set-B. Most of the ^{15}N NMR experimental values in the literature are obtained in liquid phase at finite temperatures, far from the ideal conditions that we assume in computations. Hence, comparisons of computed values with experiments are meaningful only when the solvent and finite temperature effects are incorporated. Furthermore, it is important to point out that not having a uniform set of well established experimental data due to the fact that different experiments use different conditions (different concentrations of solutions, temperature, etc.) makes comparisons with experiment even more difficult.

The experimental ^{15}N data for 28 molecules considered here are published by three different groups. The experimental values along with the conditions under which they are obtained are presented in Table 2. For the most part the results of Jameson and co-workers are obtained in neat liquids[57] while the results of Levy and co-workers[45] and Berger and co-workers[59] are obtained mainly in solution. A plot of the difference of CCSD(T)/pz3d2f computed values (for the molecules in the set-B CCSD(T)/pz3d2f values are estimated according to the schemes presented earlier) compared to the experimental values is shown in Figure 2. In contrast to the uniform 0.2−3 ppm deviation of computed results with the gas phase experiment, deviation of the computed values from the measured values of experiments in solution shows a wide variation. For example, in some cases it is as small as 1 ppm and in others it is as large as 28 ppm and can be either positive or negative. The mean absolute deviation from experiment is 12.6 ppm while the mean absolute deviations of the positive and negative chemical shielding taken separately are 15.9 and 5.2 ppm, respectively. As discussed previously, besides a couple of ppm error due to vibrational and relativistic effects, the remaining difference between the computed and measured results is entirely due to the medium effects and the residual correlation and basis set effects that are absent in the current level of theory. As a result of the variations in the measured chemical NMR shifts depending upon the experimental conditions, there are multiple values for the difference between computed (gas phase) and measured values for a given atom in a molecule. For example, in the case of NO_3^-, the measured chemical shifts vary from −12.6 to −4.0 ppm depending on the experimental conditions (a likely cause is the acidity of the medium). It is quite clear from these results that it is ill advised to directly use the computed gas phase chemical shifts to assist assignments of experiments in solution. Since there are no well established first principle based methods to incorporate solvent effects on NMR chemical shift calculations, we focus on devising an empirical correction as an alternative. We note that the success of such an empirical correction depends on whether the solvent effects can be approximately treated as an average rather than specific to individual experiments.

In the process of calibration of a new method, a statistical analysis of the differences between the computed and measured values is used to establish the accuracy and the expected error bars. For this purpose the experimental values are carefully chosen so that the differences between the two

values are small and only due to the deficiencies in the theoretical treatment of the interactions in the entire experiment rather than due to the neglect of them. But in practice, this is not always possible and when what is being neglected in the computation is large, as is the case of the solvent and finite temperature effects in this work, one can expect large and less systematic deviations. It is not uncommon in the literature that the average differences are used as a measure of the effects that are untreated (or approximated). However, it is important to emphasize that the empirical corrections such as the ones described below must be established with large data sets and should be known with respect to a quantifiable parameter that is directly influenced by the effects that are neglected in the calculation.

Strictly speaking the shielding constant difference between the experimentally measured shielding constants in the gas phase and in a solvent give a quantitative measure of that solvent effect. The measured gas phase values are often unavailable, but they can be accurately computed. Assuming that the computed values are converged to the measured gas phase values, the difference between the measured and computed results gives an estimate of the solvent effects. A plot of the difference of computed and measured chemical shifts obtained under a variety of experimental conditions against the computed absolute shielding constants of the corresponding nuclei is shown in Figure 3.

It is pertinent to note several interesting trends that can be observed in the data presented in this figure. One obvious and expected trend is the increase of the absolute difference between the computed and measured shifts as the absolute shielding constant increases. Also, within the data set that we have considered, for the positive shielding constants, the difference is also positive, and for the negative shielding constants, in contrast, the difference is either positive or negative. Furthermore, for the negative shielding constants, the difference is much smaller in comparison with that for the positive shielding constants.

NMR shielding constants are a measure of the response to an external magnetic field (B_0) due to a change in the electron density caused by bonding (relative to the bare nuclei) in the vicinity of the nuclei of interest (the effective magnetic field at the nucleus, B_{eff}, is then $B_{eff} = B_0 + \sigma B_0$ where σ may be positive or negative). We argue that, for all practical purposes, on average the solvent acts as a perturbation of the electron density; consequently, the magnitudes of the shielding constants due to the solvent effects, estimated by the difference between the computed and the measured shielding constants, are expected to show correlation with these computed shielding constants. Let us denote the shielding constants of an isolated atom σ_0 and its corresponding value when it is bonded as σ, respectively. Also, denote the changes in the shielding constants in the presence of an external medium such as a solvent as $\Delta\sigma_0$ and $\Delta\sigma$, respectively (we note that the $\Delta\sigma_0$ is not measured under normal circumstances). The shielding constant σ_s in the presence of a solvent can then be expressed as $\sigma_s \propto (\sigma + \Delta\sigma) - (\sigma_0 + \Delta\sigma_0)$. A more useful form of this expression for discussion purposes is $\sigma_s \propto (\sigma - \sigma_0) + (\Delta\sigma - \Delta\sigma_0)$, where $\sigma_g = (\sigma - \sigma_0)$ and $\Delta\sigma_s = (\Delta\sigma - \Delta\sigma_0)$ are to a good

Accuracy of Computed NMR Shifts

J. Chem. Theory Comput., Vol. 6, No. 4, 2010 **1233**

Table 2. Summary of the Reported Experimentally Measured ^{15}N NMR Chemical Shifts (ppm) and Conditions of Their Measurement

chem shift (ppm)/conditions	expt gas phase	expt liquid phase	expt solution (solvent)	Schroer	Butler
CH2N**N**			16.8 (CDCl3)[b]		
			7.8 (Et2O)[c]		
NO3−			−4.0 (satd NH4NO3)[a]	−11.5	
			−4.6 (5 M NH4NO3,2 M HNO3)[a]		
			−12.6 (7 M HNO3)[a]		
			−3.7 (satd NaNO3)[b]		
CH3NO2		0.0			
1**2**diazole			−182.0 (av, CH3OH)[b]		
			−134.7 (av, CHCl3)[b]		
			−134.0 (av, CDCl3)[c]		
			−79.8 ((CH3)2SO)[c]		
N2	−75.3 (303 K)[a]	−74, −70.2 (77 K)[a]	−70.1 (2 M HNO3)[b]		−72.0
N5+ (term.)				−100.4[e]	
C**H**2N**N**			−94.2 (CDCl3)[b]		
			−96.0 (Et2O)[c]		
HCN		−127.5 (300 K)[a],			
		−129 (309 K)[a]			
N3− (centr)			−130.4 (NaN3 in H2O)[c]	−133.7	−147
CH3CN	−126.7 (227 K)[a]	−138.0 (227 K)[a],	−140.7[b]		
		−136.4(303K)[a]			
		−137.1[c]			
CH3N**N**N			−133.2 (CDCl3)[b]		
			−129.7 (benzene)[c]		
			−134.5 (ether)[c]		
H**N**NN					
Cl**C**N		−144 (309 K)[a]			
NNO	−148 (CCl4, 303 K)[a]	−142 (193 K)[a]	−140.0 (EBBA[d])[c]		
N5+ (N2, N4)				−165.3[e]	
HN**N**N			−179.0 (ether)[c]		
CH3NN**N**			−171.0 (benzene)[c]		
1**2**diazole			−182.0 (av, CH3OH)[b]		
			−134.7 (av, CHCl3)[b]		
			−134.0 (av, CDCl3)[b]		
			−173.1 ((CH3)2SO)[c]		
CH3**N**C		−218.2[b]			
		−218.0[c]			
NN**O**	−232.3 (CCl4, 303 K)[a]	−226 (193 K)[a]	−225.0 (EBBA[d])[c]		
pyrrole		−231.4[b]	−236.4 (CCl4)[b]		
		−231.4[c]	−222.3 ((CH3)2SO)[b]		
			−235.8 (FSO3H−SbF5−SO2)[b]		
HCN**H**+				−237.3[e]	
N5+ (centr)					
CH3C**N**H+			−239.6 (FSO3H−SbF5−SO2)[b]		
			−239.2 (FSO3H−SbF5−SO2)[c]		
N3− (term.)			−280.9 (NaN3 in H2O)[c]	−281.5	−283
CH3**N**NN			−321.2 (benzene)[c]		
H**N**NN			−324.9 (ether)[c]		
(CH3)3N	−372.8[f]	−367.2[b]	−363.1 (CH3OH)[c]		
CH3NH3+			−361.4 (1 M in CH3OH)[b]		
HNCO			−346.0 (C6H12)[c]		
CH3CH2NH2			−355.4 (CH3OH, 273 K)		
NH4+			−359.6 (satd NH4NO3)[a]	−359.8	
				−361.3	
				−362.0	
				−362.7	
CH3**N**CO		−366.1[b]			
		−365.3[c]			
CH3NH2	−385.4[f]	−378.9[b]	−377.3 (CH3OH, 273 K)[c]		
NH3	−400.1 (195 K)[a]	−377.5 (195 K)[a]			
	−399.3 (302 K)[a]	−382.1 (303 K)[a]			
	−396.1 (5 atm)[b]	−381.9 (303 K)[a]			
		−380.4 (300 K)[a]			
		−380.2 (298 K)[a]			
		−380.2 (298 K)[b]			
		−376.9 (223 K)[b]			

[a] Reference 57. [b] Reference 45. [c] Reference 59. [d] EBBA: *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline. [e] Reference 37. [f] Reference 60.

approximation a measure of the gas phase shielding constant and the solvent effects, respectively. Thus, when the com-

puted gas phase (σ_g) shielding constant is positive and large, then the solvent effect, ($\Delta\rho - \Delta\rho_0$), is most likely to be
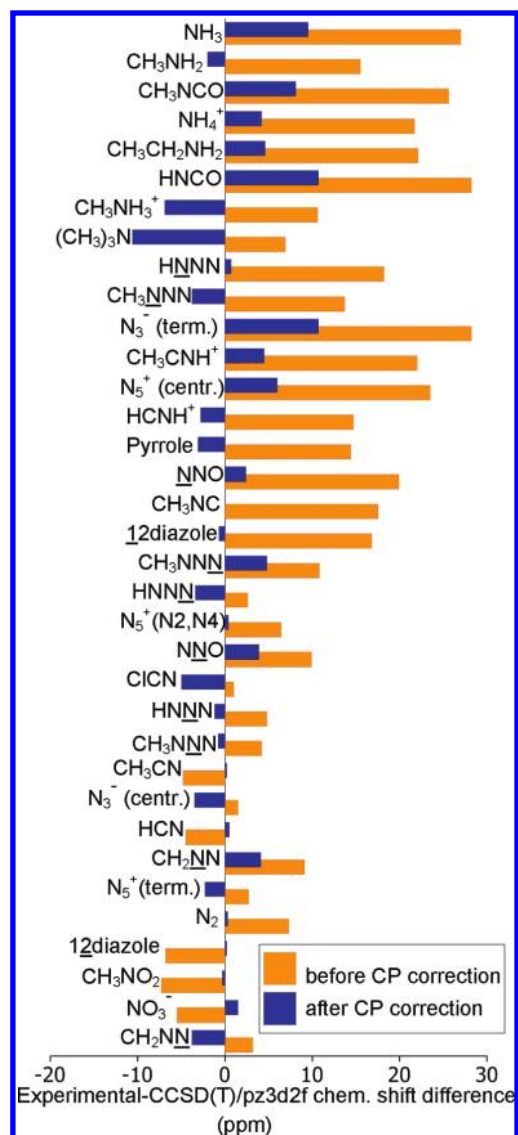
Figure 2. Differences of experimental ^{15}N NMR chemical shifts (ppm) and those calculated at the CCSD(T)/pz3d2f level with and without the empirical correction for solvent effects.

large and positive. However, when σ_g is negative, the solvent effect can be either slightly positive or negative.

A closer look at Figure 3 shows that we can identify regions of shielding constants where on average the contribution due to the medium remains unchanged. For example, we can see that, for shielding constant values in the range 0−50 ppm, the average difference is 6 ppm with the minimum and maximum differences being 1 ppm and 11 ppm, respectively. Similarly, for shielding constants in the range >50 ppm, the average is 17 ppm while the maximum and minimum differences are 7 and 28 ppm, respectively. For negative shielding constants, we can identify that the 0−(−)50 ppm range has an average error of ±5 ppm with maximum deviations of ±5 ppm and the range >(−)50 ppm has an average error of ±7 ppm while maximum and minimum deviations are ±7, respectively. These results are summarized in Tables 3 and 4.

If we use the average differences for each range listed above as the correction for the solvent effects and re-evaluate the differences between the experiment and the computed

results, after applying the proposed corrections, we obtain the results shown in Figure 2 and Table 5. We note that the mean deviation (absolute values) from the experiment of the computed gas phase results decreases from 12.6 to 3.6 ppm. Also, note that after applying the correction the mean deviations of the positive and the negative shielding constants are 4.6 and 1.6 ppm, respectively, compared with the corresponding averages prior to applying the correction, 15.9 and 5.2 ppm.

The mean deviations from experiment for the molecules in set-A and set-B are 12.1 and 14.8 ppm, respectively. The mean deviation for the group of positive chemical shifts is 15.8 ppm (set-A) and 16.4 ppm (set-B, and that for the group of negative chemical shifts is 5.0 ppm (set-A) and 6.8 ppm (set-B)). These results and the results presented in the prior section point to a general pattern that the deviation from experiment for positive shielding constant is comparatively larger than that for negative shielding constants. Comparing the behavior of sets-A and -B shows that mean deviations for set-B are only slightly higher. This might be caused by the error in the estimate used to obtain the CCSD(T)/pz3d2f chemical shift values in set-B as well as by the size of the statistical sample, since set-B only contains 6 values (5 corresponding to the positive chemical shifts and only 1 corresponding to the negative chemical shift).

Comparison of the CCSD(T)/cc-pVTZ Results with Experimental Results: Set-C. The molecules considered in set-C, further subdivided into subsets C1 and C2, having 18 or 20 atoms are the largest molecules presented in this work. As a consequence, the quality of the calculations (basis sets and theoretical method) is severely hampered. In Table 6 are presented computed ^{15}N NMR data for the molecules in set-C. They include MBPT(2) and CCSD(T) results obtained with the cc-pVDZ basis set and the MBPT(2) results obtained with cc-pVTZ, and these are currently the best possible calculations. The first observation is that the cc-pVDZ basis set, regardless of the level of theory, performs very poorly and is unsuitable for comparison with experiment. Nevertheless, the differences between the CCSD(T) and MBPT(2) obtained with the cc-pVDZ basis set are reliable and can be used to correct the MBPT(2)/cc-pVTZ results to estimate the CCSD(T)/cc-pVTZ values. These CCSD(T)/cc-pVTZ estimated values differ from 4 experimentally known values by 5.9, 11.1, 0.3, and 8.3 ppm, respectively, and, after correction for the effects of the medium, change to 0.9, 5.1, 7.3, and 1.3 ppm.

Comparison of the CCSD(T)/pz3d2f Results with Previous Theoretical Results. We have noted only a very few previous theoretical studies on ^{15}N NMR shifts, and the results from those studies along with the best values from this work and from experiment are shown in Table 7. It is evident from the results shown in Table 7 that MBPT(2) performs poorly when compared with other methods. Furthermore, the Mulliken populations which correlate with the NMR shielding indicate that the electronic structure of these molecules is inadequately described by MBPT(2). This leads us to conclude that the correlation effects beyond the MBPT(2) level must be included not only for the NMR but also for the other properties. The DFT-based methods tend
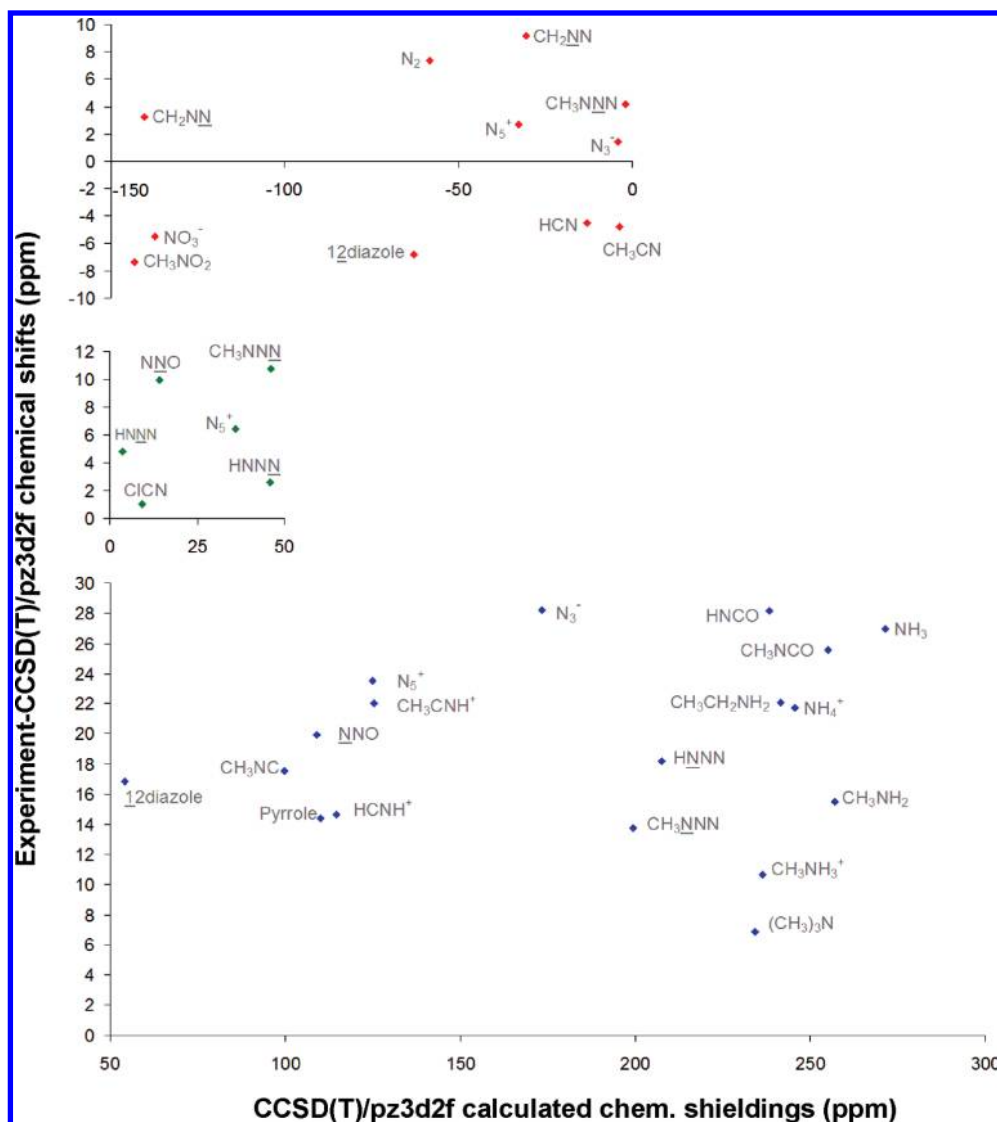
Figure 3. Relationship of the ^{15}N NMR chemical shift differences (experimental − CCSD(T)/pz3d2f, ppm) and the CCSD(T)/pz3d2f chemical shielding values (ppm).

Table 3. CP Correction to CCSD(T)/pz3d2f ^{15}N NMR Chemical Shifts for Atoms with Positive Absolute Shielding[a]

absolute chem shielding value (ppm)	0−50	>50
chem shift error − lower bound (ppm)	1	7
chem shift error − upper bound (ppm)	11	28
CP correction used − average (ppm)	6	17.5

[a] Computed chemical shifts underestimate the experimental value.

Table 4. CP Correction to CCSD(T)/pz3d2f Calculated ^{15}N NMR Chemical Shifts for Atoms with Negative Absolute Shielding[a]

absolute chem shielding value (ppm)	0−(−)50	>(−)50
chem shift error − lower bound (ppm)	−5	−7
chem shift error − upper bound (ppm)	5	7
CP correction used (ppm)	5 for positive error −5 for negative error	7 for positive error −7 for negative error

[a] If the N atom is internally polarized, the error is negative as in HCN. If the N atom is neutral, the error is positive as in N_2.

to do much better, and with the exception of a small number of DFT functional/molecule combinations, their results are consistent with the higher level computational methods. The CCSD(T)/pz3d2f results and CCSDT/qz2p chemical shifts calculated by Gauss[61] are in close agreement (the differences are 0.2, 0.6, and 2.2 ppm for terminal and central N atom in NNO and for N_2, respectively). Both CCSDT and CCSD(T) NMR shifts are in good agreement with the experimental shifts. In order to be consistent with the literature values, the CCSD(T) results in Table 7 are not corrected for solvent effects. As noted earlier, the experiments are done in solution or in some cases neat liquids, and direct comparison of

experimental results with the gas phase values is unjustified. Nonetheless, the experimental data are also included in Table 7 for the purpose of having a basis for assessing the quality of different theoretical methods.

In the interest of "predictive" quantum chemistry it would be wonderful if solution effects on a solvated molecule could be described with the same accuracy as modern quantum chemistry can describe the isolated gas phase molecules.

Table 5. Summary of ^{15}N NMR Chemical Shifts (ppm) Calculated at CCSD(T)/pz3d2f Level and CP Corrected and Their Comparison with Reported Experimental Values for the Molecules in Set-A and Set-B

chem shift (ppm)	Schroer	Butler	most recent exptl value[e]	calcd CCSD(T)/pz3d2f	CP scaling factor	CP corrected chem shift
CH$_2$NN			7.8	4.6	7	11.6
N$_5$H (N3)				3.2	7	10.2
NO$_3^-$	−11.5		−4.0	1.5	−7	−5.5
CH$_3$NO$_2$			0.0	7.3	−7	0.3
N$_5^-$				−13.5	7	−6.5
N$_5$H (N2)				−34.6	7	−27.6
12diazole			−79.8	−73.0	−7	−80.0
N$_2$		−72.0	−70.2	−77.5	7	−70.5
N$_5^+$ (term.)	−100.4[f]		−100.4	−103.1	5	−98.1
CH$_2$NN			−96.0	−105.1	5	−100.1
HCN			−127.5	−123.0	−5	−128.0
N$_5$H (N1−H)				−128.5	7	−121.5
N$_3^-$ (centr.)	−133.7	−131[g] −144 ± 3[h]	−130.4	−131.9	5	−126.9
CH$_3$CN			−137.1	−132.3	−5	−137.3
CH$_3$NNN			−129.7	−133.9	5	−128.9
HNNN			−134.5	−139.3	6	−133.3
ClCN			−144.0	−145.0	6	−139.0
NNO			−140.0	−149.9	6	−143.9
N$_5^+$ (N2, N4)	−165.3[f]		−165.3	−171.7	6	−165.7
HNNN			−179.0	−181.6	6	−175.6
CH3NNN			−171.0	−181.8	6	−175.8
12diazole			−173.1	−189.9	17.5	−172.4
CH$_3$NC			−218.0	−235.5	17.5	−218.0
NNO			−225.0	−244.9	17.5	−227.4
Pyrrole			−231.4	−245.8	17.5	−228.3
HCNH+			−235.8	−250.5	17.5	−233.0
N$_5^+$ (centr)	−237.3[f]		−237.3	−260.8	17.5	−243.3
CH$_3$CNH$^+$			−239.2	−261.2	17.5	−243.7
N$_3^-$ (term.)	−281.5	−281 to −282	−280.9	−309.1	17.5	−291.6
CH$_3$NNN			−321.2	−334.9	17.5	−317.4
HNNN			−324.9	−343.1	17.5	−325.6
(CH$_3$)$_3$N			−363.1	−370.0	17.5	−352.5
CH$_3$NH$_3^+$			−361.4	−372.0	17.5	−354.5
HNCO			−346.0	−374.2	17.5	−356.7
CH$_3$CH$_2$NH$_2$			−355.4	−377.5	17.5	−360.0
NH$_4^+$	−359.8 −361.3 −362.0 −362.7		−359.6	−381.3	17.5	−363.8
CH$_3$NCO			−365.3	−390.9	17.5	−373.4
CH$_3$NH$_2$			−377.3	−392.8	17.5	−375.3
NH$_3$			−380.2	−407.2	17.5	−389.7

[a] Reference 57. [b] Reference 45. [c] Reference 59. [d] EBBA: *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline. [e] Most recent liquid phase/solution experimental value (excluding experiments in question of Schroer et al.[43] and Butler et al.[42,67] for the sake of CP correction evaluation). [f] Reference 37. [g] Reference 67, measured in clean D$_2$O−CD$_3$OD solution. [h] Reference 67, measured for complexed azide anion in a solution containing Ce^{3+} and Ce^{4+} ions (i.e., from dearylation of 4-MeOC$_6$H$_4$N$_5$ or from N$_3^-$ anion added to a product solution after dearylation of *N*-(4-methoxyphenyl)pyrazole).

However, that does not seem yet to be possible. Consequently, crude empirical estimates are the first step.

Conclusions

The ^{15}N nuclear magnetic resonance (NMR) shielding constants computed at the many body perturbation theory and the predictive coupled cluster levels are compared with the corresponding experimental values of a series of molecules to assess corrections for solution effects. Without such corrections, it is not possible to adequately interpret results of NMR shifts for molecules like N$_5^-$, where experimental observations have been questioned. The ^{15}N CCSD(T)/

Table 6. Summary of ^{15}N NMR Chemical Shifts (ppm) Calculated at MBPT(2)/cc-pVDZ or MBPT(2)/cc-pVTZ Level, Scaled to Fit CCSD(T)/cc-pVTZ Chemical Shifts, and CP Corrected and Their Comparison with the Reported Experimental Values for the Molecules in Set-C

chem shift (ppm)	Schroer[a] expt	Butler[b] expt	calcd MBPT(2)/cc-pVDZ	calcd CCSD(T)/cc-pVDZ	calcd MBPT(2)/cc-pVTZ	CCSD(T)/cc-pVTZ	CP corr factor	CP corrected chem shift
MeOC$_6$H$_4$N$_3$ (N$_\alpha$)			−304.1	−310.1	−290.0	−295.9	17.5	−278.4
MeOC$_6$H$_4$N$_3$ (N$_\beta$)	−135.5		−129.0	−166.1	−102.4	−139.5	±5	−134.5, −144.5
MeOC$_6$H$_4$N$_3$ (N$_\gamma$)	−148.2		−339.1	−172.3	−304.0	−137.2	±5	−132.2, −142.2
MeOC$_6$H$_4$N$_5$ (N$_1$)		−80 ± 2	−132.0	−123.0	−96.7	−87.8	±5	−82.8, −92.8
MeOC$_6$H$_4$N$_5$ (N$_2$)		−22 ± 2 −28.1[c]	−105.5	−65.4	−67.1	−27.0	±7	−20.0, −34.0
MeOC$_6$H$_4$N$_5$ (N$_3$)		7 ± 2	−57.8	−29.7	−14.2	13.9	±7	20.9, 6.9

[a] Reference 43. [b] Reference 67. [c] Reference 68.

Table 7. Comparison of ^{15}N NMR Chemical Shifts (ppm) Computed at CCSD(T)/pz3d2f Level with Computed Values from the Literature (Most Recent Condensed Phase Experiments Values Also Given for Comparison although the Gas Phase Experimental Data Are Not Available in the Literature)

	MP2[a]	KS-DFT[f]	RAS-I, RAS-E[h]	B3LYP	CCSD(T)	CCSDT	experiment
CH_3NO_2	23.7[b], −71.3	15.3,6.5, 3.7, −0.1		18.6[g]	7.3		0
N_5^-	−37.9			−1.7[k]	−13.5		
N_2					−77.5	−79.7[m]	−70.2
CH_3CN	−147.3	−99.1, −111.0, −114.7, −124.5			−132.3		−137.1
C_4H_4NH (pyrrole)	−240.1	−218.1, −220.7, −221.6, −220.3			−245.8		−231.4
NNO (centr)					−149.9	−150.5[m]	−140.0
N_3^- (centr)	−159.0		−131.9, −141.1		−131.9		−130.4
NNO (term.)					−244.9	−245.1[m]	−225.0
N_3^- (term.)	−323.0		−314.6, −313.0		−309.1		−280.9
$(CH_3)_3N$	−372.7	−351.6, −352.9, −353.3, −353.4			−370.0		−363.1
CH_3NH_2	−397.9	−378.5, −380.2, −380.8, −380.2			−392.8		−377.3
NH_3	−396.5[c], −408.1[d], −412.7	−400.5, −402.1, −402.6, −401.6		−395.2[g]	−407.2		−380.2
$MeOC_6H_4N_3$ (N_α)	−290.0[e]			−310.4[k]	−295.9		−290.0[j], −293.0[k]
$MeOC_6H_4N_3$ (N_β)	−102.4[e]			−144.2[k]	−139.5		−135.5[i], −134.3[j], −137.3[k]
$MeOC_6H_4N_3$ (N_γ)	−304.0[e]			−144.3[k]	−137.2		−148.2[h], −146.1[j], −149.3[k]
$MeOC_6H_4N_5$ (N_1)[l]	−96.7[e]			−84.1[k]	−87.8		−80 ± 2[j]
$MeOC_6H_4N_5$ (N_2)[l]	−67.1[e]			−29.2[k]	−27.0		−22 ± 2[j], −28.1[k]
$MeOC_6H_4N_5$ (N_3)[l]	−14.2[e]			−18.8[k]	13.9		7 ± 2[j]

[a] MBPT(2)/pz3d2f, this work, unless specified otherwise. [b] MP2/6-311G**, see ref . [c] See ref 63. [d] MP2/6-311G*, see ref 64. [e] MBPT(2)/cc-pVTZ. [f] In general KS-DFT uses sum over state type expression with the solutions of the coupled perturbed KS equations. The choice of exchange correlation potential is usually guided by a previous calibration step. The four values correspond to the uncoupled Kohn−Sham (KS) and three levels of refinements to uncoupled KS. See ref 65 for further details. [g] B3LYP/6-311++G**, see ref 66. [h] RAS-A and RAS-E are both MCSCF with different choices of the active spaces. [i] See ref 43. [j] See ref 67. [k] RB3LYP/6-311++G(2d,p), see ref 68. [l] See Figure 4 for numbering scheme. [m] See ref 61.
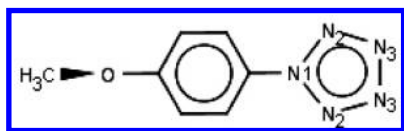
Figure 4. Structure of MBPT(2)/cc-pVDZ optimized minimum for 4-methoxyphenylpentazole ($MeOC_6H_4N_5$) and its N atom labeling.

pz3d2f, pz3p2d results presented in this work expand prior benchmark CCSD(T) calculations to include ^{15}N, and the comparison with the few known gas ^{15}N phase data (total of eight) establishes the accuracy of the ^{15}N CCSD(T) results. We observe that the CCSD(T) and MBPT(2) level shielding constant difference is small for most cases while there are a few notable exceptions. More importantly, the results are insensitive to basis set choice, and their differences can be obtained with a small cc-pVDZ basis set even when the individual values deviate significantly from the more accurate large basis set values. Since there are quite large numbers of molecules where we can obtain the MBPT(2) level chemical shifts with a suitable basis set, but not the desired CCSD(T) results, according to our findings the CCSD(T) and MBPT(2) difference can be used to correct the large basis MBPT(2) results to obtain the desired CCSD(T) estimates. Direct comparisons of the computed values with the data obtained from condensed phase experiments show a large influence from the medium and confirm that, unless the medium effects are directly incorporated in the calculations, the computed data must be corrected for the medium effects in order to be useful in practical applications. We present a systematic procedure to obtain an average correc-

tion. The error bars for the solvent effects show that for all practical purposes the same correction can be used for a range of shielding constants instead of separate corrections for each shielding constant. We show that the absolute mean error of the gas phase computed results due to the medium effects falls to 3.6 from 12.6 ppm after the proposed corrections are applied. (Within our complete set of 35 chemical shifts, the average difference between experimental liquid phase chemical shifts and the best chemical shifts calculated here was 12.6 ppm using CH_3NO_2 as an external standard and 8.9 ppm using NH_3 as an internal standard. After correcting for solvent effects, these differences decreased to 3.6 and 3.7 ppm, respectively. We are aware of the fact that, by not using NH_3 as an internal standard, our calculated NMR chemical shifts for N atoms in polar molecules might show slightly higher differences from experiment, and we stress this fact here. Since this study is related to the works of Schoer et al.[37,44] and Butler at al.,[42] who are using nitromethane as an external standard for all of their computed NMR chemical shifts, our choice in this study is not to use NH_3 as an internal standard. If the reader is interested in converting our calculated chemical shifts to those obtained by using NH_3 as an internal standard, the constant of 6.87 ppm should be added to all of our computed NMR chemical shifts and subtracted from all our CP correction factors.) Further work should attempt to incorporate at least pH effects into solvation models and related empirical estimates.

Supporting Information Available: Optimized geometries of all molecules discussed in this publication. (The computation level used for each optimization is specified in the Theoretical Calculations Section.) This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Helgaker, T.; Jaszuński, M.; Ruud, K. *Chem. Rev.* **1999**, *99*, 293.

(2) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer: Berlin, 1990; Vol. 23, p 165.

(3) Cremer, D.; Olsson, L.; Reichel, F.; Kraka, E. *Isr. J. Chem.* **1993**, *33*, 369.

(4) Gauss, J. *Ber. Bunsen. Ges. Phys. Chem.* **1995**, *99*, 1001.

(5) Pulay, P.; Hinton, J. F. In *Encyclopedia of Nuclear Magnetic Resonance*; Frant, D. M., Harris, R. K., Eds.; Wiley: Chichester, U.K., 1996; Vol. 7, p 4334.

(6) Facelli, J. C. *J. Phys. Org. Chem.* **2003**, *16*, 4327.

(7) Chesnut, D. B. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; p 245.

(8) Fleischer, U.; Kutzelnigg, W.; v. Wüllen, C. In *Encyclopedia of Computational Chemistry*; Schleyer, P.v.R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P., Schaefer, H. F., Schreiner, P. R., Eds.; Wiley: Chichester, U.K., 1998; p 1827.

(9) Bühl, M. *J. Chem. Phys.* **1993**, *99*, 1835.

(10) Gauss, J.; Stanton, J. F. *Adv. Chem. Phys.* **2002**, *123*, 355.

(11) Klemp, C.; Bruns, M.; Gauss, J.; Häussermann, U.; Stösser, G.; v.Wüllen, L.; Jansen, M.; Schnöckel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9099.

(12) Ochsenfeld, C.; Brown, S. P.; Schnell, I.; Gauss, J.; Spiess, H. W. *J. Am. Chem. Soc.* **2001**, *123*, 2597.

(13) Brown, S. P.; Schaller, T.; Seelbach, U. P.; Koziol, F.; Ochsenfeld, C.; Klärner, F.-G.; Spiess, H. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 717.

(14) Siehl, H.-U.; Müller, T.; Gauss, J. *J. Phys. Org. Chem.* **2003**, *16*, 577.

(15) Price, D. R.; Stanton, J. F. *Org. Lett.* **2002**, *4*, 2809.

(16) Gauss, J. *Chem. Phys. Lett.* **1992**, *191*, 614.

(17) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629.

(18) Bartlett, R. J.; Musial, M. *Rev. Mod. Phys.* **2007**, *79*, 291.

(19) Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **1995**, *102*, 251.

(20) Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **1995**, *103*, 3561.

(21) Stanton, J. F.; Gauss, J.; Siehl, H.-U. *Chem. Phys. Lett.* **1996**, *262*, 183.

(22) Stanton, J. F. *J. Chem. Phys.* **1996**, *104*, 2574.

(23) Jaszuński, M.; Helgaker, T.; Ruud, K.; Bak, K. L.; Jørgensen, P. *Chem. Phys. Lett.* **1994**, *220*, 154.

(24) Barszczewicz, A.; Helgaker, T.; Jaszuński, M.; Jørgensen, P.; Ruud, K. *J. Chem. Phys.* **1994**, *101*, 6822.

(25) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1994**, *221*, 91.

(26) Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898.

(27) Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 606.

(28) Rauhut, G.; Puyear, S.; Wolinski, K.; Pulay, P. *J. Phys. Chem.* **1996**, *100*, 6310.

(29) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

(30) Olsson, L.; Cremer, D. *J. Chem. Phys.* **1995**, *105*, 8995.

(31) Sundholm, D.; Gauss, J.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *243*, 264.

(32) von Philipsborn, W.; Mueller, R. *Angew. Chem., Int. Ed.* **1986**, *25*, 383.

(33) Mason, J. *Chem. Rev.* **1981**, *81*, 205.

(34) Witanowski, M.; et al. *J. Magn. Reson.* **1998**, *131*, 54.

(35) Solum, M. S.; et al. *J. Am. Chem. Soc.* **1997**, *119*, 9804.

(36) Auer, A. A.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2003**, *118*, 10407.

(37) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004.

(38) Stanton, J. F. Private communication.

(39) Ferris, K; Bartlett, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 8302.

(40) Perera, S. A.; Bartlett, R. J. *Chem. Phys. Lett.* **1999**, *314*, 381.

(41) Fau, S.; Wilson, J.; Bartlett, R. J. *J. Phys. Chem. A* **2002**, *106*, 4639.

(42) Butler, R. N.; Stephens, J. C.; Burke, L. A. *Chem. Commun.* **2003**, 1016.

(43) Schroer, T.; Haiges, R.; Schneider, S.; Christe, K. O. *Chem. Commun.* **2005**, 1607.

(44) Perera, S. A.; Gregusova, A.; Bartlett, R. J. *J. Phys. Chem. A* **2009**, *113*, 3197.

(45) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley Interscience: New York, 1979; pp 27−107.

(46) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.

(47) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

(48) Udier-Blagovic, M.; De Tirado, P. M.; Pearlman, S. A.; Jorgensen, W. L. *J. Comput. Chem.* **2004**, *25*, 1322.

(49) Tzeli, D.; Mavridis, A.; Xantheas, S. S. *J. Chem. Phys.* **2000**, *112*, 6178.

(50) Aces II, University of Florida version: Stanton, J. F.; Gauss, J.; Perera, S. A.; Yau, A. D.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K.-K.; Rozycko, P.; Sekino, H.; Huber, C.; Pittner, J. Bartlett, R. J. Aces II; Quantum Theory Project, University of Florida: Gainesville, FL. Integral packages included are VMOL (Almlöf, J.; Taylor, P.R.),VPROPS (Taylor, P. R.), and. ABACUS (Helgaker, T.; Aa. Jensen, H.J.; Jorgensen, P.; Olsen, J.; Taylor, P.R.).

(51) ACES II Mainz−Austin−Budapest version: Stanton, J. F.; Gauss, J.; Watts, J. D.; Szalay, P. G.; Bartlett, R. J.; Auer, A. A.; Bernholdt, D. B.; Christiansen, O.; Harding, M. E.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Jusélius, J.; Lauderdale, W. J.; Metzroth, T.; Michauk, C.; Price, D. R.; Ruud, K.; Schiffmann, F.; Tajti, A.; Varner, M. E.; Vázquez, J. Aces II. The integral packages: MOLECULE (Almlöf, J.; Taylor, P. R.), PROPS (Taylor, P. R.), andABACUS (Helgaker, T.; Aa. Jensen, H. J.; Jørgensen, P.; Olsen, J.).

(52) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. A. *J. Chem. Phys.* **1992**, *96*, 6796.

Accuracy of Computed NMR Shifts

J. Chem. Theory Comput., Vol. 6, No. 4, 2010 **1239**

(53) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(54) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(55) Witanowski, M.; Stefaniak, L.; Januszewski, H. *Nitrogen NMR*; Witanowski, M., Webb, G. A., Eds.; Plenum Press: New York, 1973; pp 245−254.

(56) Webb, G. A.; Witanowski, M. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1985**, *94*, 241.

(57) Jameson, C. J.; Jameson, A. K.; Oppusunggu, D.; Wille, S.; Burrell, P. M.; Mason, J. *J. Chem. Phys.* **1981**, *74*, 81.

(58) Jameson, C. J. *Chem. Rev.* **1991**, *91*, 1375.

(59) Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR-Spektroskopie von Nichtmetallen, Bd. 2*; Wiley-VCH: New York, 1992; pp 27−107.

(60) Witanowski, M.; Stefaniak, L.; Webb, G. A. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1977; Vol. 7, p 117.

(61) Gauss, J. *J. Chem. Phys.* **2002**, *116*, 4773.

(62) Hathaway, B. A.; Day, G.; Lewis, M.; Glaser, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2713.

(63) Dokalik, A.; Kalchhauser, H.; Mikenda, W.; Schweng, G. *Magn. Reson. Chem.* **1999**, *37*, 895.

(64) Barfield, M.; Fagerness, P. *J. Am. Chem. Soc.* **1997**, *119*, 8699.

(65) Fadda, E.; Casida, M. E.; Salahub, D. R. *J. Phys. Chem. A* **2003**, *107*, 9924.

(66) Alkorta, I.; Elguero, J. *Struct. Chem.* **1998**, *9*, 187.

(67) Butler, R. N.; Hanniffy, J. M.; Stephens, J. C.; Burke, L. A. *J. Org. Chem.* **2008**, *73*, 1354.

(68) Burke, L. A.; Butler, R. N.; Stephens, J. C. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 1697.