Prediction of Nitrogen and Oxygen NMR Chemical Shifts in Organic Compounds by Density Functional Theory

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Received: May 8, 1996; In Final Form: August 14, 1996⊗

Sum-over-states density functional perturbation theory (SOS-DFPT) and Hartree−Fock (HF) theory based on the "individual gauge for localized orbitals" (IGLO) scheme were used to calculate ^{13}C, ^{14}N/^{15}N, and ^{17}O NMR chemical shifts of 23 molecules. Employing the (11s7p2d/6s2p)[7s6p2d/4s2p] basis set, SOS-DFPT chemical shifts were obtained that are clearly better than HF- or UDFT-based chemical shifts, as is reflected by mean absolute deviations of 2.8 (SOS-DFPT), 7.6 (UDFT), and 5.6 ppm (HF) for ^{13}C chemical shifts, 11.8, 22.1, and 100.5 ppm for ^{14}N/^{15}N chemical shifts, and 36.4, 57.2, and 45.7 ppm for ^{17}O chemical shifts with regard to experimental values. By estimating appropriate gas phase values for ^{14}N/^{15}N chemical shifts from measured solvent effects, average errors of SOS-DFPT chemical shifts are reduced to 3 ppm, which is close to uncertainties in experimental values. SOS-DFPT is the method of choice for predicting reasonably accurate NMR chemical shifts at relatively low computational cost even in cases where correlation corrections are large. However, further improvements of SOS-DFPT are necessary to calculate more reliable ^{17}O shift values of conjugated π-systems.

1. Introduction

In previous work[1] we investigated the reliability of sum-over-states density functional perturbation theory (SOS-DFPT)[2] for the calculation of ^{13}C, ^{14}N/^{15}N, and ^{17}O NMR chemical shifts in those cases where accurate experimental gas phase data are available. SOS-DFPT chemical shifts were compared with experimental and theoretical values calculated with uncoupled density functional theory (UDFT), Hartree-Fock (HF) theory, and second-order Møller−Plesset perturbation theory (MP2). It turned out that SOS-DFPT represents an attractive method for calculating NMR chemical shifts with relatively high accuracy at rather low computational cost.

Since SOS-DFPT is basically a semiempirical method, its performance depends strongly on its calibration. For example, DFT-based methods largely overestimate paramagnetic shift contributions due to inaccuracies in DFT orbital energies. This deficiency is compensated within SOS-DFPT by an ad hoc orbital energy correction term that has been calibrated with the help of appropriate test calculations on small molecules.[2] Calibration will depend on the exchange-correlation functional used, the method of evaluating the Coulomb term J, integration techniques applied, etc. For example, we have found that the commonly used approximation of the Coulomb term J with the help of auxiliary functions leads to an underestimation of electron−electron repulsion. As a consequence, electrons can cluster more tightly around a nucleus, thus increasing diamagnetic shielding, which is normally underestimated by DFT methods.[1] In addition, DFT energies of occupied MOs become more negative, energy differences between occupied and virtual orbitals larger, and paramagnetic shift contributions smaller. Both effects prevent NMR chemical shifts from becoming too positive, thus leading to reasonable values provided paramagnetic contributions have been calibrated appropriately.

Exact calculation of the Coulomb term requires a new calibration of SOS-DFPT. If this is done with regard to both diamagnetic and paramagnetic shielding contributions, NMR chemical shifts in satisfactory agreement with measured gas phase values are obtained.[1] In our previous work, the following

conclusions concerning the calculation of NMR chemical shifts with the SOS-DFPT approach were drawn.

(1) The SOS-DFPT method leads to NMR chemical shift values that are significantly improved over those based on HF theory particularly in cases where large correlation effects play an important role.

(2) SOS-DFPT NMR shieldings are too small because of an underestimation of electron clustering in the vicinity of the nucleus, which is typical of DFT. This deficiency of DFT becomes obvious when calculating the Coulomb term J exactly as done in this and in previous work.[1] Because of the underestimation of absolute shieldings, DFT-based chemical shifts are larger up to 16 ppm, where the deviation is proportional to the number of electrons of the atom in question. This has to be considered when calibrating SOS-DFPT.

(3) In cases in which paramagnetic contributions do not play an important role, a simple correction of the diamagnetic contribution in combination with an exact calculation of J leads to accurate NMR chemical shift values that are comparable to the GIAO-MP2 values of Gauss.[3] For example, the mean absolute deviation of SOS-DFPT ^{13}C chemical shifts corrected by diamagnetic shift contribution of -5.8 ppm was found to be 2.3 ppm (GIAO-MP2: 1.2 ppm) in a study of 13 molecules with 17 different C nuclei, for which accurate experimental gas phase values are available.

(4) Scaling of the paramagnetic shift corrections suggested by Malkin and co-workers by a factor of 4/3 seems to lead to reliable ^{14}N/^{15}N chemical shifts that are more accurate than the GIAO-MP2 chemical shifts of Gauss.[3]

(5) It seems that one has to apply even larger paramagnetic shift corrections when calculating ^{17}O NMR chemical shifts with SOS-DFPT. If this is done, SOS-DFPT ^{17}O chemical shifts differ from experimental values on the average by just 3 ppm.

Conclusions 4 and 5 are tentative because of the limited number of reliable experimental gas phase values in the case of ^{14}N/^{15}N and ^{17}O chemical shifts. Both $\delta(^{14}$N/^{15}N) and δ-(^{17}O) values are often largely influenced by electron correlation effects, which makes their prediction by HF theory unreliable. Although correlation-corrected methods exist by which nitrogen

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SCHEME 1
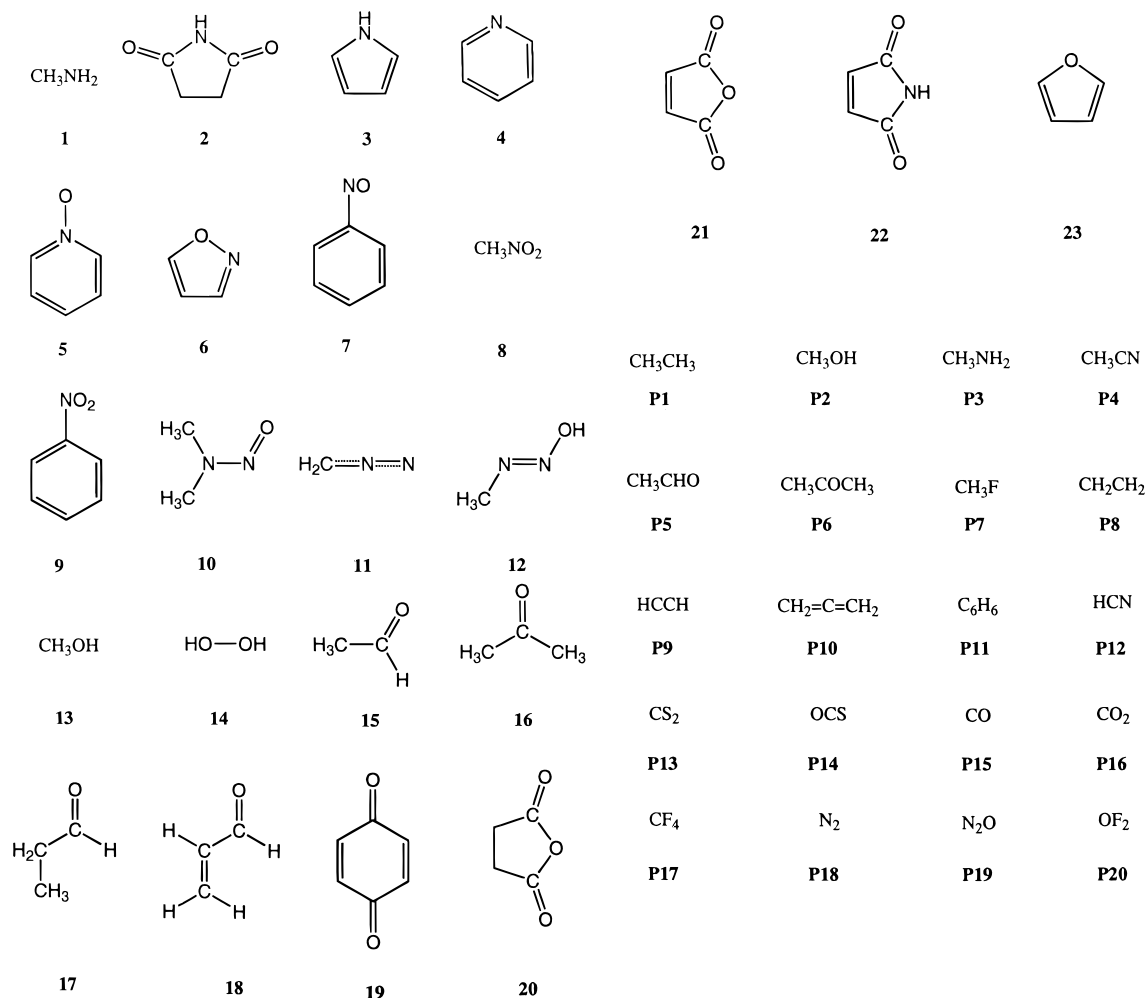
and oxygen chemical shifts can be predicted at virtually any desired accuracy,[3-10] at present these methods are too expensive to be used for larger molecules. In view of these limitations, the possibility of getting reliable $^{14}N/^{15}N$ and ^{17}O chemical shifts at rather low computational cost is attractive and could represent a stimulus for increased application of $^{14}N/^{15}N$ and ^{17}O NMR spectroscopy, which at the moment is less frequently used because of experimental limitations. The chemical shifts of $^{14}N/^{15}N$ and ^{17}O nuclei are in general more sensitive to molecular structure and conformation than either ^{1}H or ^{13}C NMR chemical shifts. This could be used for structure determination of N- or O-containing compounds along the lines of the NMR/ab initio/ IGLO method[11] provided understanding of the structural dependence of $^{14}N/^{15}N$ and ^{17}O nuclear magnetic shieldings is enhanced.

In view of the possibility that SOS-DFPT may lead to reliable predictions and a better understanding of $^{14}N/^{15}N$ and ^{17}O NMR chemical shifts, a set of 23 N- and O-containing molecules **1−23**, shown in Scheme 1, is investigated in this work.

Contrary to previous work,[1] compounds are considered for which only solution phase NMR chemical shifts are known. This requires careful consideration of the sensitivity of $^{14}N/^{15}N$ and ^{17}O magnetic shieldings with regard to solvent effects. The latter are particularly problematic for $\delta(^{17}O)$ values, which is documented by the fact that, for example, $\delta(^{17}O)$ of acetone varies from 559 ppm in aqueous solution to 605 ppm in neat liquid and to 624 ppm in infinite dilute alkane solvents (relative to gaseous H_2O),[12-14] thus spanning a shift region of 65 ppm. Experimentally, it is often necessary to use strongly polar

solvents or neat liquids, which makes a comparison with calculated shift values (corresponding to gas phase values) difficult.

Where possible, we have chosen experimental data from measurements in solvents with low dielectric constant and low complexation ability such as alkanes or chlorinated alkanes to keep uncertainties due to solvent effects as low as possible. This has been especially difficult for ^{17}O shifts, for which in many solvents strong electrostatic interactions or the possibility of hydrogen bonding has to be considered. To make a reasonable assessment of solvent effects in these cases, we have used known solvent effects of electronically similar compounds. Also, we have compared whenever possible SOS-DFPT shifts with the corresponding MP2 values. As shown in the discussion, correlation effects for the majority of chemical shift values investigated in this work are considerably larger than solvent effects, and therefore, our comparison of HF and SOS-DFPT NMR chemical shifts is still conclusive.

In the present investigation, we have not included those molecules for which chemical shifts measured in the gas phase are available since these have already been discussed in ref 1 (see molecules **P1−P20** in Scheme 1). Instead, we have particularly selected those molecules for comparison which are known to require large correlation corrections of both the dynamic and nondynamic type. In this way, limitations of the use of the SOS-DFPT approach become more apparent as this was possible in our first investigation. This is particularly true in the case of calculated ^{17}O NMR chemical shifts, for which we have not repeated calculations on alcohols, ethers, and other

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molecules with singly bonded O. Satisfactory shift values for these molecules are already obtained at the HF-IGLO level of theory so that SOS-DFPT calculations are not absolutely necessary in these cases. Of course, inclusion of these molecules in the comparison would considerably improve agreement between SOS-DFPT and experimental shift values, which has to be considered in the final discussion.

2. Theory

In a sum-over-states perturbation theory of nuclear magnetic shielding,[2] the exact wave function of the ground state is expanded in a Taylor series in the magnetic field vector **B** and the perturbed part of the wave function is expressed in terms of the excited states of the zero-order problem according to

$$\psi_0(\mathbf{B}) = \psi_0^{(0)} + i\mathbf{B} \sum_{K \neq 0} \mathbf{C}_K \psi_K^{(0)} + ... \quad (1)$$

The first-order coefficients $\mathbf{C}_K$ are determined by

$$\mathbf{C}_K = \frac{\langle \psi_0^{(0)} | H^{(\mathbf{B})} | \psi_K^{(0)} \rangle}{E_0^{(0)} - E_K^{(0)}} \quad (2)$$

where

$$H^{(\mathbf{B})} = \frac{1}{i} \frac{\partial}{\partial \mathbf{B}} H \quad (3)$$

The nuclear magnetic shielding tensor is given by

$$\boldsymbol{\sigma} \equiv \frac{\partial^2 E}{\partial \boldsymbol{\mu} \, \partial \mathbf{B}} = \langle \psi_0^{(0)} | H^{(\boldsymbol{\mu},\mathbf{B})} | \psi_0^{(0)} \rangle - 2 \sum_{K \neq 0} \mathbf{C}_K \langle \psi_0^{(0)} | H^{(\boldsymbol{\mu})} | \psi_K^{(0)} \rangle \quad (4)$$

where

$$H^{(\boldsymbol{\mu})} = \frac{1}{i} \frac{\partial}{\partial \boldsymbol{\mu}} H \quad (5)$$

$$H^{(\boldsymbol{\mu},\mathbf{B})} = \frac{\partial^2}{\partial \boldsymbol{\mu} \, \partial \mathbf{B}} H \quad (6)$$

and $\boldsymbol{\mu}$ is the nuclear magnetic dipole vector of the nucleus in question. In the SOS-DFPT formalism, the ground state wave function $\psi_0^{(0)}$ is approximated by the reference determinant Φ obtained from an ordinary Kohn–Sham DFT calculation. Accordingly, the set of excited state wave functions $\psi_K^{(0)}$ is approximated by single-replacement determinants Φ_i^a formed from the orbitals of the reference determinant, and the excitation energy $E_0^{(0)} - E_K^{(0)}$ is approximated by the difference between the corresponding Kohn–Sham orbital energies $\epsilon_i - \epsilon_a$ corrected by an energy term $\Delta E_{i \to a}^{xc}$ so that

$$E_0^{(0)} - E_K^{(0)} = \epsilon_i - \epsilon_a - \Delta E_{i \to a}^{xc} \quad (7)$$

Malkin and co-workers[2] combined SOS-DFPT with the individual gauge for localized orbitals (IGLO) formalism developed by Kutzelnigg at the HF level to solve the gauge-origin problem of magnetic shielding calculations.[15] Several expressions are given by Malkin and co-workers for the term $\Delta E_{i \to a}^{xc}$, leading to a set of different SOS-DFPT methods. On the basis of the results of our previous investigation[1] we use in this work exclusively the Loc2 approximation of Malkin and co-workers (denoted here as SOS-DFPT(Loc2)), which is given by eq 8:

$$\Delta E_{i \to a}^{xc} = \frac{2}{3} \left(\frac{3}{4\pi} \right)^{1/3} \int \rho^{\uparrow}(\mathbf{r})^{(-2/3)} \rho_i(\mathbf{r}) \, \rho_a(\mathbf{r}) \, dr \quad (8)$$

where ρ_p ($p = i, a$) is the electron density of an electron in orbital p and $\rho^{\uparrow}$ is the total α spin density.

As has been pointed out by van Wüllen,[16] SOS-DFPT/IGLO is, apart from the excitation energy correction term $\Delta E_{i \to a}^{xc}$, identical to the (IGLO version of) uncoupled density functional theory (UDFT), which can be derived by differentiating the expression for the Kohn–Sham energy according to $\boldsymbol{\sigma} = \partial^2 E / (\partial \boldsymbol{\mu} \, \partial \mathbf{B})$. Lee and co-workers[17] have argued that the reason for the failure of UDFT in predicting accurate nuclear magnetic shieldings results from the known deficiency of presently used density functionals in correctly assigning the values of orbital energies. In this context, the SOS-DFPT approach can be seen as a way of approximating correct UDFT based on the exact exchange-correlation potential.

3. Computational Methods

SOS-DFPT(Loc2) and UDFT-IGLO have been programmed and implemented into the ab initio package COLOGNE-94,[18] as described in ref 1. Again, DFT calculations were based on the exact evaluation of the Coulomb term *J* without using auxiliary basis sets, as done in the original SOS-DFPT method implemented in the program system DeMon.[19,20]

All chemical shift calculations were performed with a combination of the Becke exchange[21] and the PW91 correlation functionals[22,23] using the (11s7p2d/6s2p)[7s6p2d/4s2p] basis set developed by Kutzelnigg and co-workers.[24] While in the previous investigation[1] we exclusively used geometries optimized at the MP2/TZ2P level, in this work we have determined DFT equilibrium geometries using the same combination of exchange and correlation functionals as in the chemical shift calculations. These optimizations were performed with the Gaussian-94[25] program system employing the 6-311G(2d,2p) basis, which is TZ+2P quality (see supporting information). DFT/TZ+2P geometries are in general equal to or better than MP2 geometries and, accordingly, sufficiently accurate for the purpose of this work. Only in some exceptional cases were MP2/TZ2P geometries taken from ref 3.

Appropriate reference values for getting relative chemical shifts were obtained by using CH_4 (carbon), NH_3 (nitrogen), and H_2O (oxygen). Experimental values are normally given as shifts relative to internal tetramethylsilane (TMS) (carbon) and liquid water (oxygen) and as shieldings relative to liquid nitromethane as external reference (nitrogen). These data have been transformed and expressed as shifts relative to $CH_4(g)$, $NH_3(g)$, and $H_2O(g)$ using known experimental data:[26-28]

$$\delta_{CH_4(g)} = \delta_{TMS(g)} + 7.0 \quad (9)$$

$$\delta_{NH_3(g)} = 400.9 - \sigma_{CH_3NO_2} \quad (10)$$

and

$$\delta_{H_2O(g)} = \delta_{H_2O(l)} + 36.1 \quad (11)$$

where δ is the relative chemical shift for a given nucleus indicating sign inversion when replacing absolute shieldings by relative chemical shifts. When using nitromethane as a reference, one chooses relative chemical shifts to possess the same sign as absolute shieldings, which we have indicated by using $\sigma_{CH_3NO_2}$ rather than $\delta_{CH_3NO_2}$ in eq 10. Since neat nitromethane is used as an external reference and since solvent effects on

TABLE 1: Calculated and Experimental Carbon (^{13}C) Chemical Shifts (δ) in ppm Relative to Gaseous CH$_4$[a]

molecule	sym.	atom	HF-IGLO	UDFT-IGLO	SOS-DFPT-IGLO (Loc2)	SOS-DFPT-IGLO (TMS)[b]	SOS-DFPT-IGLO (corr)[c]	expt[d]
17, propanal	C_s	C$_1$	212.4	220.1	213.5	209.7	207.7	209.7
		C$_2$	41.0	53.7	53.8	50.0	48.0	43.7
		C$_3$	10.8	14.7	15.7	11.9	9.9	12.2
18, *trans*-propenal	C_s	C$_1$	205.2	210.5	206.6	202.8	200.8	200.3
		C$_2$	149.0	157.7	156.9	153.1	151.1	143.0
		C$_3$	148.7	154.7	152.6	148.8	146.8	143.4
19, *p*-C$_4$H$_4$(CO)$_2$	D_{2h}		202.6	212.1	208.3	204.5	202.5	194.0
19, *p*-C$_4$H$_4$(CO)$_2$			147.8	147.7	150.2	146.4	144.4	143.4
20, C$_2$H$_4$(CO)$_2$O	C_{2v}		185.0	190.0	189.0	185.2	183.2	179.5
2, C$_2$H$_4$(CO)$_2$NH	C_{2v}		191.1	191.1	190.0	186.2	184.2	186.0
20, C$_2$H$_4$(CO)$_2$O	C_{2v}		29.3	40.3	41.4	37.6	35.6	35.2
2, C$_2$H$_4$(CO)$_2$NH	C_{2v}		31.1	42.0	43.1	39.3	37.3	37.0
21, C$_2$H$_2$(CO)$_2$O	C_{2v}		177.4	185.6	184.8	181.0	179.0	172.9
22, C$_2$H$_2$(CO)$_2$NH	C_{2v}		183.5	187.5	186.4	182.6	180.6	179.2
21, C$_2$H$_2$(CO)$_2$O	C_{2v}		148.8	151.2	150.9	147.1	145.1	144.4
22, C$_2$H$_2$(CO)$_2$NH	C_{2v}		148.2	149.0	149.2	145.4	143.4	142.8
23, furan	C_{2v}	C$_2$	158.1	158.4	157.2	153.4	151.4	150.6
		C$_3$	118.8	123.5	122.6	118.8	116.8	117.4
3, pyrrole	C_{2v}	C$_2$	130.7	128.7	128.1	124.3	122.3	124.3
		C$_3$	117.9	122.6	121.5	117.7	115.7	114.6
4, pyridine	C_{2v}	C$_2$	167.6	167.4	165.9	162.1	160.1	156.9
		C$_3$	130.2	137.5	137.1	133.3	131.3	130.8
		C$_4$	152.0	148.9	148.3	144.5	142.5	143.0
5, pyridine *N*-oxide	C_{2v}	C$_2$	159.3	156.7	155.8	152.0	150.0	145.6
		C$_3$	135.1	140.1	139.6	135.8	133.8	132.8
		C$_4$	136.4	130.2	129.8	126.0	124.0	132.3
6, isoxazole	C_s	C$_3$	172.5	162.6	160.1	156.3	154.3	157.0
		C$_4$	105.9	116.1	115.2	111.4	109.4	107.5
		C$_5$	180.8	173.3	171.2	167.4	165.4	165.9
8, CH$_3$NO$_2$	C_s		67.5	74.0	74.0	70.2	68.2	68.2
9, PhNO$_2$	C_{2v}	C$_1$	160.7	166.6	167.0	163.2	161.2	155.4
		C$_2$	138.8	139.0	139.1	135.3	133.3	130.6
		C$_3$	137.1	143.6	143.1	139.3	137.3	136.4
		C$_4$	149.8	149.3	148.9	145.1	143.1	141.6
10, Me$_2$N-NO	C_s	C(*cis*)	31.1	33.6	34.4	30.6	28.6	39.1
		C(*trans*)	41.4	49.5	50.0	46.2	44.2	46.9
11, H$_2$CNN	C_{2v}		32.1	28.4	27.5	23.7	21.7	30.1
mean abs. dev.			5.6	7.6	6.9	3.8	2.8	

[a] The nucleus considered is underlined or given in column 3. Calculated with the (11s7p2d/6s2p)[7s6p2d/4s2p] basis of Kutzelnigg and co-workers.[24] BPW91/6-311G(2d,2p) geometries. [b] Obtained by using tetramethylsilane (TMS) as primary computational reference (see text). [c] Obtained by adding a diamagnetic shift correction of -5.8 ppm (see text). [d] Experimental shifts from ref 54.

^{13}C shieldings in TMS are normally very small,[29] eq 10 and 9 are used directly in the comparison with calculated gas phase values.

4. Results

Calculated ^{13}C, ^{14}N/^{15}N, and ^{17}O NMR chemical shifts of the 23 molecules investigated are listed together with the corresponding experimental shifts in Tables 1, 2, and 3. Deviations of HF-IGLO and SOS-DFPT(Loc2) shifts from experimental values are presented in Figures 1 (^{14}N/^{15}N shifts) and 2 (^{17}O shifts) in the form of bar diagrams. Table 4 gives a summary of measured solvent effects on NMR chemical shifts.

4.1. Carbon Chemical Shifts. Table 4 reveals that methyl ^{13}C shifts are hardly influenced by solvent effects. Stronger solvent effects of 3−5 ppm have been measured for the C atoms of keto or cyano groups. However, this is still smaller than uncertainties in calculated ^{13}C chemical shifts, which vary between 7 and 10 ppm at the HF level of theory. It seems that polar solvents such as dioxane or chloroform lead always to a downfield shift of ^{13}C values, which can be understood in the following way. A polar CX bond with X being more electronegative than C becomes somewhat more polar in solution phase due to the electrostatic interactions between solute and solvent. In solution, the C nucleus is somewhat more deshielded depending on the polarity and dielectric constant of the solvent.

For aromatic or, in general, conjugated compounds these effects are difficult to predict, and solvent shifts can be both positive and negative. However, in general, solvent effects are rather small for $\delta(^{13}$C) so that we refrain from discussing them here in more detail and, instead, compare calculated gas phase δ-(^{13}C) values directly with the corresponding experimental values measured in solution.

For HF, UDFT, and SOS-DFPT, mean errors from a comparison of 37 calculated and measured ^{13}C shift values are 6−7 ppm (Table 1), which suggests that neither correlation effects nor paramagnetic effects play an important role for the molecules considered. In our previous comparison,[1] which was exclusively based on measured gas phase values, HF, UDFT, and SOS-DFPT mean errors for ^{13}C shifts were 11.0, 7.7, and 5.8 ppm, respectively, suggesting slight improvements of shift values caused by the use of density functional theory. On the other hand, it is remarkable that similar or even somewhat higher accuracy is obtained with all methods despite the fact that only 7 out of 37 calculated $\delta(^{13}$C) values belong to methyl groups while all other C atoms participate in multiple bonding. This suggests some error cancelation of solvent and calculational effects.

As discussed already in our previous work,[1] the majority of DFT-based ^{13}C chemical shifts are too positive compared to experimental values. We have connected this observation with

TABLE 2: Calculated and Experimental Nitrogen (^{14}N, ^{15}N) Chemical Shifts (δ) in ppm Relative to Gaseous NH$_3$[a]

molecule	sym.	HF-IGLO	UDFT-IGLO	SOS-DFPT-IGLO (Loc2)	expt[c]	solvent	ϵ	estimated gas phase value
1, CH$_3$N$\underline{\text{H}}_2$[b]	C_s	11.7	21.7	21.5	30.3	H$_2$O	78.5	15 ± 3
2, C$_2$H$_4$(CO)$_2$N$\underline{\text{H}}$	C_{2v}	174.4	205.3	204.2	182.9	H$_2$O	78.5	203 ± 5
3, pyrrole	C_{2v}	153.5	168.5	167.2	168.2[d]	CHCl$_3$	4.8	168 ± 3
4, pyridine	C_{2v}	367.2	357.9	347.4	346.3	gas phase	1	346.3
5, pyridine N-oxide	C_{2v}	378.1	336.4	333.2	324.4	cyclohexane	2.0	328 ± 3
6, isoxazole	C_s	455.5	434.0	422.9	403.6	DMSO	46.7	416 ± 3
7, PhNO	C_s	1354.1	1082.3	898.7	936.9	Et$_2$O	4.3	?
8, CH$_3$NO$_2$	C_s	525.7	396.8	387.5	392.4	cyclohexane	2.0	392 ± 3
9, PhNO$_2$	C_{2v}	510.1	389.3	384.2	388.7[e]	CCl$_4$	2.2	389 ± 3
10, Me$_2$N-$\underline{\text{N}}$O	C_s	802.3	571.8	537.2	555.8	CHCl$_3$	4.8	?
10, Me$_2$$\underline{\text{N}}$-NO	C_s	262.0	268.1	256.1	251.2	CHCl$_3$	4.8	251 ± 3
11, H$_2$C$\underline{\text{N}}$N	C_{2v}	583.8	428.3	398.4	414.9	CH$_3$OD	32.6	400 ± 5
11, H$_2$CN$\underline{\text{N}}$	C_{2v}	268.2	314.3	303.1	308.3	CH$_3$OD	32.6	302 ± 3
12, *anti*-Me$\underline{\text{N}}$NOH	C_s	547.3	451.7	420.3	367.1	CH$_3$OD	32.6	?
12, *anti*-MeN$\underline{\text{N}}$OH	C_s	560.1	505.3	476.7	588.1	CH$_3$OD	32.6	?
mean abs. dev.		101.0	30.4	21.2				
mean abs. dev. without **12**		100.5	22.1	11.8				

[a] The nucleus considered is underlined. Calculated with the (11s7p2d/6s2p)[7s6p2d/4s2p] basis of Kutzelnigg and co-workers.[24] BPW91/6-311G(2d,2p) geometries except where noted otherwise. For estimated gas phase values, see text. [b] MP2/TZ2P geometry from ref 3. [c] Experimental shifts from ref 53 except where noted otherwise. [d] Reference 32. [e] Reference 36.

TABLE 3: Calculated and Experimental Oxygen (^{17}O) Chemical Shifts (δ) in ppm Relative to Gaseous H$_2$O[a]

molecule	sym.	HF-IGLO	UDFT-IGLO	SOS-DFPT-IGLO (Loc2)	expt[c]	solvent	ϵ
13, CH$_3$O$\underline{\text{H}}$[b]	C_s	−12.4	5.9	6.3	−0.9[d]	neat liquid	32.6
14, H$_2$O$_2$[b]	C_2	193.0	232.7	219.1	210.1	H$_2$O	78.5
15, CH$_3$CHO[b]	C_s	698.2	700.5	658.3	628.1	neat liquid	21.8
16, Me$_2$CO[b]	C_{2v}	660.7	674.7	639.4	624.0[e]	alkane	~2
17, propanal	C_s	669.4	666.6	627.4	615.6	neat liquid	18.5
18, *trans*-propenal	C_s	664.3	691.0	660.1	615.1	neat liquid	
19, p-C$_6$H$_4$(CO)$_2$	D_{2h}	699.2	801.2	760.8	671.2	toluene	2.4
20, C$_2$H$_4$(C$\underline{\text{O}}$)$_2$O	C_{2v}	448.7	450.3	442.7	412.1	CH$_3$CN	37.5
20, C$_2$H$_4$(CO)$_2$$\underline{\text{O}}$	C_{2v}	325.2	387.4	383.3	337.1	CH$_3$CN	37.5
2, C$_2$H$_4$(C$\underline{\text{O}}$)$_2$NH	C_{2v}	425.2	450.5	442.0	409.6	CH$_3$CN	37.5
21, C$_2$H$_2$(C$\underline{\text{O}}$)$_2$O	C_{2v}	470.8	502.7	491.0	437.1	CH$_3$CN	37.5
21, C$_2$H$_2$(CO)$_2$$\underline{\text{O}}$	C_{2v}	272.6	329.0	325.7	288.1	CH$_3$CN	37.5
22, C$_2$H$_2$(C$\underline{\text{O}}$)$_2$NH	C_{2v}	457.7	516.5	502.2	447.1	CH$_3$CN	37.5
23, furan	C_{2v}	267.6	308.9	304.2	272.1[f]	CH$_2$Cl$_2$	9.1
5, pyridine N-oxide	C_{2v}	363.4	500.2	487.3	385.1	CH$_3$CN	37.5
6, isoxazole	C_s	399.6	430.8	423.1	386.1[g]	neat liquid	
7, PhNO	C_s	2212.4	1926.1	1532.4	656.1	not known	
8, CH$_3$NO$_2$	C_s	746.6	698.8	668.0	641.1	not known	
9, PhNO$_2$	C_{2v}	691.3	638.2	617.1	611.1[h]	CH$_3$CN	37.5
10, Me$_2$N-N$\underline{\text{O}}$	C_s	994.2	787.7	720.4	696.1[i]	neat liquid	
mean abs. dev.		123.5	117.9	78.4			
mean abs. dev. excl. **7**		45.7	57.2	36.4			

[a] The nucleus considered is underlined. Calculated with the (11s7p2d/6s2p)[7s6p2d/4s2p] basis of Kutzelnigg and co-workers.[24] BPW91/6-311G(2d,2p) geometries except where noted otherwise. [b] MP2/TZ2P geometry from ref 3. [c] Experimental shifts from ref 12 except where noted otherwise. [d] Reference 48. [e] References 13, 14. [f] Reference 49. [g] Reference 50. [h] Reference 51. [i] Reference 52.

the basic deficiency of DFT-based methods to underestimate electron clustering in the vicinity of the nucleus, which probably results from the fact that the homogeneous electron gas is used as a starting point to model the electron distribution in a molecule. An underestimation of electron clustering leads to Fock matrix elements and energies of occupied orbitals, which are both too positive. The consequences for diamagnetic and paramagnetic contributions to shieldings (or chemical shifts) are that the former are too small and the latter too large, thus yielding too small (negative) shieldings and too large (positive) chemical shifts. While the latter effect is well-known, the former effect can only be seen if the Coulomb term J is exactly calculated as done in this and in our previous work.[1] In the case of ^{13}C chemical shifts, for which paramagnetic effects play a minor role, the underestimation of diamagnetic contributions can be corrected by changing from CH$_4$ to TMS as a reference. The underestimation of diamagnetic shielding effects is larger for TMS (−11 ppm) than for CH$_4$ (−7 ppm), which leads to error cancelation since for most investigated ^{13}C chemical shifts

errors are in the range −10 to −15 ppm. Accordingly, the calculated mean absolute deviation of SOS-DFPT ^{13}C chemical shifts decreases from 5.8 to 3.8 ppm when using TMS rather than CH$_4$ as a reference (Table 1).

As an alternative to changing the reference, one can introduce a diamagnetic correction term of −5.8 ppm or scale final shift values by a factor of 0.93.[1] Using the first alternative, we obtain the corrected SOS-DFPT(Loc2) values listed in Table 1. They agree reasonably with experimental values, deviating from the latter on the average by just 2.8 ppm. A similar accuracy is obtained when improving UDFT values by a diamagnetic shift correction of −7.7 ppm determined in our previous paper.[1] Again, this confirms that paramagnetic shift contributions play a minor role for the ^{13}C chemical shifts investigated and that both UDFT and SOS-DFPT cover part of the correlation effects that are necessary to achieve a higher accuracy than HF-IGLO.

4.2. Nitrogen Shifts. As shown in Table 4, solvent effects of ^{14}N/^{15}N chemical shifts can be as large as 20−30 ppm, in particular when H-bonding is involved. However, for solvents

TABLE 4: Measured Solvent Effects in ppm for ^{13}C, ^{15}N, and ^{17}O NMR Chemical Shifts[a]

molecule	dipole moment	solvent	ϵ	$\Delta\delta$ (ppm)
		^{13}C Chemical Shifts		
CH$_3$CN	4.0	dioxane	2.2	3.4
CH$_3$CN	4.0	dioxane	2.2	−0.9
CH$_3$CHO	2.69	CDCl$_3$	4.8	4.9
CH$_3$CHO	2.69	CDCl$_3$	4.8	−0.2
(CH$_3$)$_2$CO	2.88	CDCl$_3$	4.8	4.8
(CH$_3$)$_2$CO	2.88	CDCl$_3$	4.8	0.5
		^{15}N Chemical Shifts		
NH$_3$	1.55	Me$_2$O	5.0	10.8
		neat liquid	16.9	19.0
		H$_2$O	78.5	22.5
CH$_3$CN	4.0	cyclohexane	2.0	2.5
		benzene	2.3	−1.4
		Et$_2$O	4.3	−1.4
		DMSO	46.7	−5.7
		CHCl$_3$	4.8	−6.2
		CH$_3$OH	32.6	−11.0
pyridine	2.19	cyclohexane	2.0	−3.1
		benzene	2.3	−6.5
		DMSO	46.7	−8.5
		CHCl$_3$	4.8	−14.1
		CH$_3$OH	32.6	−26.5
		H$_2$O	78.5	−29.7
pyridine *N*-oxide	3.80	cyclohexane	2.0	0 (assumed)
		Et$_2$O	4.3	−2.3
		benzene	2.3	−4.9
		DMSO	46.7	−9.2
		CHCl$_3$	4.8	−10.3
		CH$_3$OH	32.6	−21.1
		H$_2$O	78.5	−30.0
CH$_3$NO$_2$	3.46	cyclohexane	2.0	0 (assumed)
		CCl$_4$	2.2	1.4
		Et$_2$O	4.3	4.6
		CHCl$_3$	4.8	4.7
		benzene	2.3	4.1
		DMSO	46.7	10.5
		CH$_3$OH	32.6	6.5
		H$_2$O	78.5	10.5
PhNO$_2$	4.22	CCl$_4$	2.2	0 (assumed)
		CHCl$_3$	4.8	2.6
		^{17}O Chemical Shifts		
(CH$_3$)$_2$CO	2.88	cyclohexane	2.0	0 (assumed)
		neat liquid	20.7	−19
		H$_2$O	78.5	−65

[a] Solvent shifts from refs 12, 13, 14, 53, 55.

with small dielectric constants (cyclohexane, benzene, CCl$_4$, see Table 4) solvent effects are smaller than 10 ppm. Both upfield and downfield shifts are possible, which makes predictions on the sign of a solvent shift for a particular compound in a specific solvent rather difficult.

Both Table 2 and Figure 1 reveal that SOS-DFPT(Loc2) δ-(^{14}N/^{15}N) values are significantly closer to experimental shifts than the corresponding HF values. The calculated mean deviations from experimental shifts for 12 compounds with 15 shift values are 101 ppm for HF-IGLO, 30 ppm for UDFT-IGLO, and 21 ppm for SOS-DFPT-IGLO (Table 2). Considering a 550 ppm spread of experimental values, calculated mean absolute deviations correspond to 18, 5, and 4% error, respectively. According to Figure 1, in some cases error bars are considerably larger than in other cases, and therefore, we will discuss results in detail in the following.

The experimental shifts of methylamine (**1**) and succinimide (**2**) are both measured in water,[27,30] which means that they could severely be influenced by solvent effects. The change in the nuclear magnetic shift of the nitrogen atom in ammonia when going from gas phase to infinite dilute water solution is +22.5 ppm.[27] This change in δ(^{14}N/^{15}N) can be understood when

considering that H-bonding to N leads to a withdrawal of negative charge from the N atom and, thereby, a deshielding of the N nucleus. If N is not directly involved in H-bonding, as is the case for CH$_3$NO$_2$, the deshielding effect is just 10.5 ppm (Table 4). If solvent shifts of 10 and 20 ppm are taken as lower and upper bounds for the corresponding effect in **1**, then its gas phase chemical shift will be between 20 and 10 ppm. Hence, the SOS-DFPT(Loc2) value of 21.5 ppm is probably a reasonable prediction of the chemical shift of **1** in the gas phase, which is supported by a MP2 value of 15 ppm,[3] taken in this work as a reliable estimate of the gas phase value. For **2**, magnitude and sign of the solvent effect should differ from that in **1** since N in **2** is part of a conjugated system involving the two carbonyl groups. This situation is similar to that of pyridine and pyridine *N*-oxide, for which an upfield shift of 30 ppm has been observed in aqueous solution (Table 4). Assuming that H-bonding also involves the N atoms of these molecules, H-bonding seems to increase the electronegativity of N and, thereby, leads to a clustering of electrons at N, which is supported by the relatively large polarizability of the π-system. Since π-conjugation in **2** is less developed than in pyridine, it is reasonable to assume a diamagnetic shielding effect of about 20 rather than 30 ppm due to the solvent H$_2$O. Accordingly, a gas phase value of 203 ± 5 ppm can be expected, which is in good agreement with the SOS-DFPT(Loc2) value of 204 ppm, but differs by 30 ppm from the HF value of 174 ppm (Table 2).

Among the four heteroaromatic molecules pyrrole (**3**), pyridine (**4**), pyridine *N*-oxide (**5**), and isoxazole (**6**), the experimental shift values of **3**, **4**, and **5** are expected to be free or almost free of solvent effects since they were measured either in the gas phase (**4**) or in weakly polar solvents such as cyclohexane (**5**) or CDCl$_3$ (**3**).[31,32] The shift value of **6** was measured in dimethyl sulfoxide (DMSO),[33] which due to its high dielectric constant of 46.7[34] and complexation ability can lead to solvent shifts of −8 to −12 ppm (Table 4). The SOS-DFPT(Loc2) shift values for **3**, **4**, and **5** agree with the corresponding experimental values within 1, 1, and 9 ppm (Table 2), while in the case of **6** calculated and experimental shifts differ by 19 ppm. Considering the solvent effects for cyclohexane (−3 ppm) and DMSO in the cases of **4** and **5** (Table 4), gas phase values of 328 ± 3 and 416 ± 3 ppm can be expected for **5** and **6**, respectively,[31] which are just 5−6 ppm smaller than the corresponding SOS-DFPT(Loc2) values.

The experimental ^{14}N/^{15}N shifts of nitromethane (**8**) and nitrobenzene (**9**) have been measured in cyclohexane[35] and tetrachloromethane[36] and, accordingly, should be close to the corresponding gas phase values (compare with Table 4). This is in line with the fact that the SOS-DFPT(Loc2) values for **8** and **9** are both within 5 ppm of the experimental values. Deviations for the nitroso nitrogen in nitrosobenzene (**7**) and dimethylnitrosamine (**10**) are significantly larger (38 and 19 ppm, Table 2), but still small (7−8%) considering calculated correlation effects of 455 and 265 ppm in **7** and **10**. It is not possible in these cases to make any predictions with regard to solvent effects; however, it is likely that both solvent effects and not covered correlation effects are responsible for the deviations between SOS-DFPT and experimental values. Also, difficulties in determining the exact equilibrium geometry of a nitroso compound might play a role. The HF and SOS-DFPT shifts for the amine nitrogen of **10** differ by just 11 and 5 ppm from the experimental value (Table 2), suggesting that electron correlation plays a smaller role in this case.

The experimental shifts of the diazo compound H$_2$CNN (**11**) and the diazotate *anti*-MeNNOH (**12**) were measured in deuterated methanol,[37] which interacts with **11** and **12** via H-

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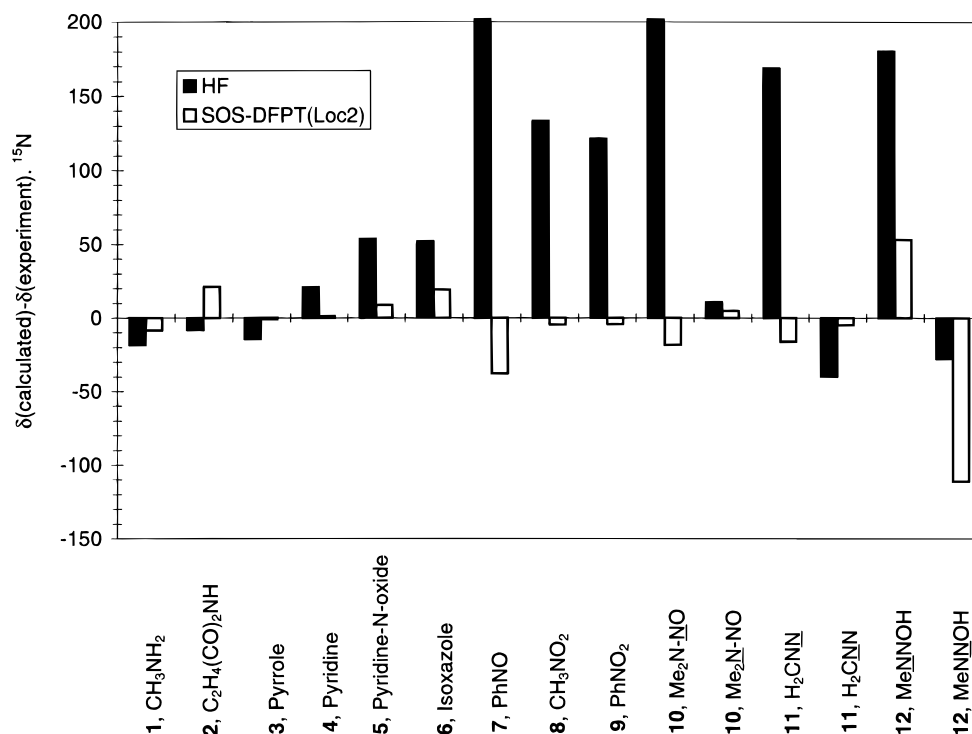
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Figure 1. Deviations (in ppm) of calculated ^{15}N chemical shifts from experimental values as obtained by HF (black bars) and SOS-DFPT(Loc2) (white bars).

bonding, thus leading to considerable solvent effects in chemical shifts. Since the terminal N atom of **11** should primarily be involved in H-bonding, we tentatively assign a solvent shift of maximally 15 ppm (similar to that predicted for **1** on the basis of MP2 calculations), thus leading to a gas phase value of 400 ± 5 ppm. The central N atom of **11** resembles more the N atom in CH_3NO_2, and therefore, it is reasonable to assume a deshielding effect of 6.5 ppm (Table 4), in line with a gas phase value of 302 ± 3 ppm. Deviations of SOS-DFPT(Loc2) shifts from estimated gas phase values are just 2 ppm for both N atoms in **11**. It is noteworthy in this connection that Gauss and Stanton[38] predict for **11** gas phase values of 408.3 and 297.5 ppm, respectively, on the basis of CCSD(T)/PZ(3df) calculations, which are close to our estimates. For **12**, reasonable predictions of solvent effects cannot be made since H-bonding may lead to relatively large changes in its electronic structure. On the other hand, it cannot be excluded that the calculated differences between SOS-DFPT and experimental shifts (53, N–Me; 111 ppm, N–OH) are partially caused by deficiencies of the SOS-DFPT approach with regard to covering important correlation and/or paramagnetic effects.

Excluding **12** from the comparison, the mean absolute deviation of SOS-DFPT(Loc2) shift values is only 11.8 ppm. In view of correlation effects up to 450 ppm (**7**) and uncertainties in experimental shift values because of unknown solvent effects, the good agreement between theory and experiment suggests that, in the case of ^{14}N/^{15}N chemical shifts, SOS-DFPT leads to a major improvement compared to HF-based chemical shift methods and can replace much more costly correlation-corrected methods. This conclusion is fully confirmed when considering just those molecules for which gas phase values can be estimated. A mean deviation of just 3 ppm is obtained, which should be about the magnitude of uncertainties in estimated gas phase values. An ab initio calculation of ^{14}N/^{15}N chemical shifts with the same accuracy would require correlated ab initio methods of the multiconfigurational SCF (MCSCF) or coupled-cluster (CC) type that are far too costly to be applied for the larger molecules considered in this work (some of the smaller

molecules such as **11** have been investigated by CCSD or even CCSD(T)[7,38].

4.3. Oxygen Shifts. Agreement between calculated and experimental [17]O chemical shifts is much lower than in the case of the ^{14}N/^{15}N shifts, as is reflected by mean absolute deviations of 123 (HF-IGLO), 118 (UDFT-IGLO), and 78 ppm (SOS-DFPT, Table 3), respectively. Clearly, SOS-DFPT(Loc2) values are in better agreement with experiment by about 30−40% than is the case for the corresponding HF values (Figure 2). However, even if one considers the fact that measured $\delta(^{17}O)$ values cover a region of about 700 ppm, one has to realize that agreement between SOS-DFPT and experiment is poor compared to results obtained for $\delta(^{13}C)$ and $\delta(^{14}N/^{15}N)$. Possible reasons for these discrepancies have to be discussed in the following.

The chemical shift of the two singly bonded oxygen atoms in methanol (**13**) and hydrogen peroxide (**14**) should be little affected by correlation effects. Thus, both HF and SOS-DFPT-(Loc2) give reasonably accurate predictions for these chemical shifts (Table 3, Figure 2), where it is not clear how solvent effects will change experimental shifts.

For the carbonyl oxygens of acetaldehyde (**15**), acetone (**16**), propanal (**17**), and *trans*-propenal (**18**), SOS-DFPT(Loc2) shift values agree clearly better with experimental values than the corresponding HF or UDFT values, indicating that both correlation and paramagnetic effects play a role in these cases. The measured [17]O shift value of acetone (624.0 ppm) should be close to the true gas phase value since it has been determined by dilution studies in three different alkane solvents and subsequently extrapolated to infinite dilution.[13,14] Hence, it is likely that the SOS-DFPT value of 639 ppm (Table 3) is 10−15 ppm too high. The [17]O shifts of **15**, **17**, and **18** were measured in neat liquids, which could imply significant solvent effects. However, the MP2 value for **15** (636.5 ppm[3]) is just 8.4 ppm higher than the experimental value of 628.1 ppm measured in neat liquid. Considering that MP2 overestimates correlation effects, the SOS-DFPT shift of 658 ppm might be actually closer to the gas phase value than the MP2 shift, probably exceeding
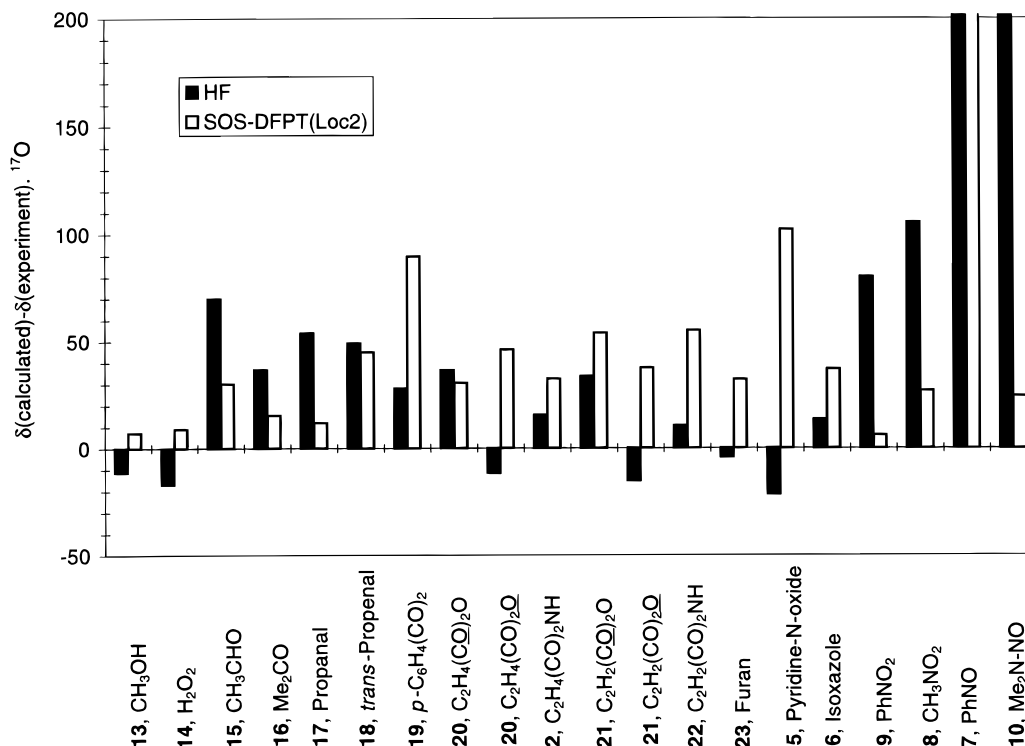
Figure 2. Deviations (in ppm) of calculated ^{17}O chemical shifts from experimental values as obtained by HF (black bars) and SOS-DFPT(Loc2) (white bars).

it by not more than 10 ppm. Since solvent effects should be even lower in the case of **17**, the measured shift of 616 ppm should be within 8 ppm of the gas phase value, and accordingly, the SOS-DFPT value of 627 ppm should be rather close to the latter. In any case, SOS-DFPT(Loc2) leads to an improvement of 20−40 ppm for the ^{17}O values of **15**, **16**, and **17** in comparison to the corresponding HF values (Table 3). This is not true for **18**, for which the SOS-DFPT(Loc2) value is only 4 ppm lower than the HF value, but 45 ppm larger than the experimental value of 615 ppm. There is no reason to suspect either that solvent effects are substantially larger or that correlation effects are substantially lower for **18** than for **17**. Therefore, the computed deviation from experiment seems to represent the actual deviation from the gas phase value (45 ppm) and, thereby, a shortcoming of the DFPT approach.

For *p*-benzoquinone (**19**), succinic anhydride (**20**), maleic anhydride (**21**), maleimide (**22**), furan (**23**), pyridine *N*-oxide (**5**), and isoxazole (**6**), the SOS-DFPT(Loc2) method leads on the average to a deviation of 52 ppm (Table 3), while HF values differ by just 19 ppm, where calculated values are mostly too large. Shift measurements for **20−23** as well as **5** were carried out in acetonitrile, which is a very polar solvent ($\epsilon = 37.5$). Molecule **19** was measured in toluene, **6** in neat liquid, and **23** in CH_2Cl_2, which is still too polar ($\epsilon = 9$) to exclude significant solvent effects. Likewise, although the aromatic solvents have low dielectric constants, they can interact with aromatic solutes by specific complexation. In all these cases, solvation will increase charge separation in the molecule, which means that the O atoms become more negatively charged. As a consequence, ^{17}O values in solution are more upfield than the corresponding gas phase values. However, it is unlikely that solvent effects are of a magnitude that they are responsible for the large deviations of SOS-DFPT values from experiment found for **19−23**, **5**, and **6**. Since the same basis sets and geometries have been used for the HF and SOS-DFPT calculations, the relatively poor performance of the SOS-DFPT(Loc2) method for conjugated compounds seems to indicate some intrinsic error

SCHEME 2
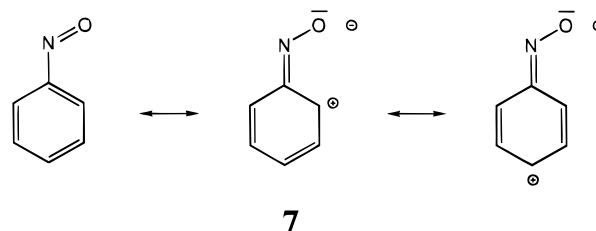
of the SOS-DFPT method itself that does not show up for C and N shifts or O shifts of saturated molecules.

For the nitro and nitroso compounds **7−10** (Table 3), reasonable SOS-DFPT(Loc2) shifts are obtained (deviations 6−27 ppm, Table 3) with the exception of molecule **7** (deviation: 876 ppm). The latter molecule represents a typical multireference problem, and therefore, it is difficult to get a reasonable ^{17}O chemical shift of **7** with a single-determinant approach despite a correlation correction of almost 700 ppm obtained at the SOS-DFPT level of theory. It is interesting to note that the inherent correlation corrections of SOS-DFPT are sufficient in the case of the N shift of **7** (deviation: 38 ppm, Table 2). Probably, this has to do with the fact that nondynamic correlation effects influence the charge distribution at O stronger than at N, as may be illustrated by the dominant resonance structures of **7** (Scheme 2).

If one excludes molecule **7** from the comparison, the mean absolute deviation between SOS-DFPT and experimental shift values decreases from 78 ppm to 36 ppm. The corresponding HF and UDFT errors are 46 and 57 ppm (Table 3), which is considerably higher than the 20 ppm deviation that one gets at the HF-IGLO level for O-containing molecules that do not possess a conjugated π-system.[39] If just these molecules are considered, SOS-DFPT errors are in the range 10−15 ppm, suggesting a 30−40% improvement with regard to HF values. Obviously, the intentional choice of a considerable number of critical cases leads to the relatively large mean error of 36 ppm.
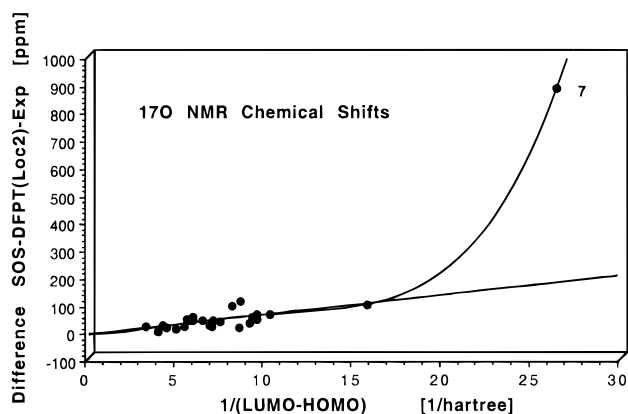
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Figure 3. Deviations (in ppm) of SOS-DFPT(Loc2) ^{17}O chemical shifts from experimental values given as a function of $1/[\epsilon(LUMO) - \epsilon(HOMO)]$ (see text).

5. Discussion and Conclusions

Results presented in this work clearly confirm the tentative conclusions of our previous report.[1] The SOS-DFPT(Loc2) method can be used to predict carbon and nitrogen chemical shifts with an accuracy that otherwise would be obtainable only with the help of highly correlated ab initio methods. This is especially true for systems with considerable correlation effects such as nitro and diazo compounds for which multiconfigurational SCF or coupled-cluster methods would be needed to achieve the same level of accuracy. For most of the systems studied, errors in the calculated nitrogen shifts are smaller than typical solvent effects for the same atom. SOS-DFPT(Loc2) provides an improvement of calculated shift values by 70−90% compared to the corresponding HF-IGLO values.

Additional calibration of diamagnetic and/or paramagnetic contributions in the case of the N chemical shifts as done in our previous work[1] is not advisable since uncertainties in experimental values due to solvent effects do not make it possible to achieve an accuracy that is higher than 3 ppm. For both ^{13}C and $^{14}N/^{15}N$ chemical shifts this accuracy has been achieved by SOS-DFPT(Loc2) calculations, which provides a sufficient basis for discussing, for example, solvent effects in the case of $^{14}N/^{15}N$ chemical shifts.

Two caveats, however, are necessary concerning the calculation of (a) typical multireference systems and (b) ^{17}O chemical shifts. DFT can cover only part of the multireference effects and, therefore, will fail if the latter become too large. A typical example is **7**, for which errors in calculated chemical shifts extensively exceed those found for other molecules. In Figure 3, deviations Δ between SOS-DFPT and experimental ^{17}O chemical shift values are plotted against the energy gap between HOMO and LUMO. As far as O atoms within a conjugated π-system are concerned, there is a linear relationship of Δ values to $1/(\epsilon(LUMO) - \epsilon(HOMO))$, which suggests that in these cases there is still a considerable error in paramagnetic shielding contributions despite the Loc correction of SOS-DFPT. The other Δ values scatter strongly around this relationship, which is not surprising in view of possible solvent effects of 10−30 ppm. Figure 3 also demonstrates the fact that **7** represents an exception since there is almost a exponential dependence (indicated in Figure 3) on $1/(\epsilon(LUMO) - \epsilon(HOMO))$ in this case. This confirms that the correct treatment of correlation effects more than that of paramagnetic effects is the problem when calculating the $\delta(^{17}O)$ value of **7**.

A similar relationship between deviations Δ and $1/(\epsilon(LUMO) - \epsilon(HOMO))$ can be found for UDFT ^{17}O NMR chemical shifts. It underlines the necessity of introducing appropriate orbital

energy corrections when calculating paramagnetic contributions to chemical shifts. Although these contributions depend on the sum of all excitation energies expressed by appropriate orbital energy differences, the strongest impact on the paramagnetic shielding term will result from the lowest excitation energy represented by the difference $\epsilon(LUMO) - \epsilon(HOMO)$. In the case of conjugated π-systems, this difference will be relatively small and rather sensitive to errors in the energy of the HOMO. In addition, there is more than just one excitation energy with a relatively small value so that error progression in the calculation of the paramagnetic term increases more than for a saturated molecule. As a consequence, paramagnetic contributions to the ^{17}O chemical shifts are still overestimated by SOS-DFPT even when using the somewhat larger Loc2 rather than the Loc1 correction factor. Figure 3 clearly reveals that Loc2 is not sufficient in these cases and that a recalibration of paramagnetic shift contributions is needed for ^{17}O chemical shift calculations with SOS-DFPT.

This conclusion is confirmed by the fact that use of the linear relationship shown in Figure 3 leads to a general improvement of ^{17}O chemical shifts so that the mean absolute deviation between SOS-DFPT and experimental shifts decreases from 36.4 to 13.6 ppm (excluding **7**), which indicates that part of the solvent effects is also absorbed by these corrections. A similar improvement can be obtained for UDFT chemical shifts if deviations are compared with the corresponding difference $\epsilon(LUMO) - \epsilon(HOMO)$. One finds a stronger coupling between these quantities, which simply reflects the fact that the Loc corrections also have to be covered in the case of UDFT chemical shifts.

A recalibration of the Loc correction in the case of ^{17}O chemical shifts has to cope with three different problems.

(1) Oxygen nuclear magnetic shieldings are more sensitive to the correct calculation of both diamagnetic and paramagnetic shielding contributions. (2) An underestimation of diamagnetic shielding terms typical of DFT[1] should be more important for oxygen than for nitrogen or carbon. (3) ^{17}O chemical shifts are more sensitive to solvent effects than $^{14}N/^{15}N$ or ^{13}C shifts; however, exact solvent shifts are hardly known in this case.

In general, correlation corrections become more important with an increasing number of electrons, increased clustering of electrons in limited space, an increasing number of electron lone pairs, and a larger anisotropy of the charge distribution, where, of course, some of these factors depend on each other.[40] Clearly, electron correlation effects should be more important for oxygen than for nitrogen. Oxygen is more electronegative than nitrogen, and therefore, its orbitals are more contracted, which means that its electrons are forced into smaller space, which makes electron correlation more complicated. For example, it is well-known that three-electron correlation effects become more important with increasing electronegativity of an atom.[40] In the same way, pair correlation for an electron lone pair is more pronounced than for a bonding electron pair because the available space for a lone pair is much smaller than for a bonding pair. Oxygen possesses one electron lone pair more than nitrogen, and as a consequence, even pair correlation is larger for O than for N.

For a given basis set and method, the description of an O-containing molecule is always more difficult than for a N-containing molecule of similar electronic structure. Apart from this, one has to consider specific errors in the case of conjugated systems. HF theory exaggerates the polarity of the CO bond with the result that partial charges at O are too large, thus leading to large diamagnetic shieldings. Simple correlation methods such as MP2 often underestimate the polar character of a polar bond and, therefore, also underestimate diamagnetic

TABLE 5: Comparison of Calculated and Experimental Dipole Moments (in Debyes)[a]

molecule	sym.	DFT	expt[c]
1, CH_3NH_2[b]	C_s	1.34	1.31
2, $C_2H_4(CO)_2NH$	C_{2v}	2.00	
3, pyrrole	C_{2v}	1.88	1.84
4, pyridine	C_{2v}	2.24	2.19
5, pyridine *N*-oxide	C_{2v}	3.80	
6, isoxazole	C_s	2.92	
7, PhNO	C_s	3.94	
8, CH_3NO_2	C_s	3.43	3.46
9, $PhNO_2$	C_{2v}	4.54	4.22
10, Me_2N-NO	C_s	4.05	
11, H_2CNN	C_{2v}	1.71	1.50
12, *anti*-MeNNOH	C_s	1.72	
13, CH_3OH[b]	C_s	1.63	1.70
14, H_2O_2[b]	C_2	1.75	2.20
15, CH_3CHO[b]	C_s	2.78	2.69
16, Me_2CO[b]	C_{2v}	2.98	2.88
17, propanal	C_s	2.68	2.52
18, *trans*-propenal	C_s	3.29	3.12
19, p-$C_6H_4(CO)_2$	D_{2h}	0	0
20, $C_2H_4(CO)_2O$	C_{2v}	4.41	
21, $C_2H_2(CO)_2O$	C_{2v}	4.06	
22, $C_2H_2(CO)_2NH$	C_{2v}	1.52	
23, furan	C_{2v}	0.61	0.66

[a] BPW91/6-311G(2d,2p) geometries except where noted otherwise. [b] MP2/TZ2P geometries from ref 3. [c] From ref 34.

shielding of electronegative atoms. These effects should become particularly critical in those cases in which the CO bond is part of a conjugated system. Then, high-level correlation-corrected ab initio methods are needed to correctly describe the charge distribution at O.

In the present case, there is no indication that SOS-DFPT leads to a seriously inaccurate charge distribution at O. For example, the calculated dipole moments agree rather well with known experimental values (Table 5). Therefore, errors in diamagnetic shielding contributions for ^{17}O should be, apart from a systematic factor or diamagnetic shielding correction similar to that found for ^{13}C chemical shifts, similar or even smaller than those obtained at the MP2 level. There is no reason to believe that the relatively large SOS-DFPT deviations of ^{17}O values for conjugated systems result from errors in the diamagnetic part of magnetic shieldings.

This leaves one with the most important problem in ^{17}O chemical shift calculations, namely, the reliable determination of solvent shifts. One cannot expect that in the near future accurate solvent shifts will be measured for a large variety of molecules. We think that this data material has to be provided by theory, for example by combining SOS-DFPT with appropriate solvent models. One will have to consider both changes in ^{17}O NMR chemical shifts due to changes in geometry caused by the solvent and the direct influence of the solvent on chemical shifts as has been described by Cremer and co-workers.[11,41,42] Work is in progress to provide a first account of calculated solvent effects.

In conclusion, the following results of this work should be stressed.

(1) ^{13}C chemical shifts are calculated with the SOS-DFPT-(Loc2) method with an accuracy of 3 ppm provided (a) a diamagnetic correction term of -5.8 ppm is added to compensate for an overestimation of diamagnetic deshielding typical of DFT and (b) solvent effects are not larger than a few ppm.

(2) In those cases in which reasonable gas phase $\delta(^{14}N/^{15}N)$ values can be estimated, SOS-DFPT(Loc2) leads to shift values that differ by just 3 ppm from experimental values. This observation provides further support to the recent suggestion that the Loc2 correction happens to cover diamagnetic and

paramagnetic deficiencies of a UDFT calculation of $^{14}N/^{15}N$ chemical shifts.

(3) SOS-DFPT $\delta(^{17}O)$ values differ from measured solution phase values on the average by 36 ppm. Agreement can be improved to 13 ppm by correcting shift values with the help of calculated HOMO−LUMO energy differences. This indicates that the Loc correction has to be readjusted for ^{17}O chemical shifts. In connection with the recalibration of the Loc correction, a systematic investigation of solvents effects for ^{17}O chemical shifts will be necessary.

(4) SOS-DFPT fails to lead to reasonable shift values in the case of molecules with strong multireference character such as nitrosobenzene (**7**). Otherwise, SOS-DFPT seems to cover a large part of electron correlation effects, thus leading to an accuracy of calculated chemical shifts that is close to GIAO-MP2 chemical shift values.

Supporting Information Available: Optimized BPW91/6-311G(2d,2f) geometries for molecules **1**−**23** in Cartesian coordinates (8 pages). Ordering information is given on any current masthead page.

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JP961316P