Sum-over-states density functional perturbation theory: Prediction of reliable ^{13}C, ^{15}N, and ^{17}O nuclear magnetic resonance chemical shifts

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Sum-over-states density functional perturbation theory (SOS-DFPT) has been used to calculate ^{13}C, ^{15}N, and ^{17}O NMR chemical shifts of 20 molecules, for which accurate experimental gas-phase values are available. Compared to Hartree–Fock (HF), SOS-DFPT leads to improved chemical shift values and approaches the degree of accuracy obtained with second order Møller–Plesset perturbation theory (MP2). This is particularly true in the case of ^{15}N chemical shifts where SOS-DFPT performs even better than MP2. Additional improvements of SOS-DFPT chemical shifts can be obtained by empirically correcting diamagnetic and paramagnetic contributions to compensate for deficiencies which are typical of DFT. © *1996 American Institute of Physics.* [S0021-9606(96)01544-9]

I. INTRODUCTION

The calculation of chemical shifts is one of the most successful contributions of *ab initio* quantum chemistry to problems of interest within experimental chemistry. The development of practically useful methods for chemical shift calculations based on Hartree–Fock (HF) theory[1–4] as well as on the random phase approximation (RPA)[5] has made it possible to obtain accurate theoretical predictions of especially ^{13}C chemical shifts in molecules large enough to be of interest for experimental chemists. The dominant role of NMR spectroscopy in the investigation of newly synthesized molecules together with the fact that the HF-based methods for calculating chemical shifts often give sufficient accuracy has made chemical shift calculations an important and often used tool to verify and/or interpret the results of the analysis of measured NMR spectra. Chemical shift calculations are used to predict the outcome of NMR measurements and to test whether the result of such a measurement can resolve the question at hand.

However, there are many molecules for which HF-based calculations of NMR chemical shifts are unreliable due to electron correlation effects. Such molecules are for example organic compounds with multiple bonding involving heteroatoms such as nitrogen or oxygen, hypervalent compounds, transition metal compounds, etc. Today there are methods based on traditional *ab initio* methodology such as Møller–Plesset (MP) perturbation theory,[6–8] coupled-cluster (CC) theory,[9,10] and multiconfigurational SCF (MCSCF) theory[11,12] as well as on the polarization propagator approximation (PPA),[13] which can provide predictions of chemical shifts at virtually any desired accuracy for systems with large correlation effects. However, even the cheapest of these methods represents a large increase in computational cost compared to the HF methods. Thus these correlated methods are limited with regard to their application to small molecules. At the same time there is a considerable need for calculating NMR chemical shifts of biochemical compounds

and transition metal compounds, which require a method that covers electron correlation effects. Even in those cases, for which HF accuracy of NMR chemical shift calculations is sufficient, a method that is substantially less costly than HF would be beneficial.

Although density functional theory (DFT) has proven to be both cost effective and to cover a substantial amount of correlation effects, it has not been as successful with regard to the calculation of chemical shifts. Early attempts using the uncoupled density functional theory (UDFT) approach in combination with the individual gauge for localized orbitals (IGLO)[14] and the gauge including atomic orbital (GIAO)[15] methods did not provide the performance one hoped to achieve with a DFT method.

Vignale *et al.*[16–19] pointed out that the theoretical foundations of DFT were not valid in the presence of a magnetic field, and they formulated a generalization of DFT termed current-density functional theory (CDFT), which is also valid in a magnetic field. It was believed that the inaccuracy of the UDFT scheme was due to the nonvalidity of ordinary DFT and that a formulation in terms of the theoretically correct CDFT would provide a better accuracy. Recent investigations by Lee, Handy, and Colwell,[20] however, indicate that the missing current-density dependence in standard DFT is not of major importance. Lee and co-workers argue that the main problem is the known deficiency of currently used density functionals to lead to erroneous orbital energies. They also point out that the critical dependence of DFT-based NMR chemical shifts on reasonable orbital energies explains the success of the sum-over-states density functional perturbation theory (SOS-DFPT) method which was introduced by Malkin *et al.*[21] in form of a mixture between DFT and a sum-over-states theory for nuclear magnetic shielding. Since the SOS-DFPT method corrects DFT orbital energies, it leads to a substantial improvement relative to UDFT in a number of studies of various systems with special emphasis on transition metal compounds.[21–26]

One has to realize that DFT is essentially a semiempir-

ical method, results of which can depend on the approximations and adjustments made within the method. In this respect, NMR chemical shifts calculated with SOS-DFPT will depend on the exchange-correlation functional used, corrections of DFT orbital energies, the method of evaluating the Coulomb term J, integration techniques applied, etc. For example, we have found in this work that the way of calculating Coulomb interactions between electrons can influence both diamagnetic and paramagnetic contributions to NMR chemical shifts. Modern DFT programs[27,28] approximate J by expanding the molecular electron density $\rho(\mathbf{r})$ in terms of atom-centered auxiliary basis sets $\alpha(\mathbf{r})$ according to

$$\rho(\mathbf{r}) \approx \sum_{\alpha} c_{\alpha} \alpha(\mathbf{r}) = \widetilde{\rho}(\mathbf{r}). \tag{1}$$

Since

$$J = \frac{1}{2} \int \rho(\mathbf{r}_1) \frac{1}{r_{12}} \rho(\mathbf{r}_2) d\tau = \frac{1}{2} \langle \rho | \rho \rangle, \tag{2}$$

the costly calculation of two-electron integrals can be avoided by setting

$$\widetilde{J} = \tfrac{1}{2} \langle \widetilde{\rho} | \widetilde{\rho} \rangle, \tag{3}$$

where the coefficients c_{α} are determined by minimizing the integral

$$\langle \rho - \widetilde{\rho} | \rho - \widetilde{\rho} \rangle. \tag{4}$$

In this way, one guarantees that

$$J \geqslant \widetilde{J}, \tag{5}$$

where the difference between exact Coulomb term J and $\widetilde{J}$ depends on both the primary and the auxiliary basis sets employed. All previous SOS-DFPT calculations have been carried out with the program system DeMon of Salahub and co-workers,[29,30] which is based on the use of auxiliary basis sets for calculating J. This may considerably affect the calculation of NMR chemical shifts so that it becomes difficult to separate between orbital energy, correlation (density functional), and auxiliary basis set dependent changes in calculated NMR chemical shifts. Therefore, we will refrain from using approximation (3) in this work and, instead, evaluate the Coulomb term J exactly. This will lead to more costly calculations on the one side, however, on the other side we will obtain a basis for the analysis of SOS-DFPT NMR chemical shifts and the question how orbital energy corrections and correlation corrections can most effectively be combined in this method.

The advantage of using correlation corrected methods for calculating NMR chemical shifts becomes already obvious when investigating ^{13}C NMR chemical shifts although correlation effects on chemical shifts are moderate in these cases. However, much stronger correlation effects are found when calculating ^{15}N and ^{17}O NMR chemical shifts.[7] Despite the fact that ^{15}N and ^{17}O NMR spectroscopy is not a popular field of current experimental research, there are a number of reasons that make the accurate prediction of ^{15}N, and ^{17}O chemical shifts highly desirable. For example, structural el-

ements with unsaturated NC, NO, NN, etc., linkages appear commonly in organic and biochemically interesting compounds. The chemical shifts of especially ^{15}N and ^{17}O are sensitive to their chemical environment making combined theoretical and experimental investigations of them a powerful tool for predicting structure and even conformation. Indeed, the possibility of making accurate theoretical predictions of ^{15}N and ^{17}O chemical shifts would certainly help to make ^{15}N and ^{17}O NMR spectroscopy more popular than it is today. Another area of interest in ^{15}N and ^{17}O NMR spectroscopy is the study of solvation phenomena since both ^{15}N and especially ^{17}O chemical shifts are sensitive to solvation effects. Therefore, a combination of measured and calculated ^{15}N and ^{17}O chemical shifts should lead to useful insights into the mechanism of solvation.

In this paper, we present the results of a systematic SOS-DFPT investigation of the ^{13}C, ^{15}N, and ^{17}O NMR chemical shifts of 20 molecules. Only systems, for which accurate experimental gas-phase chemical shifts are available, are considered. Extensive comparisons are made with HF-, MP2-, and UDFT-based calculations of NMR chemical shifts. In particular, we will investigate in which way DFT inherent correlation effects lead to an improvement of calculated ^{13}C, ^{15}N, and ^{17}O NMR chemical shifts. For this purpose, we will separate correlation effects from those effects that are due to approximations of the Coulomb part or an improved representation of orbital energies within DFT theory.

II. THEORY

Malkin and co-workers have given an explicit description of the UDFT-IGLO method.[14] A detailed derivation of the HF-IGLO equations can be found in a review by Kutzelnigg[31] and in the original papers by Kutzelnigg[1] and by Schindler and Kutzelnigg.[2] The UDFT-IGLO equations are easily obtained by replacing the exchange operator $\hat{K}$ by the exchange-correlation potential v_{xc} of DFT and deleting the exchange commutator terms, which arise due to the non-local nature of the exchange operator and which complicate HF-IGLO theory. Van Wüllen[32] has discussed the IGLO method on the basis of the current density functional theory of Vignale and Rasolt.[16–19] From this theory the UDFT-IGLO method follows as a special case by removing the assumption that the exchange-correlation energy functional depends on the probability current density.

For a closed shell molecule, the UDFT-IGLO expression for the nuclear magnetic shielding tensor is

$$\boldsymbol{\sigma}_A = 2 \sum_i \langle \phi_i^{(0)} | \widetilde{h}_{i,A}^{(\boldsymbol{\mu},\mathbf{B})} | \phi_i^{(0)} \rangle - 4 \sum_i \langle \phi_i^{(0)} | \widetilde{h}_{i,A}^{(\boldsymbol{\mu})} | \widetilde{\phi}_i^{(\mathbf{B})} \rangle, \tag{6}$$

where the ϕ_i:s are doubly occupied Kohn–Sham orbitals localized according to the criterion of Foster and Boys[33] and the index A refers to the nucleus in question. The one-electron operators are defined by

$$^{\alpha,\beta}\widetilde{h}_{i,A}^{(\boldsymbol{\mu},\mathbf{B})}=\frac{\partial^2}{\partial\mu_\alpha\partial B_\beta}\widetilde{h}_{i,A}$$

$$=\frac{e^2}{2c^2}\frac{\delta_{\alpha\beta}(\mathbf{r}-\mathbf{R}_i)\cdot(\mathbf{r}-\mathbf{R}_A)-(\mathbf{r}-\mathbf{R}_i)_\alpha(\mathbf{r}-\mathbf{R}_A)_\beta}{|\mathbf{r}-\mathbf{R}_A|^3},$$

(7)

and

$$\widetilde{h}_{i,A}^{(\boldsymbol{\mu})}=\frac{1}{i}\frac{\partial}{\partial\boldsymbol{\mu}}\widetilde{h}_{i,A}=-\frac{e}{c}\frac{(\mathbf{r}-\mathbf{R}_A)\times\boldsymbol{\nabla}_i}{|\mathbf{r}-\mathbf{R}_A|^3}.$$

(8)

The first-order occupied Kohn–Sham orbitals $\{\widetilde{\phi}_i^{(\mathbf{B})}\}$ are expanded in terms of the zero-order orbitals according to

$$\widetilde{\phi}_i^{(\mathbf{B})}=\sum_j\mathbf{U}_{ji}\phi_j^{(0)}+\sum_b\mathbf{U}_{bi}\phi_b^{(0)}.$$

(9)

The occupied–occupied part of the matrix $\mathbf{U}$ represents the projection of the first-order orbitals onto the zero-order occupied orbitals and is not uniquely defined. It is chosen as

$$\mathbf{U}_{ji}=-\frac{e}{2c}\langle\phi_j^{(0)}|\Lambda_j^{(\mathbf{B})}-\Lambda_i^{(\mathbf{B})}|\phi_i^{(0)}\rangle,$$

(10)

where

$$\Lambda_j^{(\mathbf{B})}=\tfrac{1}{2}(\mathbf{R}_j\times\mathbf{r}),$$

(11)

which is compatible with the orthonormality restriction of the Kohn–Sham orbitals. If one defines

$$\mathbf{Y}_{ai}=\langle\phi_a^{(0)}|\widetilde{h}_i^{(\mathbf{B})}|\phi_i^{(0)}\rangle-\frac{e}{c}\sum_j\ (\langle\phi_a^{(0)}|\Lambda_i^{(\mathbf{B})}-\Lambda_j^{(\mathbf{B})}|\phi_j^{(0)}\rangle$$

$$\times\langle\phi_j^{(0)}|\hat{f}_i^{(0)}|\phi_i^{(0)}\rangle),$$

(12)

where the virtual orbitals $\{\phi_a^{(0)}\}$ are the normal canonical ones and the one-electron operator $\widetilde{h}_i^{(\mathbf{B})}$ is

$$\widetilde{h}_i^{(\mathbf{B})}=\frac{1}{i}\frac{\partial}{\partial\mathbf{B}}\widetilde{h}_{i,A}=-\frac{e}{2c}(\mathbf{r}-\mathbf{R}_i)\times\boldsymbol{\nabla}_i,$$

(13)

then the virtual-occupied part of the matrix $\mathbf{U}$ will be given by

$$\mathbf{U}_{ai}=\sum_k\left(\frac{\Sigma_j\mathbf{Y}_{aj}c_{kj}}{\epsilon_k-\epsilon_a}\right)c_{ki},$$

(14)

where the matrix c is the transformation matrix from canonical to localized orbitals.

In the SOS-DFPT theory of Malkin and co-workers,[21] nuclear magnetic shielding is expressed by a sum-over-states formula in terms of the exact ground and excited state wave functions. In this formulation, the wave function in a magnetic field is expanded according to

$$\Psi_0(\mathbf{B})=\Psi_0^{(0)}+i\mathbf{B}\sum_{K\neq0}\mathbf{C}_K\Psi_K^{(0)}+\cdots,$$

(15)

where the coefficients are determined by

$$\mathbf{C}_K(\mathbf{B})=\frac{\langle\Psi_0^{(0)}|H^{(\mathbf{B})}(\mathbf{B})|\Psi_K^{(0)}\rangle}{E_0^{(0)}-E_K^{(0)}}.$$

(16)

The nuclear magnetic shielding is given by

$$\boldsymbol{\sigma}=\langle\Psi_0^{(0)}|H^{(\mu,\mathbf{B})}|\Psi_0^{(0)}\rangle-2\sum_{K\neq0}\mathbf{C}_K\langle\Psi_0^{(0)}|H^{(\mu)}|\Psi_K^{(0)}\rangle.$$

(17)

Malkin and co-workers proceed by approximating the ground state wave function $\Psi_0^{(0)}$ by the single-determinant wave function Φ of the Kohn–Sham reference state and the set of excited state wave functions by single-replacement determinants Φ_i^a formed from $\Psi_0^{(0)}$. The excitation energy $E_0^{(0)}-E_K^{(0)}$ is approximated by the orbital energy difference $\epsilon_i-\epsilon_a$ corrected by an energy term $\Delta E_{i\rightarrow a}^{\mathrm{xc}}$ so that

$$E_0^{(0)}-E_K^{(0)}=\epsilon_i-\epsilon_a-\Delta E_{i\rightarrow a}^{\mathrm{xc}}.$$

(18)

Using the IGLO ansatz for the Kohn–Sham orbitals leads to equations identical to Eqs. (6)–(14) with Eq. (14) replaced by

$$\mathbf{U}_{ai}=\sum_k\left(\frac{\Sigma_j\mathbf{Y}_{aj}c_{kj}}{\epsilon_k-\epsilon_a-\Delta E_{k\rightarrow a}^{\mathrm{xc}}}\right)c_{ki}.$$

(19)

Malkin and co-workers suggested several expressions for the excitation energy correction $\Delta E_{i\rightarrow a}^{\mathrm{xc}}$ of which the ''Loc1'' and ''Loc2''[21] approximations will be considered in this work. Approximation Loc1 implies

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

(20)

and Loc2

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

(21)

where $\rho_q=\varphi_q^*\varphi_q$, $\rho^\uparrow=\Sigma_i^{\mathrm{occ},\alpha}\rho_i$, and $\rho=\rho^\uparrow+\rho^\downarrow$. We will denote these two variants of the SOS-DFPT method as SOS-DFPT(Loc1) and SOS-DFPT(Loc2) whenever clarification is needed.

The purpose of the $\Delta E_{i\rightarrow a}^{\mathrm{xc}}$ terms is to increase the magnitude of the excitation energies thereby reducing paramagnetic contributions to nuclear magnetic shieldings. Since shieldings calculated at the UDFT level are generally too paramagnetic, a reduction of the paramagnetic contribution leads to significant improvement of SOS-DFPT chemical shifts in most cases. This becomes clear when considering the fact that SOS-DFPT, apart from the term $\Delta E_{i\rightarrow a}^{\mathrm{xc}}$, is identical to the UDFT theory of describing NMR chemical shifts. In recent work, Lee, Handy, and Colwell[20] argue that errors in nuclear magnetic shieldings calculated with UDFT are mainly due to the known deficiency of existing density functionals of estimating the energies of higher occupied orbitals too high, which leads to an overestimation of paramagnetic contributions. In view of this, the usefulness of the SOS-DFPT method can be understood by regarding $\Delta E_{i\rightarrow a}^{\mathrm{xc}}$ as a level shift correction for the erroneous orbital energies that adjusts orbital energy differences $\epsilon_i-\epsilon_a$ to correct Kohn–Sham values.

TABLE I. Absolute NMR shieldings as calculated with different numerical implementations of UDFT and SOS-DFPT.[a]

Molecule	Nucleus	UDFT-GIAO[b] this work	UDFT-IGLO this work	UDFT-IGLO Ref. 21	SOS-DFPT (Loc1) this work	SOS-DFPT (Loc1) Ref. 21
PN	P	−16.4	−13.6	3.4	39.3	55.1
	N	−399.7	−397.8	−392.4	−353.6	−348.8
CO	C	−12.5	−12.2	−8.6	3.3	6.4
	O	−78.1	−76.7	−66.5	−53.2	−43.8
F_2		−272.7	−273.0	−257.5	−227.7	−214.0
N_2		−83.1	−82.6	−75.6	−66.0	−59.5
H_2CO	C	−26.6	−25.6	−24.2	−16.6	−15.0
	O	−447.2	−447.5	−440.4	−399.3	−393.1
Mean abs. dev.[c]			1.1	8.4		7.6

[a]All calculations done with the $(11s7p2d/6s2p)[7s6p2d/4s2p]$ basis of Kutzelnigg and co-workers (Ref. 38) using the Becke (Ref. 35) exchange and PERDEW-86 (Ref. 63) correlation functionals. Geometries from (Ref. 64) and (Ref. 65) (H_2CO).
[b]Calculations with GAUSSIAN 94 (Ref. 46).
[c]Mean absolute deviation in ppm refers always to differences with regard to data given in the previous column.

III. IMPLEMENTATION AND COMPUTATIONAL DETAILS

The UDFT-IGLO and SOS-DFPT methods described above were implemented within the COLOGNE 94[34] program system. $\Delta E_{i \to a}^{xc}$ was obtained by numerical integration of Eqs. (20) and (21). The Coulomb term J was exactly calculated without using auxiliary basis sets as done in the original SOS-DFPT method implemented in the program system DeMon.[29,30] In benchmark calculations, absolute UDFT-IGLO chemical shifts were checked by comparison with the corresponding UDFT-GIAO values (see Table I), which differ by 0.3 (F in F_2) up to 2.8 ppm (P in PN). In view of the fact that exact agreement between IGLO and GIAO chemical shifts can only be obtained with an infinitely large basis set, a mean absolute deviation between IGLO and GIAO chemical shifts of 1.1 ppm (Table I) was considered to be reasonable.

It is interesting to note that UDFT-IGLO calculations of Malkin and co-workers[21] carried out with the same basis set, functional, and geometry lead to shielding values that on the average are 8 ppm more positive than UDFT values calculated in this work (see Table I). The same observation can be made with regard to the corresponding SOS-DFPT(Loc1) values of Malkin and co-workers, which are between 2 and 16 ppm (mean absolute deviation 8 ppm, Table I) larger than SOS-DFPT(Loc1) shieldings calculated here. For both UDFT and SOS-DFPT shieldings, deviations increase linearly with the number of electrons if atoms of the same period of the Periodic Table are considered. This suggests that diamagnetic shielding as calculated in the program DeMon is somewhat larger and it is reasonable to relate this difference to the different ways of calculating the Coulomb term J in this and previous work. We will pay special attention to this possibility in the following.

All DFT calculations of chemical shifts discussed in this work were performed with a combination of the Becke exchange[35] and the PW91 correlation functionals[36,37] using

the $(11s7p2d/6s2p)[7s6p2d/4s2p]$ basis set developed by Kutzelnigg and co-workers (denoted by them as basis III) for chemical shift calculations with the IGLO method.[38] To make results comparable with those of Malkin and co-workers,[21] Cartesian rather than spherical d functions were employed. The $[7s6p2d/4s2p]$ basis is of similar size as the $(11s7p2d/6s2p)[6s4p2d/3s2p]$ basis employed by Gauss in his GIAO-MP2 benchmark calculations[7] and, therefore, guarantees that comparisons with GIAO-MP2 results will reveal DFT and correlation specific rather than basis set dependent differences in calculated NMR chemical shifts. To complement the set of available reference data, GIAO-MP2 calculations were performed for molecules CS_2 and OCS using both a $(12s8p3d)[8s7p3d]$ and a $(11s7p2d)[7s6p2d]$ basis[38] for sulfur and applying the program package ACES II.[39]

Comparison of calculated and experimental NMR chemical shifts is exclusively done for molecules, for which reliable gas phase values of $\delta(^{13}C)$, $\delta(^{15}N)$, and $\delta(^{17}O)$ are available.[40–42] In this way, any discrepancies due to solvent effects are excluded. Since most of the molecules considered were previously investigated by Gauss at the HF-GIAO, MP2-GIAO levels[7] and even at the CCSD-GIAO level,[10] reliable *ab initio* data are available for testing the performance of DFT in the case of chemical shift calculations. Accurate experimental gas-phase geometries are not available for most of the systems considered and, therefore, MP2/TZ2P equilibrium geometries from Ref. 7 were used for all molecules. In two cases, in which MP2/TZ2P geometries were not available, geometries were optimized at the MP2/cc-pVTZ[43–45] level using the GAUSSIAN 94[46] program.

IV. RESULTS

Tables II–IV present calculated and experimental ^{13}C, ^{15}N, and ^{17}O chemical shifts of molecules **1**–**20**. Values of $\delta(^{13}C)$, $\delta(^{15}N)$, and $\delta(^{17}O)$ shifts are given relative to gaseous CH_4, NH_3, and H_2O, respectively. Nuclear magnetic shield-

TABLE II. Calculated and experimental ^{13}C chemical shifts (δ) in ppm relative to gaseous CH_4.[a]

Molecule	Sym.	HF-IGLO	HF-GIAO[c]	UDFT-IGLO	SOS-DFPT-IGLO (Loc1)	SOS-DFPT-IGLO (Loc2)	SOS-DFPT-IGLO (TMS)[d]	GIAO-MBPT(2)[c]	Exp.[e]
1, CH_3CH_3	D_{3d}	11.9	11.7	16.5	17.0	17.1	13.3	13.5	14.2
2, CH_3OH	C_s	53.0	52.0	64.8	64.7	64.6	60.8	59.3	58.5
3, CH_3NH_2	C_s	32.6	31.9	41.1	41.2	41.1	37.3	36.6	36.8
4, $\underline{C}H_3CN$	C_{3v}	5.1	4.8	10.4	11.2	11.4	7.6	7.9	7.4
5, $\underline{C}H_3CHO$	C_s	33.5	33.5	42.5	42.5	42.4	38.6	38.7	37.9
6, $\underline{C}H_3COCH_3$	C_{2v}	32.6	32.2	40.2	40.7	40.8	37.0	37.0	37.1
7, CH_3F	C_{3v}	72.3	71.6	86.2	86.0	85.8	82.0	79.7	78.3
8, CH_2CH_2	D_{2h}	135.5	135.8	141.4	138.3	137.2	133.4	130.3	130.6
9, $CHCH$	$D_{\infty h}$	80.8	81.8	82.3	81.4	81.0	77.2	78.2	77.9
10, $\underline{C}H_2CCH_2$	D_{2d}	81.0	81.7	85.1	83.9	83.4	79.6	80.6	79.9
10, $CH_2\underline{C}CH_2$	D_{2d}	239.6	240.0	238.5	234.4	233.0	229.2	227.5	224.4
11, C_6H_6	D_{6h}	140.9	140.6	144.1	143.7	143.5	139.7	137.5	137.9
12, HCN	$C_{\infty v}$	125.8	127.5	120.1	116.2	114.9	111.1	114.2	113.0
4, $CH_3\underline{C}N$	C_{3v}	134.0	135.1	130.2	127.6	126.7	122.9	125.4	121.3
13, CS_2[b]	$D_{\infty h}$	255.1	255.8	204.7	202.1	201.2	197.4	191.7	203.1
14, OCS[b]	$C_{\infty v}$	188.3	187.5	166.2	164.1	163.4	159.6	159.2	165.1
15, CO	$C_{\infty v}$	223.6	224.9	206.6	191.9	187.6	183.8	190.4	194.1
16, CO_2	$D_{\infty h}$	147.2	147.9	138.7	138.1	137.9	134.1	138.0	136.3
5, $CH_3\underline{C}HO$	C_s	212.4	211.3	219.9	214.2	212.4	208.6	200.3	201.8
6, $CH_3\underline{C}OCH_3$	C_{2v}	220.5	218.8	226.0	221.7	220.3	216.5	207.3	208.2
17, CF_4	T_d	119.6	116.4	150.4	150.6	150.6	146.8	137.1	130.6
Mean abs. dev.		11.0	11.5	7.7	6.0	5.8	3.7	2.2	
Mean abs. dev (without **13**, **14**, **15**, **17**)		6.8	7.2	7.4	5.9	5.4	2.3	1.2	

[a]Geometries from Ref. 7 except where noted otherwise. All calculations were carried out with the $(11s7p2d/6s2p)[7s6p2d/4s2p]$ of Kutzelnigg and co-workers (Ref. 38) except where noted otherwise. For molecules with more than one unique carbon nucleus, the nucleus considered is underlined.
[b]MP2/cc-pVTZ geometry: CS: 1.557 Å (CS_2); CS: 1.561 Å, CO: 1.165 Å (OCS).
[c]From (Ref. 7) except **13** and **14**.
[d]Obtained by using tetramethylsilane (TMS) as primary computational reference instead of CH_4 (see the text).
[e]From Ref. 40.

ings for the reference molecules are listed in Table V. HF-GIAO and MP2-GIAO chemical shifts published by Gauss[7] have been included into Tables II–IV for comparison. Deviations between calculated and experimental chemical shifts are presented graphically in Figs. 1–3.

The different treatment of the gauge problem at the IGLO and GIAO level of theory leads to different require-ments on quality and size of the basis set used for NMR chemical shift calculations. However, for sufficiently large basis sets as those used in this work, IGLO and GIAO per-form equally well. In such a case, any deviations between HF-IGLO and HF-GIAO chemical shifts are indicative of remaining basis set deficiencies. The IGLO and GIAO chemical shifts in Tables II–IV reveal that calculated differ-

TABLE III. Calculated and experimental ^{15}N chemical shifts (δ) in ppm relative to gaseous NH_3.[a]

Molecule	Sym.	HF-IGLO	HF-GIAO[b]	UDFT-IGLO	SOS-DFPT-IGLO (Loc1)	SOS-DFPT-IGLO (Loc2)	SOS-DFPT-IGLO (corr)[c]	GIAO-MBPT(2)[b]	Exp.[d]
12, HCN	$C_{\infty v}$	317.4	318.6	306.7	294.0	290.0	285.1	275.2	284.9
4, CH_3CN	C_{3v}	307.3	309.2	295.2	284.8	281.5	276.9	263.0	272.6
18, N_2	$D_{\infty h}$	387.3	391.3	354.5	338.3	333.4	325.9	321.1	326.1
19, $\underline{N}NO$	$C_{\infty v}$	207.9	210.9	172.8	166.4	164.4	165.6	141.1	165.0
19, $N\underline{N}O$	$C_{\infty v}$	310.1	310.8	263.8	259.2	257.8	252.5	242.4	253.2
Mean abs. dev.		45.6	47.8	18.2	8.2	5.3	1.2	11.8	

[a]Geometries from Ref. 7. All calculations were carried out with the $(11s7p2d/6s2p)[7s6p2d/4s2p]$ basis of Kutzelnigg and co-workers (Ref. 38). For molecules with more than one unique nitrogen nucleus, the nucleus considered is underlined.
[b]From Ref. 7.
[c]Obtained after scaling shifts by 0.93 and applying a paramagnetic correction proportional to $1/[\epsilon(LUMO)-\epsilon(HOMO)]$ (see the text).
[d]Taken from Ref. 41.

TABLE IV. Calculated and experimental ^{17}O chemical shifts (δ) in ppm relative to gaseous H_2O.[a]

Molecule	Sym.	HF-IGLO	HF-GIAO[c]	UDFT-IGLO	SOS-DFPT-IGLO (Loc1)	SOS-DFPT-IGLO (Loc2)	SOS-DFPT-IGLO (corr)[d]	GIAO-MBPT(2)[c]	Exp.[e]
14, OCS[b]	$C_{\infty v}$	242.2	248.5	246.8	240.4	238.4	241.0	227.3	236.1
15, CO	$C_{\infty v}$	416.4	422.0	405.6	383.5	377.0	382.6	392.2	386.3
16, CO_2	$D_{\infty h}$	106.7	112.2	114.1	112.4	111.8	104.0	103.8	100.6
19, N_2O	$C_{\infty v}$	172.2	177.7	163.8	158.8	157.3	146.3	138.6	143.4
20, OF_2	C_{2v}	799.7	801.0	988.3	920.0	899.8	815.9	824.6	817.1
Mean abs. dev.		17.8	22.0	47.0	27.4	23.9	3.2	5.6	
Mean abs. dev. (without **20**)			17.7	23.5	16.0	8.6	9.2		

[a]Geometries from Ref. 7 except where noted otherwise. All calculations were carried out with the $(11s7p2d/6s2p)[7s6p2d/4s2p]$ basis of Kutzelnigg and co-workers (Ref. 38) except were noted otherwise.
[b]MP2/cc-pVTZ geometry: CS: 1.561 Å, CO: 1.165 Å (OCS).
[c]From Ref. 7 except **14**.
[d]Obtained after scaling shifts by 0.93 and applying a paramagnetic correction proportional to $1/[\epsilon(LUMO) - \epsilon(HOMO)]$ (see the text).
[e]Taken from Ref. 42.

ences are in general a few ppm. Differences increase from $\delta(^{13}C)$ to $\delta(^{15}N)$, and $\delta(^{17}O)$, reflecting an increasing magnitude of basis set incompleteness errors in this sequence. In no case, however, are basis set incompleteness errors large enough to dominate deviations between experimental and calculated NMR chemical shift values. Therefore, we will consider these deviations as being method rather than basis set dependent. Since HF-IGLO and HF-GIAO lead to almost identical values for the majority of molecules considered in this work, we will refer to them simply as ''HF'' values not distinguishing any longer between IGLO and GIAO. In the same way, GIAO-MP2 NMR chemical shifts will be referred to as ''MP2'' chemical shifts.

A. ^{13}C chemical shifts

Figure 1(a) presents absolute deviations of calculated $\delta(^{13}C)$ values from the experimental values for both UDFT, SOS-DFPT(Loc1), and SOS-DFPT(Loc2) methods. Mean absolute deviations of calculated chemical shifts with regard to experimental values are given in Table II. HF-IGLO and HF-GIAO deviations are almost identical (11.0 and 11.5 ppm) where the relatively large average errors are mainly due to the shift values of those molecules [CS_2 (**13**), OCS (**14**), CO (**15**), and CF_4 (**17**)] that require elaborate correla-

TABLE V. ^{13}C, ^{15}N, and ^{17}O nuclear magnetic shieldings σ (in ppm) of reference molecules.[a]

Molecule	Sym.	HF-IGLO	UDFT-IGLO	SOS-DFPT-IGLO (Loc1)	SOS-DFPT-IGLO (Loc2)
CH_4	T_d	196.1	189.8	191.2	191.6
NH_3	C_{3v}	261.6	258.6	260.1	260.6
H_2O	C_{2v}	322.4	320.8	323.2	324.0

[a]Geometries from Ref. 7. All shielding values calculated with the $(11s7p2d/6s2p)[7s6p2d/4s2p]$ basis of Kutzelnigg and co-workers (Ref. 38).
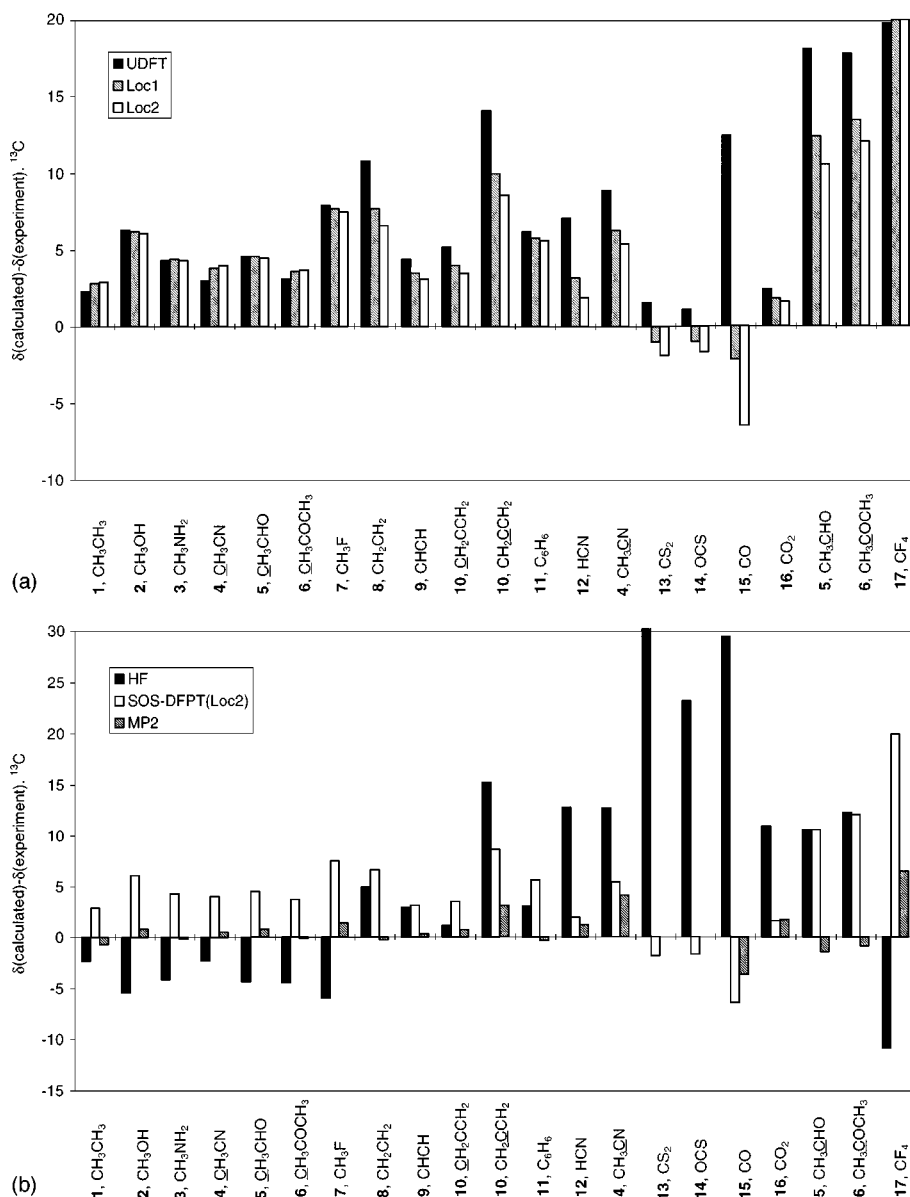
tion treatments. By excluding the latter molecules from the comparison mean absolute deviations of 6.8 and 7.2 ppm are obtained similar to what has been found by other authors.[47–49] UDFT reduces mean absolute deviations from 11 to 7.7 ppm where Fig. 1(a) reveals that UDFT chemical shifts are always too large. SOS-DFPT leads to another improvement of mean absolute deviations by about 2 ppm (Loc1: 6.0, Loc2: 5.8 ppm, Table II) where the Loc2 approach is marginally better than the Loc1 approach. However, the best agreement between theory and experiment is achieved at the GIAO-MP2 level of theory as is documented by mean values of 2.2 ppm.[7] Neither for DFT- or MP2-based methods it plays a major role whether critical cases such as **13**, **14**, **15**, and **17** are included into the comparison (Table II) although the chemical shift of CF_4 is difficult to describe for most of the methods considered in this work. Satisfactory results can only be obtained in this case if higher order correlation effects are included into the calculation as has been demonstrated by Gauss and Stanton.[10]

In the following we will discuss computed chemical shifts in more detail considering structural features of the molecules investigated. Molecules **1–7** contain methyl carbon bonded to various functional groups by a single bond while molecules **8–11** contain multiple-bonded carbon. Figure 1(a) reveals that for the first group of molecules UDFT, SOS-DFPT(Loc1) and SOS-DFPT(Loc2) $\delta(^{13}C)$ values are identical within 1 ppm suggesting that paramagnetic effects[50] do not play an important role in these cases and that diamagnetic contributions are similarly treated by the three methods.[50] For **8–11**, UDFT and SOS-DFPT values differ by 1–5 ppm due to a stronger influence of paramagnetic contributions in these molecules, thus making the impact of the orbital energy correction on the magnitude of the total chemical shifts larger. The Loc2 approximation for orbital energy differences, which is larger by a factor of 4/3 than the corresponding Loc1 correction, leads to a larger damping of paramagnetic effects and, therefore, produces somewhat

FIG. 1. (a) Deviations (in ppm) of calculated $\delta(^{13}C)$ values from experimental values as obtained by UDFT (black bars), SOS-DFPT(Loc1) (shaded bars), and SOS-DFPT(Loc2) methods (white bars). (b) Deviations (in ppm) of calculated $\delta(^{13}C)$ values from experimental values as obtained by HF (black bars), SOS-DFPT(Loc2) (white bars), and MP2 (shaded bars).

lower chemical shifts in slightly better accord with the corresponding experimental values.

This effect is even more pronounced for $\delta(^{13}C)$ values of the nitrile and carbonyl groups in **4**, **5**, **6**, and **12**. For these molecules, SOS-DFPT leads to clearly better chemical shifts than UDFT where the Loc2 correction performs somewhat better than the Loc1 correction. Only in the cases of CS_2 (**13**), OCS (**14**), and CO (**15**), does the Loc2 correction lead to $\delta(^{13}C)$ values that are smaller than the corresponding experimental ones by maximally 6.5 ppm. It is interesting to note that in all other cases, UDFT and SOS-DFPT shifts are always larger than experimental values. The largest discrepancy between theory and experiment is obtained for CF_4 [(**17**, 20 ppm, Table II)], which is also unusual as UDFT and SOS-DFPT lead to the same $\delta(^{13}C)$ of 150 ppm (Table II).

Contrary to results obtained by Malkin and co-workers,[21] we find that Loc2 rather than Loc1 leads to somewhat better chemical shifts and, therefore, we continue by considering just SOS-DFPT(Loc2) values in the following.

In Fig. 1(b), SOS-DFPT(Loc2) results are compared to the results obtained at the HF or MP2 level of theory. If correlation corrections and paramagnetic contributions to chemical shifts are relatively small, SOS-DFPT(Loc2) values follow closely trends in measured $\delta(^{13}C)$ values although calculated values are 4–5 ppm too large thus leading to an accuracy, which is lower than that of MP2, but higher than that of HF. The improvement in accuracy becomes particularly clear when considering molecules with larger correlation (and/or paramagnetic) effects such as **10** or **12–16**, for which SOS-DFPT(Loc2) results are clearly better than HF
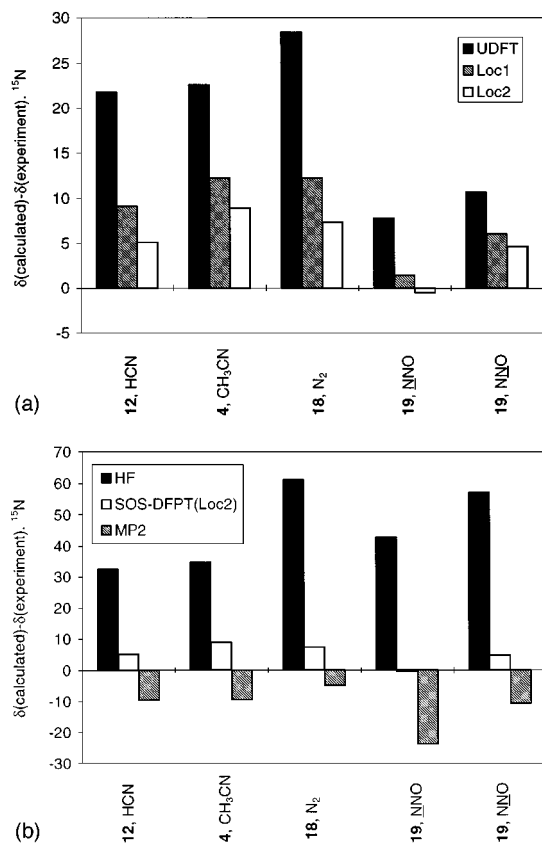
FIG. 2. (a) Deviations (in ppm) of calculated $\delta(^{15}N)$ values from experimental values as obtained by UDFT (black bars), SOS-DFPT(Loc1) (shaded bars), and SOS-DFPT(Loc2) (white bars). (b) Deviations (in ppm) of calculated $\delta(^{15}N)$ values from experimental values as obtained by HF (black bars), SOS-DFPT(Loc2) (white bars), and MP2 (shaded bars).

FIG. 3. (a) Deviations (in ppm) of calculated $\delta(^{17}O)$ values from experimental values as obtained by UDFT (black bars), SOS-DFPT(Loc1) (shaded bars), and SOS-DFPT(Loc2) (white bars). (b) Deviations (in ppm) of calculated $\delta(^{17}O)$ values from experimental values as obtained by HF (black bars), SOS-DFPT(Loc2) (white bars), and MP2 (shaded bars).

results leading to an accuracy close to that of the MP2-GIAO method. However, SOS-DFPT chemical shifts of the carbonyl carbons of **5** and **6** are not improved compared to the corresponding HF values both being 10–12 ppm too high (Table II). As mentioned above, SOS-DFPT(Loc2) performs also poor in the case of **17**.

Although SOS-DFPT(Loc2) $\delta(^{13}C)$ values represent an improvement with regard to HF-based values, their accuracy does not come close to MP2 shift values because they are in general too positive. This result is unexpected in view of the fact that DFT methods cover a considerable part of electron correlation and SOS-DFPT(Loc2), in particular, compensates for the deficiencies of DFT methods when calculating chemical shifts.

On the other hand, our results confirm and extend the findings of previous investigations on other type of molecules including transition metal compounds.[21–23,25] In cases where the correlation effects are small and, therefore, the HF method performs well, there are only small improvements in calculated $\delta(^{13}C)$ values due to the use of DFT. However, these improvements are obtained at considerably lower cost which make DFT-based methods for calculating chemical shifts highly attractive.
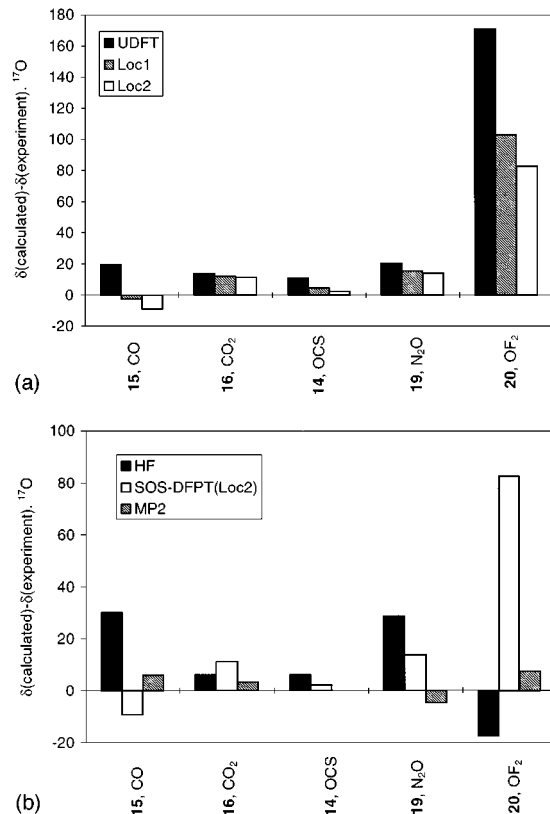
B. ^{15}N chemical shifts

In Fig. 2(a), UDFT and SOS-DFPT (Loc1 and Loc2) $\delta(^{15}N)$ values are compared for molecules **12**, **4**, **18**, and **19**. In these cases correlation effects and paramagnetic contributions are rather large and, accordingly, significant differences between the performance of the three DFT methods can be observed. Mean deviations from experimental values decrease in the order UDFT (mean deviation: 18.2 ppm, Table III), SOS-DFPT(Loc1) (8.2), SOS-DFPT(Loc2) (5.3), where SOS-DFPT seems to outperform even MP2 (11.8 ppm). However, in view of the limited number of cases considered, it is premature to draw such conclusions.

The largest deviation of SOS-DFPT(Loc2) values from experiment is 9 ppm [**4**, see Fig. 2(b)] while at the MP2 level this is −24 ppm for the terminal nitrogen in N_2O (**19**). Molecule **19** is a 4π system similar to ozone and is known to be a typical multireference system, which is difficult to calculate. One could wonder whether the MP2/TZ2P geometry used in this work as well as in the MP2-GIAO calculations guarantees an accurate calculation of $\delta(^{15}N)$. However, more recent calculations at the MP2-GIAO level using experimental equilibrium geometries do not deviate more than 5 ppm from MP2 values obtained with MP2/TZ2P geometries,[9,10] i.e., the discrepancy for the terminal N nucleus of **19** is not

caused by errors in the geometry used. However, by including more correlation effects at the CCSD or MP4(SDQ) level, $\delta(^{15}N)$ values for the terminal and central nitrogen are calculated [CCSD: 169 and 264 ppm; MP4(SDQ): 165 and 258 ppm[9,10]] that are in considerably better agreement with experiment. Clearly, deviations at the MP2 level are caused by deficiencies of the method to cover strong correlation effects. DFT seems to be able to cover these effects thus leading to satisfactory $\delta(^{15}N)$ values.

C. ^{17}O chemical shifts

There are only a few reliable experimental gas-phase values for $\delta(^{17}O)$, which has to do with the experimental difficulties in measuring ^{17}O shifts. Table IV and Figs. 3(a) and 3(b) present calculated and experimental $\delta(^{17}O)$ values for **14**, **15**, **16**, **19**, and **20**.

With the exception of the $\delta(^{17}O)$ value of OF_2, SOS-DFPT(Loc2) data compare fairly well with experiment and are better than the corresponding HF values. The mean absolute deviation of SOS-DFPT(Loc2) shifts for **14–19** is 9.2 ppm which is somewhat larger than the corresponding mean absolute deviations obtained for $\delta(^{13}C)$ (5.8) and $\delta(^{15}N)$ (5.3). However, if OF_2, (**20**) is included in the comparison, the mean absolute deviations of DFT-based chemical shifts are larger or similar to HF-based chemical shifts due to the fact that errors are five to ten times larger for the former than the latter methods.

V. DISCUSSION AND CONCLUSIONS

Contrary to previous investigations by Malkin and co-workers,[21] we find that SOS-DFPT(Loc2) rather than SOS-DFPT(Loc1) leads to somewhat better NMR chemical shift values for the molecules considered in this work. Actually, SOS-DFPT(Loc1) and SOS-DFPT(Loc2) perform similarly in the case of $\delta(^{13}C)$ (Table II) while in the case of $\delta(^{15}N)$ and $\delta(^{17}O)$ (Tables III and IV) improvements of 10%–30% can be achieved with SOS-DFPT(Loc2). SOS-DFPT chemical shifts seem to be on the average always better than UDFT chemical shifts, which in turn seem to be better than chemical shift values calculated at the HF level of theory. Of course, one has to note that the set of $\delta(^{15}N)$ and $\delta(^{17}O)$ values calculated is rather small (due to the lack of sufficiently accurate experimental gas phase values) and, therefore, not representative. For example, this is reflected by calculated $\delta(^{17}O)$ values, which are clearly better at the HF rather than the DFT level of theory.

Despite the fact that the number of calculated $\delta(^{15}N)$ and $\delta(^{17}O)$ values is rather small, some interesting observations can be made when comparing the shift values of Tables II–IV. Apart from a few exceptions, DFT-based chemical shifts are always more positive than experimental values. As already mentioned in connection with the data of Table I, UDFT-IGLO and SOS-DFPT shieldings published by Malkin and co-workers[21] are up to 16 ppm higher than shieldings calculated in this work. We connect this observation with the fact that in the present work the Coulomb term J has been exactly calculated according to Eq. (2). Approxi-

mating J according to Eq. (3) as done by Malkin and co-workers, leads to underestimation of electron repulsion [see inequality (5)] and two important consequences for the calculation of NMR shieldings can result:

(1) Any underestimation of Coulomb repulsion causes an enhanced clustering of electrons in the vicinity of the nucleus. In this way, electron–nucleus attraction is maximized and the total energy of the system in question is lowered. However, clustering of electrons in the vicinity of the nucleus also causes enhanced shielding of the nucleus and, by this, an increase of diamagnetic shielding.

(2) The magnitude of orbital energies depends on the magnitude of the electron–nucleus attraction term. If the latter becomes more negative, orbital energies will also become more negative. Thus an underestimation of the Coulomb term leads to an intrinsic correction of DFT orbital energies with the result that, in addition to the Loc correction, paramagnetic contributions to NMR chemical shifts are reduced.

As far as NMR chemical shifts are concerned, effects (1) and (2) will be reduced to zero if reference molecule and target molecule have similar structures and all paramagnetic contributions to NMR shieldings are rather small. However, for target molecules with structures considerably different from that of the appropriate reference molecule, both effects have to be considered. For example, if the target molecule contrary to the reference molecule possesses polar bonds, then effect (1) on diamagnetic shieldings will be much higher than in the reference molecule. Similarly, effect (2) will play a larger role for unsaturated molecules with low lying excited states rather than the (saturated) reference molecule. In general, we can expect an increasing importance of effects (1) and (2), the more target and reference molecule differ in structure. Both effects will lead to a decrease of NMR chemical shifts.

Hence, part of the success of the SOS-DFPT method is based on a cancellation of errors caused by approximating the Coulomb term and overestimating paramagnetic contributions due to deficiencies of DFT orbital energies. In this respect, it is not surprising that we find that the Loc2 rather than the Loc1 approximation leads to somewhat better NMR chemical shifts. For Loc2, the prefactor of the level shift correction is increased from 0.5 to 0.66 [compare with Eqs. (20) and (21)] thus partially compensating for changes in chemical shifts due to the use of the exact Coulomb term and an increase of paramagnetic contributions. In this respect, one might wonder whether it is useful at all to apply any of the Loc corrections suggested by Malkin and co-workers.

For most ^{13}C chemical shifts listed in Table II, paramagnetic contributions at the IGLO level should be rather small, which is confirmed by (a) the relatively small sensitivity of SOS-DFPT results with regard to the choice of the orbital correction and (b) the similarity of UDFT and SOS-DFPT chemical shifts. This simplifies the analysis of calculated ^{13}C chemical shifts, which has to be based on an analysis of calculated shieldings. All DFT shieldings turn out to be too small where the error increases with the anisotropy of the distribution of negative charge at the C atom. For example, for CH_4, which has a more spherical charge distribution sur-

rounding the C nucleus, the error is just -7 ppm,[51–53] while for **7** the error increases to -15 ppm as a result of the large anisotropy of the electron distribution at C caused by the F atom. The fact that ^{13}C shieldings are too small is a result of the use of density functionals, which are derived from the homogenous electron gas anisotropically corrected by Beckes gradient correction[35] and an appropriate correlation functional derived either from the electron gas or from helium calculations.[36,37,54–56] Clearly these corrections cannot compensate for a major deficiency of the homogenous electron gas distribution, namely, that the clustering of electrons at the nucleus because of stabilizing electron–nucleus attraction is underestimated. This, for example, leads to diagonal Fock matrix elements which are too positive and, as a consequence, to orbital energies which are too high thus artificially increasing the paramagnetic contributions to shielding. In the case of ^{13}C shieldings, a more direct effect is that the C nucleus is too much deshielded in a DFT calculation, diamagnetic effects are underestimated, and shieldings become too small.

Variation of the functional used does not improve the DFT inherent underestimation of diamagnetic effects. However, there are other ways to correct the diamagnetic contributions. One was implicitly used by Malkin and co-workers[21] when determining the Coulomb term J according to Eq. (3) [although the authors probably did not consider this consequence of Eq. (3)]. An underestimation of J leads to increased clustering of electrons around the nucleus and, thereby, to larger diamagnetic contributions and an implicit correction of DFT shieldings. This improvement can be enhanced for chemical shifts by using an appropriate reference. For example, Malkin and co-workers[21] used CH_4 with its experimental CH bond length ($r_0 = 1.094$, $r_g = 1.107$ Å[57]) as reference rather than CH_4 with the experimentally derived or calculated r_e value of the CH bond length (exp: $r_e = 1.085$,[58] MP2: $r_e = 1.083$ Å[7]), which is about 0.01–0.02 Å shorter than measured r_0 or r_g values. We calculate that this choice leads to an improvement of SOS-DFPT ^{13}C chemical shifts by 3–6 ppm and explains the good agreement between the chemical shifts of Malkin and co-workers and experimental shift values.

Since we believe that in the long run it is of advantage to consistently use *ab initio* r_e geometries both for reference and target molecules when calculating NMR chemical shifts and since we have intentionally refrained from approximating the Coulomb term J, we investigated other ways of improving diamagnetic contributions. A simple correction is achieved by choosing a reference that electronically is closer to the target molecules than CH_4 and, therefore, guarantees some cancellation of errors in calculated diamagnetic shielding contributions. One obvious choice is TMS, which compared to CH_4 has a more anisotropic charge distribution at the C atoms and, therefore, possesses a diamagnetic shielding error of -11 ppm[51,59]). By using TMS rather than CH_4, SOS-DFPT ^{13}C chemical shifts are improved on the average by 2 ppm thus leading to a mean absolute deviation of 3.7 rather than 5.8 ppm (Table II).

An alternative way to improve SOS-DFPT chemical shifts is to add a diamagnetic shielding correction (e.g., -5.8 ppm in the present case) or to scale SOS-DFPT(Loc2) values by a factor of 0.93. In both cases, one obtains SOS-DFPT chemical shifts of similar accuracy (mean absolute deviation: 3.9 ppm) as those obtained with TMS as a reference. When excluding the somewhat problematic molecules **13**, **14**, **15**, and **17** from the comparison, a mean absolute deviation of 2.3 ppm is obtained for corrected SOS-DFPT chemical shifts, which approaches the corresponding mean absolute deviation for MP2 (1.2 ppm, Table II).

It is interesting to note that a similar degree of accuracy (mean absolute deviation: 4.6 ppm) can be achieved if for UDFT chemical shifts diamagnetic shielding contributions are corrected by -7.7 ppm. Further improvements of UDFT shifts can be obtained by analysing discrepancies from experimental values that are >6 ppm. It turns out that these differences increase linearly with the term $1/(\epsilon_{LUMO} - \epsilon_{HOMO})$. If this dependence on the HOMO-LUMO gap is included as a paramagnetic correction to UDFT chemical shifts, shift values are obtained that deviate from experimental values on the average by just 2.9 ppm. Obviously, any simple correction of the basic deficiency of DFT, namely, to lead to orbital energies that are too positive, is sufficient to obtain improved chemical shift values.

In view of the discussion of DFT-based ^{13}C chemical shifts, the surprisingly good performance of SOS-DFPT(Loc2) in the case of ^{15}N chemical shifts has to be seen under a different perspective. Again, ^{15}N shieldings are too small and the corresponding shift values become too positive. This is clearly reflected by the UDFT chemical shifts of Table III and a mean absolute deviation of 18.2 ppm. Scaling UDFT values by a factor of 0.93 [as found in the case of $\delta(^{13}C)$ values] leads to improved chemical shifts that differ on the average by just 3.6 ppm from experimental values. This error can be further reduced if remaining differences are expressed as a linear function of $1/(\epsilon_{LUMO} - \epsilon_{HOMO})$ and paramagnetic correction terms are added to scaled UDFT ^{15}N chemical shifts.

If the same procedure is applied to SOS-DFPT(Loc2) chemical shifts, one obtains chemical shifts that are 10 to 15 ppm smaller than experimental values. Introducing positive (rather than negative) paramagnetic corrections in dependence on $1/(\epsilon_{LUMO} - \epsilon_{HOMO})$ leads to corrected SOS-DFPT chemical shifts in excellent agreement with experiment (mean absolute deviation: 1.2 ppm, Table III). These observations indicate that in the case of ^{15}N NMR chemical shifts the combination of an exact description of J and application of the Loc2 correction leads to a fortuitous cancellation of errors and hence rather accurate chemical shifts for the molecules considered. Actually, however, the Loc2 correction is somewhat too large if one considers that after scaling a positive rather than negative paramagnetic correction term has to be added.

Both SOS-DFPT(Loc1), SOS-DFPT(Loc2) (corrected or uncorrected) and MP2 ^{15}N chemical shifts correlate closely with experimental values (R^2 values of 0.999 or 1.000). This indicates that relative trends in ^{15}N chemical shifts are correctly described by these methods and that correlation effects

are similarly covered by both SOS-DFPT and MP2. The fact that correlation effects are large for the molecules considered is reflected by the large deviations of HF-IGLO and HF-GIAO shifts from experimental values. Clearly, SOS-DFPT or an appropriately corrected UDFT method represent major improvements relative to HF in the case of $\delta(^{15}N)$ calculations.

Similar as in the case of ^{15}N chemical shifts, the small number of calculated $\delta(^{17}O)$ values makes it difficult to draw any conclusions. In addition, the comparison between calculated and experimental $\delta(^{17}O)$ values is dominated by the fact that DFT-based methods overestimate the $\delta(^{17}O)$ value of OF_2 by 80 to 170 ppm while HF-based methods underestimate this value by less than 20 ppm (Table IV). Again, improved $\delta(^{17}O)$ values are obtained by scaling them with a factor of 0.93 and introducing a paramagnetic correction in dependence of $1/(\epsilon_{LUMO}-\epsilon_{HOMO})$ (see corrected values in Table IV). Values of similar accuracy can be obtained from UDFT chemical shifts when improving them in the same way as SOS-DFPT values.

In summary, we can state that DFT-based methods such as UDFT or SOS-DFPT predict chemical shifts of ^{13}C, ^{15}N, and ^{17}O in small molecules with an accuracy that is clearly better than that of standard Hartree–Fock theory and approaches that of correlated methods such as second-order perturbation theory. For the molecules considered, DFT seems to provide a consistent assessment of correlation effects for ^{13}C, ^{15}N, and ^{17}O NMR chemical shifts. This advantage of DFT-based methods for NMR chemical shift calculations is somewhat flawed by a systematic underestimation of diamagnetic shieldings that was not observed in previous work since the use of approximated two-electron Coulomb interactions leads to a partial cancellation of this effect. We note that simple scaling of chemical shifts or the introduction of a fixed diamagnetic correction can easily compensate for this problem.

The second problem concerns the Loc correction of paramagnetic contributions to NMR shieldings. Rather simple corrections such as the introduction of a $1/(\epsilon_{LUMO}-\epsilon_{HOMO})$ dependent correction factor as done in this work can solve this problem. The Loc corrections of Malkin and co-workers correspond to a particular set up of the DFT approach as for example to the way of calculating the Coulomb term J. They cannot be generally transferred to other DFT programs that handle the calculation of Coulomb and exchange-correlation terms differently. Hence the Loc2 correction in combination with an exact evaluation of the Coulomb term leads to somewhat better chemical shifts than the Loc1 approximation recommended by Malkin and co-workers. Neither Loc2 nor Loc1 lead to the best values in the case of $\delta(^{15}N)$ and $\delta(^{17}O)$. These can only be obtained by additional corrections depending on $1/(\epsilon_{LUMO}-\epsilon_{HOMO})$. However, the limited number of $\delta(^{15}N)$ and $\delta(^{17}O)$ values considered in this work requires further investigations to suggest an improved paramagnetic correction applicable in general to DFT-based calculations of $\delta(^{15}N)$ and $\delta(^{17}O)$. Work is in progress to determine such correction factors. Apart from this, there is clearly a need to improve density

functionals in the way that a better description of the electron density surrounding the nucleus is obtained and, in this way, both diamagnetic and paramagnetic contributions to NMR shieldings are corrected.

These conclusions have to be considered in view of the fact that DFT-based methods lead to a substantial reduction of computational efforts required to perform a chemical shift calculation. For example, a calculation with the SOS-DFPT(Loc2) method requires between 30% and 50% of the CPU-time needed for the corresponding HF-IGLO calculation despite the fact that the present implementation does not make use of auxiliary basis sets to speed up calculations.

After this work had been finished, two publications appeared in the literature, which both describe the use of UDFT-GIAO to calculate NMR chemical shifts.[60,61] The accuracy of published UDFT-GIAO shifts compares with that obtained with the UDFT-IGLO approach, i.e., it is clearly lower than that obtained with the SOS-DFPT method described in this work. Rauhut and co-workers[61] associate the overestimation of paramagnetic contributions by the UDFT-GIAO method with the lack of current-dependent terms in the exchange-correlation functional rather than with the deficiencies of the DFT energy denominators of Eq. (14). They argue that deficiencies of the DFT energy denominators in the way as they are discussed in the present work should also be found for other second-order properties such as polarizabilities calculated with DFT. We note in this connection that (a) the inclusion of current-dependent terms does not lead to an improvement of DFT-based chemical shifts as was shown by Handy and co-workers[20] and (b) DFT-based polarizabilities show indeed similar deficiencies as UDFT chemical shifts.[62]

ACKNOWLEDGMENTS

[1] W. Kutzelnigg, Isr. J. Chem. **19**, 193 (1980).
[2] M. Schindler and W. Kutzelnigg, J. Chem. Phys. **76**, 1919 (1982).
[3] K. Wolinski, J. F. Hinton, and P. Pulay, J. Chem. Soc. **112**, 8251 (1990).
[4] R. Ditchfield, Mol. Phys. **27**, 789 (1974).
[5] A. E. Hansen and T. D. Bouman, J. Chem. Phys. **82**, 5035 (1985).
[6] J. Gauss, Chem. Phys. Lett. **191**, 614 (1992).
[7] J. Gauss, J. Chem. Phys. **99**, 3629 (1993).
[8] J. Gauss, Chem. Phys. Lett. **229**, 198 (1994).
[9] J. Gauss and J. F. Stanton, J. Chem. Phys. **102**, 251 (1995).
[10] J. Gauss and J. F. Stanton, J. Chem. Phys. **103**, 3561 (1995).
[11] C. v. Wüllen and W. Kutzelnigg, Chem. Phys. Lett. **205**, 563 (1993).
[12] K. Ruud, T. Helgaker, R. Kobayashi, P. Jǿrgensen, K. L. Bak, and H. J. Aa. Jensen, J. Chem. Phys. **100**, 8178 (1994).
[13] T. D. Bouman and A. E. Hansen, Chem. Phys. Lett. **175**, 292 (1990).

[14] V. G. Malkin, O. L. Malkina, and D. R. Salahub, Chem. Phys. Lett. **204**, 80 (1993).

[15] G. Schreckenbach and T. Ziegler, J. Phys. Chem. **99**, 606 (1995).

[16] G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).

[17] G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10685 (1988).

[18] M. Rasolt, G. Vignale, and F. Perrot, Int. J. Quant. Chem. Symp. **26**, 359 (1992).

[19] G. Vignale, M. Rasolt, and D. J. W. Geldart, Phys. Rev. B **37**, 2502 (1988).

[20] A. M. Lee, N. C. Handy, and S. M. Colwell, J. Chem. Phys. **103**, 10095 (1995).

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

[22] M. Kaupp, V. G. Malkin, O. L. Malkina, and D. R. Salahub, Chem. Phys. Lett. **235**, 382 (1995).

[23] M. Kaupp, V. G. Malkin, O. L. Malkina, and D. R. Salahub, J. Am. Chem. Soc. **117**, 1851 (1995).

[24] V. G. Malkin, O. L. Malkina, and D. R. Salahub, J. Am. Chem. Soc. **117**, 3294 (1995).

[25] M. Kaupp, V. G. Malkin, O. L. Malkina, and D. R. Salahub, Chem. Eur. J. **2**, 24 (1996).

[26] T. B. Woolf, V. G. Malkin, O. L. Malkina, D. R. Salahub, and B. Roux, Chem. Phys. Lett. **239**, 186 (1995).

[27] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, and R. Ahlrichs, Chem. Phys. Lett. **240**, 283 (1995).

[28] B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. **71**, 3396 (1979).

[29] A. St-Amant and D. R. Salahub, Chem. Phys. Lett. **169**, 387 (1990).

[30] A. St-Amant, Ph.D. thesis, Universite de Montréal, 1992.

[31] W. Kutzelnigg, J. Mol. Struct. (Theochem) **202**, 11 (1989).

[32] C. v. Wüllen, J. Chem. Phys. **102**, 2806 (1995).

[33] J. M. Foster and S. F. Boys, Rev. Mod. Phys. **32**, 300 (1960).

[34] E. Kraka, J. Gauss, F. Reichel, L. Olsson, Z. Konkoli, Z. He, and D. Cremer, COLOGNE 94, Göteborg University, Göteborg, 1994.

[35] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[36] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[37] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[38] W. Kutzelnigg, U. Fleischer, and M. Schindler, in *NMR, Basic Principles and Progress*, edited by P. Diehl *et al*. (Springer, Berlin, 1991), Vol. 23, p. 165.

[39] J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, Int. J. Quantum Chem. Symp. **26**, 879 (1992).

[40] A. K. Jameson and C. J. Jameson, Chem. Phys. Lett. **134**, 461 (1987).

[41] C. J. Jameson, A. K. Jameson, D. Oppusunggu, S. Wille, P. M. Burrell, and J. Mason, J. Chem. Phys. **74**, 81 (1981).

[42] R. E. Wasylishen, S. Mooibroek, and J. B. Macdonald, J. Chem. Phys. **81**, 1057 (1984).

[43] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[44] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[45] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).

[46] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Kieth, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, GAUSSIAN 94 (Revision B.3), Gaussian, Inc., Pittsburgh, 1995.

[47] M. Schindler and W. Kutzelnigg, J. Am. Chem. Soc. **105**, 1360 (1983).

[48] D. Cremer, F. Reichel, and E. Kraka, J. Am. Chem. Soc. **113**, 9459 (1991).

[49] F. Reichel, Ph.D. thesis, Universität zu Köln, 1991.

[50] Throughout this work, the differentiation between diamagnetic and paramagnetic effects is based on the IGLO approach.

[51] The absolute shielding σ_0 of CH_4 is measured to be 194.8 ppm (Ref. 52) which after rovibrational corrections (Ref. 53) increases to $\sigma_e = 198.4$ ppm thus indicating an error of $191.6 - 198.4 = -6.8$ ppm for SOS-DFPT. For TMS, rovibrational corrections are not known and, therefore, the rovibrational corrections of CH_4 are added to $\sigma_0 = 188.1$ ppm (Ref. 59) to get an estimated σ_e value of 191.7 ppm and a SOS-DFPT error of -10.9 ppm.

[52] S. G. Kukolich, J. Am. Chem. Soc. **97**, 5704 (1975).

[53] C. J. Jameson, A. C. de Dios, and A. K. Jameson, J. Chem. Phys. **95**, 1069 (1991).

[54] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[55] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 385 (1988).

[56] R. Colle and O. Salvetti, Theor. Chim. Acta **37**, 329 (1975).

[57] *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege and A. M. Hellwege (Springer, Berlin, 1976), Vol. 7.

[58] K. Kuchitsu and L. S. Bartell, J. Chem. Phys. **36**, 2470 (1962).

[59] W. T. Raynes, R. Mc Vay, and S. J. Wright, J. Chem. Soc. Faraday Trans. 2 **85**, 759 (1989).

[60] J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, J. Chem. Phys. **104**, 5497 (1996).

[61] G. Rauhut, S. Puyear, K. Wolinski, and P. Pulay, J. Phys. Chem. **100**, 6310 (1996).

[62] S. M. Colwell, C. W. Murray, N. C. Handy, and R. D. Amos, Chem. Phys. Lett. **210**, 261 (1993).

[63] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[64] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979), Vol. 4.

[65] W. J. Hehre, L. Radom, P. V. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).