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Performance of DFT for ^{29}Si NMR Chemical Shifts of Silanes

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The predictive power of DFT, HF, and MP2 ^{29}Si NMR chemical shift calculations for silane molecules, including fluoro- and methylsilanes (Si_nH_{2n+2} ($n = 1, ..., 5$), Si_nF_{2n+2} ($n = 1, ..., 3$), and SiH_mX_{4-m} ($X = F, CH_3$)) is compared. A systematic accumulation of error proportional to the number of hydrogen neighbors to silicon sites is observed for DFT for all applied exchange-correlation functionals, whereas MP2 is not affected by this problem. A proposed empirical correction scheme for DFT provides excellent agreement with experiment with any exchange-correlation functional employed in this study.

1. Introduction

Nuclear magnetic resonance (NMR) is widely used and represents a powerful tool to probe the electronic and geometric structure of molecules as well as of solids. Indeed, NMR chemical shifts (δ), directly related to the nuclear magnetic shielding (σ), are very much dependent on the local geometry around the investigated nucleus and also on its electronic environment. Predicting structures and compositions of complex systems through modeling NMR shifts is thus a reachable goal, but it necessitates that an accuracy of few parts per million can be achieved in the calculations.

Numerous methods have been developed for the calculation of nuclear magnetic shielding in molecules since the fundamental formulation of its theory by Ramsey.[1] Most of these methods are based on the Hartree−Fock (HF) perturbation theory. Linear combination of atomic orbitals (LCAO) "ab initio" calculations with large basis sets were performed within the coupled Hartree−Fock perturbation theory (CHF) as early as the 1960's by Lipscomb[2] and others. Significant progress has been achieved by the use of gauge independent atomic orbitals (GIAO) in the CHF calculations.[3] Remarkable success was reached in the calculations of shielding constants in molecules also by the development of gauge transformation methods (e.g., individual gauge for local orbitals (IGLO),[4] continuous-transformation schemes (of atoms in molecules,[5] of origin of current density, CTOCD[6]).

In addition to HF and post HF, density functional theory (DFT) has become a standard tool for efficient and accurate calculations of the electronic and cohesive properties, as well as molecular structures. However, within a rigorous theory for calculations of nuclear magnetic shielding, DFT has to be extended to a current density functional theory (CDFT).[7] This was formally realized by Bieger et al.[8] However, up to now there have been no useful current density functionals available. Nonetheless a great success has been reached in application of DFT to magnetic shielding calculations in molecules just using an "uncoupled perturbation treatment" (UCPT), i.e., neglecting current contributions to the exchange-correlation potential and to the vector potential, as already proposed by Bieger et al.[8] For an overview, see, e.g., refs 9−14.

First principles NMR methods have shown a very large development of applications in all domains, with an increased interest for in situ reactions,[15,16] proteins,[17,18] zeolites,[19−22] and systems containing transition metals.[12,23,24] ^{29}Si NMR spectra (including MAS NMR spectra for Si-containing solids) have the interesting characteristics to display large δ variations with local structure, involving the first and second shells of neighbors. This behavior holds for molecules such as silanes, where the δ values spread over 170 ppm (see, e.g., Marsmann[26] for an overview for Si compounds) and also for solids such as zeolites showing a variation range of around 15 ppm with respect to geometry changes or substitution of a silicon center with another element.[27,28]

As a test set of the accuracy that could be expected concerning ^{29}Si NMR shifts with various environments, we have chosen the silane molecules. The silanes will give us the possibility to study trends by systematic variation of their structures (isomers, substituent effects−replacing hydrogen by alkyl groups or halogens, etc.).

The first and simplest approach to the interpretation of the ^{29}Si NMR chemical shift was based on its dependence on the atomic charge, which could be related to the electronegativity of the substituents.[29,30] In zeolites, empirical relations have been widely used to relate chemical shifts to the local structure, like average SiOSi bond angles, Si− Si distances, and the number of aluminum neighbors.[31] However, it is quite obvious that such simple models cannot describe correctly the variation of the chemical shifts in silanes, where substituent electronegativities do not vary much whereas the variation of the chemical shifts is quite large (∼170 ppm).

On the other hand, purely empirical formulas, considering the skeleton of the silane, work very well, such as the scheme proposed by Hahn.[32] It predicts the ^{29}Si NMR chemical shifts with an accuracy of ∼2 ppm and considers only structural information of the given site and its next neighbors.

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TABLE 1: Bond Lengths and Angles of Selected Compounds Calculated in This Work Compared with Literature Values[a]

		LDA/ DZVP	B3LYP/ 6-31G*[55]	expt[56]	expt[57]
SiH_4	Si−H	1.503	1.486	1.490	1.480 (IR)
Si_2H_6	Si−Si	2.331	2.350	2.331	2.331 (ED)
	Si−H	1.495	1.489	1.492	1.492
SiF_4	Si−F	1.578	1.563	1.566	1.553 (ED)
SiH_3F	Si−H	1.502			1.484 (MW, IR)
	Si−F	1.622	1.613	1.593	1.593
	∠HSiH	110.3			110.6
SiH_2F_2	Si−F	1.606	1.601	1.577	
$SiHF_3$	Si−H	1.480			1.5201 (MW)
	Si−F	1.591	1.590	1.562	1.5624
	∠HSiF	108.8			110.6
Si_2F_6	Si−Si	2.317			2.317 (ED)
	Si−F	1.592			1.564
SiH_3CH_3	Si−H	1.506	1.490	1.485	
	Si−C	1.878	1.889	1.867	
	∠HSiH	108.5	110.9	108.9	
$SiH(CH_3)_3$	Si−H	1.511	1.489	1.492	
	Si−C	1.877	1.891	1.873	
	∠HSiC	109.2	108.7	108.8	
TMS	Si−C	1.877		1.875	

[a] All lengths are given in angstroms and angles in degrees. From ref 57 the experimental technique is given and indicated as in original (IR (infrared), ED (electron diffraction), MW (microwave)).

In this paper, we present ^{29}Si NMR calculations on silanes and substituted silane molecules, comparing various methods and showing that, surprisingly, for DFT quite large deviations from experiment can be obtained when the number of hydrogens bonded to silicon is increasing. An empirical correlation scheme is proposed to provide reliable chemical shifts as a function of of the atoms surrounding silicon sites.

2. Computational Details

Geometries have been optimized within the local density approximation (LDA) associated with the VWN functional for correlation[33] and DZVP basis functions.[34] Frequency calculations were performed on optimized geometries, and no negative frequencies were observed, ensuring that all structures are local minima on the potential energy surface. These calculations were performed using the AllChem program package.[35]

Calculated geometries of selected molecules are compared with experiment and other calculations in Table 1. The largest deviations between our geometries and experiment are found for the fluorosilanes, i.e., the Si−F bond (0.03 Å), whereas Si−H bonds generally agree within 0.02 Å, Si−Si within 0.01 Å, and bond angles within 1.5°.

Nuclear magnetic shieldings have been calculated employing the deMon-NMR package[36] on molecular orbitals computed using AllChem.[35] The IGLO technique,[4] partially with the ad hoc corrections proposed by Malkin et al.[10] (indicated as LOC1), was chosen. Separation of DFT and property package has the advantage that shifts can be calculated using different methods (IGLO, LOC1, change of localization procedures) on the same set of molecular orbitals, if an uncoupled SOS theory to calculate shieldings is employed. The IGLO III basis set[37] was chosen, the adaptive grid did not exceed density differences of more than 10^{-7} au, and the GEN-A3 option (automatic generation of auxiliary functions, including *f*-functions) was used. We employed LDA (Slater-Dirac/VWN[33]) and generalized gradient approximation (GGA) (Perdew86[38]/Perdew-Wang86[39] (PW86) and the Becke88[40]/Perdew-Wang86 (B88PW86)) as exchange-correlation functionals (noted as exchange/correlation).

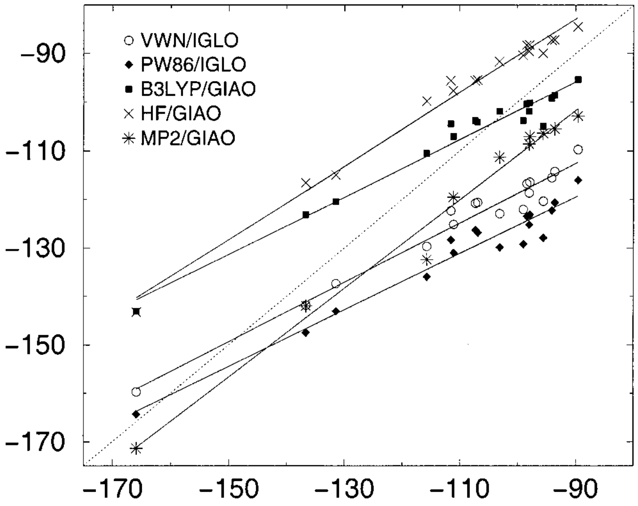

Figure 1. Scatter plot of calculated (*y*-axis) ^{29}Si chemical shifts with respect to TMS (calculated with the same method, basis, and computational details) in various methods vs experiment (*x*-axis) for silane molecules Si_nH_{2n+2}. Linear regressions are indicated, the unit slope is given as a dashed line. All values are in ppm.

Benchmark calculations have also been performed using the GIAO[3] technique and a 6-311+(2d,p) basis set on HF, MP2, Becke3[41]/LYP[42] (B3LYP), and VWN[33] (SVWN5 as Gaussian keyword) methods as implemented in the Gaussian 98 program package.[43]

3. Results and Discussion

3.1. Silanes Si_nH_{2n+2}. ^{29}Si NMR chemical shifts of silane molecules Si_nH_{2n+2}, $n = 1, ..., 5$, thus including (mono)silane, disilane, trisilane, *n*-tetrasilane and isotetrasilane, and *n*-pentasilane, isopentasilane, and neopentasilane, have been calculated. Experiments on the whole set of silanes have been carried out in C_6D_6 solution and at room temperature by Hahn,[32] and they show that silanes cover a large part of the silicon scale of magnetic shieldings, from −90 ppm to −166 ppm (values are chemical shifts with respect to tetramethylsilane, TMS). Newer experiments for the whole set of silanes are − to our best knowledge−not available at present. Since various values are reported for monosilane between −91 ppm and −95.6 ppm,[32] an experimental uncertainty of ∼5 ppm can be expected, especially because experiments are carried out in solution.

In general, silicons surrounded by a higher number of neighboring hydrogen atoms are found at lower fields. Neopentasilane is the molecule which covers the whole range of ^{29}Si NMR chemical shifts of silanes studied in this paper as internal shift, with its central silicon upfield and the other four at the smallest shift with respect to TMS, yielding thus a total internal shift of 76 ppm.

Calculated ^{29}Si NMR chemical shifts are compared with experiment in Table 2, and their correlation with experiment is given in Table 3.

Figure 1 shows the correlation of selected calculated and measured chemical shifts for silanes. The DFT-based methods correlate well with experiment, but too small slopes are obtained for all applied functionals. The tendency of the results obtained with the hybrid functional (B3LYP) to shift by ∼15 ppm toward the HF-based results can also be seen clearly. This holds especially for the chemical shift of the central silicon in

fTABLE 2: ^{29}Si NMR Chemical Shifts of Silane Molecules Si_nH_{2n+2} with Respect to TMS

	VWN			PW86		B88PW86		B3LYP	HF	MP2	
	IGLO	LOC1	GIAO	IGLO	LOC1	IGLO	LOC1	GIAO	GIAO	GIAO	expt
SiH_4	120.3	−123.7	−117.9	−127.9	−131.5	−116.4	−119.8	−105.0	−90.0	−106.4	−95.6
Si_2H_6	−122.9	−122.9	−120.3	−129.9	−130.0	−120.2	−119.9	−101.9	−91.7	−111.3	−103.1
Si_3H_8 (1)	−118.6	−117.6	−115.9	−125.2	−124.3	−116.3	−115.1	−101.9	−89.6	−108.6	−98.0
Si_3H_8 (2)	−129.7	−129.1	−126.8	−136.0	−135.6	−128.5	−127.7	−110.5	−99.8	−132.4	−115.7
n-Si_4H_{10} (1)	−116.4	−115.3	−113.7	−123.1	−122.1	−114.2	−112.8	−100.2	−88.2	−107.1	−97.8
n-Si_4H_{10} (2)	−125.1	−124.0	−122.2	−131.0	−130.0	−124.3	−122.9	−107.1	−97.7	−119.5	−111.1
i-Si_4H_{10} (1)	−114.2	−112.7	−111.6	−120.6	−119.2	−112.3	−110.6	−98.6	−87.2	−105.5	−93.6
i-Si_4H_{10} (2)	−141.9	−140.8	−139.0	−147.5	−146.5	−141.7	−140.4	−123.1	−116.5	−142.0	−136.3
n-Si_5H_{12} (1)	−116.7	−115.1	−114.0	−123.4	−121.8	−114.6	−112.8	−100.4	−88.3		−98.4
n-Si_5H_{12} (2)	−122.3	−120.8	−119.3	−128.3	−126.9	−121.7	−120.0	−104.5	−95.6		−111.5
n-Si_5H_{12} (3)	−120.7	−119.3	−117.7	−126.3	−124.9	−120.4	−118.8	−103.8	−95.7		−107.3
i-Si_5H_{12} (1)	−115.5	−113.9	−113.1	−122.2	−120.6	−114.0	−112.1	−99.2	−87.3		−94.1
i-Si_5H_{12} (2)	−137.4	−136.1	−135.3	−143.1	−141.9	−137.5	−136.0	−120.4	−114.9		−131.5
i-Si_5H_{12} (3)	−122.0	−119.1	−119.8	−129.2	−125.4	−120.2	−118.7	−104.1	−95.5		−106.9
i-Si_5H_{12} (4)	−120.6	−120.8	−118.3	−126.8	−127.9	−119.9	−118.2	−103.8	−90.1		−99.0
neo-Si_5H_{12} (1)	−109.7	−107.9	−107.4	−116.0	−114.3	−108.3	−106.3	−95.4	−84.5	−102.9	−89.6
neo-Si_5H_{12} (2)	−159.7	−158.3	−155.7	−164.3	−163.1	−160.5	−158.9	−143.1	−143.3	−171.4	−165.9
TMS	313.3	316.4	308.9	314.4	317.4	320.1	323.4	330.0	385.8	367.6	

[a] Experimental shifts are taken from ref 32. In the last row the calculated absolute ^{29}Si NMR shielding of TMS in the same method (reference) is given. All values are in ppm.

TABLE 3: Linear Regression Data of the Correlation Experimental vs Calculated ^{29}Si Chemical Shift for Silanes[a]

	uncorrected			corrected		
	a	*b*	*r*	*a*	*b*	*r*
VWN/IGLO	0.613 ± 0.029	−57.38 ± 3.21	0.984	1.11 ± 0.03	10.69 ± 3.61	0.994
VWN/LOC1	0.607 ± 0.039	−57.13 ± 4.31	0.971	1.04 ± 0.02	3.88 ± 2.46	0.997
VWN/GIAO	0.598 ± 0.030	−56.35 ± 3.32	0.982	0.99 ± 0.03	−0.62 ± 2.95	0.995
PW86/IGLO	0.584 ± 0.034	−66.91 ± 3.74	0.976	1.06 ± 0.03	6.35 ± 3.29	0.994
PW86/LOC1	0.580 ± 0.043	−66.45 ± 4.81	0.960	1.09 ± 0.03	8.97 ± 2.82	0.996
B88PW86/IGLO	0.658 ± 0.022	−51.13 ± 2.45	0.992	1.11 ± 0.04	10.76 ± 4.06	0.992
B88PW86/LOC1	0.651 ± 0.032	−50.80 ± 3.59	0.982	1.07 ± 0.03	6.29 ± 2.81	0.996
B3LYP/GIAO	0.591 ± 0.030	−42.76 ± 3.27	0.982			
HF/GIAO	0.756 ± 0.024	−14.85 ± 2.65	0.993			
MP2/GIAO	0.915 ± 0.042	−19.45 ± 4.75	0.992			

[a] On the left-hand side uncorrected and on the right-hand side empirical corrected data (see text) are given. *a* indicates the slope, *b* the intercept, and *r* the correlation coefficient.

neopentasilane, where a proper description of correlation effects is important. B3LYP does not improve the poor CHF result for this molecule, whereas LDA-, GGA-, and MP2-based calculations give the nearly correct shift.

MP2 holds this quality—despite of a small "offset" from the ideal correlation—for all the silane molecules considered. In contrast, the results of the DFT-based calculations predict a too small increase of the shift going to lower fields. Nevertheless, all DFT-based methods, including B3LYP, show a quite good correlation between measured and calculated chemical shifts within the silanes (see Table 3). A similar good correlation is obtained for the CHF and the MP2 results. Unfortunately, MP2 calculations on molecules as large as Si_5H_{12} are nearly reaching the limit of today's computing facilities[44] and could not be applied to two isomers (iso-Si_5H_{12} and *n*-Si_5H_{12}).

In Figure 2a, the results of several different exchange-correlation functionals (including B3LYP) are shown. More recent GGAs have been applied for the calculation of the critical internal ^{29}Si NMR shift of neopentasilane, yielding the values of 53.2 (Perdew-Wang 91[45]) and 47.0 ppm (G96[46]LYP), using the same computational details as in the other Gaussian benchmarks. For this compound, these functionals perform similarly as the other functionals (i.e., 50.0 ppm for IGLO-LDA) and strongly underestimate the experimental result (76 ppm), too. These results indicate that there seems to be no advantage of GGA over LDA. A similar conclusion can be drawn comparing chemical shifts calculated at GGA and LDA levels in other publications, even if the reported shieldings differ considerably (see, e.g., ref 47). We conclude thus that ^{29}Si NMR chemical shifts for silanes are insensitive to the functional employed and that—if DFT is chosen—the computationally least expensive LDA could be considered.

Figure 2b compares experiment with three different techniques to compute the shieldings, each of them using the local VWN approach. IGLO and GIAO perform very similarly, and the ad hoc corrections of the virtual orbital energies proposed by Malkin et al.[10] show little effect. The calculations visualized in Figure 2b are performed with two different basis sets (IGLO III and 6311+(2d,p)) and give similar results. Further adding of polarization functions to the IGLO III basis (one *s* and one *p* function with an exponent chosen to be $^1/_3$ of the smallest exponent for each angular momentum, respectively) gives only small differences of the internal shift of neopentasilane (47 ppm instead of 50 ppm vs 76 ppm in experiment).

Chemical shifts are known to be quite sensitive to geometries. The calculation of bond length dependency on shielding allows one to estimate the error for calculated chemical shifts due to inaccuracies in the geometry. As discussed above, the error in the calculated Si−Si and Si−H bond lengths is smaller than 0.02 Å. The maximum error is estimated to be 10 ppm for each Si type due to possible errors in the Si−H (0.5 ppm per bond for an estimated maximum error of 0.02 Å) and Si−Si (2.0 ppm per bond for 0.01 Å) bond lengths, respectively.

The core contributions to the shielding constant, which can easily be analyzed with the IGLO method, differ by less than

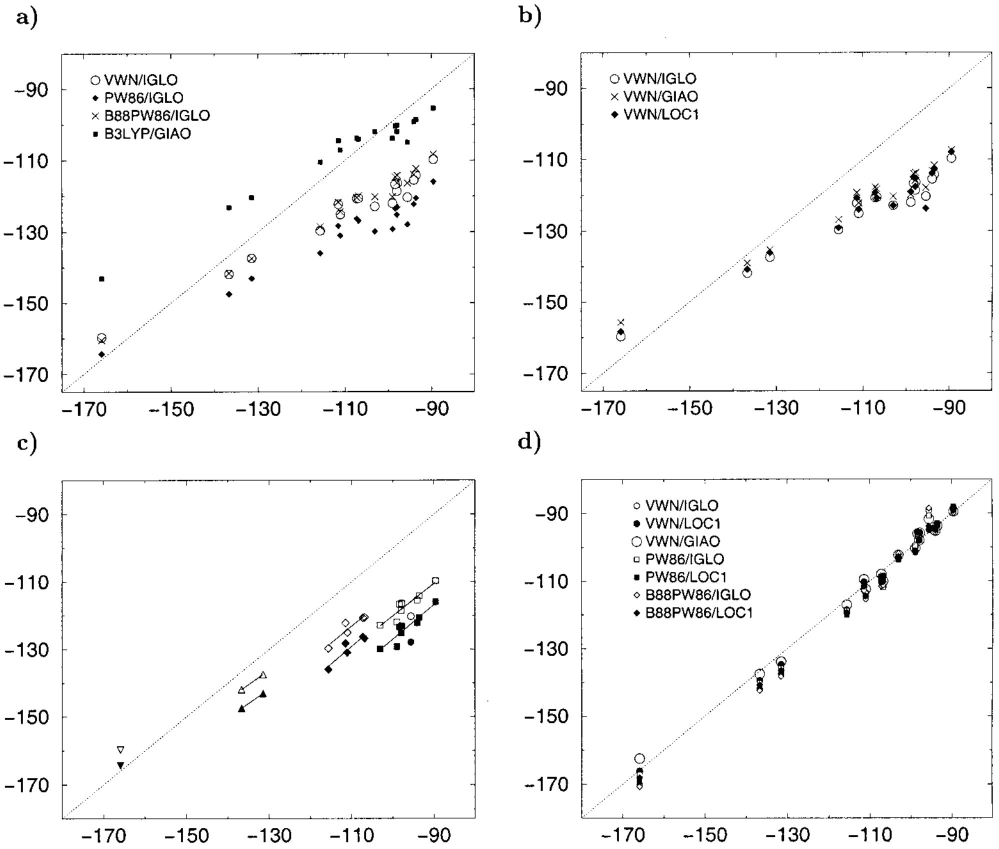

Figure 2. (a) The same set of silane molecules as in Figure 1 is studied in DFT using different exchange-correlation functionals. (b) The same set of silane molecules as in Figure 1 is studied in LDA employing different methods to calculate the shielding constants. (c) Two DFT methods from the plot of Figure 1: VWN/IGLO (empty signs) and PW86/IGLO (filled signs) are shown, while number of silicon neighbors $n_{\mathrm{Si}} = 0$ (circle), $n_{\mathrm{Si}} = 1$ (square), $n_{\mathrm{Si}} = 2$ (diamond), $n_{\mathrm{Si}} = 3$ (triangle up), and $n_{\mathrm{Si}} = 4$ (triangle down) are distinguished. Regressions for each set are given. (d) Empirically corrected ^{29}Si NMR shifts with respect to TMS of calculated silane molecules in DFT vs experiment. Conventions as in Figure 1.

TABLE 4: Linear Regression Data of the Correlation Experimental vs Calculated ^{29}Si Chemical Shift for Distinct Sites n_{Si}[a]

	n_1			n_2			n_3	
	a	*b*	*r*	*a*	*b*	*r*	*a*	*b*
VWN/IGLO	0.96 ± 0.15	−23.97 ± 14.50	0.934	1.00 ± 0.22	−13.61 ± 24.05	0.935	0.87	−12.60
VWN/LOC1	1.08 ± 0.15	−11.68 ± 14.98	0.943	1.09 ± 0.25	−2.54 ± 27.70	0.929	0.90	−8.49
VWN/GIAO	0.94 ± 0.16	−23.19 ± 15.91	0.920	0.96 ± 0.24	−14.94 ± 26.12	0.920	0.71	−35.23
PW86/IGLO	1.02 ± 0.16	−25.22 ± 15.82	0.931	1.04 ± 0.23	−15.20 ± 25.01	0.935	0.85	−10.42
PW86/LOC1	1.13 ± 0.16	−13.28 ± 15.84	0.942	1.14 ± 0.26	−2.43 ± 28.84	0.930	0.88	−5.97
B88PW86/IGLO	0.87 ± 0.16	−30.66 ± 15.87	0.908	0.92 ± 0.20	−21.11 ± 22.04	0.936	0.81	−20.44
B88PW86/LOC1	0.98 ± 0.16	−18.72 ± 15.91	0.925	1.01 ± 0.23	−9.95 ± 25.48	0.930	0.85	−16.42
B3LYP/GIAO	0.53 ± 0.13	−48.71 ± 12.37	0.862	0.71 ± 0.20	−27.96 ± 22.52	0.895	0.52	−68.98
HF/GIAO	0.51 ± 0.06	−38.73 ± 6.10	0.958	0.45 ± 0.16	−47.31 ± 17.22	0.857	0.31	−96.15

[a] *n* gives the number of neighboring silicon atoms. Other conventions as in Table 3.

0.1 ppm for the K shell, but by 9 ppm for the L shell between the central silicon of neopentasilane and monosilane.

The diamagnetic contributions to the shielding are very similar.[48] They are determined simply by the charge distribution of the occupied orbitals. The differences of the shielding constants result obviously from a different description of the paramagnetic part of the shielding, which is determined to a large extent by the unoccupied orbitals.

The DFT results show a systematic trend in their deviations from experiment. Therefore, one can divide all Si atoms of the whole set into five subsets, each containing silicon atoms with the same number of silicon neighbors n_{Si}, $n_{\mathrm{Si}} = 0, ..., 4$ (or, in the case of silanes, of hydrogen neighbors). Two of the five sets ($n_{\mathrm{Si}} = 1, 2$) contain enough values to perform a numerical analysis: if one correlates calculated and experimental chemical shifts set by set as shown in Table 4, all exchange-correlation functionals give a very good correlation with experiment and the linear slope is close to unity. However, these linear regressions are shifted against each other by ~10 ppm. This behavior is visualized for VWN/IGLO and PW86/IGLO in Figure 2c. This trend holds for all employed functionals (LDA, GGA, hybrid), for both basis sets (IGLO III or 6-311+(2d,p)) and all techniques used to calculate the shieldings (GIAO, IGLO and LOC1). We can thus conclude that all DFT methods show a systematic error proportional to the number of neighboring silicon (or hydrogen) atoms for the estimation of ^{29}Si NMR chemical shifts.

3.2. Fluorosilanes. The calculations on silanes raise the question whether the systematic error of the shifts is caused by the neighboring silicon or by the hydrogen atoms, or, in other words, if the Si−Si or the Si−H bonds are described improperly by DFT. Therefore, we calculated ^{29}Si NMR chemical shifts of fluorosilanes Si_nF_{2n+2}. Unfortunately, experimental data are restricted to three species which contain four different silicon

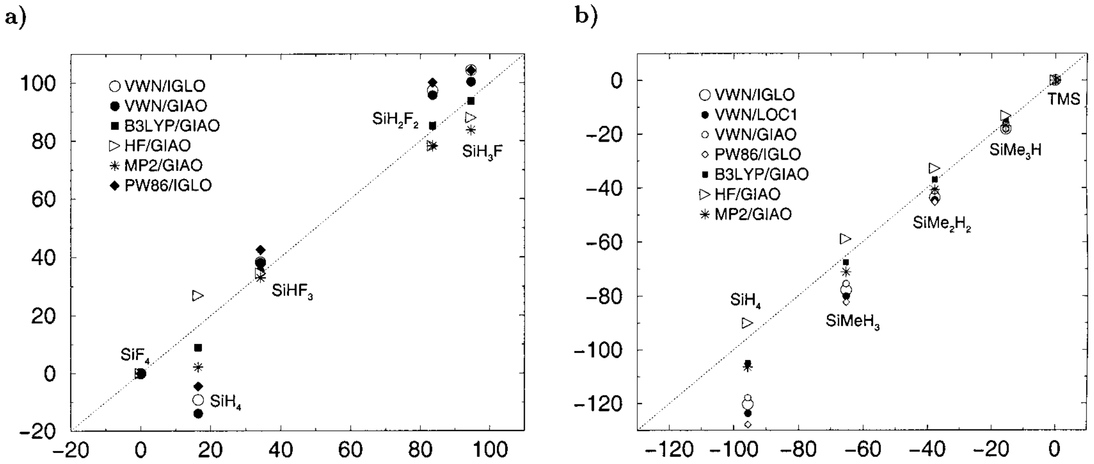

Figure 3. (a) Scatter plot of calculated ^{29}Si NMR chemical shift of fluorinated monosilane molecules $SiH_{4-x}F_x$ vs experiment with respect to SiF_4. (b) Scatter plot of calculated ^{29}Si NMR chemical shifts of methylated monosilane $SiH_{4-x}(CH_3)_x$ with respect to TMS vs experiment. Conventions as in Figure 1.

TABLE 5: Si NMR Chemical Shifts of Fluorosilanes Si_nF_{2n+2} with Respect to SiF_4 in ppm

	VWN			PW86	B3LYP	HF	
	IGLO	LOC1	GIAO	IGLO	GIAO	GIAO	expt
SiF_4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Si_2F_6	−35.5	−37.4	−39.6	−35.2	−38.0	−40.5	−35.5
Si_3F_8 (1)	−33.9	−35.9	−37.5	−33.7	−36.9	−39.3	−33.5
Si_3F_8 (2)	−100.8	−99.6	−103.2	−97.9	−99.7	−96.2	−95.7

[a] Experimental values are taken from ref 49.

sites (SiF_4, Si_2F_6, and Si_3F_8).[49] Experimental shifts are given with respect to SiF_4. The shifts of these three compounds cover a range of ~100 ppm, more than the whole set of silanes. All performed calculations give good agreement with experiment and give shifts with respect to SiF_4 with an error of less than 6 ppm (see Table 5). The very good quality of the calculated chemical shifts for fluorosilanes confirms the role of hydrogen in the inaccuracies of the calculated chemical shifts for the silanes within DFT-based methods. Interestingly, HF-based calculations match also the results of the DFT-based calculations. For these compounds, the influence of the solvent has been estimated experimentally:[49] solvents affect the ^{19}F NMR shifts by ~10 ppm, but ^{29}Si NMR chemical shifts are changed by only 1.1 ppm.

The number of basis functions for fluorine is generally much higher in standard basis sets such as IGLO III or 6311+(2d,p) than that of hydrogen. Thus, one could imagine that the improper description in silanes is caused by missing *d*-functions on the hydrogens, providing not enough virtual orbitals for the sum-over-states expansion needed to describe the perturbed wave function. However, calculating the silanes with IGLO III fluorine basis functions on hydrogen atoms does not correct the too small internal shift of neopentasilane, and therefore this argument can be dismissed.

As a next step, fluorinated monosilanes $SiH_{4-x}F_x$ were studied. Calculated ^{29}Si NMR chemical shifts are compared with experimental values[50] in Table 6 and Figure 3a. B3LYP gives an excellent agreement with experiment. This can be understood by the fact that the B3LYP values for silanes come close to experiment at low fields, where other DFT functionals work better further upfield. HF and MP2 calculations agree well with experiment, if the uncertain SiH_4 is left out in these considerations. For DFT, one can clearly see a proportionality between the difference of the calculated and experimental shift with the number of hydrogen atoms.

3.3. Methylsilanes. Table 7 and Figure 3b show that DFT methods underestimate the ^{29}Si NMR shifts for methylsilanes with respect to experiment[51] if the number of hydrogen neighbors increases. Again, all DFT methods, regardless the functional, basis set, or technique of shielding calculation, agree very well in their results. Hartree−Fock is underestimating the shift, and B3LYP is inbetween the two methods, very close to the unit slope. The MP2 method gives reasonable results but is further off the slope with respect to B3LYP. Van Wazer et al.[52] observed similar results for HF calculations with smaller basis sets than the present DFT results.

3.4 Empirical Correction for the Silanes. Empirical corrections to improve the results of *first principles* NMR calculations are quite frequently proposed in the literature. These treatments can remove the major part of systematic errors which are accumulated in the calculations. For example, recently Forsyth and Sebag[53] proposed a scheme for the description of ^{13}C NMR chemical shifts of organic compounds calculated with B3LYP on MM3 geometries. They correlated their values with experiment, fixed the slope to unity and the intercept to zero and reduced the RMS error from ~10 ppm to ~3 ppm for a variety of molecules.

Here, we suggest applying a different treatment which takes the systematic behavior of the errors into account:

$$\delta_{\mathrm{TMS}}(X) = \sigma(TMS) - \sigma(X) + n_{Si}(X)\alpha + \beta \tag{1}$$

where α is the difference of the intercepts of sets $n_{Si} = 1$ and $n_{Si} = 2$, and β is determined by the difference between the experimental and calculated shifts of the central Si atom in the trisilane. This silicon was chosen because it is located in the central area of chemical shifts of silanes. With this correction, a nearly perfect agreement between calculated and measured chemical shifts is obtained (see Table 3 and Figure 2d). Such empirical correction formulas can be used for highly accurate predictions of chemical shifts with DFT-based calculations, even though the problem of an underestimated shift, when hydrogen is bound to silicon, is not yet solved theoretically.

4. Conclusions

Calculated chemical shifts in silanes correlate quite well with experiment for all methods used in this paper. Problems occur in an accurate quantitative description of the chemical shifts as the number of hydrogen atoms bound to the Si atom is increased. Nonetheless, by empirical correction formulas DFT calculations

TABLE 6: ^{29}Si NMR Chemical Shifts of Fluorinated Monosilane SiH_xF_{4-x} with Respect to TMS in ppm

	VWN			PW86	B3LYP	HF	MP2	
	IGLO	LOC1	GIAO	IGLO	GIAO	GIAO	GIAO	expt
SiH_3F	−6.7	−11.2	−3.6	−8.1	−20.3	−28.9	−24.9	−17.4
SiH_2F_2	−13.8	−16.5	−8.6	−12.3	−28.8	−39.7	−30.4	−28.5
$SiHF_3$	−72.9	−73.7	−66.0	−69.9	−79.0	−82.5	−75.7	−77.8
SiF_4	−112.1	−110.4	−104.0	−112.4	−114.0	−116.9	−108.6	−112.0

[a] Experimental values are taken from ref 50.

TABLE 7: ^{29}Si NMR Chemical Shifts of Methylsilanes $SiH_x(CH_3)_{4-x}$ with Respect to TMS in ppm[a]

	VWN			PW86	B3LYP	HF	MP2	
	IGLO	LOC1	GIAO	IGLO	GIAO	GIAO	GIAO	expt
SiH_3CH_3	−77.8	−80.1	−75.5	−82.3	−67.6	−58.9	−71.1	−65.2
$SiH_2(CH_3)_2$	−43.6	−44.5	−41.2	−45.4	−36.9	−32.8	−40.7	−37.7
$SiH(CH_3)_3$	−18.1	−18.1	−16.3	−18.2	−14.6	−13.2	−16.9	−15.5
$Si(CH_3)_4$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] Experimental values are taken from ref 51.

can predict these shifts within an accuracy of few parts per million. There seems to be also an advantage over the HF method, if the number of Si atoms bound to the silicon atom under consideration is increased. In these cases DFT performs as well as MP2.

This trend seems to be general since it has also been observed for model clusters of siliceous zeolite frameworks: δ_{Si} values calculated for the central silicon of $Si(OSiH_3)_4$ models with CHF and with DFT-based method are very comparable. However, increasing the cluster with two other shells of neighbors improves systematically the DFT results,[22] whereas the improvement of the CHF results is not regular.

The differences between different exchange-correlation functionals within LDA and even gradient corrected LDA functionals are rather small. There are also no significant differences between the IGLO and the GIAO treatment.

Enlargement of the basis sets employed in this study does not change the results. However, the size and shape of a basis set affects the "virtual basis", the basis which is used to expand the magnetically perturbed wave function, only indirectly. Since gap energies of the HF method are about twice as big as in the case of DFT, the shape of the virtual orbital basis is expected to be rather different and might be an explanation of the big deviations we observe between DFT and (*post*) HF methods. Another indication for this argument is the almost constant shift of the DFT results with respect to HF when applying an hybrid method (cf. meaning see Figure 1).

However, the reason for the deviations of the calculated chemical shifts from the measured ones for Si with a large number of surrounding hydrogens is not yet clear. In the present paper we have checked several influences (basis sets, GIAO vs IGLO, exchange-correlation functionals, geometry, ...), but none of these factors could explain the deviations sufficiently. If we assume that MP2 calculations and experiment give correct ^{29}Si NMR chemical shifts of silanes, we can exclude that solvent effects are responsible for the deviations we observe employing DFT. Unfortunately, no information about the influence of the solvent on the ^{29}Si NMR shifts of those compounds could be found in the literature. As mentioned in the Introduction, there is still a lack of proper description for the current contributions to the exchange-correlation potential and contributions to the vector potential, as they appear in a rigorous treatment of the nuclear magnetic shielding within the current density functional theory. However, as already pointed out in refs 7 and 54, the current contributions to the vector potential are usually (apart from systems with 4f-states or superhigh magnetic fields) small, compared with the external vector potential. Concerning the contributions to V_{xc}, the situation is not as clear, but there is no obvious reason such effects should be especially important for silicons with Si−H bonds of a silicon and less important for silicons with Si−F, Si−C, or Si−Si bonds.

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