Correlation of Empirical δ(TMS) and Absolute NMR Chemical Shifts Predicted by ab Initio Computations

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A set of reference linear correlations is presented to convert ab initio quantum mechanically computed absolute chemical shielding tensors into the more common empirical δ(TMS) values. Large deviations between computed and experimental values are discussed in regards to chemical dynamics.

Computational NMR methods provide predictions of absolute chemical shift shielding tensors that need to be correlated to conventional δ(TMS) values for comparison with results from typical NMR experiments.[1–3] In an experiment, δ(TMS) values would be assigned by reference to an in situ signal for TMS or predetermined standard. In principle, one could use a similar approach computationally, by computing the absolute chemical shift for TMS and taking the difference between that value and the absolute shift computed for the nucleus in question. This approach makes the implicit assumption that a correlation exists between the absolute and empirical shifts with the form [$\delta = m\sigma + b$], where $m = 1$ and only the value for the axis shift, b, is important. Although the assumption of linearity appears to be well founded, the slope of the line is in general not 1 and is dependent on computational method and basis set. Thus, at present levels, computational ^{1}H NMR studies referenced only to TMS are inherently flawed and at least linear correlation equations are needed. Furthermore, in order to obtain useful chemical shift predictions over the full spectral window, these empirical correlations must display a high degree of linearity ($R^2 > 0.999$).[1,2] This study establishes a restricted set of reference hydrocarbons and generates empirical equations for the conversion of ab initio to δ(TMS) chemical shifts at various computational levels.[3]

Computational Considerations

Molecular structures have been optimized at the restricted Hartree–Fock (RHF) self-consistent field (SCF) level of theory with the aid of the analytically determined gradients and the search algorithms contained with GAMESS[4] and GAUSSIAN94.[5] In addition, effects of dynamic correlation have been addressed using hybrid density functional method (HDFT).[6] The HDFT methods employed two different exchange–correlation functionals, Becke's three-parameter functional[7] in combination with nonlocal correlation provided by the Lee–Yang–Parr expression,[8,9] which contains both local and nonlocal terms, B3LYP, and with the nonlocal correlation provided by the Perdew 91 expression,[10] B3PW91. For discussion of the effect of basis set on structure and magnetic properties, a variety of basis sets have been employed. These include 3-21G(nd,mp),[11] 6-31G(nd,mp),[12,13] DZV(2d,p),[14] DZV+(2d,p),[14] 6-311G(nd-,mp),[15] cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, and aug-cc-pVTZ,[16–18] where $n = 0$–2, $m = 0$–1. (Table 1). From these data, correlation lines are generated and evaluated for linear fit and slope.

Calculation of magnetic properties necessitates consideration of the gauge-invariance problem.[1,2,19,20] This problem results from the fact that the magnetic field appears in the Hamiltonian in the form of a vector potential the origin of which (gauge origin) is not fixed. A common gauge origin (CGO) may be chosen, such as the origin of the molecular coordinate system, but computations short of an infinite basis set yield magnetic properties dependent on the choice of the gauge origin. Thus, the truncated basis sets, commonly used in ab initio calculations, result in significant error due to gauge variance. More advanced solutions to this problem are the distributed origin approaches that introduce local gauge origins to define the vector potential. In these methods, the gauge factors are either explicitly contained in the atomic orbitals or in some manner incorporated into the molecular or localized molecular orbitals. One categorization of such methods for the work presented here is summarized in Table 1.

Discussion

The first issue at hand is to establish a reference set of hydrocarbons for developing the required correlation lines. We decided to use a relatively small set of structures that nonetheless span a reasonable range of chemical shifts and bonding types. The hypothesis to be tested is whether good linear correlations can be obtained over these hydrocarbons and shift positions so that the need for redundancy could be minimized. The compounds chosen were benzene δ(7.14), ethene δ(5.31), ethyne δ(1.47), ethane δ(0.88), methane δ(0.13), and TMS δ(0.00).

Fundamental problems encountered in the calculation of magnetic properties include the following: the consideration of what/where gauge origins are to be; the adequacy of basis set in terms of convergence or near-convergence to the Hartree–Fock limit; the careful examination of predicted results as a function of overall computational method.[1,2,19] We considered these issues at several levels. First, basis set adequacy and overall predictability of the test set using one of the class III methods is discussed. Second, the gauge problem is examined by carrying out calculations of absolute shieldings on the test set using several different gauge origin techniques at a variety of basis sets. Third, predictions of chemical shieldings on interesting and relevant molecules outside our test set are presented.

Although standard R^2 factors can provide a reasonable gauge of the linear fit, exceptional linearity ($R^2 > 0.999$) is needed if the results are going to be experimentally meaningful here. The

Correlation of NMR Shifts

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TABLE 1: Classification of Computational Magnetic Shielding Techniques

	method	technique	performance comments
class I	SGO[a]	gauge origin taken as the molecular origin	relatively poor performance unless Hartree−Fock basis set limit considered
class II	CSGT[b]	gauge continuously transformed back to the reference	superior to SGO methods, although still requires adequate basis set functionality. CSGT and IGAIM perform identically in most cases.
	IGAIM[c]	gauge origin taken as the basin of charge density within bonds	
class III	IGLO[d] LORG[e]	partition shielding into parts related to specific spatial regions of the molecule	significant improvements over class I and II methods, with reasonable computational effort required
	GIAO[f]	complex exponential dependence on the part of the vector potential arising from the external uniform magnetic field	efficient in terms of convergence of chemical shift values as a function of basis set. Allows reliable values with relatively smaller basis sets.

[a] Reference 19. [b] Reference 21. [c] Reference 22. [d] References 23 and 24. [e] References 25 and 26. [f] References 27 and 28.

TABLE 2: Computed (GIAO) and Experimental δ(TMS) Chemical Shifts for Reference Hydrocarbons.

method[a]	benzene	ethene	ethyne	ethane	methane	TMS	average deviation
RHF/3-21G	26.24 (6.93)	27.73 (5.51)	31.83 (1.64)	32.82 (0.70)	33.11 (0.42)	33.84 (−0.27)	0.22
RHF/3-21G(d,p)	25.1 (7.00)	26.66 (5.52)	31.08 (1.32)	31.77 (0.67)	31.97 (0.47)	32.52 (−0.05)	0.18
RHF/6-31G	25.79 (6.98)	27.43 (5.48)	31.72 (1.58)	32.64 (0.74)	33.06 (0.36)	33.68 (−0.20)	0.17
RHF/6-31G(d)	25.3 (7.16)	27.29 (5.25)	31.10 (1.57)	31.90 (0.79)	32.38 (0.33)	32.90 (−0.17)	0.11
RHF/d95+(2d,p)	24.46 (7.06)	26.37 (5.29)	30.08 (1.86)	31.33 (0.70)	31.81 (0.26)	32.34 (−0.23)	0.17
RHF/6-311g(2df,pd)	24.74 (7.19)	26.76 (5.26)	30.83 (1.38)	31.45 (0.79)	31.85 (0.41)	32.39 (−0.10)	0.11
BPW91/6-311G(2df,2p)	24.0 (7.10)	25.84 (5.41)	30.39 (1.17)	30.65 (0.93)	31.41 (0.22)	31.53 (0.10)	0.13
B3LYP/cc-pVDZ	24.16 (7.07)	25.81 (5.45)	30.13 (1.18)	30.40 (0.92)	31.04 (0.28)	31.30 (0.03)	0.12
B3LYP/cc-pVTZ	24.16 (7.15)	26.04 (5.37)	30.59 (1.06)	30.82 (0.85)	31.52 (0.18)	31.37 (0.32)	0.15
B3LYP/aug-cc-pVDZ	23.98 (7.08)	25.76 (5.42)	30.18 (1.28)	30.56 (0.93)	31.30 (0.24)	31.57 (−0.02)	0.09
B3LYP/aug-cc-pVTZ	24.07 (7.14)	25.99 (5.36)	30.54 (1.15)	30.80 (0.91)	31.45 (0.31)	31.74 (0.05)	0.11
B3LYP/DZ+(2d,p)	24.00 (6.99)	25.68 (5.44)	29.72 (1.70)	30.69 (0.80)	31.45 (0.10)	31.67 (−0.10)	0.12
B3LYP/6-311G(2df,pd)	24.32 (7.11)	26.21 (5.37)	30.67 (1.23)	30.95 (0.98)	31.65 (0.33)	32.11 (−0.10)	0.12
B3PW91/cc-pVDZ	24.05 (7.05)	25.70 (5.46)	30.06 (1.24)	30.44 (0.87)	31.07 (0.26)	31.30 (0.04)	0.11
B3PW91/cc-pVTZ	23.99 (7.12)	25.86 (5.40)	30.46 (1.17)	30.76 (0.90)	31.45 (0.26)	31.64 (0.09)	0.11
B3PW91/aug-cc-pVDZ	23.88 (7.07)	25.65 (5.43)	30.11 (1.30)	30.55 (0.89)	31.26 (0.23)	31.50 (0.01)	0.08
B3PW91/aug-cc-pVTZ	23.92 (7.12)	25.82 (5.39)	30.42 (1.19)	30.75 (0.90)	31.45 (0.26)	31.63 (0.09)	0.12
experiment	7.14	5.31	1.47	0.88	0.13	0.00	

[a] Geometry as well as property computed at the indicated level.

"closeness" of the slope to 1 is an additional criterion for choosing a linear correlation over an axis shift correction. How far does the slope have to deviate from 1 before it is necessary to use a linear correlation instead of a simple axis offset? A typical ¹H NMR spectrum spans a window of about 17 ppm, from 12 to −5 ppm on the δ scale. Proton resonances are reported to two significant figures past the decimal, but simple solvent effects on hydrocarbons can cause ca. 0.1 ppm changes. If one required less than 0.2 ppm deviation throughout the scale, that level of precision could only be achieved by an axis shift method if the slope were between 0.99 and 1.01. Thus, even methods that display impressive linear correlations but manifest a slope of 0.98 would result in serious errors in the shifts at the extremes of the spectrum, if a simple axis shift method were

used. It is with this level of scrutiny that we evaluate the following correlations.

Chemical shifts were computed using the GIAO method at a variety of different basis sets and employing RHF, DFT, and HDFT methods (Table 2). In general, the effect of increasing basis set size is to lower the value of the absolute chemical shift. Addition of polarization functionality decreases the predicted value by as much as 1 ppm for the set of molecules considered in our test set. The addition of a triple split from a double split in basis set quality tends to increase the predicted value, whereas the addition of polarization functionality tends to decrease the predicted value [e.g., compare effects seen with the Dunning basis sets]. The implementation of the density functional techniques decreases the prediction by up to 1 ppm.

TABLE 3: Correlation Parameters (Slope, Intercept, and R^2) for Reference Set of Molecules[a]

method	slope (m)	intercept (b)	R^2 factor
RHf/3-21G	−0.9476	31.79	0.9966
RHF/3-21G(d,p)	−0.9515	30.89	0.9972
RHF/6-31G	−0.9098	30.44	0.9980
RHF/6-31G(d)	−0.9660	31.61	0.9990
RHF/DZ+(2d,p)	−0.9253	29.69	0.9971
RHF/6-311G(2df,pd)	−0.9527	30.75	0.9988
BPW91/6-311G(2df,2p)	−0.9317	29.48	0.9986
B3LYP/cc-pVDZ	−0.9867	30.91	0.9985
B3LYP/cc-pVTZ	−0.9459	30.00	0.9969
B3LYP/aug-cc-pVDZ	−0.9352	29.51	0.9993
B3LYP/aug-cc-pVTZ	−0.9250	29.40	0.9984
B3LYP/DZ+(2d,p)	−0.9251	29.19	0.9988
B3LYP/6-311G(2df,pd)	−0.9256	29.62	0.9987
B3PW91/cc-pVDZ	−0.9684	30.35	0.9989
B3PW91/cc-pVTZ	−0.9186	29.15	0.9986
B3PW91/aug-cc-pVDZ	−0.9272	29.22	0.9993
B3PW91/aug-cc-pVTZ	−0.9118	28.93	0.9987

[a] Data are plotted as y_{corr} = intercept + slope × y_{calcd}.

The behavior of B3LYP vs B3PW91 is nearly identical, with the latter functional combination tending to predict slightly lower values of shifts than the former.
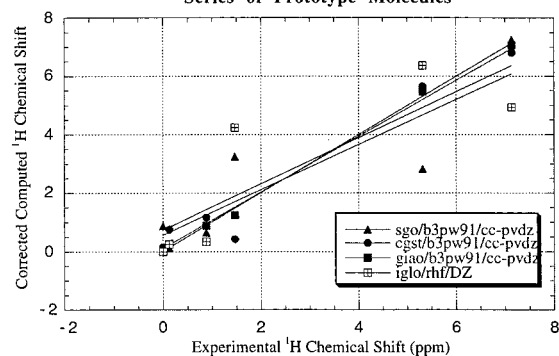
Results presented here indicate that the B3LYP/cc-pVDZ basis set gives the slope closest to 1.00 (0.987), but this value still falls short of 0.99 and therefore supports the use of a linear correlation instead of an axis offset. Almost all of the basis sets and dynamic correlation methods result in what would appear to be reasonable linear fits (0.996 < R^2 < 0.999) and slopes (0.910−0.987) (Table 3). These regression parameters can, however, be somewhat misleading. For example, although one can obtain an R^2 of 0.997 and slope of 0.948 using the 3-21G basis set, the scatter of data around the line is much greater than that for the higher levels of theory (average deviation of 0.19 vs 0.08 ppm for B3PW91/aug-cc-pVDZ). In terms of linear fit, R^2 values below 0.999 do not correlate with average variances of less than 0.10 ppm. The best overall behavior comes from hybrids of cc-pVDZ and aug-cc-pVDZ with B3LYP or B3PW91; B3PW91/aug-cc-pVDZ and B3LYP/cc-pVDZ displayed average variances of only 0.08 and 0.11 ppm, respectively. These latter methods provide predictions that well exceed the performance of empirical additivity schemes and functional group reference tables. Thus, they should be tested in structure determination applications.

In these studies, we have obtained optimized geometries as well as the respective property computation at the level indicated. Earlier, it has been emphasized that accurate geometries and wave functions are important in order to obtain shifts in good agreement with experimental results. The addition of dynamic electron correlation does not always give a much better fit or slope for NMR correlations, and coincidentally, addition of electron correlation in conjunction with lower basis sets has been observed to cause overexpanded bond lengths in annulenes.[29−31] With higher basis sets, these lengths return to normal.

Comparison of Methods of Predicting ^{1}H Chemical Shifts for a Series of Prototype Molecules

Figure 1. Plot of δ(TMS) vs absolute chemical shift computed using four methods of gauge origin.

These problems associated with the prediction of geometries likely manifest an effect on the performance of the NMR methods as well.

In addition to the effect of basis set and dynamic correlation on the prediction of chemical shifts, the data illustrate the superiority of the GIAO method over other choices of computing chemical shifts. Single gauge origin, SGO, continuous set of gauge transformation, CSGT, individual gauge for atoms in molecules, IGAIM, and individualized gauge for localized orbitals, IGLO, were compared. We note that the IGAIM method gives results identical to the CSGT results presented here, and so only the latter are reported in Table 4.

Only a subset of computational methods were chosen from that performed with our GIAO analysis in the above section. In particular, it is at the lower end of basis set choice that the major differences surface. Although fair results can be obtained with smaller basis sets in combination with the more superior gauge invariant methods, the class I and II methods require the use of larger basis sets, supplemented with polarization functionality. In particular, data in Table 4 illustrate the significant decrease in the R^2 factor that results from using the SGO or CSGT(=IGAIM) compared to GIAO methods, especially for the smallest basis sets (0.66 < R^2 < 0.83). The estimated slopes from any of these basis set choices are significantly far from 1. The superiority of the CSGT(=IGAIM) method over the SGO method comes out with the larger basis sets considered. At the cc-pVDZ level, the R^2 is already improved to 0.98 for CSGT and the slope is significantly closer to 1 (calcd, 0.87); however, only at the larger aug-cc-pVTZ basis set would CSGT have predictability (R^2 = 0.998) approaching that of GIAO. Figure 1 shows the computational methods of predicting the magnetic shielding considered above, at the level of theory that was optimal using the GIAO methodology (B3PW91/cc-pVDZ). In addition, one final comparison is made with available data of Schindler and Kutzellnigg, using their IGLO method. These data were computed at the RHF level of theory using a comparable basis set of double-ζ quality ((7,3/3) Huzinaga basis set in the

TABLE 4: Correlation Parameters (Slope, Intercept, and R^2) for Alternative Computational Methods[a]

method	intercept (b)		slope (m)		R^2 factor	
	SGO	CSGT	SGO	CSGT	SGO	CSGT
RHF/3-21G	5.17	21.50	−0.1682	−0.6567	0.8113	0.6591
RHF/6-31G	5.03	22.98	−0.1668	−0.7151	0.8069	0.6790
RHF/6-31G(d)	7.52	31.56	−0.2697	−1.025	0.7778	0.8281
RHF/6-311G(d,p)	14.68	32.21	−0.4647	−1.028	0.9229	0.9800
B3PW91/cc-pVDZ	9.97	33.18	−0.3242	−1.100	0.8802	0.9794
B3PW91/aug-cc-pVTZ	16.55	29.31	−0.5368	−0.9240	0.9479	0.9984

[a] Data are plotted as y_{corr} = intercept + slope × y_{calcd}.

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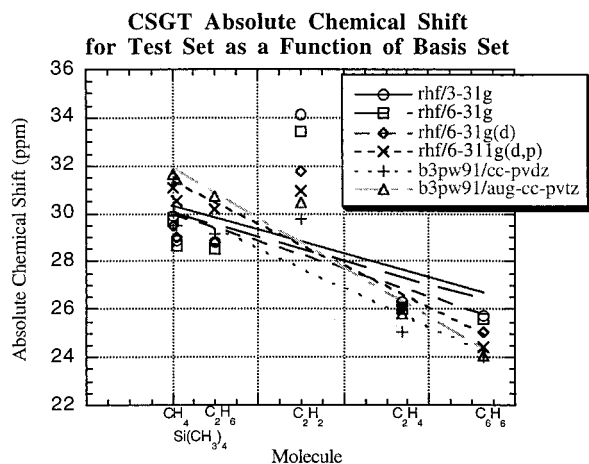
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Figure 2. Plot of δ(TMS) vs absolute chemical shift computed using CSGT(=IGAIM) at a variety of levels of theory.

contraction (4,1,1,1;2,1/2,1)[32]). As pointed out in Schindler and Kutzellnigg's paper, the agreement with experimental results is greatly improved with the addition of polarization functions. At the level shown in this plot, the IGLO method shows agreement slightly less good than the CSGT(=IGAIM) method. None of these methods outperforms GIAO. In any case, these methods do not meet the general utility standard laid out at the beginning of our discussion.

Among all the molecules considered in the test set, it is the triple-bonded system, acetylene, that appears to be the most difficult test (Figure 2). Vibrational corrections, of which more will be discussed later, may help this problem and tighten up the correlations.

The ultimate test of utility in such correlations comes from their ability to assign signals outside of the reference group of compounds on which the regression was performed. In particular, we looked at four specific hydrocarbons with novel chemical features, trisbicyclohexenobenzene, **1**,[33] corannulene, **2**,[34] dimethyldihydropyrene, **3**,[35,36] and [18]-annulene, **4**,[37] at three levels of theory (Table 5), along with their known experimental values.
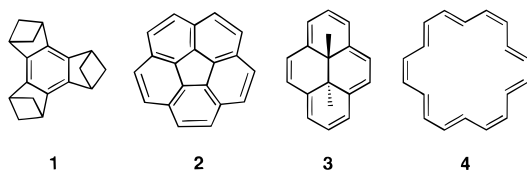
These compounds demonstrate a wide variability in their NMR signals. The predictions made by IGAIM and GIAO at

comparable basis set and correlation method show that GIAO does a better job with this set of hydrocarbons. A predictive accuracy of 0.2−0.3 ppm would seem reasonable to expect, although some glaring exceptions can be seen, especially in the case of the inner protons of **4**.

The reliability of computational NMR methods is now high enough for us to gain chemical insight when static computational values disagree with experimental observations. The weak fuzziness of the predictive character ($\pm$0.3 ppm) will likely be sorted out by incorporation of better basis sets or inclusion of solvent effects, but it is our opinion that errors significantly greater than 1 ppm are indicative of something more than failures of the static methodology. The incredible difference in accuracy between the predictions for **1**−**3** and **4** point to a special characteristic of **4**. We believe that out-of-plane librational modes may cause a significant change in the NMR properties of **4**. In general, vibrational motion perturbs chemical shifts.[2] The sensitivity of ^{13}C NMR shifts to small molecular motions has been noted in carbocation studies.[38] For many cases, this correction may be negligible, but for molecules such as **4** it is likely very important. Another conspicuous prediction is the ca. 1 ppm miss for the methyl signals in **3**. One could argue that this points to a mishandling of the ring current instead of dynamic effects. Certainly both these factors may be at play, but given the quality of the basis set, our next investigation will be to study the dynamical correction.

Effects due to molecular vibrations and librations are a likely source of variance.[39] Because the NMR predictions are made from geometries at r_0 and not r_{eq}, a vibrational correction is always missing,[2] but an additional correction arises for molecules vibrating about a symmetric structure. Although the r_{eq} may coincide with the spatially averaged structure, positive and negative spatial distortions can have the same effect on the NMR shift; therefore, some structure Δx distorted from the r_{eq} better betrays the NMR spectrum. Structures like acetylenes and annulenes have such low-energy distortion modes. This situation is also well exemplified by "highly symmetric" molecules that manifest their symmetry through time-averaging but essentially never exist in the precise high-symmetry form. Because symmetry-related distortion must have similar perturbations on the NMR shift, the average of positive and negative spatial distortions will not cancel out. For example, methane would be more closely represented by a C_{3v} than a T_d structure, acetylene would be more like C_s than C_∞, and [18]-annulene would distort out of plane to D_{3d} or C_{6v}. Specific attention to vibrational effects on the prediction of proton NMR resonances is an essential avenue for research. Inclusion of a vibrational correction into the treatment of our reference set of compounds will likely

TABLE 5: Comparison of Experimental and Computed δ(TMS) Values for 1-4

compound	exptl δ(TMS)	IGAIM BPW91/6-311G(2df,2p)		IGAIM B3PW91/cc-pVDZ		GIAO B3PW91/cc-pVDZ	
		calcd[a]	corr[b]	calcd[a]	corr[b]	calcd[a]	corr[b]
1	2.52	28.6	3.0	27.9	2.8	28.9	2.4
	2.27	29.0	2.6	28.5	2.2	29.4	1.9
	3.22	28.1	3.4	27.7	3.0	28.4	2.8
2	7.80	23.4	8.2	23.7	7.2	23.6	7.5
3	8.08	22.6	9.0	22.5	8.3	22.8	8.3
	8.62	22.1	9.5	22.0	8.3	22.2	8.8
	8.67	21.9	9.6	21.9	9.0	22.2	8.9
	−4.25	36.7	−5.2	35.9	−6.0	37.1	−5.6
4[c]	−3.0	41.8	−10.3	43.2	−13.1	43.0	−11.3
	9.0	19.9	11.7	20.1	10.9	20.2	10.8

[a] Calcd refers to the calculated value. [b] Corr refers to the corrected value using the linear regression of the test set at these levels: for IGAIM/BPW91/6-311G(2df,2p), 31.65 − 1.002(calc), R^2 = 0.9591; for IGAIM/B3PW91/cc-pVDZ, 31.64 − 1.034(calcd), R^2 = 0.9215; for GIAO/B3PW91/cc-pVDZ, 30.35 − 0.968(calcd), R^2 = 0.9989. [c] Note that even with B3PW91/DZ(2df,2p)//B3PW91/DZ(2df,2p) GIAO computations, the absolute ^{1}H chemical shift values are 42.62 and 19.80.

improve the agreement with experimental results and the linearity of the regression. Appropriate restriction of the dynamics in **4** could result in further upfield shifts of the inner protons.

Conclusions

Simple differences between computed ^{1}H NMR shift values for TMS and "test" nuclei do not provide reliable predictions for experimental δ(TMS) values. These unacceptable predictions stem from the fact that although the relationship between experimental and computed shifts can be roughly linear, presently accessible methods do not give linear correlations with slopes close enough to 1. Nonetheless, when a linear conversion formula derived from a small set of reference hydrocarbons is used, reasonable (± 0.3 ppm) predictions can be made for a test set of novel hydrocarbons. Class III methods, such as GIAO or IGLO, show the best overall performance. In cases where large discrepancies (i.e., greater than 1 ppm) are observed, we conclude that dynamical factors play an important role in perturbing the NMR spectrum.

References and Notes

(1) Chesnut, D. B. *The Ab Initio Computation of Nuclear Magnetic Resonance Chemical Shielding*; Lipkowitz, K. B., Boyd, D. B., Ed.; VCH Publishers: New York, 1997; Vol. 8.

(2) Chesnut, D. B. *Chem. Phys.* **1997**, *214*, 73−79.

(3) For leading work on ^{13}C NMR correlations, see: Forsyth, D. A.; Sebag, A. B. *J. Am. Chem. Soc.* **1997**, *119*, 9483−9494.

(4) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Albert, S. T. *Quantum Chem. Program Exchange Bull,* **1990**, *10*.

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN94-DFT*, B.1 ed.; Gaussian, Inc.: Pittsburgh, PA, 1994.

(6) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(8) Lee, T. J.; Rice, J. E. *Chem. Phys. Lett.* **1988**, *150*, 406.

(9) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(10) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(11) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939−947.

(12) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728.

(13) Hehre, W. J.; Lathan, W. A. *J. Chem. Phys.* **1972**, *56*, 5255.

(14) Dunning, T.; Hay, P. *Gaussian basis sets for molecular calculations*; Schaefer, H. F., Ed.; Plenum Press: New York, London, 1977; p 1.

(15) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

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

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

(18) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(19) Chesnut, D. B. *Ab Initio Calculations of NMR Chemical Shielding*; Webb, G. A., Ed.; Academic Press: San Diego, 1994; Vol. 29.

(20) Chesnut, D. B. *Some Recent Ab Initio Calculations of the NMR Chemical Shift*; Webb, G. A., Ed.; Academic Press: San Diego, 1989; Vol. 21.

(21) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223.

(22) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *194*, 1−8.

(23) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193.

(24) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

(25) Bouman, T. D.; Hansen, A. E. *Chem. Phys. Lett.* **1988**, *149*, 510.

(26) Hansen, A. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5035.

(27) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8521.

(28) Ditchfield, R. *J. Chem. Phys.* **1972**, *56*, 5688.

(29) Baldridge, K. K.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 745−748.

(30) Schulman, J. M.; Disch, R. L. *J. Mol. Struct.: THEOCHEM* **1991**, *234*, 213−225.

(31) Gorter, S.; Rutten-Keulemans, R.; Krever, M.; Romers, C.; Cruickshank, D. W. J. *Acta Crystallogr.* **1995**, *B51*, 1036−1045.

(32) Huzinaga, S. *Approximate Atomic Wave Functions. I*; University of Alberta: Edmonton, 1971.

(33) Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102−2103.

(34) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921−1923.

(35) Mitchell, R. H.; Lai, Y. H.; William, R. V. *J. Org. Chem.* **1979**, *44*, 4733−4735.

(36) Boekelheide, V.; Hylton, T. *J. Am. Chem. Soc.* **1967**, *89*, 1695.

(37) Gaoni, Y.; Melera, A.; Sondheimer, F.; Wolovsky, R. *Proc. R. Soc.* **1964**, 397.

(38) Schleyer, P. v. R.; Carneiro, J. W. d. M.; Koch, W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3990−3992.

(39) Forsyth, D. A.; Panyachotipun, C. *Res. Chem. Intermed.* **1996**, *22*, 725−35.