Calculation of NMR Chemical Shifts for Taxol and α-Pinene within the Generalized Gradient Approximation

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ABSTRACT: Simulations of the nuclear magnetic shielding within the generalized gradient approximation (GGA) for α-pinene and taxol were carried out to assess the performance of the method for bigger molecules. The localized orbital/local origin gauge (LORG) formalism and the modified "0.05" Becke's three-parameter exchange functional and the gradient-corrected functional of Lee, Yang, and Paar (B3LYP) proposed recently by Wilson and others was used. A modest dependence of the results on the basis set size was observed. For the current implementation, the uncoupled calculations were up to 47 times faster than the usual coupled-perturbed (CP)–gauge-invariant atomic orbital (GIAO) method and provided similar accuracy. Reproducing both the absolute as the relative chemical shifts the GGA/LORG procedure can thus be used as a faster alternative to the coupled techniques. Int J Quantum Chem 91: 277–283, 2003

Key words: DFT; generalized gradient approximation; LORG; NMR

Introduction

The density functional theory (DFT) methods revolutionized many areas of computational chemistry, because of their simplicity and low cost [1, 2]. Particularly challenging for simulations of nuclear magnetic resonance has been the generalized gradient approximation (GGA) formulation of DFT. In this case, the magnetic perturbation can be handled as a one-electron problem, which significantly reduces computational demands [3, 4]. Despite renewed interest in the past, the method is still used rather sporadically and was tested on a limited number of systems. Nevertheless, as shown below, the method can compete in performance with the usual coupled- perturbed (CP) techniques also for larger organic molecules and is stable for a broader variety of basis sets.

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Simulation techniques of nuclear magnetic resonance (NMR) parameters underwent significant development in the last three decades. For example, origin dependence of calculated chemical shifts [5, 6] was overcome in many ways. Formalism based on the gauge invariant atomic orbitals (GIAO, also called London- or magnetic field–dependent AOs) has been established as a good standard [7, 8]. Alternative theories such as LORG (localized orbital/local origin) [9], IGLO (individual gauge for localized orbitals) [10], CSGT (continuous set of gauge transformations) [11] or IGAIM (individual gauges for atoms in molecules) [11] provide similar results but differ in computational speed and problems associated with their implementation [12]. For calculation within GGA, the LORG method originally formulated for the random phase approximation [9] was found suitable in previous work [3] and is also used here.

Another important aspect of GGA that should be mentioned is the correspondence of Kohn–Sham orbital energies to electronic excitation energies [13, 14] or, more generally, to sum over states (SOS) calculations of molecular properties. Approximate DFT-SOS schemes were applied for calculations of the vibrational circular dichroism [15], Raman optical activity [16], or nuclear spin–spin coupling constants [17, 18]. In contrast to these properties, however, NMR shielding within the GGA scheme can be obtained exactly. Formally, the coupled-perturbed and sum over states formulae coincide. Thus, if suitable functional is found, accuracy of the Schrödinger limit can be achieved for simulated NMR parameters using a simple noniterative equation. The GGA scheme may not be valid when the electric current density is included in the DFT functional. Yet the current dependence has not been explored sufficiently and a vast majority of the functionals used in chemistry ignore it. Relativistic effects can be incorporated into GGA using pseudopotentials similarly as for other DFT methods [19], but this topic is not followed in the current study.

Theory and Computation

SHIELDING TENSOR IN THE GGA SCHEME

The shielding tensor for a nucleus λ consists of a diamagnetic ($\boldsymbol{\sigma}_\mathrm{d}$) and paramagnetic ($\boldsymbol{\sigma}_\mathrm{p}$) part. Within the GGA exchange and correlation energies are functions of electronic density independent of magnetic field, which leads to the following expressions for closed-shell molecules (in atomic units) [1, 4, 20]

$$\sigma_d = \Sigma_{K,occ}\langle K|[\mathbf{r}\cdot(\mathbf{r}-\mathbf{r}_\lambda)\mathbf{E}-(\mathbf{r}-\mathbf{r}_\lambda)\mathbf{r}]|\mathbf{r}-\mathbf{r}_\lambda|^{-3}|K\rangle, \tag{1}$$

$$\sigma_p = 4\Sigma_{K,occ}\Sigma_{J,virt}(\varepsilon_J-\varepsilon_K)^{-1}\langle K|\mathbf{r}\times\nabla/2|J\rangle\langle J|\mathbf{o}|K\rangle, \tag{2}$$

where K and J denote occupied and virtual orbitals, **E** is the unit tensor, **r** and $\mathbf{r}_\lambda$ are the electron and nuclear coordinates, respectively, ϵ_i orbital energies, $\mathbf{o}=|\mathbf{r}-\mathbf{r}_\lambda|^{-3}(\mathbf{r}-\mathbf{r}_\lambda)\times\nabla$. As the exact formula for construction of the Kohn–Sham orbitals and energies is unknown [3, 4, 17] an "NMR-optimized" DFT Becke3LYP$_{0.05}$ formula was proposed by Wilson et al. [3] and is used here.

THE LORG TRANSFORMATION

Current implementation of the LORG transformation is based on localized orbitals {k, small letters} obtained by the Boys localization [21]. The orbitals are related to the canonical molecular orbitals {K, capitals} by an orthonormal transformation, $|\mathrm{k}\rangle = \Sigma_\mathrm{K}\, U_\mathrm{kK}^{-1}\,|\mathrm{K}\rangle$ and provide local origins $\mathbf{r}_\mathrm{k} = \langle \mathrm{k}|\mathbf{r}|\mathrm{k}\rangle$. Note that $\langle \mathrm{k}|\mathrm{k}'\rangle=\delta_{\mathrm{kk}'}$. After some algebra we obtain the working expression for GGA-LORG NMR shielding tensors in the Kohn–Sham orbital basis,

$$\begin{aligned}\sigma_{LORG} &= \sigma_p + \sigma_d \\ &= 4\Sigma_{K,occ}\Sigma_{J,virt}(\varepsilon_J-\varepsilon_K)^{-1}\langle K|\mathbf{r}\times\nabla/2|J\rangle\langle J|\mathbf{o}|K\rangle \\ &\quad + 4\Sigma_{K,occ}\Sigma_{J,virt}\mathbf{E}_{JK}\langle J|\mathbf{o}|K\rangle \\ &\quad + \Sigma_{K,occ}\langle K|[\mathbf{r}\cdot(\mathbf{r}-\mathbf{r}_\lambda)\mathbf{E}-(\mathbf{r}-\mathbf{r}_\lambda)\mathbf{r}]|\mathbf{r} \\ &\quad - \mathbf{r}_L|^{-3}|K\rangle + \Sigma_{K,occ}\Sigma_{L,occ}\langle K||r-r_\lambda|^{-3}[\mathbf{E}(\mathbf{r} \\ &\quad - \mathbf{r}_\lambda)\cdot\mathbf{C}_{KL} - (\mathbf{r}-\mathbf{r}_\lambda)\mathbf{C}_{KL}]|L\rangle \\ &\quad + 4\Sigma_{K,occ}\Sigma_{L,occ}\mathbf{R}_{KL}\langle L|\mathbf{o}|K\rangle \\ &= \sigma_{p1}+\sigma_{p2}+\sigma_{d1}+\sigma_{d2}+\sigma_{d3}.\end{aligned} \tag{3}$$

Arbitrary vectors were introduced, $\mathbf{C}_\mathrm{KL} = \Sigma_\mathrm{k}\, U_\mathrm{Kk}\, \mathbf{r}_\mathbf{k}\, U_\mathrm{kL}^{-1}$, $\mathbf{R}_\mathrm{KJ}=\Sigma_\mathrm{L}\ \mathbf{C}_\mathrm{KL}\times\langle \mathrm{L}|\mathbf{r}/2|\mathrm{J}\rangle$ and $\mathbf{E}_\mathrm{JK} = \Sigma_\mathrm{L}\,(\epsilon_\mathrm{J}-\epsilon_\mathrm{L})^{-1}\ \mathbf{C}_\mathrm{KL}\times\langle \mathrm{L}|\ \nabla/2|\mathrm{J}\rangle$, explicit formation of which leads to fewer floating-point operations and speeds up the calculation. The terms $\boldsymbol{\sigma}_\mathrm{p1}$ and $\boldsymbol{\sigma}_\mathrm{d1}$ coincide with the common origin formulae 1–2. The terms $\boldsymbol{\sigma}_\mathrm{p2}$ and $\boldsymbol{\sigma}_\mathrm{d2}$ ensure origin independence of

TABLE I

Relative isotropic shifts for α-pinene.

	CP/GIAO					GGA/LORG					
	6-31g	6-31g**	6-31g** 0.05[a]	6-311 ++g**	AUG	6-31g	6-31g**	6-311 ++g**	6-311 ++g**[b]	AUG	Exp. (Ref. 25)
Carbons											
1	−5.4	−4.9	−4.9	−6.5	−8.6	−4.0	−5.4	−5.7	26.0	−7.0	−27.78
2	−100.3	−99.6	−97.5	−112.2	−115.1	−89.8	−92.4	−102.0	−81.2	−104.1	−189.74
3	−73.0	−72.3	−69.9	−80.4	−80.6	−66.1	−69.4	−71.2	−60.3	−72.5	−13.38
4	10.3	10.1	10.6	8.9	10.2	10.1	6.6	10.0	31.5	9.3	−13.14
5	0.2	0.4	0.5	−0.8	−0.8	2.2	1.0	−0.4	6.0	−1.1	2.87
6	[151.1]	[148.2]	[145.2]	[137.9]	[137.94]	[188.1]	[194.6]	[150.1]	[144.0]	[140.6]	[TMS-29.88]
7	8.6	8.8	9.6	10.3	9.8	9.6	6.7	11.5	11.2	11.0	−16.87
8	16.2	16.8	18.0	17.3	16.5	17.2	13.1	18.6	15.0	18.3	10.77
9	21.8	22.2	23.7	23.1	23.6	23.1	18.6	24.6	40.8	24.3	10.14
10	19.2	19.5	20.8	19.3	20.1	19.0	14.7	20.9	65.4	20.9	20.67
Ave. dev.	11.4	11.8	12.7	9.5	9.2	13.8	11.0	12.3	27.1	11.6	0.00
Mean dev.	36.7	36.8	37.1	35.2	34.6	38.4	37.7	36.3	47.6	35.8	0.00
Hydrogens											
1	0.00	0.01	−0.01	0.04	0.07	−0.42	−0.03	0.02	3.27	0.01	0.14
3	−3.37	−3.39	−3.33	−3.54	−3.52	−3.56	−3.31	−3.38	1.27	−3.35	−3.11
4a	−0.19	−0.21	−0.24	−0.34	−0.30	−0.09	−0.22	−0.22	7.19	−0.36	−0.16
4s	−0.34	−0.28	−0.32	−0.30	−0.26	0.00	−0.19	−0.21	3.22	−0.32	−0.08
5	[30.60]	[29.61]	[29.38]	[29.83]	[29.48]	[30.76]	[29.84]	[29.26]	[26.50]	[29.24]	[TMS-2.07]
7a	0.73	0.81	0.86	1.00	0.88	1.05	0.98	1.02	7.29	0.95	0.92
7s	−0.41	−0.32	−0.32	−0.31	−0.34	−0.06	−0.19	−0.23	0.95	−0.38	−0.26
8	0.43	0.48	0.51	0.34	0.36	0.95	0.88	1.05	0.65	0.34	0.81
8	0.95	1.04	1.10	0.98	1.06	0.88	0.54	0.53	1.55	1.02	0.81
8	0.93	1.01	1.07	0.95	1.03	0.96	0.91	1.07	2.13	1.53	0.81
9	1.34	1.44	1.50	1.47	1.52	1.39	1.40	1.58	2.15	1.51	1.23
9	1.34	1.43	1.49	1.43	1.53	1.37	1.41	1.58	4.19	0.55	1.23
9	0.40	0.35	0.38	0.52	0.45	1.34	0.77	0.72	5.92	0.98	1.23
10	0.32	0.43	0.48	0.27	0.41	0.43	0.34	0.40	6.86	0.36	0.41
10	0.45	0.49	0.59	0.23	0.25	0.31	0.36	0.49	4.70	0.31	0.41
10	0.23	0.33	0.38	0.14	0.25	0.16	0.23	0.32	4.28	0.20	0.41
Ave. dev.	−0.12	−0.07	−0.04	−0.12	−0.09	0.03	−0.05	0.00	2.98	−0.08	0.00
Mean dev.	0.34	0.35	0.36	0.36	0.29	0.17	0.17	0.23	3.83	0.32	0.00

Relative shifts with respect to H_6 and C_5; absolute values for these atoms are given in square brackets.

[a] The "corrected" 0.05 B3LYP functional was used in the fourth column (for CP) and for all GGA calculations (columns 7–11).

[b] All orbitals J included in Eq. (2).

the new paramagnetic and diamagnetic parts, respectively, and $\boldsymbol{\sigma}_{d3}$ is an origin-independent correction raised because of the incompleteness of the virtual orbital space. It is important to realize that the origin transformation [cf. Eqs. (1)–(3)] does not destroy the simplicity of the method lying in the virtually one-electron formalism.

Program Gaussian [22] was used for geometry optimizations and molecular energies. The NMR tensors were calculated by the program Roa [16] that reads molecular orbitals from Gaussian.

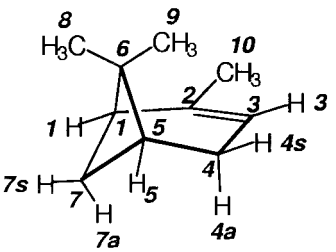

FIGURE 1. α-Pinene, numbering of carbon and hydrogen atoms.

Results and Discussion

SMALL MOLECULES

To assess basis-set dependence of the GGA method not emphasized in previous studies [3, 4] test computations were performed on a trial set of small molecules (H_2, HF, HCN, H_2O, NH_3, H_2O_2, CH_2O, CH_4, and C_2H_2) introduced by Cybulski and Bishop [23]. The results of the calculations, which can be made easily, are not listed here in detail. The following conclusions, however, appear important for computations on larger molecules: The GGA method is known to be quite sensitive to the choice of the functional [3], but the error introduced by an incomplete basis is much smaller and for medium and large bases (6-311++g**) is similar as for CP. Both methods provided results more accurate for hydrogens than for heavy atoms. Finally, the replacement of the B3LYP functional by the "0.05" functional by the standard form had rather negligible effect on computed CP shifts, unlike for the GGA results.

α-PINENE

Table I shows isotropic shifts for α-pinene (Fig. 1) as calculated by the CP and GGA methods. Relative shifts to arbitrarily selected atoms relevant for most NMR applications in chemistry are used instead of the usual TMS standard, because of additional complexity associated with computation of the standard shifts, namely, their dependence on the solvent.

Rather surprisingly, both the CP and GGA methods reproduce experimental results with approximately the same precision for all basis sets. For carbons, the GGA mean error of 38.4 ppm for the smallest basis (6–31g) is reduced only to 35.8 ppm for aug-cc-pvtz (AUG). This resembles the numbers for the CP method (36.7–34.6 ppm). Similar "basis-set independence" can be observed for the hydrogen atoms. Thus the two approaches can be considered as equivalent simulation techniques for NMR. In other words, most of the differences between computed and experimental chemical shifts are not related to the CP or GGA approximations but stem from other simplifications, analysis of which goes behind the topic of this study. Also the absolute isotropic shielding constants (indicated in the square brackets for the reference atoms) converge reasonably well with the basis set size for both methods.

As mentioned above for the small molecule set, replacement of the B3LYP functional by the $B3LYP_{0.05}$ form does not cause any qualitative change for α-pinene. This can be seen by comparison of the third and fourth columns in the Table I for the 6-31g** basis set for the CP calculation. On the other hand, such a change would have a dramatic effect on the GGA results, as found previously [3].

For the 6-311++g** basis and the GGA scheme, a trial calculation using all orbitals {J} in the expression of the paramagnetic tensor [see Eq. (2)] is presented in Table I, column 10. Although at the limit of exact wavefunction same values should be obtained, the inclusion of the occupied orbitals significantly worsens actual results, namely, for the hydrogen relative shifts. This can perhaps be explained by particular optimization of the 0.05 functional, not including all the orbital space. However, such formalism simplifies the theory (term $\boldsymbol{\sigma}_{d3}$ disappears from Eq. (3) and may find suitable applications for future functionals.

TAXOL

The taxol molecule was chosen as a popular example of even larger systems previously used for NMR benchmark calculations [12]. Its geometry

TABLE II

Relative isotropic shifts of ^{13}C in taxol.

	CP/GIAO HF/6-31g*	CP/GIAO B3L/6-31g*	CP/GIAO BPW/6-31g*	GGA/LORG $B3L_{0.05}$/6-31g*	Exp. (Ref. 12)
1	−83.4	−63.2	−58.0	−55.9	−69.7
2	−76.4	−60.2	−55.8	−54.1	−70.4
3	−75.5	−59.5	−55.1	−53.4	−70.4
4	−82.5	−62.1	−56.8	−53.7	−68.4
5	−76.6	−56.4	−51.3	−49.9	−68.4
6	−80.5	−65.8	−62.0	−60.7	−79.4
7	−120.4	−96.0	−89.4	−87.1	−108.4
9	4.3	8.4	9.0	6.6	3.6
10	−88.6	−72.1	−68.3	−64.3	−75.0
11	−75.1	−57.2	−52.4	−51.2	−68.4
12	−75.4	−57.4	−52.5	−50.9	−68.4
13	−78.1	−60.1	−55.4	−53.5	−70.1
14	−78.2	−60.4	−55.7	−53.9	−70.1
15	−76.4	−58.6	−53.9	−52.6	−73.3
16	−19.9	−14.2	−12.9	−13.3	−14.6
17	−129.0	−108.4	−102.4	−100.6	−114.1
19	−16.6	−12.4	−11.5	−12.8	−13.7
20	−95.1	−78.9	−73.9	−72.0	−83.4
21	−82.5	−70.3	−66.4	−65.7	−74.6
22	15.0	15.9	16.2	15.1	15.4
23	−17.7	−16.3	−16.4	−16.6	−20.4
24	14.7	21.5	24.6	22.6	22.9
25	35.5	45.8	48.7	44.3	43.8
26	27.2	36.9	40.3	38.7	31.7
27	29.6	38.2	41.5	39.2	36.8
28	−20.2	−15.1	−13.8	−15.4	−16.9
29	−157.3	−139.0	−133.6	−128.5	−145.0
30	[147.9]	[126.3]	[124.4]	[173.0]	[TMS-58.6]
31	40.5	50.4	53.9	50.1	49.1
32	−126.3	−104.3	−97.5	−97.3	−112.6
33	29.1	41.8	45.4	41.6	37.8
34	−13.7	−13.4	−13.7	−12.8	−13.6
35	18.3	24.9	27.2	25.1	23.0
36	−26.5	−22.6	−21.1	−19.7	−25.8
37	−25.4	−21.2	−19.4	−19.5	−22.5
38	−18.0	−12.1	−9.9	−9.7	−17.9
39	11.4	14.1	14.9	13.6	13.0
40	−126.8	−105.1	−98.5	−98.8	−111.8
41	28.5	40.2	43.5	40.0	36.0
42	−20.0	−16.2	−15.1	−16.0	−16.3
43	−118.4	−98.4	−92.7	−94.2	−108.4
44	−75.0	−60.8	−57.2	−57.3	−70.5
45	−83.2	−62.3	−57.0	−54.4	−71.6
46	−85.9	−64.9	−59.6	−56.2	−71.6
47	−74.9	−60.3	−56.2	−54.8	−70.1
48	−74.8	−59.9	−55.7	−54.0	−70.1
49	−85.9	−65.0	−59.6	−57.3	−75.1
Average Deviation	−6.9	6.0	9.6	9.9	0
Mean Deviation	8.3	7.3	11.2	12.2	0

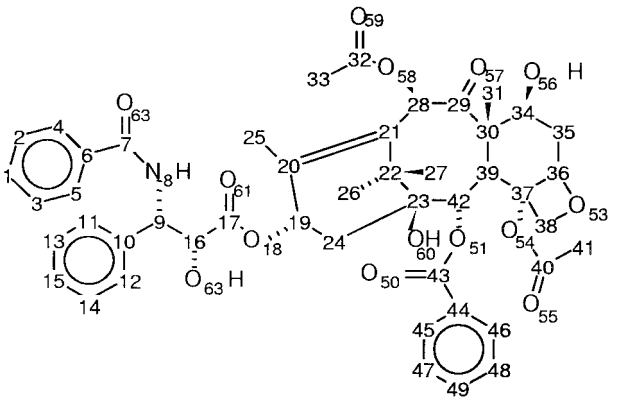

FIGURE 2. Taxol, arbitrary numbering of heavy atoms used in Table II.

was optimized at the BPW91/6-31G** level, starting from an X-ray structure of taxol carbamate [24]. The NMR shifts calculated in the 6-31g* basis for carbon atoms are collected in Table II; the numbering corresponds to Figure 2. Three approximations (HF, B3LYP (B3L), and BPW91 (BPW), columns 2–4 in Table II) for the CPU method are compared with the GGA results and experimental shifts. For the B3L functional the GGA results are slightly worse than for CP (cf. the mean deviations of 12.2 and 7.3 ppm, respectively), but this difference is minor with respect to the variations of carbon shifts and comparable to the change caused if the other (HF, BPW91) functionals are used for CP. Generally, the computed shifts faithfully follow experimental values and can thus be used for assignments of many NMR peaks. Apparently, similarly as for α-pinene, the precision for neither method is accurate enough for a complete modeling of experimental spectrum.

COMPUTATIONAL TIMES

Computer demands are heavily dependent on implementation; nevertheless, the simple formalism of the GGA method indicated in the introduction suggests a significant difference between the CP and GGA methods. As apparent from the theory only one-dimensional integrals are needed for the GGA, computation of which takes a fraction of the time needed for a single-point energy calculation. For the computations on α-pinene and taxol CPU times and required disk space are listed in Table III. An atom-by-atom computation of the tensor is implemented in the Roa program for GGA, which is not convenient for systems with many atoms and small basis sets. This is reflected in the computational times for taxol, only slightly more favorable for GGA than for CP. However, dramatic differences in required CPU times could be observed for α-pinene. The CP method is several times more time-consuming than is GGA, and the difference sharply increases as the basis size grows. Both methods require approximately the same disk space, needed for the storage of the one-electron integrals, the number of which increases as N^2, where N is the number of basis functions.

TABLE III

Times and disk spaces needed for NMR computations.

Number of basis functions	CPU time (min)		Disk space (MB)	
	LORG	GIAO	LORG	GIAO
α-pinene				
122 (6-31G)	3	20	12	20
230 (6-31G**)	13	78	37	36
342 (6-31++G**)	36	434	80	64
950 (aug-cc-pVTZ)	488	23023	500	322
Taxol				
1185 (6-31G*)	3240	4560	680	500

Different computers were used; the times were projected for one MIPS R10000/250MHz processor. All calculations were done with the $B3L_{0.05}$ functional.

The results indicate viability of the GGA methods, namely because of computational advantages. The computation of NMR shifts presented above appears more universal than a similar SOS approach to simulations of spin–spin interaction constants [18]. The latest, more advanced GGA scheme [25] overcomes the need of the empirical 0.05 functional by a self-consistent computation based on the electron densities less dependent on the parameterization.

Conclusions

The generalized gradient approximation can be used for precise computations of absolute and relative NMR shifts. The method is simpler than CP methods and therefore results in significant savings of required CPU time. Calculation of absolute isotropic shieldings in smaller bases was found to be less accurate for GGA than for CP, unlike for bigger basis sets. For relative shifts in α-pinene and taxol accuracies of both methods were found to be comparable. A significant disadvantage of the GGA

represents the empirical construction of the DFT functional, which prevents a systematic improvement of the accuracy.

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