

**Computational Studies of the  $^{13}\text{C}$  and  $^1\text{H}$  NMR  
Isotropic Chemical Shifts Using Density Functional  
Optimized Geometries. Adamantane and  
2,4-Methano-2,4-dehydroadamantane  
(a [3.1.1]Propellane) as Case Studies**

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The  $^{13}\text{C}$  and  $^1\text{H}$  chemical shift values computed at HF, BLYP and B3LYP/6-311G(d,p) levels of theory, for the BLYP/6-31G(d,p) optimized geometries of adamantane and 2,4-methano-2,4-dehydroadamantane, are reported and compared with the available experimental data. Except for the »inverted« carbon atoms, the HF values are superior to the DFT ones when the isotropic shifts with respect to TMS are in question. However, in case of the relative shifts computed with respect to the most deshielded center within the molecule, the DFT methods yield significantly better agreement with the experiment than the HF. The most probable reason for these findings may be the cancellation of errors arising from the inappropriate description of the paramagnetic contributions to the overall shielding tensor within the Kohn-Sham approach when an internal standard (within a molecule) is chosen, instead of an external one. The CSGT relative shift values correlate better with the experiment than the GIAO ones, the correlations being significantly superior at DFT than at the corresponding HF level of theory.

*Key words:* magnetic shielding, isotropic chemical shifts, *ab initio* calculations, density functional theory, adamantane, 2,4-methano-2,4-dehydroadamantane, inverted carbons.

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## INTRODUCTION

Accurate predictions of molecular response properties to external fields are of general significance in various areas of chemical physics. This especially refers to the second-order magnetic response properties, since the magnetic resonance based techniques have gained substantial importance in chemistry and biochemistry. Thus, the computed  $^{13}\text{C}$  chemical shifts are frequently used as an aid in identification of reactive ionic species,<sup>1-3</sup> while the prediction of environmental dependence of the chemical shifts in case of amino acid carbon atoms might be very helpful in elucidating the three-dimensional protein structures.<sup>4</sup>

The quantities of primary interest in due course are the nuclear magnetic shielding tensors,<sup>5</sup> defined as the mixed second derivative of the energy ( $E$ ) with respect to the magnetic moment of the X-th nucleus ( $\vec{m}_X$ ) and the external magnetic field ( $\vec{B}$ ):

$$\sigma_X^{\alpha\beta} = \frac{\partial^2 E}{\partial B^\alpha \partial m_X^\beta}$$

(where Greek superscripts denote the corresponding vector or tensor components).

It has been long recognized that prediction of the second-order magnetic response properties from the first principles, within a finite basis approximation, requires a gauge-independent algorithm.<sup>6-10</sup> Although the first such algorithm, due to Ditchfield<sup>8</sup> (based on previous works of London) appeared almost three decades ago, chemically reasonable predictions of NMR properties for molecular systems of moderate size have not been possible until recently. Within the mentioned methodology (known as GIAO – gauge independent atomic orbitals), the gauge-invariance is achieved using explicitly field-dependent basis functions.<sup>8-10</sup> Application of the GIAO approach to molecular systems was significantly improved by an efficient application of the method to the *ab initio* SCF calculations, using techniques borrowed from analytic derivative methodologies.<sup>9,10</sup> An efficient alternative to the GIAO procedure is the CSGT (continuous set of gauge transformations) algorithm<sup>6,11-13</sup> due to Keith and Bader (and its variant known under the acronym IGAIM – individual gauge for atoms in molecules).<sup>11-13</sup> Within this methodology, the nuclear magnetic shielding tensor is expressed through the induced first-order electronic current density. An accurate calculation of the last quantity by performing a gauge transformation for each point in space leads to gauge-invariant values of the shielding tensors. It has been shown that both methodologies are very useful, although it seems that the GIAO procedure is somewhat superior since it exhibits a faster convergence of the calculated properties upon extension of the basis set used.<sup>6,14-18</sup>

It is worth mentioning at this point that other methodologies, such as IGLO<sup>19,20</sup> (individual gauge for localized orbitals) and LORG<sup>21,22</sup> (localized orbital/local origin) *etc.*, have been proposed and their performances tested on a wide variety of molecular systems.<sup>23–26</sup> However, taking into account the computational cost and the effectiveness of calculation, the GIAO and CSGT methods seem to be preferable from many aspects at the present state of this subject.

It is important from the methodological aspect to study the performances of various methods for achievement of gauge invariance, especially with respect to inclusion of the dynamical electron correlation effects<sup>27</sup> and the basis set size.<sup>6</sup> Several studies of this type have been recently published,<sup>14,28–34</sup> although it does not seem that a definitive conclusion on the optimal choice of computational method has been reached. This especially refers to the problem of inclusion of dynamical electron correlation effects into the *ab initio* calculations of the second order magnetic response properties. Although the GIAO-MBPT and CC methodologies have been recently proposed<sup>35–39</sup> and successfully applied, they are computationally demanding for even modest size molecules, which are of interest to organic chemists. On the other hand, the density functional methodologies<sup>39–40</sup> offer an effective alternative to the conventional correlated methods, due to their significantly lower computational cost.

Since the Hohenberg-Kohn theorem,<sup>41</sup> it is known that the electronic energy of a given molecular system is a definite functional of the corresponding density,<sup>39–41</sup> but the exact form of this functional is not explicitly known. Various types of such (exchange and correlation) functionals have been proposed<sup>42–48</sup> either on a more mathematical or physical basis. Practically all of the proposed functionals were constructed primarily having the energetics of molecular systems in mind. However, some of them (mainly the gradient corrected ones) have been shown to be remarkably accurate in prediction of other molecular properties, such as harmonic force constants.<sup>49–51</sup> It is thus of certain interest to test their performances for prediction of the second order magnetic response properties. Several systematic studies have already been devoted to this subject<sup>14,34</sup> but mainly with respect to correlation between the computed isotropic shieldings and the measured chemical shifts. It seems that little attention has been paid to the question of performances of various theoretical approaches regarding the prediction of the relative shielding values with respect to a given center within the same molecule.

In the present paper, we report a HF SCF and density functional study of isotropic  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts for two characteristic systems: adamantane, characterized by a highly stiffened structure, and 2,4-methano-2,4-dehydroadamantane (a [3.1.1]propellane) – a system with »inverted« carbon atoms.<sup>52,53</sup> We have used optimized geometries at the gradient-cor-

rected density functional level of theory<sup>39,40</sup> with a DZP quality basis set both for the systems of interest and the standard for calculation of isotropic chemical shifts (TMS). The performances of various density functional methodologies and the conventional HF SCF procedure in predicting both the <sup>13</sup>C and <sup>1</sup>H isotropic chemical shifts and the relative shifts with respect to the most deshielded center within a given molecule were tested. Also, the efficiency of GIAO, CSGT and IGAIM algorithms for achieving gauge independence was tested with respect to the previously mentioned physical properties.

## COMPUTATIONAL DETAILS

Full geometry optimizations of adamantane and 2,4-methano-2,4-dehydroadamantane, as well as of tetramethylsilane (TMS), were performed in redundant internal coordinates with Berny's optimization algorithm<sup>54</sup> (calculating the energy derivatives analytically). Geometry optimizations were performed at the gradient-corrected density functional level of theory using a combination of Becke's exchange functional<sup>43</sup> with the Lee-Yang-Parr correlation one<sup>45</sup> (the methodology denoted as BLYP). The standard 6-31G(d,p) basis set of DZP quality was used for orbital expansion in solving the Kohn-Sham equations.<sup>42</sup> The stationary points found on the molecular potential energy hypersurfaces were characterized by numerical harmonic vibrational analyses. The absence of both imaginary frequencies (negative eigenvalues of the Hessian matrices) confirmed that the stationary points correspond to real minima, instead of being saddle points. Complete harmonic vibrational analyses of the mentioned species will be published elsewhere.

### *Calculations of Isotropic Chemical Shifts*

The <sup>1</sup>H and <sup>13</sup>C NMR shielding tensors for the BLYP/6-31G(d,p) optimized geometries of the mentioned species were calculated using three previously discussed methodologies for achievement of gauge independence: Gauge Independent Atomic Orbitals (GIAO) method, Continuous Set of Gauge Transformations (CSGT) methodology and the Individual Gauge for Atoms in Molecules (IGAIM) approach (for a more thorough description of these methods, see the following chapter). These calculations were performed at various theoretical levels, both with and without inclusion of the dynamical electron correlation effects using a TZP quality basis set 6-311G(d,p) for orbital expansion. The standard Hartree-Fock (HF/6-311G(d,p)) as well as BLYP/6-311G(d,p) and B3LYP/6-311G(d,p) levels of theory were employed. The B3LYP methodology is based on a combination of Becke's three-parameter adiabatic connection exchange functional<sup>48</sup> with the LYP correlation one. In all density functional calculations, the fine (75, 302) grid was used for numerical integration.<sup>39,40</sup> Note that while the BLYP methodology is non-hybrid (it includes no HF exchange), the B3LYP one contains an admixture of HF exchange (*i.e.* is of hybrid form).

The isotropic shielding values, defined as:

$$\sigma_{\text{iso}} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$$

( $\sigma_{ii}$  being the principal tensor components) were used to calculate the isotropic chemical shifts  $\delta$  with respect to TMS ( $\delta_{\text{iso}}^{\text{X}} = \sigma_{\text{iso}}^{\text{TMS}} - \sigma_{\text{iso}}^{\text{X}}$ ).

It is worth noting at this point that the exchange and correlation functionals used in the present work for calculation of magnetic shielding properties do not include the magnetic field dependence explicitly.<sup>34</sup> However, they have been shown to yield rather accurate predictions of some other molecular properties.<sup>34,49</sup> The overall success of density functional quantum chemistry in predicting other molecular properties, such as vibrational spectra,<sup>49-51</sup> has stimulated work on further application of this methodology.

### *Methods for Achievement of Gauge Invariance*

Since a comparison of various methods for achievement of gauge invariance is presented in this work, a brief description of the employed techniques is presented in this chapter.

Within the general SCF approach, the expression for the shielding tensor components for nucleus X reduces to:

$$\sigma_{\text{X}}^{\alpha\beta} = \frac{\partial^2 \mathbf{E}}{\partial B^\alpha \partial m_{\text{X}}^\beta} = \left\langle \hat{h}^{(B^\alpha, m_{\text{X}}^\beta)} \mathbf{P} \right\rangle + \left\langle \hat{h}^{m_{\text{X}}^\beta} \mathbf{P}^{B^\alpha} \right\rangle$$

where the first and higher order derivatives are denoted with superscripts showing the variables with respect to which the differentiation is to be performed, while  $\mathbf{P}$  is the density matrix. The derivatives of the Hamiltonian are given by:

$$h_{\mu\nu}^{m_{\text{X}}^\beta} = \left\langle \chi_\mu \left| \hat{h}^{m_{\text{X}}^\beta} \right| \chi_\nu \right\rangle \quad ; \quad h_{\mu\nu}^{(B^\alpha, m_{\text{X}}^\beta)} = \left\langle \chi_\mu \left| \hat{h}^{(B^\alpha, m_{\text{X}}^\beta)} \right| \chi_\nu \right\rangle$$

where:

$$\hat{h}^{m_{\text{X}}^\beta} = -\frac{i}{c} \frac{[(\vec{r} - \vec{R}_{\text{X}}) \times \vec{\nabla}]_\beta}{|\vec{r} - \vec{R}_{\text{X}}|^3} \quad \text{and} \quad \hat{h}^{(B^\alpha, m_{\text{X}}^\beta)} = \frac{i}{2c^2} \frac{\vec{r}(\vec{r} - \vec{R}_{\text{X}})\delta_{\alpha\beta} - \vec{r}_\alpha(\vec{r} - \vec{R}_{\text{X}})_\beta}{|\vec{r} - \vec{R}_{\text{X}}|^3}$$

The derivative of the density matrix with respect to the magnetic field components is obtained by solving the corresponding coupled-perturbed equations.

Within the GIAO methodology, for calculation of magnetic properties, explicitly field-dependent wavefunctions are used, of the following form:

$$\chi_\mu(\vec{B}) = \exp\left[-\frac{i}{2c}(\vec{B} \times \vec{R}_\mu) \cdot \vec{r}\right] \cdot \chi_\mu(\vec{0})$$

where  $\chi_\mu$  is the basis function  $\vec{R}_\mu$  position vector, while  $\chi_\mu(\vec{0})$  denotes the (usual) field-independent function.

On the other hand, the CSGT approach is based on the expression for the shielding tensor components for nucleus X in terms of the induced first-order electronic current density  $J^{(1)}(r)$ :

$$\sigma_X^{ab} = \frac{\partial^2 E}{\partial B^a \partial m_X^\beta} = -\frac{1}{Bc} \int [\vec{r}_X \times J_a^{(1)}(r) / r_X^3]_\beta d\vec{r}_X$$

Within this method, the gauge-invariance is achieved by accurate calculation of the induced first order electronic current density, performing a gauge transformation for each point in space.

## RESULTS AND DISCUSSION

The optimized geometry parameters for adamantane at the BLYP/6-31G(d,p) level of theory, along with the experimental electron diffraction data, are presented in Table I. As can be seen, the agreement between theory and experiment is very good. Since structural data are not available for 2,4-methano-2,4-dehydroadamantane, the optimized BLYP/6-31G(d,p) parameters for this system are compared with the available data for [1.1.1]propellane (Table II). The agreement is again very good. The structures of adamantane and 2,4-methano-2,4-dehydroadamantane, together with the atomic numbering scheme for the second system, are shown in Figures 1 and 2 respectively.

It has been long recognized that accurate predictions of molecular geometries are essential for reliable calculations of magnetic properties. Although it is sometimes convenient to use the available experimental geometry, in order to have consistent results for both of the studied systems, we relied on the DFT optimized geometries. Since the agreement with the available experimental data is rather good, and further, it has been recognized that the derivatives of the form  $(\partial\sigma/\partial q_i)$  ( $q_i$  being a geometry parameter) are rather small for both  $^{13}\text{C}$  and  $^1\text{H}$  shieldings,<sup>55</sup> we regard the adopted approach as fully appropriate.

The computed isotropic  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts (with respect to TMS) for adamantane and 2,4-methano-2,4-dehydroadamantane, at both the HF/6-311G(d,p) as well as at the density functional BLYP/6-311G(d,p) and B3LYP/6-311G(d,p) levels of theory (employing both GIAO and CSGT methods for achievement of gauge independence) are presented in Tables III, V and VII. On the other hand, in Tables IV, VI and VIII, the relative shift values with respect to the most deshielded atoms in the structures of adamantane and 2,4-methano-2,4-dehydroadamantane are given. Since the IGAIM values at the corresponding levels of theory yield essentially the same results as CSGT, only the latter are presented in Tables III–VIII. The following conclusions can be straightforwardly derived on the basis of presented data.

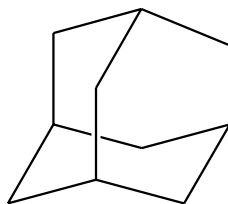


Figure 1. Adamantane.

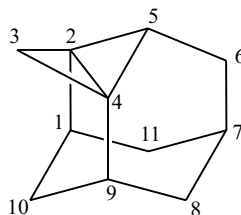


Figure 2. [3.1.1]propellane; Structure and atomic numbering.

On an absolute scale, the predicted isotropic  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts for adamantane at the HF level of theory are in excellent agreement with the experiment, the GIAO values being superior in the case of  $^{13}\text{C}$  shield-

TABLE I  
The experimental<sup>52</sup> and optimized (BLYP/6-31G(d,p)) geometry parameters for adamantane

Parameters <sup>a</sup>	Experimental	BLYP/6-31G(d,p)
Distances		
C(s)–C(t)	1.540(2)	1.5558
C(s)–H	1.112(4)	1.1052
C(t)–H	1.112(4)	1.1048
Angles		
C(s)–C(t)–C(s)	109.8 (5)	109.35
C(t)–C(s)–C(t)	108.8(10)	
C(s)–C(t)–H		110.08
C(t)–C(s)–H		110.08
H–C(s)–H	116.9(60)	106.77

<sup>a</sup> »s« and »t« denote a secondary and tertiary carbon atom, respectively.

TABLE II

The BLYP/6-31G(d,p) optimized geometry parameters for 2,4-methano-2,4-dehydroadamantane, together with the selected experimental data for [1.1.1]propellane

Parameters	Experimental	BLYP/6-31G(d,p)
Distances		
C(1)–C(2)	–	1.5443
C(2)–C(3)	–	1.5146
C(2)–C(4)	1.596	1.5993
C(2)–C(5)	–	1.5232
C(5)–C(6)	1.525	1.5253
C(6)–C(7)	–	1.5499
C(7)–C(11)	–	1.5595
C(11)–C(1)	–	1.5576
C(1)–C(10)	–	1.5646
C(1)–H	1.106	1.1032
C(3)–H <sub>ax</sub>	–	1.0987
C(3)–H <sub>eq</sub>	–	1.0936
C(5)–H	1.106	1.1023
C(6)–H	1.106	1.1045
C(7)–H	1.106	1.1038
C(8)–H <sub>eq</sub>	–	1.1042
C(8)–H <sub>ax</sub>	–	1.1040
C(10)–H <sub>eq</sub>	–	1.1016
C(10)–H <sub>ax</sub>	–	1.1044
Angles		
C(2)–C(3)–C(4)	–	63.7
C(2)–C(5)–C(4)	–	63.3
C(2)–C(5)–C(6)	–	118.6
C(1)–C(10)–C(9)	–	100.6
C(11)–C(7)–C(8)	–	111.4

ings, while the CSGT method performs slightly better in the case of the <sup>1</sup>H ones. The density functional levels of theory, even with a TZP quality basis set are less reliable on an absolute scale. Similar conclusions are valid in the case of 2,4-methano-2,4-dehydroadamantane, as well. Namely, except for the inverted carbons and two of their nearest neighbors (atoms 1, 2, 4 and 9), the HF/6-311G(d,p) <sup>13</sup>C isotropic shieldings agree excellently with the experimentally measured ones. The CSGT algorithm yields a better



TABLE III

Theoretical and experimental  $^{13}\text{C}$  and  $^1\text{H}$  isotropic chemical shifts (with respect to TMS, all values in ppm) for adamantane (all calculations performed with the 6-311G(d,p) basis set)

Method	$\text{C(t)}^{\text{a}}$		$\text{C(s)}^{\text{a}}$	
	CSGT	GIAO	CSGT	GIAO
BLYP	40.4	38.8	44.8	44.7
B3LYP	36.8	34.8	42.5	41.6
HF	27.6	26.8	34.5	33.6
Experimental	26.6		33.5	

Method	$\text{H(t)}^{\text{a}}$		$\text{H(s)}^{\text{a}}$	
	CSGT	GIAO	CSGT	GIAO
BLYP	1.6	1.8	1.8	1.9
B3LYP	1.5	1.7	1.7	1.8
HF	1.1	1.2	1.3	1.3
Experimental	1.1		1.2	

<sup>a</sup> »s« and »t« denote a secondary and tertiary carbon or hydrogen atom, respectively.

TABLE IV

Theoretical and experimental  $\delta_{\text{iso}}(\text{C(s)}) - \delta_{\text{iso}}(\text{C(t)})$  and  $\delta_{\text{iso}}(\text{H(s)}) - \delta_{\text{iso}}(\text{H(t)})$  values (in ppm) for adamantane (all calculations performed with the 6-311G(d,p) basis set)<sup>a</sup>

Method	$\delta_{\text{iso}}(\text{C(s)}) - \delta_{\text{iso}}(\text{C(t)})^{\text{a}}$	
	CSGT	GIAO
BLYP	4.4	5.9
B3LYP	5.7	6.8
HF	6.9	6.8
Experimental	6.9	

Method	$\delta_{\text{iso}}(\text{H(s)}) - \delta_{\text{iso}}(\text{H(t)})^{\text{a}}$	
	CSGT	GIAO
BLYP	0.2	0.1
B3LYP	0.2	0.1
HF	0.2	0.1
Experimental	0.1	

<sup>a</sup> »s« and »t« denote a secondary and tertiary carbon or hydrogen atom, respectively.

TABLE V

Theoretical (GIAO)  $^{13}\text{C}$  and  $^1\text{H}$  and experimental  $^{13}\text{C}$  isotropic chemical shifts (with respect to TMS, all values in ppm) for 2,4-methano-2,4-dehydroadamantane (all calculations performed with the 6-311G(d,p) basis set)

Atom	Experiment	HF	BLYP	B3LYP
C1	44.0	34.7	45.4	43.2
C2	24.2	18.0	31.9	29.7
C3	40.9	42.9	44.5	44.8
C4	24.2	18.0	31.9	29.7
C5	64.4	64.4	72.0	70.9
C6	30.8	30.5	37.8	36.1
C7	26.6	27.2	37.0	34.7
C8	34.2	33.6	41.6	39.7
C9	44.0	34.7	45.4	43.2
C10	50.1	48.5	56.5	55.1
C11	34.2	33.6	41.6	39.7
H(C1)	–	2.0	2.5	2.4
H <sub>eq</sub> (C3)	–	2.0	2.1	2.1
H <sub>ax</sub> (C3)	–	1.1	1.0	1.1
H(C5)	–	2.0	2.3	2.3
H'(C6)	–	1.7	2.0	1.9
H''(C6)	–	1.7	2.0	1.9
H(C7)	–	1.4	1.8	1.7
H <sub>eq</sub> (C8)	–	1.3	1.7	1.6
H <sub>ax</sub> (C8)	–	1.2	1.6	1.5
H(C9)	–	2.0	2.5	2.4
H <sub>eq</sub> (C10)	–	2.0	2.6	2.5
H <sub>ax</sub> (C10)	–	1.4	2.0	1.8
H <sub>eq</sub> (C11)	–	1.3	1.7	1.6
H <sub>ax</sub> (C11)	–	1.2	1.6	1.5

overall agreement with the experimental values than GIAO. It is worth noting that the HF CSGT chemical shifts for the inverted carbons as well as their nearest neighbors are in significantly better agreement with the experiment than the HF GIAO values. The DFT methods perform significantly better than the HF in the case of inverted carbons. Although inclusion of the dynamical electron correlation may be certainly significant for these centers, the good performances of DFT methods in such cases may be re-

TABLE VI

Theoretical (GIAO)  $\delta_{\text{iso}}(\text{C}(5)) - \delta_{\text{iso}}(\text{C}(i))$  and  $\delta_{\text{iso}}(\text{H}_{\text{eq}}(10)) - \delta_{\text{iso}}(\text{H}(i))$  and experimental  $\delta_{\text{iso}}(\text{C}(5)) - \delta_{\text{iso}}(\text{C}(i))$  values (in ppm) for 2,4-methano-2,4-dehydroadamantane (all calculations performed with the 6-311G(d,p) basis set)

Atom	Experiment	HF	BLYP	B3LYP
C1	20.4	29.7	26.6	27.7
C2	40.2	46.4	40.1	41.2
C3	23.5	21.5	27.5	26.1
C4	40.2	46.4	40.1	41.2
C5	0.0	0.0	0.0	0.0
C6	33.6	33.9	34.2	34.8
C7	37.8	37.2	35.0	36.2
C8	30.2	30.8	30.4	31.2
C9	20.4	29.7	26.6	27.7
C10	14.3	15.9	15.5	15.8
C11	30.2	30.8	30.4	31.2
H(C1)	–	0.0	0.1	0.1
H <sub>eq</sub> (C3)	–	0.0	0.5	0.4
H <sub>ax</sub> (C3)	–	0.9	1.6	1.4
H(C5)	–	0.0	0.3	0.2
H'(C6)	–	0.3	0.6	0.6
H''(C6)	–	0.3	0.6	0.6
H(C7)	–	0.6	0.8	0.8
H <sub>eq</sub> (C8)	–	0.7	0.9	0.9
H <sub>ax</sub> (C8)	–	0.8	1.0	1.0
H(C9)	–	0.0	0.1	0.1
H <sub>eq</sub> (C10)	–	0.0	0.0	0.0
H <sub>ax</sub> (C10)	–	0.6	0.6	0.7
H <sub>eq</sub> (C11)	–	0.7	0.9	0.9
H <sub>ax</sub> (C11)	–	0.8	1.0	1.0

garded as fortious, *i.e.* as being due to cancellation of errors. It has been firmly established that the currently available exchange and correlation functionals are not *a priori* expected to yield accurate magnetic properties of molecular systems. This is due to several reasons. First, the developed functionals have been parametrized for calculation of energetic properties, and are thus expected to perform best for calculations of such properties.<sup>34,39,40</sup>

TABLE VII

Theoretical (CSGT (IGAIM))  $^{13}\text{C}$  and  $^1\text{H}$  and experimental  $^{13}\text{C}$  isotropic chemical shifts (with respect to TMS, all values in ppm) for 2,4-methano-2,4-dehydroadamantane (all calculations performed with the 6-311G(d,p) basis set)

Atom	Experiment	HF	BLYP	B3LYP
C1	44.0	37.7	45.9	45.6
C2	24.2	21.5	31.7	31.9
C3	40.9	45.2	44.2	46.4
C4	24.2	21.5	31.7	31.9
C5	64.4	66.0	70.4	71.5
C6	30.8	32.2	37.3	37.4
C7	26.6	30.5	38.2	37.7
C8	34.2	35.6	41.4	41.4
C9	44.0	37.7	45.9	45.6
C10	50.1	50.2	56.0	56.5
C11	34.2	35.6	41.4	41.4
H(C1)	–	2.1	2.1	2.2
H <sub>eq</sub> (C3)	–	1.9	1.6	1.8
H <sub>ax</sub> (C3)	–	1.1	0.6	0.8
H(C5)	–	2.0	1.9	2.0
H'(C6)	–	1.7	1.6	1.7
H''(C6)	–	1.7	1.6	1.7
H(C7)	–	1.5	1.5	1.6
H <sub>eq</sub> (C8)	–	1.6	1.5	1.6
H <sub>ax</sub> (C8)	–	1.5	1.4	1.5
H(C9)	–	2.1	2.1	2.2
H <sub>eq</sub> (C10)	–	2.1	2.2	2.3
H <sub>ax</sub> (C10)	–	1.7	1.7	1.8
H <sub>eq</sub> (C11)	–	1.6	1.5	1.6
H <sub>ax</sub> (C11)	–	1.5	1.4	1.5

Further, due to the underestimation of the  $\varepsilon_a - \varepsilon_i$  energy differences (where the subscript  $a$  refers to virtual orbitals, while  $i$  refers to occupied ones), the DFT methods overestimate the paramagnetic shielding terms, leading to »too deshielded« centers. Namely, the paramagnetic contribution to the overall shielding tensor component within the DFT GGA approximation is given by:<sup>34</sup>

TABLE VIII

Theoretical (CSGT (IGAIM))  $\delta_{\text{iso}}(\text{C}(5)) - \delta_{\text{iso}}(\text{C}(i))$  and  $\delta_{\text{iso}}(\text{H}_{\text{eq}}(10)) - \delta_{\text{iso}}(\text{H}(i))$  and experimental  $\delta_{\text{iso}}(\text{C}(5)) - \delta_{\text{iso}}(\text{C}(i))$  values (in ppm) for 2,4-methano-2,4-dehydroadamantane (all calculations performed with the 6-311G(d,p) basis set)

Atom	Experiment	HF	BLYP	B3LYP
C1	20.4	28.3	24.5	25.9
C2	40.2	44.4	38.7	39.6
C3	23.5	20.8	26.2	25.1
C4	40.2	44.4	38.7	39.6
C5	0.0	0.0	0.0	0.0
C6	33.6	33.8	33.1	34.1
C7	37.8	35.5	32.2	33.8
C8	30.2	30.4	29.0	30.1
C9	20.4	28.3	24.5	25.9
C10	14.3	15.8	14.4	15.0
C11	30.2	30.4	29.0	30.1
H(C1)	—	0.0	0.1	0.1
H <sub>eq</sub> (C3)	—	0.2	0.6	0.5
H <sub>ax</sub> (C3)	—	1.0	1.6	1.5
H(C5)	—	0.1	0.3	0.3
H'(C6)	—	0.4	0.6	0.6
H''(C6)	—	0.4	0.6	0.6
H(C7)	—	0.6	0.7	0.7
H <sub>eq</sub> (C8)	—	0.5	0.7	0.7
H <sub>ax</sub> (C8)	—	0.6	0.8	0.8
H(C9)	—	0.0	0.1	0.1
H <sub>eq</sub> (C10)	—	0.0	0.0	0.0
H <sub>ax</sub> (C10)	—	0.4	0.5	0.5
H <sub>eq</sub> (C11)	—	0.5	0.7	0.7
H <sub>ax</sub> (C11)	—	0.6	0.8	0.8

$$\sigma_{\text{p}}^{\text{X}\alpha\beta} = - \sum_{j=1}^n \sum_{b=n+1}^m \frac{\langle b | l^\alpha | j \rangle \langle j | l_{\text{X}}^\beta r_{\text{X}}^{-3} | b \rangle + \langle b | l_{\text{X}}^\alpha r_{\text{X}}^{-3} | j \rangle \langle j | l^\beta | b \rangle}{(\varepsilon_b - \varepsilon_j)}$$

where  $r_{\text{X}}$  is the electron distance from nucleus X,  $l$  is the angular momentum operator, while the Greek superscripts denote vector or tensor components. As can be seen from Tables V and VII, the density functional calculations lead to exactly »too deshielded« centers if we compare the computed  $\delta$

values with the experiment. From the physical viewpoint, the underestimation of the  $\varepsilon_a - \varepsilon_i$  terms is due to the fact that the functionals that are currently in use for DFT calculations vanish too quickly to zero. This leads to wrong Kohn-Sham solutions for the virtual states, as the exchange-correlation functional has wrong behavior, being severely too shallow. Therefore, any perturbation theoretic approach based on these solutions would lead to erroneous predictions. In a very recent study, an attempt to overcome this weak point of the GGA approximation was presented, based on the usage of two novel functionals – HCTH, and its asymptotically corrected variant – HCTH(AC).<sup>34</sup> Another efficient algorithm for improvement of these results is based on Malkin’s sum-over-states density functional perturbation theory (SOS-DFPT) where level shift corrections are applied to the Kohn-Sham orbital energies.<sup>34</sup> It is worth noting that the last approach leads to a substantial improvement in the calculated magnetic properties. Regarding the method for achievement of gauge invariance, for the present case, at the BLYP level, the CSGT algorithm is slightly superior to GIAO. On the other hand, at the hybrid B3LYP level, GIAO is found to be slightly superior.

In order to further test the performances of the employed methodologies with respect to both inclusion of dynamical electron correlation effects and the way of achieving gauge independence, we have tabulated the relative isotropic shifts (with respect to the most deshielded centers within the studied molecules) and compared these values with the experimental ones. Contrary to the previous discussion, the DFT results were found to be superior to the HF ones in the present case. The performances of pure (BLYP) and hybrid (B3LYP) DFT methods with respect to prediction of the relative shieldings within the molecule are rather close, as can be seen from the root mean square values of the deviations from experimental data (Table IX). This conclusion is a rather important one, since it implies that the density functional description of the magnetic properties of centers within a molecule (on a relative scale) is superior to the HF SCF. Such findings may be probably attributed to the fact that the errors arising from the inappropriate description of virtual states within the Kohn-Sham approach cancel when the computed values are referred to a particular center within the same molecule, instead of to an *external* standard, such as TMS.

Regardless of the level of theory employed, the calculated CSGT relative shift values (with respect to the most deshielded center within the molecule) for 2,4-methano-2,4-dehydroadamantane were found to correlate better with the experimental values, compared to the GIAO ones. However, the DFT values correlate better with the experimental ones than the corresponding HF ones. The plots of the computed (at HF and DFT levels, with the CSGT method) *vs.* the experimental <sup>13</sup>C relative shifts are shown in Figure 3. The parameters obtained by linear regression analyses are summarized in Table X.

TABLE IX

The RMS deviations of the computed absolute and relative shifts (at various theoretical levels) from the experimental data

Method		HF	BLYP	B3LYP
GIAO	Absolute	4.839	6.748	5.209
	Relative	4.839	3.054	3.352
CSGT	Absolute	3.518	6.619	6.847
	Relative	3.999	2.695	2.706

TABLE X

The parameters of correlation equations of the form:  $[\delta_{\text{iso}}(\text{C}(5)) - \delta_{\text{iso}}(\text{C}(i))]_{\text{theor.}} = a + b \times [\delta_{\text{iso}}(\text{C}(5)) - \delta_{\text{iso}}(\text{C}(i))]_{\text{exp.}}$  together with the  $r^2$  values

Method		$a$	$b$	$r^2$
GIAO	HF	2.08	1.03	0.9063
	BLYP	3.68	0.91	0.9481
	B3LYP	3.57	0.94	0.9483
CSGT	HF	2.17	0.99	0.9176
	BLYP	3.03	0.88	0.9522
	B3LYP	3.18	0.91	0.9532

## CONCLUSIONS

Theoretical  $^{13}\text{C}$  and  $^1\text{H}$  chemical shift values (with respect to TMS) and the relative shifts (with respect to the most deshielded center in the molecule) are reported for adamantane and 2,4-methano-2,4-dehydroadamantane. The mentioned parameters were computed at HF, BLYP and B3LYP/6-311G(d,p) levels of theory, for the BLYP/6-31G(d,p) optimized geometries. The CSGT, IGAIM and GIAO algorithms for achievement of gauge invariance were employed. Except for the inverted carbon atoms, the computed chemical shifts (with respect to TMS) at the HF level of theory are in significantly better agreement with the experiment (the CSGT method being superior to GIAO), while the DFT values are systematically too deshielded. The last finding may be attributed to the inappropriate description of paramagnetic contribution to the shielding tensor within the Kohn-Sham approach. On the contrary, the relative shielding values (with respect to the most deshielded center within the molecule) computed at DFT levels are su-

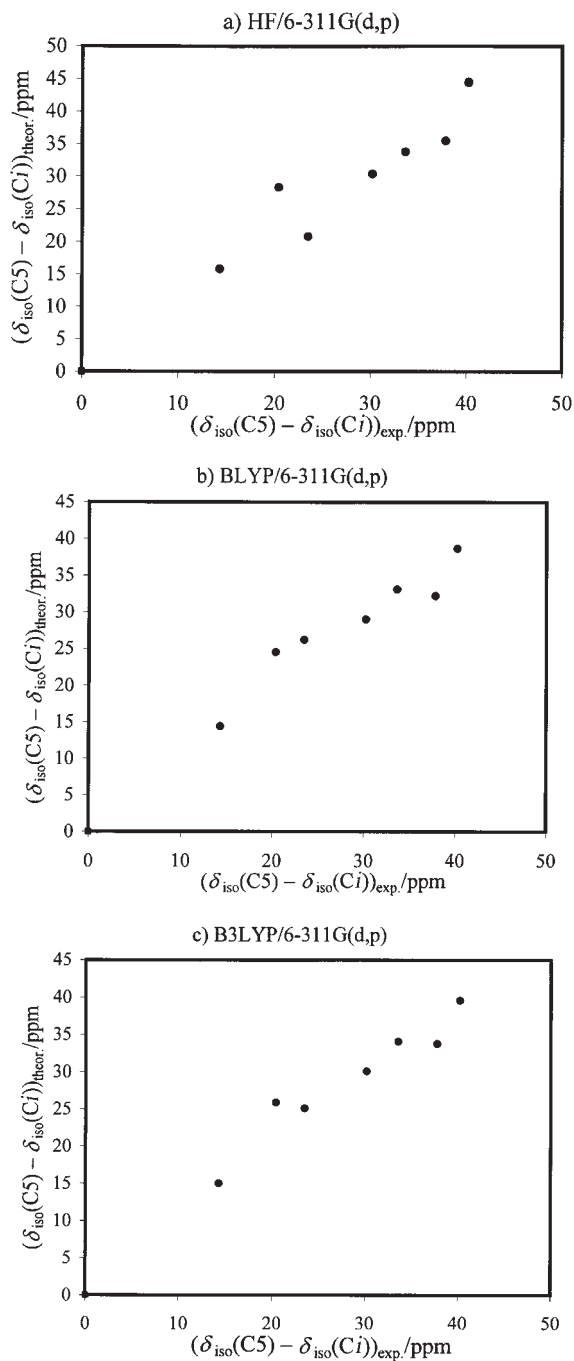


Figure 3. Plots of the computed *vs.* experimental  $^{13}\text{C}$  relative shifts, at the HF and the two DFT levels, with the CSGT method.



perior to the HF ones. It thus seems that, although inferior to both HF and other correlated methods on an absolute scale, DFT methods may be successfully applied when the relative shieldings within the molecular system are of interest. The CSGT relative shift values correlate better with the experimental ones than the GIAO ones, regardless of the level of theory. For a given algorithm for achievement of gauge invariance, the correlations are significantly better at the DFT than at the HF level of theory. The proposed approach can be potentially useful in an extended way to predict the chemical shifts of the highly anharmonic systems, such as hydrogen-bonded ones. However, such systems require averaging over the nuclear wavefunction.

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**SAŽETAK****Proračun  $^{13}\text{C}$  i  $^1\text{H}$  NMR izotropnih kemijskih pomaka za geometrije optimizirane metodama DFT. Adamantan i 2,4-metano-2,4-dehidroadamantan ([3.1.1]propelan) kao modelni sustavi***Dražen Vikić-Topić i Ljupčo Pejov*

Vrijednosti  $^{13}\text{C}$  i  $^1\text{H}$  kemijskih pomaka izračunane su s HF, BLYP i B3LYP/6-31G(d,p) metodama, za BLYP/6-31G(d,p) optimizirane geometrije adamantana i 2,4-metano-2,4-dehidroadamantana, tj. [3.1.1]propelana, te uspoređene s eksperimentalnim podacima. Za sve atome, osim za invertirane atome ugljika, izračunane vrijednosti izotropnih kemijskih pomaka, u odnosu na TMS, bolje su kada se koristi metoda HF nego metoda DFT. Kada se računaju relativni kemijski pomaci, prema najodsjenjenijem centru u molekuli, metode DFT daju znatno bolje slaganje s eksperimentalnim podacima nego metoda HF. Najvjerojatniji razlog tome je poništavanje pogrešaka, koje proizlaze zbog neodgovarajućeg udjela paramagnetnog doprinosa ukupnom tenzoru zasjenjenja u teorijskom pristupu Kohn-Sham, u slučaju kada se koristi standard unutar molekule. Relativni pomaci izračunani CSGT pristupom bolje koreliraju s eksperimentalnim podacima nego oni proračunani GIAO pristupom, pri čemu je slaganje s eksperimentom bitno bolje za metode DFT nego za metodu HF.