

# Nuclear shielding constants by density functional theory with gauge including atomic orbitals

Trygve Helgaker,<sup>a)</sup> Philip J. Wilson, Roger D. Amos, and Nicholas C. Handy  
*Department of Chemistry, University of Cambridge, CB2 1EW, United Kingdom*

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Recently, we introduced a new density-functional theory (DFT) approach for the calculation of NMR shielding constants. First, a hybrid DFT calculation (using 5% exact exchange) is performed on the molecule to determine Kohn–Sham orbitals and their energies; second, the constants are determined as in nonhybrid DFT theory, that is, the paramagnetic contribution to the constants is calculated from a noniterative, uncoupled sum-over-states expression. The initial results suggested that this semiempirical DFT approach gives shielding constants in good agreement with the best *ab initio* and experimental data; in this paper, we further validate this procedure, using London orbitals in the theory, having implemented DFT into the *ab initio* code DALTON. Calculations on a number of small and medium-sized molecules confirm that our approach produces shieldings in excellent agreement with experiment and the best *ab initio* results available, demonstrating its potential for the study of shielding constants of large systems. © 2000 American Institute of Physics.  
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## I. INTRODUCTION

It is now apparent that, because of its simplicity and low cost, density-functional theory (DFT) is a computational chemistry methodology that is making important contributions. Since the introduction of generalized-gradient approximation (GGA) exchange-correlation functionals and hybrid functionals, there have been thousands of DFT studies involving molecular structure and energetics. Essentially, the stage has now been reached where the DFT methodology represents a useful tool for the study of molecular energetics and structure, providing accurate results at low cost.

More recently, the DFT methodology has been extended to various time-dependent properties (in particular dynamical polarizabilities and excitation energies)<sup>1–4</sup> as well as to magnetic properties. The calculation of NMR chemical shifts, in particular, constitutes an important challenge for computational chemistry.<sup>5</sup> One popular DFT approach is that taken by Malkin *et al.*,<sup>6</sup> in which improved shieldings are obtained by shifting the excitation energies in the uncoupled paramagnetic sum-over-states expression; in the present paper, we explore a slightly different approach, in which the improvement in the excitation energies is achieved by using a reoptimized functional.<sup>7</sup>

In GGA theory, the magnetic Hessian (the only part of the Kohn–Sham Hessian needed for shieldings) is diagonal, implying that there are no coupled equations to be solved in the calculation of the paramagnetic contribution to the shieldings, significantly reducing the computational cost for large systems. More precisely, in the GGA approximation, the formulas for the dia- and paramagnetic contributions to the shieldings are given by

$$\sigma_d^{A\alpha\beta} = \sum_j (j | (\mathbf{r} \cdot \mathbf{r}_A \delta^{\alpha\beta} - r_A^\alpha r_A^\beta) r_A^{-3} | j), \quad (1)$$

$$\sigma_p^{A\alpha\beta} = - \sum_j \sum_b \frac{(b | l^\alpha | j)(j | l_A^\beta r_A^{-3} | b) + (b | l_A^\alpha r_A^{-3} | j)(j | l^\beta | b)}{\epsilon_b - \epsilon_j}, \quad (2)$$

where we have used standard notation and the summations are over the occupied and unoccupied orbitals, denoted by *j* and *b*, respectively. Since these expressions contain no two-electron contributions, they depend only indirectly on the functional used in the calculation, that is, only through the appearance of the canonical orbitals and orbital energies in the expressions.

Obviously, the success of this theory depends crucially on the orbitals and orbital energies delivered by the functional. For consistency, we ought to use a GGA functional to determine the orbitals and their energies; however, since the exact Kohn–Sham functional is unknown, it is entirely appropriate to use any functional that delivers good orbitals and energies. Thus, in our previous paper, we showed that a reoptimized hybrid functional gives orbitals and energies which, when substituted into Eqs. (1) and (2), give good chemical shifts for molecules containing first- and second-row atoms.<sup>7</sup> In particular, for the hybrid functional B3LYP, the best results are obtained by using 5% rather than 20% Hartree–Fock exchange. Since all functionals are approximate, it does not cause us concern that the functional used for magnetic properties is distinct from the one used for electrostatic properties.

Our first calculations with this new DFT approach<sup>7</sup> used the LORG algorithm<sup>8</sup> for the location of the gauge origin; in this paper, our purpose is to validate further the method using London orbitals or gauge including atomic orbitals

<sup>a)</sup>Permanent address: Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway.

(GIAOs).<sup>9,10</sup> To this end, we have taken the opportunity to instal DFT algorithms into the *ab initio* code DALTON.<sup>11</sup>

In the next section, the DFT implementation into DALTON is briefly described, as well as the installation of the above scheme for NMR chemical shifts. In Sec. III, we present some computational details and a comparison of DFT shieldings obtained with and without the use of GIAOs. In Sec. IV, we present calculations of NMR chemical shifts for some systems that are recognized as presenting a challenge to quantum chemists, namely, *cis*- and *trans*-N<sub>2</sub>F<sub>2</sub>, and 1-cyclopropylcyclopropylidenemethyl-cation.<sup>5</sup>

## II. THEORY

The present implementation of DFT theory for the calculation of chemical shieldings using London orbitals is based on a previous implementation of shieldings at the Hartree–Fock level in the program system DALTON.<sup>12</sup> In the present section, we describe briefly those aspects of the DFT implementation of London orbitals for the calculation of NMR shieldings that are different from Hartree–Fock theory.

In principle, the only modifications needed to turn a Hartree–Fock code into a DFT code is to replace the Hartree–Fock exchange contributions to the energy and other quantities such as the Fock matrix by the corresponding exchange-correlation contributions of DFT theory. In hybrid theories, the Hartree–Fock exchange is not completely removed but rather scaled by some factor. In the following, we shall assume that the Hartree–Fock exchange has been everywhere correctly scaled and concentrate solely on the exchange-correlation contributions of DFT theory. Before describing the implementation of shieldings, we note that the current implementation of DFT in DALTON is based on that in CADPAC, using the same routines for generating the abscissas and weights for the density quadrature and for the functionals; the optimized energies are therefore identical to those produced by CADPAC. Moreover, the DALTON implementation used in this paper is a preliminary one in that it does not utilize point-group symmetry; also, there is no efficient screening of quadrature points and of the contributions from the individual orbitals at each point. There are, however, no limitations with respect to the types of basis sets that can be used (segmented or generally contracted with spherical-harmonic or Cartesian components) and molecular gradients have also been coded.

There exist several formulations of coupled-perturbed Hartree–Fock theory. These are equivalent in the sense that they all give the same numerical results but different in that they represent the electronic energy by means of different parameters. In some formulations, the redundant MO coefficients are the basic variables; in other formulations, the basic variables are a set of nonredundant orbital-rotation parameters. We shall not concern ourselves with the details of these formulations here, but note that all time-independent second-order Hartree–Fock properties are conveniently expressed in terms of the total energy and the Fock matrix and their partial derivatives with respect to the external perturbations. In particular, in order to calculate Hartree–Fock chemical shieldings, we need to calculate the total energy  $E$

and its second-order partial derivatives  $\partial^2 E / \partial \mathbf{B} \partial \mathbf{M}_K |_0$  (which contribute to the diamagnetic shielding) as well as the Fock matrix  $\mathbf{F}$  and its first-order partial derivatives  $\partial \mathbf{F} / \partial \mathbf{B} |_0$  and  $\partial \mathbf{F} / \partial \mathbf{M}_K |_0$  (which contribute to the paramagnetic shielding). As indicated by our notation, all differentiations are carried out for zero external field  $\mathbf{B} = \mathbf{0}$  and for zero magnetic moments  $\mathbf{M}_K = \mathbf{0}$ . To turn an existing Hartree–Fock code into a Kohn–Sham code, we need only to extend the evaluation of these quantities to include the contributions from the exchange-correlation potential.

Before considering these partial derivatives, we recall that, in the London theory of magnetic properties, the AOs depend explicitly on the external magnetic field and will therefore make contributions to all partial derivatives with respect to the external field (some of these derivatives may be zero by symmetry). Consider an AO  $\chi_\alpha$  centered on the nucleus A, whose position in space is  $\mathbf{A}$ . For a chosen gauge origin  $\mathbf{O}$ , the corresponding London atomic orbital is given by

$$\omega_\alpha = \exp\left[-\frac{1}{2} i \mathbf{B} \times (\mathbf{A} - \mathbf{O}) \cdot \mathbf{r}\right] \chi_\alpha(\mathbf{r}_A), \quad (3)$$

where  $\mathbf{r}$  is the position of the electron relative to the origin of the coordinate system and  $\mathbf{r}_A$  is the position of the electron relative to  $\mathbf{A}$ . The overlap distribution of two London orbitals  $\omega_\alpha$  and  $\omega_\beta$  is therefore

$$\Omega_{\alpha\beta} = \omega_\alpha^* \omega_\beta = \exp\left(\frac{1}{2} i \mathbf{B} \times \mathbf{R}_{AB} \cdot \mathbf{r}\right) \chi_\alpha \chi_\beta, \quad (4)$$

where

$$\mathbf{R}_{AB} = \mathbf{A} - \mathbf{B}. \quad (5)$$

Note that, because of the use of the London orbitals, the electron density depends *explicitly* on the magnetic field,

$$\rho(\mathbf{r}, \mathbf{B}) = \sum_{\alpha\beta} D_{\alpha\beta} \exp\left(\frac{1}{2} i \mathbf{B} \times \mathbf{R}_{AB} \cdot \mathbf{r}\right) \chi_\alpha \chi_\beta. \quad (6)$$

In this expression, the  $D_{\alpha\beta}$  are the elements of the density matrix. However, because of the special form of this explicit dependence, the first derivative of the density with respect to the field at zero field is equal to zero,

$$\left. \frac{\partial \rho(\mathbf{r}, \mathbf{B})}{\partial \mathbf{B}} \right|_{\mathbf{B}=\mathbf{0}} = \frac{1}{2} i \sum_{\alpha\beta} (\mathbf{R}_{AB} \times \mathbf{r}) D_{\alpha\beta} \chi_\alpha \chi_\beta = \mathbf{0}. \quad (7)$$

This result follows from the fact that, whereas  $D_{\alpha\beta}$  is symmetric with respect to the permutation of orbitals  $\alpha$  and  $\beta$ , the position vector  $\mathbf{R}_{AB}$  is antisymmetric with respect to such a permutation. The same result holds for the gradient of the density  $\nabla \rho$ . Since the evaluation of shieldings involves only first derivatives with respect to the field  $\mathbf{B}$ , there will be no contributions to the shieldings from the explicit field-dependence of the density on the magnetic field.

The calculation of the exchange-correlation contribution to the energy involves the integration over all space of some functional  $F(\rho, \zeta)$  that depends only on the density  $\rho$  and the norm of its gradient  $\zeta = |\nabla \rho|$ ,

$$E_{xc} = \int F(\rho, \zeta) d\mathbf{r}. \quad (8)$$

Since the exchange-correlation energy does not depend explicitly on the nuclear magnetic moments, it makes no contribution to the second partial derivative of the total energy with respect to the external field and the nuclear moments,

$$\left. \frac{\partial^2 E_{xc}}{\partial \mathbf{B} \partial \mathbf{M}_K} \right|_{\mathbf{B}=\mathbf{0}, \mathbf{M}_K=\mathbf{0}} = \mathbf{0}. \quad (9)$$

Thus, in converting a Hartree–Fock code into a Kohn–Sham code, there are no modifications to be made to the diamagnetic contribution to the shieldings.

Let us next consider the modifications that must be made in the construction of the derivative Fock matrices in order to obtain the corresponding derivative Kohn–Sham matrices. The exchange-correlation contribution to the Kohn–Sham matrix takes the form

$$F_{\alpha\beta}^{xc} = \int v_{xc} \Omega_{\alpha\beta} d\mathbf{r}, \quad (10)$$

where the exchange-correlation potential is given by

$$v_{xc} = \frac{\delta E_{xc}}{\delta \rho} = \frac{\partial F}{\partial \rho} - \nabla \cdot \frac{\partial F}{\partial \nabla \rho}. \quad (11)$$

Clearly, since neither the overlap distribution nor the exchange-correlation potential depends explicitly on the nuclear magnetic moments, it will make no contribution to the derivatives of the Kohn–Sham matrix with respect to the nuclear magnetic moments,

$$\left. \frac{\partial F_{\alpha\beta}^{xc}}{\partial \mathbf{M}_K} \right|_{\mathbf{M}_K=0} = \mathbf{0}. \quad (12)$$

However, since the overlap distributions depend explicitly on the external field, the derivatives of the exchange-correlation contribution to the Kohn–Sham matrix with respect to the external field will not vanish. Carrying out the differentiation, we obtain

$$\left. \frac{\partial F_{\alpha\beta}^{xc}}{\partial \mathbf{B}} \right|_{\mathbf{B}=\mathbf{0}} = \frac{1}{2} i \int (\mathbf{R}_{AB} \times \mathbf{r}) v_{xc} \chi_\alpha \chi_\beta d\mathbf{r}. \quad (13)$$

Note that there is no contribution from the density itself (for the reasons discussed above) and that the differentiated exchange-correlation part of the Kohn–Sham matrix is imaginary and antisymmetric with respect to permutation of the indices  $\alpha$  and  $\beta$ . Note also that the contribution from the exchange-correlation potential to the differentiated Kohn–Sham matrix is easily coded, at least in a scheme that involves numerical quadrature.

In practice, the evaluation of the Kohn–Sham matrix in terms of the exchange-correlation potential is rather expensive and is often avoided by partial integration (exact in the limit of exact integration), giving the following scheme:

$$F_{\alpha\beta}^{xc} = \int \frac{\partial F}{\partial \rho} \Omega_{\alpha\beta} d\mathbf{r} + \int \frac{\partial F}{\partial \zeta} \frac{\nabla \rho}{\zeta} \cdot \nabla \Omega_{\alpha\beta} d\mathbf{r}. \quad (14)$$

Using this expression, the partial derivative with respect to the external field becomes

$$\begin{aligned} \left. \frac{\partial F_{\alpha\beta}^{xc}}{\partial \mathbf{B}} \right|_{\mathbf{B}=\mathbf{0}} &= \frac{1}{2} i \int (\mathbf{R}_{AB} \times \mathbf{r}) \\ &\times \left[ \frac{\partial F}{\partial \rho} \chi_\alpha \chi_\beta + \frac{\partial F}{\partial \zeta} \frac{\nabla \rho}{\zeta} \cdot \nabla (\chi_\alpha \chi_\beta) \right] d\mathbf{r} \\ &+ \frac{1}{2} i \int \left( \mathbf{R}_{AB} \times \frac{\nabla \rho}{\zeta} \right) \frac{\partial F}{\partial \zeta} \chi_\alpha \chi_\beta d\mathbf{r}. \end{aligned} \quad (15)$$

Again, we see that the coding of this term is simple, involving essentially no quantities that are not also needed for the quadrature of the undifferentiated exchange-correlation part of the Kohn–Sham matrix.

In conclusion, to turn an existing Hartree–Fock shieldings program into a Kohn–Sham program, only the code for the construction of the right-hand side of the coupled-perturbed equations involving the external field needs to be modified. The modification consists of scaling the exchange part of the Hartree–Fock potential and adding the corresponding DFT contribution (13) or alternatively (15).

### III. COMPUTATIONAL DETAILS AND COMPARISON WITH NON-GIAO CALCULATIONS

We begin by investigating the effect of size of the basis set and the treatment of the gauge-origin problem on the shieldings in the test molecules HF, H<sub>2</sub>O, CO, and F<sub>2</sub> and by comparing the convergence properties of our new B3LYP<sub>GGA</sub><sup>0.05</sup> functional<sup>7</sup> with the Hartree–Fock method and conventional DFT functionals. This is particularly important in view of the fact that, for the accurate prediction of shieldings, the B3LYP<sub>GGA</sub><sup>0.05</sup> functional provides a viable alternative to the expensive post-Hartree–Fock *ab initio* methods. We have chosen the same basis sets and geometries as used in the previous investigations by Ruud *et al.*<sup>12</sup> and by Lee *et al.*,<sup>13</sup> which highlighted the more rapid basis set convergence of GIAOs over the IGLO and single-origin gauges within the framework of Hartree–Fock, MCSCF, and DFT methods.

We investigate the performance of the three Huzinaga basis sets HII, HIII, and HIV,<sup>14</sup> which are fairly large in size (the HII is comparable to TZP in quality). In addition, we include the smaller DZP basis,<sup>15</sup> bearing in mind that, for large molecules, only smaller basis sets are viable [for example, Häser *et al.* utilized the DZP basis set in their GIAO-HF NMR shielding calculations on C<sub>60</sub> and C<sub>70</sub> (Ref. 16)].

For linear and symmetric top molecules the isotropic shielding constants are defined by

$$\bar{\sigma} = \frac{1}{3} (\sigma_{\parallel} + 2\sigma_{\perp}), \quad (16)$$

where  $\sigma_{\parallel}$  refers to the component along the major molecular axis and  $\sigma_{\perp}$  is the component in the direction perpendicular to it. Anisotropies are given by

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}. \quad (17)$$

For all other molecular symmetries,

$$\bar{\sigma} = \frac{1}{3} \text{tr } \sigma \quad (18)$$

and

TABLE I. (a) Basis set and gauge dependence of the SCF and DFT isotropic shieldings ( $\sigma_{\text{iso}}$ ). All values in ppm. (b) Basis set and gauge dependence of the SCF and DFT anisotropic shieldings ( $\Delta\sigma$ ). All values in ppm.

Molecule	Nucl.	Basis	$N^a$	SCF			DFT-GIAO			Best <i>ab initio</i> <sup>b</sup>	Expt.	
				CHF	LORG	GIAO	B3LYP	BLYP	B3LYP <sup>0.05</sup> <sub>GGA</sub>			
(a)	HF	F	DZP	21	391.9	391.9	413.8	406.5	402.7	410.7		
			II	29	394.3	394.3	412.6	408.2	406.0	413.5		
			III	47	408.3	408.3	410.9	407.9	406.2	413.6		
			IV	77	410.9	410.9	410.4	406.9	405.1	412.6	418.6	419.7±6.0
	H <sub>2</sub> O	O	DZP	26	297.0	297.0	323.1	316.8	313.1	322.6		
			II	35	295.2	295.2	328.4	327.1	326.0	334.1		
			III	57	316.9	316.9	320.8	319.2	317.9	326.7		
			IV	97	320.7	320.7	320.5	319.1	317.9	326.7	337.9	357.6±17.2
	CO	C	DZP	32	5.5	-2.7	-8.8	4.1	9.0	30.3		
			II	46	-14.7	-17.3	-20.5	-15.2	-11.6	10.9		
			III	74	-20.4	-21.1	-22.9	-18.8	-15.5	7.4		
			IV	114	-23.1	-23.2	-23.7	-18.9	-15.3	7.3	5.6	2.8±0.9
O		DZP	32	-69.9	-79.9	-69.9	-58.4	-53.7	-17.5			
		II	46	-92.1	-93.4	-84.3	-80.5	-76.9	-39.5			
		III	74	-83.9	-84.3	-84.3	-81.7	-78.1	-40.7			
		IV	114	-84.5	-84.6	-84.2	-81.0	-77.1	-40.0	-52.9	-36.7±17.2	
F <sub>2</sub>	F	DZP	32	-162.2	-177.4	-154.7	-220.2	-234.5	-150.1			
		II	46	-178.9	-185.0	-157.0	-240.6	-259.3	-171.1			
		III	74	-177.0	-179.2	-175.3	-261.8	-281.6	-189.7			
		IV	114	-168.0	-168.4	-167.3	-252.1	-271.7	-181.3	-186.5	-192.8	
(b)	HF	F	DZP	21	135.3	135.3	102.5	113.1	118.8	106.3		
			II	29	131.8	131.8	104.0	111.0	114.5	102.5		
			III	47	110.4	110.4	106.5	111.0	113.4	101.7		
			IV	77	106.1	106.1	106.9	112.0	114.8	102.9	94.3	93.8
	H <sub>2</sub> O	O	DZP	26	56.5	56.5	46.1	43.9	42.8	41.8		
			II	35	61.4	61.4	41.1	33.8	30.1	30.7		
			III	57	56.7	56.7	55.6	51.8	49.8	48.4		
			IV	97	57.6	57.6	57.1	54.4	52.9	51.1	46.5	...
	CO	C	DZP	32	398.5	410.9	420.0	402.8	396.0	363.5		
			II	46	428.7	432.6	437.3	431.9	427.4	393.0		
			III	74	437.3	438.4	441.2	437.6	433.3	398.4		
			IV	114	441.3	441.4	442.1	437.5	432.9	398.3	401.0	406.1±1.4
O		DZP	32	721.2	736.2	720.4	703.2	696.2	641.3			
		II	46	754.1	756.1	742.4	736.5	731.1	674.4			
		III	74	742.0	742.7	742.7	738.5	733.2	676.5			
		IV	114	742.7	742.7	742.2	737.2	731.4	675.2	694.6	676.1±26	
F <sub>2</sub>	F	DZP	32	976.0	999.7	964.8	1062.4	1084.0	956.6			
		II	46	1001.1	1010.6	968.3	1093.8	1122.0	989.0			
		III	74	998.3	1001.8	995.9	1125.7	1155.4	1016.9			
		IV	114	984.4	985.1	983.4	1110.6	1140.1	1003.8	1011.7	1050±50	

<sup>a</sup> $N$  represents the total number of basis functions.<sup>b</sup>Experimental and GIAO-CCSD(T) values taken from Ref. 27.

$$\Delta\sigma = \sigma_{\alpha\alpha} - \frac{1}{2}(\sigma_{\beta\beta} + \sigma_{\gamma\gamma}), \quad (19)$$

where  $\sigma_{ii}$  are the principal tensor components such that  $\sigma_{\alpha\alpha}$  is the largest component.<sup>17</sup>

The basis set and gauge dependence of the shielding isotropies and anisotropies are presented in Tables I(a) and I(b), respectively, where the latter are known to be more sensitive to basis set quality. For the DZP and three Huzinaga basis sets, we compare Hartree–Fock shielding constants using the single-origin, LORG and GIAO gauge methods. For the GIAO-DFT calculations, we use the B3LYP,<sup>18</sup>

LDA,<sup>19</sup> BLYP,<sup>20</sup> and B3LYP<sup>0.05</sup><sub>GGA</sub> functionals. The single-origin and LORG-HF values were calculated using the CADPAC package;<sup>17</sup> the GIAO-HF and GIAO-DFT calculations were performed using the DALTON package. In order that the CADPAC and DALTON calculations may be compared on an equal level, Cartesian basis functions are used in both cases. For comparison, we have also listed the best *ab initio* and experimental values.

For the HF and H<sub>2</sub>O molecules (which are well described at the Hartree–Fock level) as well as for the more

difficult CO and F<sub>2</sub> molecules, the convergence of the Hartree–Fock isotropic and anisotropic shieldings using GIAOs is significantly better than the corresponding single-origin/LORG values for the smaller DZP and HII basis sets. The LORG value show significant improvement at the HIII level and have converged to the corresponding GIAO values for HIV (for the difficult F<sub>2</sub> molecule, the HIII values have not completely converged to the HIV ones). Similar basis set trends are also seen for the GIAO-DFT isotropic and anisotropic shielding values. It noteworthy that our new B3LYP<sub>GGA</sub><sup>0.05</sup> functional provides poor agreement with the reference *ab initio* and experimental data using the smaller DZP basis set (this is most pronounced for the CO molecule). However, compared to the conventional functionals B3LYP and BLYP, B3LYP<sub>GGA</sub><sup>0.05</sup> does produce a slightly smaller gap in the shielding values between HII and HIII.

From these observations, it is clear that triple-zeta rather than double-zeta quality basis sets are required to describe accurately the shielding properties in these test molecules at both the Hartree–Fock and DFT levels of theory. The improved flexibility of HIII over HII (due to the presence of deeper core functions and more polarization functions in the former) provides a similar level of accuracy compared to the more computationally expensive HIV. For this reason, we use the HIII basis set in all subsequent calculations.

#### IV. RESULTS AND DISCUSSION

We have calculated the Hartree–Fock and DFT (B3LYP, LDA, BLYP, and B3LYP<sub>GGA</sub><sup>0.05</sup>) NMR shieldings within the GIAO framework for <sup>13</sup>C, <sup>15</sup>N, <sup>17</sup>O, and <sup>19</sup>F nuclei in 14 molecules (containing between one to eight heavy atoms) which possess significant electron correlation effects. All calculations utilised the HIII basis sets of Huzinaga and were performed with the DALTON program. To further reduce computational effort, we used spherical rather than Cartesian basis functions in the next set of calculations. In the CO molecule, for example, this reduces the total number of basis functions from 74 to 70 (using the HIII basis), while producing only a negligible change in the calculated shieldings.

The geometries used in our calculations were obtained from the following references: CH<sub>2</sub>, CF<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, linear CO<sub>2</sub> and N<sub>2</sub>O as well as cyclic CO<sub>2</sub> and N<sub>2</sub>O from Ref. 21; *cis*- and *trans*-N<sub>2</sub>F<sub>2</sub> from Ref. 22; C<sub>6</sub>H<sub>6</sub> and CF<sub>4</sub> from Ref. 23; C<sub>2</sub>H<sub>3</sub><sup>+</sup> and C<sub>7</sub>H<sub>9</sub><sup>+</sup> from Ref. 24; and C<sub>6</sub>H<sub>5</sub>N<sub>2</sub><sup>+</sup> from Ref. 26. In this work, we define the mean absolute error as a percentage

$$d_{\bar{P}}(\text{ref}) = \frac{100}{N} \sum_{M=1}^N \left| \frac{P_{\text{calc}}^M - P_{\text{ref}}^M}{P_{\text{ref}}^M} \right|, \quad (20)$$

where  $P_{\text{calc}}^M$  is the DFT evaluated shielding parameter,  $M$  represents a particular nuclear center,  $N$  is the total number of centers, and  $P_{\text{ref}}^M$  represents the best post Hartree–Fock *ab initio* shieldings or experimental values using the center of the error bars.

The GIAO-HF and GIAO-DFT isotropic shieldings are presented in Table II. It is well known that conventional DFT functionals produce values that are too deshielded relative to experiment and this is again born out from the results in

Table II. Analysis of the mean absolute percentage errors shown at the foot of Table II indicate that, amongst the conventional functionals, similar errors are obtained between the hybrid (B3LYP) and nonhybrid GGA (BLYP) functionals, which in turn represent an improvement over LDA. Overall, the DFT results are superior to the coupled-perturbed Hartree–Fock ones. Our new functional B3LYP<sub>GGA</sub><sup>0.05</sup> provides a significant improvement over the conventional DFT functionals, with an accuracy equal to the best *ab initio* data.

In addition to the isotropic shieldings, it is instructive to consider how the individual tensor components obtained using the B3LYP<sub>GGA</sub><sup>0.05</sup> functional compare with the corresponding best *ab initio* values. As an example, we consider the CH<sub>2</sub> carbene molecule, which displays strong static correlation effects in the *xx* tensor component as discussed by van Wüllen *et al.*<sup>21</sup> For example, the calculated B3LYP<sub>GGA</sub><sup>0.05</sup> <sup>13</sup>C shielding components  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and  $\sigma_{zz}$  in CH<sub>2</sub> are -2101, 215, and -325 ppm, respectively, and compare favourably with the reference MCSCF values of -2120, 201, and -237 ppm. Similar good agreement is also observed for the <sup>1</sup>H shielding tensors; -69, 29, and 16 ppm (B3LYP<sub>GGA</sub><sup>0.05</sup>), and -71, 29, and 18 ppm (MCSCF).

Previous LORG-B3LYP<sub>GGA</sub><sup>0.05</sup> shielding calculations<sup>7</sup> on the linear CO<sub>2</sub> and N<sub>2</sub>O molecules at the HIV basis set level produced values that were in good agreement with the reference data. The corresponding GIAO values obtained with the smaller HIII basis set are included in Table II for comparison and show that the LORG and GIAO shieldings are in similar agreement. In addition, we also present CO<sub>2</sub> and N<sub>2</sub>O at their cyclic geometries, which represent structures far removed from the global minima of the linear species. The B3LYP<sub>GGA</sub><sup>0.05</sup> shielding values provide a marked improvement over the conventional DFT values when compared to the reference MCSCF values of van Wüllen.<sup>21</sup> Once again, the calculated B3LYP<sub>GGA</sub><sup>0.05</sup> <sup>13</sup>C shielding components  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and  $\sigma_{zz}$  in the cyclic CO<sub>2</sub> molecule (-281, 91, and 31 ppm for <sup>13</sup>C and -281, 124, and -40 ppm for <sup>17</sup>O) compare favorably with the corresponding MCSCF values (-295, 98.3, and 45.2 ppm for <sup>13</sup>C; and -297.5, 156.3, and -15.0 ppm for <sup>17</sup>O).

Gauss and Stanton have calculated GIAO-CCSD(T) <sup>13</sup>C shieldings in a series of vinyl cations (using a triple-zeta quality basis on the carbon atoms) and obtained nearly perfect agreement with the experimental values.<sup>24</sup> They concluded that correlation contributions to the shieldings were significant and found that the shielding of the C<sub>α</sub> atom (which is significantly deshielded) in the 1-cyclopropylcyclopropylidenemethyl-cation can only be accurately reproduced at the CCSD(T) level. However, the prohibitive computational cost (about one month CPU time) for molecular systems of this size means that such high-level correlated methods cannot be routinely applied. Since our new B3LYP<sub>GGA</sub><sup>0.05</sup> functional has been shown to provide a viable alternative to such high-level correlated methods<sup>7</sup> (the corresponding B3LYP<sub>GGA</sub><sup>0.05</sup> calculation required about 1 day CPU time), we present our own DFT shielding calculations for this cation together with the smaller C<sub>2</sub>H<sub>3</sub><sup>+</sup> system. They provide a severe test to the DFT functionals, bearing in mind that correlation contributions to the shieldings are significant (i.e., about 100 ppm for the C<sub>α</sub> atom in C<sub>2</sub>H<sub>3</sub><sup>+</sup>). From Table

TABLE II. Experimental and calculated DFT-GIAO isotropic shieldings ( $\sigma_{\text{iso}}$ , in ppm).

Molecule	Nucl.	SCF	B3LYP	LDA	BLYP	B3LYP <sub>GGA</sub> <sup>0.05</sup>	Best <i>ab initio</i>	Expt.
CH <sub>2</sub>	H	-42.7	-29.9	-62.6	-24.5	-8.1	-7.8 <sup>a</sup>	...
	C	-1496.1	-1253.1	-2004.2	-1135.6	-736.7	-718 <sup>a</sup>	...
CF <sub>2</sub>	C	-140.7	-145.8	-151.4	-139.3	-96.0	-101 <sup>a</sup>	...
	F	-5.0	-77.6	-117.5	-92.0	-30.9	-34 <sup>a</sup>	...
CF <sub>4</sub>	C	78.6	44.6	37.3	35.8	50.7	64.4 <sup>b</sup>	64.5 <sup>g</sup>
	F	277.9	236.2	219.2	224.6	244.1	...	...
NO <sub>2</sub> <sup>-</sup>	N	-680.8	-473.4	-427.4	-420.1	-333.2	-360 <sup>a</sup>	-368 <sup>a</sup>
	O	-559.2	-502.1	-492.1	-474.0	-354.5	-382 <sup>a</sup>	-342 ± 20 <sup>a</sup>
linear-CO <sub>2</sub>	C	51.6	48.2	48.7	48.5	60.8	63.5 <sup>b</sup>	58.8 <sup>g</sup>
	O	221.2	211.3	207.9	210.0	224.9	236.4 <sup>c</sup>	243 ± 17 <sup>a</sup>
cyclic-CO <sub>2</sub>	C	-95.5	-93.3	-93.1	-87.9	-53.2	-50.6 <sup>a</sup>	...
	O	-162.8	-138.8	-138.4	-130.2	-65.6	-52.1 <sup>a</sup>	...
linear-N <sub>2</sub> O	N <sub>term</sub>	63.5	81.1	87.5	87.3	106.6	100.5 <sup>c</sup>	99.5 <sup>c</sup>
	N <sub>cent</sub>	-32.3	-11.9	-3.0	-5.2	14.2	5.3 <sup>c</sup>	11.3 <sup>c</sup>
	O	174.9	172.7	179.1	173.4	194.4	198.8 <sup>c</sup>	200.5 <sup>c</sup>
cyclic-N <sub>2</sub> O	N	-177.1	-171.0	-171.3	-169.3	-122.0	-87.3 <sup>a</sup>	...
	O	104.1	53.4	44.8	37.1	89.9	87.4 <sup>a</sup>	...
<i>cis</i> -N <sub>2</sub> F <sub>2</sub>	N	-194.8	-183.7	-172.9	-175.5	-131.5	-100.9 <sup>d</sup>	-119.8 <sup>d</sup>
	F	91.6	14.5	-6.2	-3.3	46.3	80.7 <sup>d</sup>	52.8 <sup>d</sup>
<i>trans</i> -N <sub>2</sub> F <sub>2</sub>	N	-299.4	-266.3	-256.3	-255.8	-202.1	-165.5 <sup>d</sup>	-181.7 <sup>d</sup>
	F	126.0	40.3	14.5	18.4	67.4	103.7 <sup>d</sup>	95.1 <sup>d</sup>
C <sub>6</sub> H <sub>6</sub>	C	54.9	43.0	39.9	40.9	56.7	64.0 <sup>b</sup>	57.2 <sup>g</sup>
C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	C <sub>α</sub>	-254.7	-183.1	-165.7	-165.7	-124.4	-143.0 <sup>e</sup>	...
	C <sub>β</sub>	123.7	108.6	107.2	105.8	114.6	129.2 <sup>e</sup>	...
C <sub>7</sub> H <sub>9</sub> <sup>+</sup>	C <sub>α</sub>	-88.6	-68.9	-65.2	-62.8	-36.3	-36.6 <sup>e</sup>	...
	C <sub>β</sub>	141.8	124.5	120.6	120.3	131.8	145.6 <sup>e</sup>	...
	C <sub>β'</sub>	180.2	155.4	149.7	148.6	160.6	175.2 <sup>e</sup>	...
	C <sub>γ</sub>	158.5	132.7	125.6	125.5	138.7	152.1 <sup>e</sup>	...
	C <sub>γ'</sub>	156.9	133.7	128.1	127.1	139.9	156.5 <sup>e</sup>	...
C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> <sup>+</sup>	N <sub>α</sub>	16.9	-0.9	-8.1	-6.5	18.5	41.8 <sup>f</sup>	15.9 <sup>f</sup>
	N <sub>β</sub>	-100.0	-96.9	-102.3	-97.0	-54.8	-62.4 <sup>f</sup>	-73.5 <sup>f</sup>
<i>d</i> σ <sub>iso</sub> (Expt.)		60.4	51.2	52.4	51.7	12.4	13.7	...
<i>d</i> σ <sub>iso</sub> (Best)		89.4	68.1	86.1	61.6	18.5	...	...

<sup>a</sup>IGLO-MCSCF (Ref. 21).<sup>b</sup>GIAO-MBPT(2) (Ref. 23).<sup>c</sup>GIAO-CCSD (Ref. 29).<sup>d</sup>GIAO-FV CASSCF (Ref. 22).<sup>e</sup>GIAO-CCSD(T) (Ref. 24).<sup>f</sup>LORG-SCF (Ref. 26) (not included in the error analysis).<sup>g</sup>Reference 28.

II, it is clear that the computed values for the less shielded C<sub>α</sub> atoms in both cations are significantly too deshielded at the Hartree-Fock and DFT levels with the latter providing some improvement. The B3LYP<sub>GGA</sub><sup>0.05</sup> values provide increased accuracy and, in the case of the C<sub>7</sub>H<sub>9</sub><sup>+</sup> cation, are in excellent agreement with the CCSD(T) value. Furthermore, analysis of the principal shielding tensor components of the B3LYP<sub>GGA</sub><sup>0.05</sup> functional (-173.9, 67.4, and -25 ppm for the σ<sub>xx</sub>, σ<sub>yy</sub>, and σ<sub>zz</sub> components, respectively) reveals that the σ<sub>xx</sub> and σ<sub>yy</sub> components are in good agreement with the corresponding CCSD(T) values (-184.9, 70.4, and 4.6 ppm, respectively) compared with, for example, the conventional B3LYP functional (-215.0, 29.8, and -21.5 ppm, respectively). For the more shielded carbon atoms, the Hartree-Fock values are found to be in good agreement with the CCSD(T) values and are superior in quality to the DFT shieldings, with B3LYP<sub>GGA</sub><sup>0.05</sup> improving upon the conventional DFT shieldings.

In a similar manner to Stanton *et al.*,<sup>25</sup> we compare the experimental NMR spectrum with the computed GIAO-SCF,

GIAO-LDA, GIAO-B3LYP<sub>GGA</sub><sup>0.05</sup>, and GIAO-CCSD(T) spectra for the 1-cyclopropylcyclopropylidene-methyl-cation in Fig. 1. The absolute shieldings were converted to relative shifts using calculated shieldings for the internal reference CH<sub>4</sub> [using Stanton's MBPT(2) optimized R(CH) bond length] of 195.3 ppm (Hartree-Fock), 193.0 ppm (LDA), and 192.8 ppm (B3LYP<sub>GGA</sub><sup>0.05</sup>). For comparison, the corresponding GIAO-CCSD(T)<sup>13</sup>C shielding value for CH<sub>4</sub> was 201.4 ppm. Relative shifts with respect to TMS were obtained using δ(CH<sub>4</sub>) values of -1.3 ppm and -3.9 ppm for Hartree-Fock and correlated/DFT calculations.

Challoner *et al.*<sup>26</sup> have reported the experimental <sup>15</sup>N shielding tensor data for the 5-methyl-2-diazobenzenesulphonic acid hydrochloride molecule, in which the two nitrogen nuclei in the diazo moiety exhibit markedly different shieldings; they also performed *ab initio* LORG-SCF shielding calculations on the model compound C<sub>6</sub>H<sub>5</sub>N<sub>2</sub><sup>+</sup> whose geometry was first optimized at the SCF/6-31G\* level (where the resulting N-N bond distance

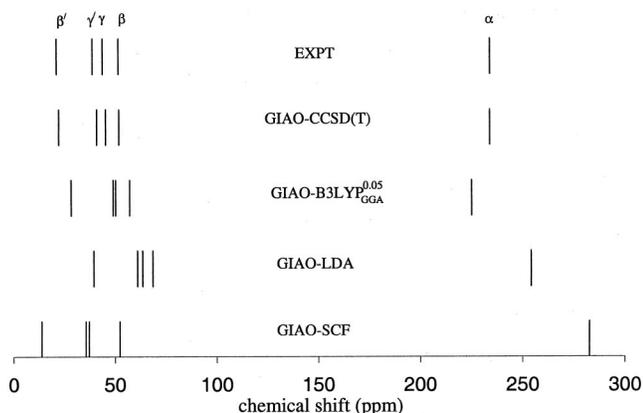


FIG. 1. Comparison between the experimental and calculated  $^{13}\text{C}$  GIAO chemical shifts of the 1-cyclopropylcyclopropylidene-methyl-cation (all values in ppm).

was found to be in good agreement with experiment). Using the same geometry, we calculated the Hartree–Fock and DFT shieldings for the  $N_\alpha$  (adjacent N atom to the benzene ring) and  $N_\beta$  (terminal N atom) as shown in Table II. For both N atoms, the conventional DFT values are too deshielded. Both the Hartree–Fock and B3LYP $_{\text{GGA}}^{0.05}$  methods provide good agreement with experiment for the  $N_\alpha$  shieldings; for the  $N_\beta$  atom, the B3LYP $_{\text{GGA}}^{0.05}$  scheme provides a small improvement over the Hartree–Fock method.

A more detailed analysis of the individual shielding tensor components highlights the superior performance of the B3LYP $_{\text{GGA}}^{0.05}$  scheme over the Hartree–Fock method. For the  $N_\alpha$  atom, the experimental  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and  $\sigma_{zz}$  shielding components are  $-133.3$ ,  $-133.3$ , and  $314.2$  ppm, respectively. Although the Hartree–Fock and B3LYP $_{\text{GGA}}^{0.05}$  isotropic shieldings are similar, the individual shielding tensor components of the latter ( $-135.9$ ,  $-115.2$ , and  $306.5$  ppm) are superior in quality to the former ( $-174.2$ ,  $-172.5$ , and  $397.5$  ppm). Similarly, for the  $N_\beta$  atom the B3LYP $_{\text{GGA}}^{0.05}$  tensors ( $-196.5$ ,  $-124.8$ , and  $156.8$ ) are in better agreement with the experimental shielding tensors ( $-229.8$ ,  $-166.8$ , and  $176.2$ ) compared with the Hartree–Fock values ( $-286.3$ ,  $-211.5$ , and  $197.8$ ). For comparison, Challoner *et al.*<sup>26</sup> found that the calculated (LORG-SCF/6-31G\*\*) principal shielding tensor components for both N atoms were in rather good agreement with the experimental values especially for the  $\sigma_{xx}$  and  $\sigma_{yy}$  components (the  $\sigma_{zz}$  shielding component were found to be too strongly shielded).

## V. CONCLUSIONS

This paper extends the size of the molecules studied in our previous B3LYP $_{\text{GGA}}^{0.05}$  shielding studies to include larger systems with up to eight heavy atoms. For this reason, London orbitals, which are known to provide the optimum way of tackling the gauge-origin problem, have been utilized in the calculations.

Since these molecules possess significant electron correlation effects, they represent a severe challenge to DFT methods. It is therefore encouraging to see that the calculated

GIAO-B3LYP $_{\text{GGA}}^{0.05}$  NMR shieldings provide accurate results with a quality that matches the best available *ab initio* data. They represent a significant improvement over the conventional DFT functionals studied here. The full potential of the GIAO-B3LYP $_{\text{GGA}}^{0.05}$  scheme therefore lies in the accurate prediction of shielding constants in larger molecules where the computational cost is prohibitive for high-level correlated methods.

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