

# GIAO shielding constants and indirect spin–spin coupling constants: performance of density functional methods

Thomas W. Keal <sup>a</sup>, David J. Tozer <sup>a,\*</sup>, Trygve Helgaker <sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK

<sup>b</sup> Department of Chemistry, University of Oslo, PO Box 1033, Blindern, N-0315 Oslo, Norway

Received 3 March 2004; in final form 6 April 2004

Available online 1 June 2004

## Abstract

The performance of the KT1 and KT2 exchange–correlation functionals is assessed for the determination of GIAO nuclear magnetic resonance shielding constants and indirect spin–spin coupling constants. For 14 highly correlated molecules containing light, main group nuclei, the functionals provide isotropic shieldings that are more than twice as accurate as those of BLYP and B3LYP. For 11 other molecules, they provide spin–spin coupling constants that are of variable quality. The spin–spin results highlight the sensitivity of the Fermi-contact term to exchange–correlation functional and are consistent with previous observations using a self-interaction corrected functional.

© 2004 Elsevier B.V. All rights reserved.

## 1. Introduction

The calculation of nuclear magnetic resonance (NMR) parameters is an important aspect of theoretical chemistry. Within Kohn–Sham density functional theory (DFT) [1], shielding constants and chemical shifts are relatively easy to compute, particularly for generalised gradient approximation (GGA) functionals where an uncoupled formalism is appropriate. For light, main-group nuclei, shielding constants from conventional GGAs and hybrid exchange–correlation functionals tend to be significantly too deshielded [2]. A number of approaches have been developed to try to improve shielding accuracy [3–7]. Calculations of indirect spin–spin coupling constants are somewhat less common. In part, this can be attributed to the complexity of the calculations, particularly when all four Ramsey mechanisms (diamagnetic spin–orbit, paramagnetic spin–orbit, spin–dipole, and Fermi-contact) are included. For examples, see [4,8–13].

In a recent study [14], we developed two new GGAs, designed specifically to provide high-quality shielding

constants for light, main-group nuclei. Both functionals are linear combinations of Dirac local density exchange [15], Vosko–Wilk–Nusair (VWN) local correlation [16], and a simple gradient expansion term, corrected to prevent asymptotic divergence. The first functional, denoted KT1, satisfies the uniform electron gas condition, whilst the second, denoted KT2, relaxes this condition through a fit to thermochemical data. The preliminary study [14] demonstrated that both functionals can provide isotropic and anisotropic shieldings of light, main-group nuclei that are 2–3 times more accurate than those of conventional GGAs and hybrid functionals. The results approach correlated *ab initio* quality. The KT2 functional has also been shown [17] to provide high-quality chemical shifts (shielding constants relative to reference nuclei).

To date, our investigations of KT1 and KT2 have used the CADPAC [18] implementation of the localised-orbital/local-origin (LORG) formalism [19] for the location of the gauge origin, which imposes a limit on the size of system that can be studied when there is an external magnetic field perturbation. To resolve this, we have implemented the functionals in the DALTON [20] program, which uses the gauge including atomic orbital (GIAO) scheme [21,22].

\* Corresponding author. Fax: +44-191-384-4737.

E-mail address: [D.J.Tozer@durham.ac.uk](mailto:D.J.Tozer@durham.ac.uk) (D.J. Tozer).

The aims of the present manuscript are threefold. First, we validate our implementation by comparing DALTON GIAO isotropic shieldings with CADPAC LORG values. Second, we extend our KT1/KT2 shielding constant investigations to a new set of challenging, highly correlated systems, including charged species, non-equilibrium geometries, and larger molecules with up to 16 atoms; attention is paid to both isotropic shieldings and individual tensor components. And third, we investigate the performance of KT1 and KT2 for the determination of indirect spin–spin coupling constants. This final aspect is particularly relevant in light of observations made by Patchkovskii et al. [4]. These authors used a self-interaction corrected (SIC) exchange–correlation functional, within an optimised effective potential framework. Like KT1 and KT2, their SIC functional gave significantly improved shielding constants. However, their spin–spin couplings were of variable quality, due to the sensitivity of the Fermi-contact term. The present study will establish the quality of spin–spin couplings from KT1 and KT2. Results and conclusions are presented in Sections 2 and 3, respectively.

## 2. Results

### 2.1. Comparison of LORG and GIAO shieldings

Table 1 compares KT1 and KT2 isotropic shieldings determined using the LORG formalism in the CADPAC program with those obtained using the GIAO formalism in DALTON. The molecules are those considered in [14], using the near-experimental geometries detailed in [6]. All calculations use the Huzinaga IV basis set [23,24] (denoted HIV) with Cartesian basis functions. The LORG and GIAO results are in very good agreement, with the small discrepancies arising due to the different gauge treatments; we have confirmed that converged electronic energies from the two codes agree to within numerical integration grid error ( $\sim 10^{-6}E_h$ ). Note that for molecules containing second-row atoms, the LORG results in Table 1 differ slightly from those in [14] since, in that investigation (and others [6,25]), we used a slightly smaller version of the HIV basis for second-row atoms, as detailed in [5].

Table 1  
LORG and GIAO isotropic shielding constants, in ppm, determined using the HIV basis set

Molecule	Nucleus	KT1		KT2	
		LOGR	GIAO	LOGR	GIAO
HF	F	412.0	410.9	412.4	411.4
H <sub>2</sub> O	O	330.7	330.5	329.6	329.5
CH <sub>4</sub>	C	196.4	196.3	195.2	195.1
CO	C	10.4	9.9	7.4	6.9
	O	−56.1	−55.9	−57.1	−56.9
N <sub>2</sub>	N	−55.8	−56.0	−59.7	−59.9
F <sub>2</sub>	F	−193.6	−193.0	−211.0	−210.4
O'OO'	O'	−1246.3	−1246.0	−1278.7	−1278.4
	O	−796.9	−796.6	−809.1	−808.9
PN	P	46.6	46.9	47.1	47.3
	N	−358.8	−358.3	−361.5	−361.0
H <sub>2</sub> S	S	741.5	742.4	735.7	736.3
NH <sub>3</sub>	N	265.9	266.1	264.5	264.6
HCN	C	87.2	86.9	86.0	85.7
	N	−18.6	−18.8	−19.4	−19.6
C <sub>2</sub> H <sub>2</sub>	C	120.5	120.3	120.4	120.2
C <sub>2</sub> H <sub>4</sub>	C	64.3	64.1	63.2	63.0
H <sub>2</sub> CO	C	−3.0	−3.3	−4.7	−4.9
	O	−383.8	−383.5	−379.6	−379.3
N'NO	N'	106.8	106.4	102.1	101.7
	N	14.2	13.5	12.2	11.4
	O	184.1	184.3	177.5	177.6
CO <sub>2</sub>	C	65.0	64.0	63.7	62.8
	O	224.5	224.4	221.6	221.4
OF <sub>2</sub>	O	−516.7	−516.4	−534.0	−533.7
H <sub>2</sub> CNN'	C	170.1	169.9	167.4	167.2
	N	−37.5	−37.9	−41.7	−42.1
	N'	−128.3	−128.7	−138.4	−138.8
HCl	Cl	961.3	965.2	958.6	962.3
SO <sub>2</sub>	S	−149.5	−148.5	−156.8	−155.9
	O	−244.6	−244.8	−251.8	−251.8
PH <sub>3</sub>	P	600.5	601.6	596.0	596.9

## 2.2. Isotropic shielding constants

Having established a valid implementation, we now extend our investigation of KT1 and KT2 GIAO shielding constants. We consider the 14 highly correlated systems studied previously by Helgaker et al. [26], using the same Huzinaga III (HIII) basis set [23,24] with spherical-harmonic basis functions. Details of the geometries are given in [26]. Isotropic shieldings are presented in Table 2. For comparison, DFT shieldings determined using the Dirac–VWN [15,16] local density approximation (LDA), the Becke–Lee–Yang–Parr [33,34] GGA (BLYP) and the hybrid B3LYP [35] functional are also presented, together with reference ab initio data and (where available) experimental data from [26]. Mean absolute errors  $|d|$  and mean absolute per-

centage errors  $|d|%$  are presented, relative to both ab initio and experiment.

All errors reduce in moving from LDA to BLYP, although the mean absolute errors increase slightly in moving from BLYP to B3LYP. This is one of the few properties where hybrids are inferior to GGAs; see [25] for a detailed investigation of the effect of exact exchange on shieldings. LDA, BLYP, and B3LYP all give shieldings that are significantly too deshielded. In moving to KT1 and KT2, the shieldings improve significantly, with both functionals giving mean absolute and mean absolute percentage errors that are more than a factor of two smaller than those of BLYP. The results support our earlier observations [14] that KT1 and KT2 provide improved quality shieldings for neutral molecules at near-equilibrium geometries. Furthermore, they

Table 2  
GIAO isotropic shielding constants, in ppm, determined using the HIII basis set

Molecule	Nucleus	LDA	BLYP	B3LYP	KT1	KT2	ab initio	Experimental <sup>g</sup>
CH <sub>2</sub>	H	-62.5	-24.5	-29.8	-19.8	-16.8	-7.8 <sup>a</sup>	
	C	-2003.2	-1135.3	-1252.6	-915.7	-868.8	-718 <sup>a</sup>	
CF <sub>2</sub>	C	-151.4	-139.3	-145.8	-91.2	-94.5	-101 <sup>a</sup>	
	F	-117.6	-92.0	-77.6	-64.7	-60.5	-34 <sup>a</sup>	
CF <sub>4</sub>	C	37.3	35.8	44.6	53.7	52.2	64.4 <sup>b</sup>	64.5
	F	219.2	224.6	236.2	231.9	231.9		
NO <sub>2</sub> <sup>-</sup>	N	-427.4	-420.1	-473.4	-350.5	-360.8	-360 <sup>a</sup>	-368
	O	-492.1	-474.0	-502.1	-396.6	-409.0	-382 <sup>a</sup>	-342 ± 20
Linear-CO <sub>2</sub>	C	48.7	48.5	48.3	63.2	61.9	63.5 <sup>b</sup>	58.8
	O	207.9	210.1	211.4	222.0	218.9	236.4 <sup>c</sup>	243 ± 17
Cyclic-CO <sub>2</sub>	C	-93.1	-87.9	-93.3	-52.1	-55.6	-50.6 <sup>a</sup>	
	O	-138.4	-130.2	-138.8	-77.3	-89.6	-52.1 <sup>a</sup>	
Linear-N <sub>2</sub> O	N <sub>term</sub>	87.5	87.3	81.1	105.6	100.8	100.5 <sup>c</sup>	99.5
	N <sub>cent</sub>	-3.0	-5.2	-11.9	12.5	10.4	5.3 <sup>c</sup>	11.3
	O	179.1	173.4	172.7	183.0	176.3	198.8 <sup>c</sup>	200.5
Cyclic-N <sub>2</sub> O	N	-171.3	-169.3	-171.0	-126.5	-132.3	-87.3 <sup>a</sup>	
	O	44.8	37.1	53.4	82.0	68.4	87.4 <sup>a</sup>	
<i>cis</i> -N <sub>2</sub> F <sub>2</sub>	N	-172.9	-175.5	-183.7	-137.1	-143.2	-100.9 <sup>d</sup>	-119.8
	F	-6.2	-3.3	14.5	27.2	21.7	80.7 <sup>d</sup>	52.8
<i>trans</i> -N <sub>2</sub> F <sub>2</sub>	N	-256.3	-255.8	-266.3	-208.4	-216.9	-165.5 <sup>d</sup>	-181.7
	F	14.5	18.4	40.3	47.5	42.9	103.7 <sup>d</sup>	95.1
C <sub>6</sub> H <sub>6</sub>	C	39.9	40.9	43.0	61.0	59.6	64.0 <sup>b</sup>	57.2
C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	C <sub>α</sub>	-165.7	-165.7	-183.1	-128.7	-132.5	-143.0 <sup>e</sup>	
	C <sub>β</sub>	107.2	105.8	108.6	121.2	120.0	129.2 <sup>e</sup>	
C <sub>7</sub> H <sub>9</sub> <sup>+</sup>	C <sub>α</sub>	-64.8	-62.5	-68.6	-37.1	-39.4	-36.6 <sup>e</sup>	
	C <sub>β</sub>	120.8	120.4	124.7	136.0	134.7	145.6 <sup>e</sup>	
	C <sub>β'</sub>	149.7	148.6	155.4	162.1	160.9	175.2 <sup>e</sup>	
	C <sub>γ</sub>	125.4	125.3	132.5	139.9	138.5	152.1 <sup>e</sup>	
C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> <sup>+</sup>	C <sub>γ'</sub>	128.1	127.0	133.6	141.9	140.5	156.5 <sup>e</sup>	
	N <sub>α</sub>	-8.0	-6.5	-0.8	17.0	14.5	41.8 <sup>f</sup>	15.9
	N <sub>β</sub>	-102.4	-97.2	-97.1	-64.2	-69.5	-62.4 <sup>f</sup>	-73.5
$ d $ (experimental)		44.5	42.5	46.2	17.6	19.3	11.3	
$ d $ (ab initio)		91.4	56.7	62.8	23.7	24.3		
$ d %$ (experimental)		52.4	51.7	51.1	15.5	16.6	13.7	
$ d %$ (ab initio)		86.1	61.6	68.0	28.5	28.1		

<sup>a</sup> IGLO-MCSCF [27].

<sup>b</sup> GIAO-MBPT(2) [28].

<sup>c</sup> GIAO-CCSD [29].

<sup>d</sup> GIAO-FV CASSCF [30].

<sup>e</sup> GIAO-CCSD(T) [31].

<sup>f</sup> LORG-SCF [32] (not included in any error analysis).

<sup>g</sup> See [26].

demonstrate that the functionals can also work well for charged species and geometries that are far from equilibrium. To put the results into further context, the corresponding mean absolute errors for Hartree–Fock are 64.7 ppm (vs. experiment) and 79.9 ppm (vs. best ab initio) [26]. We note that KT1 and KT2 are slightly inferior to the B3LYP<sup>0.05</sup><sub>GGA</sub> method [5], for which the mean absolute errors are 12.4 ppm (vs. experiment) and 15.0 ppm (vs. best ab initio) [26]. However, B3LYP<sup>0.05</sup><sub>GGA</sub> is less theoretically rigorous as it determines uncoupled shieldings using orbitals from a non-multiplicative Kohn–Sham operator. For the systems in Table 2 where experimental data is available, KT1 and KT2 are inferior to the correlated ab initio methods.

Each value in Table 2 is the sum of a diamagnetic and a paramagnetic contribution. For each nucleus, we have

examined the variation in these quantities with exchange–correlation functional. In all cases, the diamagnetic contribution varies very little – the average values are 391.6, 393.2, 393.0, 395.2, and 396.3 ppm for LDA, BLYP, B3LYP, KT1, and KT2, respectively. The variation in the total shielding can therefore be attributed almost entirely to the variation in the paramagnetic term, whose average values are –486.0, –455.9, –460.6, –423.1, and –426.4 ppm, respectively. For a GGA functional, this paramagnetic term has an explicit inverse dependence on the occupied–virtual eigenvalue differences and it is commonly assumed that the excess deshielding from conventional GGAs arises due to underestimation of these eigenvalue differences. In line with this argument, we do observe that for all the molecules in Table 2, the HOMO–LUMO eigenvalue

Table 3  
Indirect spin–spin coupling constants, in Hz, determined using the HIII-su3 basis set

Molecule		LDA	BLYP	B3LYP	KT1	KT2	Experimental <sup>a</sup>
HF	<sup>1</sup> J <sub>HF</sub>	395.9	390.0	439.3	344.7	335.1	538.0
CO	<sup>1</sup> J <sub>CO</sub>	26.7	22.7	19.4	25.8	27.3	15.7
<sup>14</sup> N <sup>15</sup> N	<sup>1</sup> J <sub>NN</sub>	4.3	3.1	1.8	3.9	3.9	1.7
H <sub>2</sub> O	<sup>1</sup> J <sub>OH</sub>	–65.7	–72.6	–76.9	–66.2	–68.1	–86.0
	<sup>2</sup> J <sub>HH</sub>	–3.3	–6.4	–8.1	–6.3	–10.4	–8.2
HC <sup>15</sup> N	<sup>1</sup> J <sub>CN</sub>	–8.1	–12.6	–18.1	–5.1	–5.5	–20.5
	<sup>1</sup> J <sub>CH</sub>	223.9	284.3	284.4	250.8	279.5	262.2
	<sup>2</sup> J <sub>NH</sub>	–6.3	–5.9	–7.5	–4.0	–3.0	–8.2
<sup>14</sup> NH <sub>3</sub>	<sup>1</sup> J <sub>NH</sub>	37.0	44.9	45.4	40.8	43.5	44.1
	<sup>2</sup> J <sub>HH</sub>	–5.0	–9.1	–10.4	–8.2	–12.5	–10.3
CH <sub>4</sub>	<sup>1</sup> J <sub>CH</sub>	100.2	133.3	132.2	117.1	128.4	120.0
	<sup>2</sup> J <sub>HH</sub>	–7.3	–12.5	–13.3	–10.6	–15.6	–12.1
C <sub>2</sub> H <sub>2</sub>	<sup>1</sup> J <sub>CC</sub>	176.8	201.0	204.9	175.4	180.9	184.8
	<sup>1</sup> J <sub>CH</sub>	215.8	277.0	274.2	251.6	280.9	243.0
	<sup>2</sup> J <sub>CH</sub>	48.9	57.2	55.9	58.2	58.7	53.1
	<sup>3</sup> J <sub>HH</sub>	6.5	10.3	11.0	10.8	14.9	9.7
C <sub>2</sub> H <sub>4</sub>	<sup>1</sup> J <sub>CC</sub>	51.4	69.5	73.1	53.0	56.3	66.7
	<sup>1</sup> J <sub>CH</sub>	128.0	166.7	166.1	148.6	164.6	151.2
	<sup>2</sup> J <sub>CH</sub>	1.4	0.1	–1.4	2.7	–0.2	–1.2
	<sup>2</sup> J <sub>HH</sub>	4.5	4.9	3.4	6.3	3.5	2.0
	<sup>3</sup> J <sub>cis</sub>	10.0	13.1	13.1	12.1	14.6	10.5
	<sup>3</sup> J <sub>trans</sub>	14.7	20.5	20.2	20.8	25.0	16.7
C <sub>2</sub> H <sub>6</sub>	<sup>1</sup> J <sub>CC</sub>	11.4	21.8	24.5	11.4	13.2	34.5
	<sup>1</sup> J <sub>CH</sub>	103.9	137.2	136.4	121.1	133.4	125.2
	<sup>2</sup> J <sub>CH</sub>	–2.3	–3.9	–4.6	–2.8	–4.8	–4.7
	<sup>2</sup> J <sub>HH</sub>	–5.0	–9.1	–10.0	–7.3	–11.8	
C <sub>6</sub> H <sub>6</sub>	<sup>1</sup> J <sub>CC</sub>	42.6	56.7	60.1	42.1	45.0	56.1
	<sup>2</sup> J <sub>CC</sub>	0.5	–0.3	–1.8	0.4	–1.2	–1.7
	<sup>3</sup> J <sub>CC</sub>	9.8	10.5	11.2	8.9	9.6	9.4
	<sup>1</sup> J <sub>CH</sub>	129.9	167.2	166.8	149.6	166.4	153.8
	<sup>2</sup> J <sub>CH</sub>	3.3	3.1	2.0	4.4	2.8	1.4
	<sup>3</sup> J <sub>CH</sub>	6.1	7.9	8.1	7.8	8.6	7.0
	<sup>4</sup> J <sub>CH</sub>	–0.3	–0.8	–1.3	–0.6	–1.1	–1.0
	<sup>3</sup> J <sub>HH</sub>	6.9	9.0	8.8	8.3	9.5	7.0
	<sup>4</sup> J <sub>HH</sub>	1.2	1.6	1.3	2.0	1.9	1.2
	<sup>5</sup> J <sub>HH</sub>	0.2	0.5	0.8	0.4	0.9	0.6
d  (all)		12.9	10.0	8.0	10.8	12.6	
d  <sup>b</sup>		9.1	6.0	5.3	5.5	7.0	
d /% (all)		45.7	29.5	15.2	49.4	35.8	

<sup>a</sup> All experimental values include vibrational corrections, except C<sub>2</sub>H<sub>6</sub>. See [12,13].

<sup>b</sup> Excluding <sup>1</sup>J<sub>HF</sub> in HF.

differences from KT1 and KT2 are notably larger than those of LDA and BLYP – see [14] for a quantitative assessment of KT1/KT2 eigenvalues.

The reduced deshielding is also evident in individual tensor components. For example, van Wüllen and Kutzelnigg [27] have highlighted a very strong deshielding  $xx$  component in the C shielding tensor of CH<sub>2</sub> (carbene), due to excitation from the lone pair (molecule in  $xz$  plane). Their multiconfigurational self-consistent field (MCSCF)  $\sigma_{xx}$ ,  $\sigma_{yy}$ ,  $\sigma_{zz}$  values are –2120, 201, and –237 ppm, respectively. By comparison, our BLYP components are –3228, 209, and –387 ppm, demonstrating that the excess deshielding observed in the isotropic value arises primarily from the  $xx$  component. The corresponding KT2 values of –2494, 216, and –328 ppm, respectively, are notably closer to MCSCF, although there is further room for improvement. The same authors also considered tensor components for CF<sub>2</sub> and for CO<sub>2</sub> and N<sub>2</sub>O at non-equilibrium cyclic geometries. We have confirmed that for all these cases, the MCSCF values reported are better reproduced with KT1/KT2 than with BLYP.

### 2.3. Indirect spin–spin coupling constants

Finally, we investigate the performance of KT1 and KT2 for the calculation of indirect spin–spin coupling constants. We use the procedure described in [11], in-

cluding all four Ramsey mechanisms, and consider 11 molecules drawn from [12] and [13]. Following [12], all calculations use the Huzinaga III basis set, augmented with three tight  $s$  functions (HIII-su3) with spherical-harmonic basis functions. Near-experimental geometries are taken from [6] (except for C<sub>6</sub>H<sub>6</sub>, for which  $r_{CC} = 1.392$  Å,  $r_{CH} = 1.086$  Å, and C<sub>2</sub>H<sub>6</sub>, for which  $r_{CC} = 1.526$  Å,  $r_{CH} = 1.088$  Å,  $\theta_{CCH} = 107.4^\circ$ ,  $\theta_{HCH} = 111.5^\circ$ ). The results are presented in Table 3, together with LDA, BLYP, B3LYP, and reference data. The reference data, which is taken from the earlier references, corresponds to the experimental coupling constants, corrected for vibrational contributions (determined at the B3LYP level). The coupling in HF is particularly challenging and so mean absolute errors are presented both including and omitting this quantity. Mean absolute percentage errors are also presented.

The couplings improve notably from LDA to BLYP to B3LYP, although the KT1 and KT2 results are of variable quality. They perform particularly poorly for systems such as HF and CO, but are relatively accurate for many of the CC and CH couplings. When HF is omitted from the error analysis, the KT1 mean absolute error is close to that of B3LYP, whilst the KT2 error is slightly inferior to BLYP. Both functionals yield relatively large percentage errors.

Table 4 presents the diamagnetic spin–orbit (DSO), paramagnetic spin–orbit (PSO), spin–dipole (SD) and

Table 4

Diamagnetic spin–orbit (DSO), paramagnetic spin–orbit (PSO), spin–dipole (SD) and Fermi-contact (FC) contributions, in Hz, to selected indirect spin–spin coupling constants

	LDA	BLYP	B3LYP	KT1	KT2	Experimental
HF, $^1J_{\text{HF}}$						
DSO	0.3	0.3	0.3	0.4	0.3	
PSO	199.7	203.4	201.3	198.4	198.0	
SD	5.3	3.4	1.3	4.0	1.5	
FC	190.6	182.9	236.4	141.9	135.3	
Total	395.9	390.0	439.3	344.7	335.1	538.0
CO, $^1J_{\text{CO}}$						
DSO	0.1	0.1	0.1	0.1	0.1	
PSO	15.1	14.5	14.3	13.7	14.0	
SD	–4.8	–5.7	–6.1	–5.2	–5.7	
FC	16.4	13.8	11.1	17.3	18.9	
Total	26.7	22.7	19.4	25.8	27.3	15.7
HC <sup>15</sup> N, $^1J_{\text{CH}}$						
DSO	0.5	0.4	0.4	0.4	0.4	
PSO	–0.5	–0.4	–1.0	–0.4	–0.4	
SD	0.7	0.6	0.5	0.6	0.7	
FC	223.3	283.7	284.4	250.1	278.8	
Total	223.9	284.3	284.4	250.8	279.5	262.2
C <sub>2</sub> H <sub>2</sub> , $^1J_{\text{CC}}$						
DSO	0.0	0.0	0.0	0.0	0.0	
PSO	6.6	7.1	8.4	5.9	6.3	
SD	8.4	10.8	11.6	8.8	10.5	
FC	161.8	183.2	184.9	160.6	164.1	
Total	176.8	201.0	204.9	175.4	180.9	184.8

Fermi-contact (FC) contributions to the following selected couplings:  $^1J_{\text{HF}}$  in HF,  $^1J_{\text{CO}}$  in CO,  $^1J_{\text{CH}}$  in  $\text{HC}^{15}\text{N}$ , and  $^1J_{\text{CC}}$  in  $\text{C}_2\text{H}_2$ . These couplings were chosen because they exhibit significant variation across the functionals; KT1 and KT2 perform poorly for the first two, but are relatively accurate for the latter two. For all four couplings the DSO contributions are very small and are almost independent of functional. The magnitude of the PSO contributions are smaller with KT1 and KT2 than with LDA and BLYP. This is to be expected, since the PSO term has an explicit inverse dependence on the occupied-virtual eigenvalue differences and so is somewhat analogous to the paramagnetic contribution to the shielding constant, which reduces in magnitude with KT1 and KT2; it has been suggested [4] that such a reduction in the PSO magnitude is desirable. The variation in the PSO term with functional is, however, relatively small and does not explain the observed variation in the total coupling constants. The variation in the SD term, though significant as a percentage of its value, is also relatively small in absolute terms. It is clear from Table 4 that for all four couplings, the variation in the total coupling constant with exchange-correlation functional is dominated by the variation in the FC term.

Our spin–spin observations are therefore consistent with the SIC findings of Patchkovskii et al. [4]. The introduction into a functional of the appropriate characteristics necessary for high quality shielding constants can lead to significant changes in the Fermi-contact term, which can affect the quality of the total spin–spin coupling constants.

### 3. Conclusion

The KT1 and KT2 GGA exchange-correlation functionals have been implemented in the DALTON program. GIAO isotropic shieldings are in good agreement with LORG values for the HIV basis set. The functionals were used to calculate isotropic shielding constants for 14 highly correlated molecules. In line with previous observations, KT1 and KT2 give shieldings that are a significant improvement over those from conventional functionals. They are successful for both charged and neutral species, and for equilibrium and non-equilibrium geometries. The improvement can be traced almost exclusively to the paramagnetic contribution. The functionals were then used to determine indirect spin–spin coupling constants for 11 molecules. The results are of variable quality and do not represent an improvement over conventional functionals. This can be traced to the sensitivity of the Fermi-contact term to exchange-correlation functional, and is consistent with the SIC findings of Patchkovskii et al. [4].

### Acknowledgements

We are grateful to the EPSRC for studentship support (TWK) and to Aron J. Cohen for assistance in checking our implementation of spin–spin couplings.

### References

- [1] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.
- [2] P.J. Wilson, R.D. Amos, N.C. Handy, Mol. Phys. 97 (1999) 757.
- [3] V.G. Malkin, O.L. Malkina, M.E. Casida, D.R. Salahub, J. Am. Chem. Soc. 116 (1994) 5898.
- [4] S. Patchkovskii, J. Autschbach, T. Ziegler, J. Chem. Phys. 115 (2001) 26.
- [5] P.J. Wilson, R.D. Amos, N.C. Handy, Chem. Phys. Lett. 312 (1999) 475.
- [6] P.J. Wilson, D.J. Tozer, Chem. Phys. Lett. 337 (2001) 341.
- [7] J. Poater, E. van Lenthe, E.J. Baerends, J. Chem. Phys. 118 (2003) 8584.
- [8] V.G. Malkin, O.L. Malkina, D.R. Salahub, Chem. Phys. Lett. 221 (1994) 91.
- [9] R.M. Dickson, T. Ziegler, J. Phys. Chem. 100 (1996) 5286.
- [10] V. Sychrovský, J. Gräfenstein, D. Cremer, J. Chem. Phys. 113 (2000) 3530.
- [11] T. Helgaker, M. Watson, N.C. Handy, J. Chem. Phys. 113 (2000) 9402.
- [12] T.A. Ruden, O.B. Lutnaes, T. Helgaker, K. Ruud, J. Chem. Phys. 118 (2003) 9572.
- [13] M. Pecul, T. Helgaker, Int. J. Mol. Sci. 4 (2003) 143.
- [14] T.W. Keal, D.J. Tozer, J. Chem. Phys. 119 (2003) 3015.
- [15] P.A.M. Dirac, Proc. Cambridge Philos. Soc. 26 (1930) 376.
- [16] S.J. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.
- [17] M.J. Allen, T.W. Keal, D.J. Tozer, Chem. Phys. Lett. 380 (2003) 70.
- [18] R.D. Amos et al., CADPAC 6.5, The Cambridge Analytic Derivatives Package, 1998.
- [19] A.E. Hansen, T.D. Bouman, J. Chem. Phys. 82 (1995) 5035.
- [20] T. Helgaker et al., DALTON Release 1.2, An Electronic Structure Program, 2001.
- [21] R. Ditchfield, J. Chem. Phys. 56 (1972) 5688.
- [22] K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.
- [23] S. Huzinaga, Approximate Atomic Functions, University of Alberta, Edmonton, 1971.
- [24] W. Kutzelnigg, U. Fleischer, M. Schindler, in: NMR-Basic Principles and Progress, vol. 23, Springer, Heidelberg, 1990.
- [25] P.J. Wilson, D.J. Tozer, J. Chem. Phys. 116 (2002) 10139.
- [26] T. Helgaker, P.J. Wilson, R.D. Amos, N.C. Handy, J. Chem. Phys. 113 (2000) 2983.
- [27] C. van Wüllen, W. Kutzelnigg, J. Chem. Phys. 104 (1996) 2330.
- [28] J. Gauss, J. Chem. Phys. 99 (1993) 3629.
- [29] J. Gauss, J.F. Stanton, J. Chem. Phys. 102 (1995) 251.
- [30] M. Jaszuński, T. Helgaker, K. Ruud, Magn. Reson. Chem. 34 (1996) 646.
- [31] J. Gauss, J.F. Stanton, J. Mol. Struct.: Theochem 398–399 (1997) 73.
- [32] R. Challoner, R.K. Harris, J.A. Tossell, J. Magn. Reson. 126 (1997) 1.
- [33] A.D. Becke, Phys. Rev. A. 38 (1988) 3098.
- [34] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B. 37 (1988) 785.
- [35] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.