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Spin–orbit corrections to NMR shielding constants from density functional theory. How important are the two-electron terms?

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Abstract

A recently developed density functional theory (DFT) ansatz for the calculation of one-electron spin–orbit (SO) corrections to NMR chemical shifts has been extended to include two-electron SO operators. The performance of different approximations is evaluated in calculations of ^{1}H and ^{13}C nuclear shieldings in the hydrogen halides, the halomethanes, and in iodobenzene. Two-electron contributions are significant relative to the one-electron contributions for fluorine substituents (ca. 30–35%) but decrease for the heavier halogens (ca. 6–7% for iodine). A mean-field approximation to the two-electron SO integrals performs excellently, with negligible deviations from the 'exact' results, thus opening the way to calculations on large systems. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The importance of relativistic effects on NMR properties has recently received increased attention, as both scalar (spin-free) relativistic effects and spin–orbit (SO) coupling have to be considered for compounds containing heavy atoms [1]. In particular, SO-induced heavy-atom effects on NMR chemical shifts have been studied in some detail. They may affect significantly even the nuclear shieldings of light atoms bound to heavier atoms like Br or I [2–7].

While early investigations of SO effects on chemical shifts were based on semi-empirical methods [8] more recently approaches based on density functional theory (DFT) [2,3,6,7] or on the Hartree–Fock approximation

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[4,5] have been implemented and applied. Most calculations included only the one-electron SO operator [2–4,6,7], or an effective one-electron SO operator in conjunction with a pseudopotential treatment [5]. The importance of the two-electron SO contributions for a reliable calculation of NMR chemical shifts has thus remained unclear. Here we report on the explicit implementation of two-electron SO integrals in the DFT-based deMon–NMR code, as well as on validation calculations for the ^{1}H shifts in the hydrogen halides and for the ^{13}C shifts in the halogenomethanes.

The explicit calculation of all two-electron SO matrix elements quickly becomes very demanding computationally (with respect to both disk space and computer time) with increasing system size. We have therefore also implemented and tested a mean-field approximation to the two-electron SO integrals [9]. This mean-field method has been applied successfully to SO energy splittings in SO CI calculations. It is of interest to evaluate its performance in the context of DFT calculations of NMR chemical shifts. It is hoped that this approach will allow the inclusion of the two-electron SO contributions even for relatively large systems of chemical interest, with a modest computational effort that is compatible with the underlying, relatively inexpensive, DFT approach. As a simple example, two-electron SO effects on all ^{1}H and ^{13}C nuclear shieldings in iodobenzene, C_6H_5I, have been evaluated (one-electron SO contributions alone have been discussed recently for this system [6]).

2. Method

In the presence of an external magnetic field, SO interactions produce non-zero spin density even in formally closed-shell systems, as they mix a ground-state singlet with excited triplet states. This SO-induced spin density may take part in magnetic interactions in molecules (or, e.g., in solids). The interaction with the magnetic moments of the nuclei may lead to hyperfine structure which in principle might be observed by EPR spectroscopy. Moreover, the SO interaction is the leading term for the electronic g-tensor of EPR spectroscopy. Questions associated with EPR spectroscopy are outside the scope of the present Letter. However, the SO-induced spin density contributes to the NMR shielding tensors, in particular via a Fermi-contact (FC) mechanism. The theoretical background of this question has been discussed elsewhere [2,4] and recently a general qualitative concept has been delineated [6] which relates these interactions to the FC mechanism of indirect nuclear spin–spin coupling.

To calculate the SO corrections to the nuclear shielding tensor, we use a DFT-based third-order perturbation theory approach developed recently [2]. We include the FC operator through finite perturbation theory (FPT). Based on the perturbed Kohn–Sham orbitals (spin-polarized by the FC operator), we then employ a sum-over-states ansatz to calculate the SO corrections to the NMR shielding tensor. The final expressions (in the case of a common gauge origin) are as follows (λ_N is the parameter specifying the finite perturbation):

$$\sigma_{N,vu}(\text{SO}) = \frac{\sigma_{N,vu}^{\alpha}(\lambda_N) + \sigma_{N,vu}^{\beta}(\lambda_N)}{\lambda_N} = \frac{\sigma_{N,vu}^{\alpha,p}(\lambda_N) + \sigma_{N,vu}^{\beta,p}(\lambda_N)}{\lambda_N} \tag{1}$$

$$\sigma_{N,vu}^{\alpha,p}(\lambda_N) = \frac{e\hbar}{2mc} \sum_{k}^{\text{occ}} \sum_{a}^{\text{virt}} \frac{\left\langle \psi_k^{\alpha,0}(\lambda_N) \mid L_{iv} \mid \psi_a^{\alpha,0}(\lambda_N) \right\rangle \left\langle \psi_a^{\alpha,0}(\lambda_N) \mid H_{iu}^{\text{SO}} \mid \psi_k^{\alpha,0}(\lambda_N) \right\rangle}{\varepsilon_k^0 - \varepsilon_a^0 - \Delta E_{k \to a}^{0,\text{xc}}} \tag{2}$$

and a corresponding expression for $\sigma_{N,vu}^{\beta,p}$. Superscripts p indicate that paramagnetic shielding terms are considered, superscripts '0' denote wavefunctions and energies unperturbed by the external magnetic field. Taking $\Delta E_{k \to a}^{0,\text{xc}} = 0$ in Eq. (2) (and for β spin) corresponds to the simple uncoupled DFT approach. The uncoupled equations result from the lack of a dependency of the commonly used exchange-correlation

functionals on the induced paramagnetic current density [10]. Within the LOC1 approximation of the SOS–DFPT method [11,12] we introduce a simple correction term

$$\Delta E_{k \to a}^{0,\text{xc}} = \frac{1}{2}\left(\frac{3}{4}\pi\right)^{1/3} \int \rho(0,\boldsymbol{r})^{(-2/3)} \rho_k(0,\boldsymbol{r})\, \rho_a(0,\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} \tag{3}$$

to account in part for such deficiencies of the functional.

In the above expressions, and in what follows, we use the following notation: $\boldsymbol{r}_{iN} = \boldsymbol{r}_i - \boldsymbol{r}_N$, $\boldsymbol{B}$ is the external magnetic field, $\boldsymbol{\sigma}_N$ the shielding tensor for nucleus N, subscripts i and j refer to electrons, subscript N refers to a nucleus, and u and v represent Cartesian components of vectors and tensors. We have used the following operators:

$$H_{iu}^{\text{SO}} = \frac{e\hbar}{2mc}\left(\sum_N \frac{Z_N L_{iNu}}{r_{iN}^3} - \sum_{j \neq i} \frac{L_{ju}^i}{r_{ij}^3} - 2\sum_{j \neq i} \frac{L_{iu}^j}{r_{ij}^3}\right) \tag{4}$$

and

$$L_{iu} = -i(\boldsymbol{r}_i \times \nabla_i)_u; \quad L_{iNu} = -i(\boldsymbol{r}_{iN} \times \nabla_i)_u; \quad L_{ju}^i = -i(\boldsymbol{r}_{ij} \times \nabla_j)_u. \tag{5}$$

In our previous Letter [2] we included only the one-electron SO operator (first term in Eq. (4)). In the present work, the two-electron SO and spin–other-orbit terms (second and third terms in Eq. (4)) have also been implemented, by interfacing the EAGLE code [3] to our program. Since the exact calculation of the resulting two-electron integrals is demanding computationally (in particular when compared to the underlying, relatively inexpensive DFT approach), we implement a mean-field approximation [9] to the two-electron SO terms.

Note that we presently neglect the spin-dipolar (SD) contribution to the hyperfine interaction. At the Hartree–Fock level, the SD contribution has been found to account for only ca. 2–3% of the FC term for light atom shieldings in the neighborhood of heavier nuclei [4,5]. This point is mentioned again in the discussion.

The main idea of the mean-field SO approximation has been explained in Ref. [9]. In what follows, we give a brief summary. The two-electron terms of the SO operator basically describe a shielding of the nuclear charges (the 'bare nuclear potential', cf. the first term in Eq. (4)) by the electrons (mainly by the core shells at the same atom). This leads to the conclusion that an effective one-electron (Fock-type) operator should be sufficient to describe the dominant contributions of the SO operator between valence–valence singly excited Slater determinants, and that matrix elements between Slater determinants, which are doubly excited with respect to each other, can be neglected. Generalizing the matrix element between singly excited determinants to the case of partially filled shells leads to the Fock-type generalization

$$\begin{aligned}
H_{ij}^{\text{SO-mf}} = &\langle i|H^{\text{SO}}(1)|j\rangle + \sum_M^{\text{mf-orbs.}} \text{occ}(M)\big[\langle iM\alpha|H^{\text{SO}}(1,2)|jM\alpha\rangle + \langle iM\beta|H^{\text{SO}}(1,2)|jM\beta\rangle \\
&- \langle iM\alpha|H^{\text{SO}}(1,2)|M\alpha j\rangle - \langle iM\beta|H^{\text{SO}}(1,2)|M\beta j\rangle - \langle M\alpha i|H^{\text{SO}}(1,2)|jM\alpha\rangle \\
&- \langle M\beta i|H^{\text{SO}}(1,2)|jM\beta\rangle\big]
\end{aligned} \tag{6}$$

where i and j are spin orbitals and Ms are the (partially) occupied orbitals generating the electronic charge distribution to interact with. $\text{occ}(M)$ is the occupation number of orbital M. As the inner shells are, for practical purposes, independent of the valence occupation, one common set of orbitals can be chosen to generate effective integrals to be used for several valence excited states at the same time. As the computation of the effective integrals requires the two-electron integrals in the full molecular basis set, no computational savings have been made up to this point.

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[3] EAGLE is a code for the calculation of integrals of the Breit–Pauli SO Hamiltonian over molecular Cartesian Gaussian functions, written by Praphull Chandra.

For significant simplifications in the calculation of the integrals, further approximations have to be made. A more detailed analysis [13] of the contributions to the mean-field integrals leads to an omission of all multi-centre one- and two-electron integrals. This amounts essentially to a calculation of the shielding of the nuclear charge by the core electrons for each atom separately. This one-center approximation reduces the number of two-electron integrals to be calculated significantly. Moreover, it allows advantage to be taken of full spherical symmetry and thus the separation of the integrals into pure radial and angular parts. In particular, the contraction of the integrals in the primitive basis set can be carried out already in the radial part, reducing the computational demands dramatically.

While this short description of the mean-field SO approximation has been based on its usual use in SO CI calculations, the same types of arguments apply to the present Kohn–Sham based perturbation theory. In a DFT framework one may argue that, in the calculation of the SO integrals, the mean-field approximation makes use of a sum of state-averaged atomic densities instead of the true molecular density in the core region. During an expansion in atomic basis functions, it is further possible to neglect all terms between different centers (one-center approximation).

3. Computational details

The calculations have been carried out using a modified version of the deMon–KS program [14] augmented by the deMon–NMR code [12]. All calculations of SO corrections to the nuclear shieldings have been obtained with the Perdew and Wang exchange functional [15] and the Perdew correlation functional (PP) [16] whereas the uncorrected (nonrelativistic) chemical shifts were calculated with the more recent Perdew/Wang exchange-correlation functional (PW91) [17] (see Refs. [2,3,12] for further computational details). We have used two different sizes of basis sets: (a) the moderately sized basis set BII of Kutzelnigg et al. (also known as IGLO-II) [18] and (b) a very large, fully uncontracted (UP) basis derived from Partridge's basis sets [19], leading to the sizes 16s4p (H), 18s13p4d (C,F), 20s15p4d (Cl), 22s17p11d (Br), and 27s20p14d (I) (see Refs. [2,3] for the detailed construction). While all six cartesian components of the d-functions were kept in the nonrelativistic shielding calculations, the s-like component was dropped in the calculations of the SO corrections, for compatibility with the SO integral codes (cf. below).

A FINE angular grid with 32 (for the calculation of the chemical shifts) or 64 (for the SO corrections) points of radial quadrature [12,14] was employed. We used experimental structures for the hydrogen halides and for iodobenzene [20]. For the halomethanes, the structures have been optimized at the Hartree–Fock level, using quasi-relativistic effective-core potentials for carbon and halogen [21] together with (4s4p1d)/[2s2p1d] and (5s5p1d)/[3s3p1d] valence basis sets for carbon [21] and halogen [22], respectively. A (4s1p)/[2s1p] basis was employed for hydrogen [23]. The optimization results are given in Table 1.

Integrals over the full Breit–Pauli SO operator [24] were evaluated by means of the EAGLE program (see footnote 3). This program is based on methods for the evaluation of operators which are expressible as derivatives of the Coulomb potential [25]. The integrals of the Breit–Pauli operator are of this type, but also the

Table 1
Optimized structures for the halomethanes CH_3X (X = F, Cl, Br, I)[a]

X	$r(C–X)$	$r(C–H)$	$\angle(X–C–H)$
F	1.365	1.081	108.6
Cl	1.799	1.077	107.8
Br	1.948	1.077	107.5
I	2.167	1.077	107.2

[a]HF optimizations with quasi-relativistic ECPs (see text). Distances in Å, angles in degs.

integrals over the spin-dependent part of the Douglas–Kroll-transformed no-pair operator are accessible using these methods.

For the calculation of the mean-field integrals, the atomic mean-field integral program AMFI has been used, which was recently developed by one of us (BS). In addition to the Breit–Pauli integrals [24] employed in the present work, it is also capable of calculating the SO integrals for the no-pair SO operator obtained by the free-particle Douglas–Kroll transformation. Detailed information on the no-pair SO operator can, e.g., be found in Ref. [26]. The AMFI code uses the one-center approximation for both one- and two-electron SO integrals (see discussion above). The code is based on spherical harmonic d-functions, and thus the s-like contaminant has been projected out in the preceding deMon–KS calculation (cf. above).

4. Results

4.1. [1]H shifts of the hydrogen halides

Table 2 gives SO corrections to the ^{1}H shieldings in HX (X = F, Cl, Br, I) computed by different methods (cf. discussion above). The calculations with the AMFI code involve the one-center approximation even for the one-electron SO integrals. Comparison to the one-electron contributions computed with the EAGLE code (without the one-center approximation) shows clearly that this is an excellent approximation.

Table 2 also shows that the two-electron contributions are far from being negligible. They amount to ca. 30% of the one-electron contributions for HF, but their relative importance decreases for the heavier halogens, down to ca. 7% for HI. Fig. 1 compares the computational results obtained with the larger UP basis set to experiment. As found previously [2,4,8] the nonrelativistic calculations cannot reproduce the large increase in the shielding from HF to HI, which is clearly an SO effect, as shown by the SO-corrected results. The two-electron SO corrections are opposite to the one-electron contributions, as expected, and thus reduce to some extent the overall magnitude of the (strongly shielding) SO corrections. This improves slightly the agreement with experiment in all cases. In view of the relatively constant deviations from experiment from HF through HBr, we think that the remaining discrepancies arise largely in the nonrelativistic DFT calculations rather than from the SO corrections. The almost perfect agreement with experiment for HI might be due to a cancellation of errors.

At this stage, a more detailed comparison to experiment is not warranted, as for a more quantitative study other, as yet neglected, contributions need to be addressed. (i) Ro-vibrational corrections are expected to be large for the present ^{1}H shieldings. The bond-distance dependence of the SO contributions (and thus their change upon inclusion of ro-vibrational effects) may be quite different than that of the nonrelativistic shielding alone. We have started an investigation into this matter. (ii) Spin-dipolar contributions to the hyperfine interactions have been neglected. At the HF level, these have been found to account for ca. 2–3% of the FC interactions (i.e. their inclusion will further increase the ^{1}H shieldings) [4,5]. (iii) Scalar relativistic effects might become significant with iodine, in particular their coupling with the SO contributions [4]. (iv) Basis-set incompleteness is expected to give too small (shielding) SO contributions, but may also influence the nonrelativistic results (the deMon–KS program version employed does not handle f-functions). Larger basis sets increase the SO contributions by providing a larger virtual MO space for the perturbation expansion and by decreasing the relevant energy differences between occupied and virtual MOs (note the analogy to the treatment of electron correlation by perturbation theory). This is confirmed by comparing the BII and UP basis set results (see Table 2). The SO contributions generally increase with basis set expansion. In contrast, the nonrelativistic shielding values are reduced by ca. 0.8–1.0 ppm for HF and HCl, but not for the heavier halides.

The exact treatment of all two-electron SO integrals quickly becomes demanding computationally with increasing system size (as will be illustrated below). Table 2 thus also includes results obtained with the mean-field approximation for the two-electron SO integrals. This method works excellently (even while

Table 2
SO corrections to ^{1}H shieldings in hydrogen halides (in ppm)[a]

| | Basis | σ (nonrel.) | 1e–SO | | (1e + 2e)–SO | | $\sigma_{exp.}$ [b] | $\sigma_{exp.} - \sigma_{nonrel.}$ |
			EAGLE	AMFI	EAGLE	AMFI(HF)[c]		
HF	BII	30.04	0.16	0.17	0.11	0.11	28.89	− 1.15
	UP	29.09	0.17	0.18	0.12	0.12		− 0.20
HCl	BII	31.72	0.80	0.80	0.65	0.65	31.06	− 0.66
	UP	30.98	0.91	0.90	0.74	0.73		+ 0.08
HBr	BII	31.25	4.18	4.18	3.75	3.76	34.96	+ 3.71
	UP	31.27	4.86	4.87	4.38	4.38		+ 3.69
HI	BII	31.65	11.59	11.58	10.79	10.78	43.86	+ 12.21
	UP	31.74	13.30	13.29	12.38	12.37		+ 12.12

[a]Uncorrected shieldings obtained with IGLO gauge, PW91 functional and 32 points of radial quadrature. SO corrections with common gauge on X, P86 functional, and 64 radial points.
[b]Experimental shielding for HF from Ref. [30]. Values for HCl, HBr, and HI are gas-phase shifts from Ref. [31] converted to absolute shieldings using $\sigma(CH_4) = 30.61$ [32].
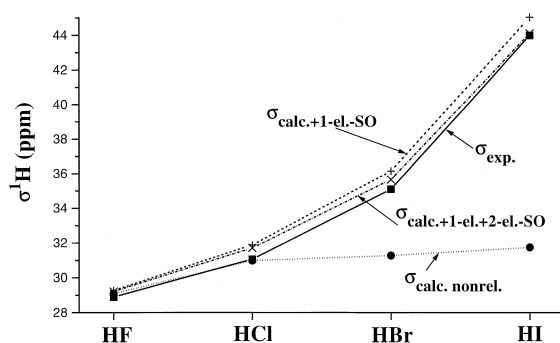[c]Atomic density matrix calculated at the HF level. Results with a DFT-based density matrix are identical (see text).

Fig. 1. Comparison of computed and experimental ^{1}H shieldings for the hydrogen halides (see Table 2 for numerical data). Calculations with UP basis sets. The AMFI results are used for the SO corrections.

including the one-center approximation), with deviations from the exact two-electron results of only ca. 0.01 ppm for the ^{1}H shieldings. This result confirms the remarkable performance of the mean-field approximation noted previously for SO splittings [9,13].

To calculate the mean-field SO integrals, atomic one-electron density matrices are required. These atomic calculations may in principle be carried out at various theoretical levels. From a practical point of view, it is of course desirable to use the same method as is used for the full molecular calculation (in the present case DFT calculations with the deMon code). To estimate the sensitivity of the results to the choice of the atomic one-electron density matrix, we have compared a Hartree–Fock derived density matrix [AMFI(HF)], as well as the one obtained from the deMon–DFT calculations [AMFI(DFT)]. The results turn out to be identical, i.e. the choice does not appear to be critical. Table 2 thus includes only the AMFI(HF) data.

Table 3 evaluates the use of mixed basis sets, i.e. of using the moderate BII basis on one atom together with the large UP basis on the other atom. As expected, for the ^{1}H shieldings it is more important to have a large basis on hydrogen, as the FC operator probes the spin density at the NMR nucleus, which is particularly basis-set dependent. It appears to be somewhat less important to have a large basis on the heavy neighboring (spin–orbit) atom. Thus, results with the BII basis on the halogen but with the UP basis on hydrogen agree excellently with the full UP basis results. In contrast, the results with the BII basis only on hydrogen are much closer to the full BII basis results. This type of a ''locally dense basis-set approximation'' [27,28] may also be used to reduce the computational effort for very large systems, e.g. those with many heavy atoms.

The most important advantage of the mean-field approximation is of course the significantly increased computational efficiency (with respect to both disk space and computer time). To give the reader an idea of the timings of different parts of the code for the DFT calculation of SO corrections to nuclear shieldings at different levels of approximation, Table 4 summarizes some results for the hydrogen halides. The second column gives the timings for the SCF part of the code, i.e. the CPU time required for the calculation of the Kohn–Sham MOs (single-point calculation, the number of SCF iterations is given). The other columns summarize the timings for the deMon–NMR steps, using different methods (codes) for the calculation of the one- and two-electron SO integrals. The calculation of the SO corrections with only the one-electron SO integrals by the EAGLE code requires only about 20–30% of the time needed to obtain the nonrelativistic (perturbed) wavefunction. The explicit calculation of the one- and two-electron SO integrals (with the EAGLE code) increases this ratio significantly, to ca. 400–500% of the Kohn–Sham part. Since this increased computer time is accompanied by a dramatic increase of the disk space needed to store the 2-electron SO integrals, the full-blown calculation of the two-electron SO corrections becomes impractical already for relatively small molecules.

In contrast, the calculation of one- and two-electron SO terms within the mean-field approximation (as implemented in the AMFI code) is not significantly more expensive than the calculation of the one-electron

Table 3
Basis set effects on SO corrections to ^{1}H shieldings (in ppm) in hydrogen halides

	Basis	Basis size [a]	1e (EAGLE)	(AMFI)	1e + 2e (AMFI(HF))
HF	UP	109	0.17	0.18	0.12
	BII	29	0.16	0.17	0.11
	BII(H) [b]	87	0.16	0.17	0.11
	BII(X) [c]	51	0.17	0.18	0.12
HCl	UP	109	0.91	0.90	0.73
	BII	43	0.80	0.80	0.65
	BII(H) [b]	87	0.80	0.80	0.65
	BII(X) [c]	65	0.88	0.88	0.71
HBr	UP	167	4.86	4.87	4.38
	BII	73	4.18	4.18	3.76
	BII(H) [b]	145	4.35	4.36	3.91
	BII(X) [c]	95	4.81	4.82	4.33
HI	UP	199	13.30	13.29	12.37
	BII	93	11.59	11.58	10.78
	BII(H) [b]	177	11.82	11.81	11.00
	BII(X) [c]	115	13.31	13.29	12.37

[a] Number of contracted basis functions.
[b] Mixed basis with BII on H but UP on X.
[c] Mixed basis with UP on H but BII on X.

terms only (Table 4). Thus, at the mean-field SO level, the computation of the SO integrals requires only a relatively small fraction of the computer resources for the overall shielding computations. Note, that the uncontracted UP basis set represents essentially the worst case for the performance of the AMFI code, as no use is made of the contraction of the integrals already in the radial part (one of the main advantages of the code).

4.2. ^{13}C shifts of the methyl halides

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Table 5 gives the SO corrections to the ^{13}C chemical shifts in the halogenomethanes CH$_3$X. Fig. 2 compares graphically nonrelativistic and SO-corrected results to experiment. First of all, we compare different choices of

Table 4
Timings for various steps in the calculation of SO corrections to ^{1}H shieldings in HX (X = F, Cl, Br, I) [a]

	AO [b]	SCF part (deMon)	1e (EAGLE)	(1e + 2e) (AMFI) [c]	(EAGLE) [d]
HF	109	116 (25 iter.)	32	33	481
HCl	117	170 (29 iter.)	41	45	559
HBr	167	480 (34 iter.)	112	130	2116
HI	199	834 (36 iter.)	182	246	3930

[a] Times (in s) on a HP9000-C160 workstation.
[b] Number of contracted basis functions.
[c] Mean field approximation.
[d] Full evaluation of all 2-electron SO integrals.

Table 5
SO correction to ^{13}C shieldings (in ppm) in CH_3X (X = F, Cl, Br, I)

| | Basis | σ (nonrel.) | Gauge origin | 1e–SO | | (1e+2e)–SO | | $\sigma_{exp.}$ [b] | $\sigma_{exp.} - \sigma_{nonrel.}$ |
				EAGLE	AMFI [c]	EAGLE	AMFI [c]		
CH_3F	BII	119.98	on F	0.65	0.70	0.46	0.48	116.8	−3.2
	BII	119.98	on C	0.66	0.74	0.47	0.50		
	UP	111.29	on F	0.62	0.65		0.44		+5.5
	UP	111.29	on C	0.61	0.68		0.46		
CH_3Cl	BII	162.78	on Cl	2.22	2.21	1.82	1.82	162.5	−0.3
	BII	162.78	on C	1.95	1.97	1.62	1.62		
	UP	153.39	on Cl	2.43	2.41		1.98		+9.1
	UP	153.39	on C	2.24	2.25		1.86		
CH_3Br	BII	171.09	on Br	11.33	11.19	10.23	10.14	178.5	+7.4
	BII	171.09	on C	10.73	10.67	9.74	9.66		
	UP	162.81	on Br	11.99	11.93		10.79		+15.7
	UP	162.81	on C	11.06	11.05		10.04		
CH_3I	BII	188.76	on I	28.95	28.83	27.03	26.99	212.1	+23.3
	BII	188.76	on C	21.92	21.86	20.58	20.56		
	UP	181.11	on I	29.66	29.55		27.64		+31.0
	UP	181.11	on C	22.91	22.90		21.47		

Dependence on the choice of gauge origin [a].

[a] Perturbation parameter $\lambda = 0.00001$. Nonrelativistic shieldings with IGLO gauge, SO corrections with common gauge as indicated.
[b] Experimental shifts (in ppm) versus TMS from Ref. [33] converted to absolute shieldings, using $\sigma^{13}C(TMS) = 187.9$ ppm derived from $\sigma^{13}(CO) = 0.9$ ppm [30].
[c] The AMFI calculations include the one-center approximation.

common gauge origin for the calculation of the SO corrections, either on the halogen or on the carbon nucleus (Table 5). This choice matters significantly, increasingly so for the heavier halogens. For these, the better choice certainly is the heavy halogen nucleus. However, for molecules containing several heavy atoms no such simple choice can be made. Thus, distributed gauges (e.g. as in the IGLO or GIAO procedures) are needed. In this context we found that the IGLO choice involves the danger of numerical instabilities, due to the separate localization of α and β orbitals in the present implementation [2,6]. While these difficulties of the IGLO approach for the calculation of SO corrections to chemical shifts can be overcome (and are not always severe), GIAO procedures might be preferable from a purely theoretical point of view, as they do not involve any localization procedure (in fact, both methods have their individual advantages in the MO analysis of the SO
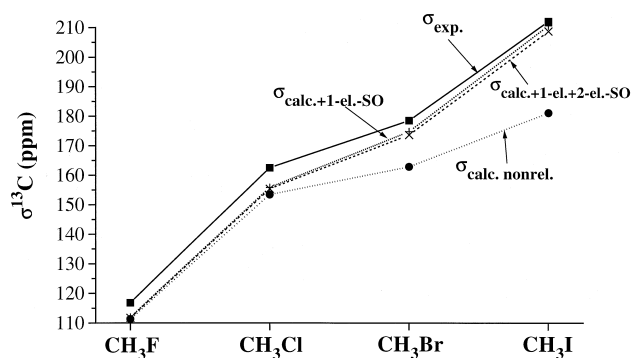

Fig. 2. Comparison of computed and experimental ^{13}H shieldings for the methyl halides (see Table 5 for numerical data). Calculations with UP basis sets and common gauge origin at the halogen nucleus for the SO corrections. The AMFI results are used for the SO corrections.

Table 6
SO corrections to ^{13}C and ^{1}H shieldings in iodobenzene (in ppm)

Nucleus	1e–SO (EAGLE)	(AMFI)	(1e + 2e)–SO (AMFI)
C_{ipso}	33.19	33.08	30.85
C_{ortho}	− 1.55	− 1.56	− 1.47
C_{meta}	− 0.43	− 0.50	− 0.46
C_{para}	0.29	0.22	0.18
H_{ortho}	− 0.26	− 0.26	− 0.25
H_{meta}	0.24	0.19	0.19
H_{para}	0.09	0.05	0.05

[a] Basis BII, perturbation parameter $\lambda = 0.00001$.

corrections, as the GIAO approach gives canonical MO contributions whereas the IGLO approach gives an analysis in terms of localized MOs). Both options will be pursued in our future work.

As for the ^{1}H shifts in the hydrogen halides, the two-electron SO contributions account for ca. 30% of the one-electron terms for the fluorine compound and thus reduce the SO shift considerably. Also as for HX, the importance of the two-electron terms drops to ca. 6–7% for the iodine compound. The one-center approximation for the calculation of the one-electron SO integrals again works well, with deviations from the exact results below 1%. The mean-field approximation to the two-electron SO integrals performs excellently, with negligible errors compared to the other error sources (e.g. basis set effects, neglected spin-dipolar term, DFT errors).

In contrast to the ^{1}H shieldings in the hydrogen halides, the ^{13}C shieldings in the methyl halides are already underestimated by the calculations including the one-electron SO corrections only. Therefore, the two-electron SO contributions worsen the agreement with experiment slightly. In view of the relatively constant deviation from experiment for $CH_{3}F$ through $CH_{3}Br$ it appears that, as for the hydrogen halides, the discrepancies arise in the nonrelativistic shieldings rather than in the computation of the SO corrections. The particularly good agreement with experiment for $CH_{3}I$ might again be due to error compensation. We note again, that a deeper comparison to experiment is not warranted at this stage, due to various other factors that need to be considered (see discussion in Section 4.1).

4.3. ^{13}C and ^{1}H shifts in iodobenzene

Table 6 compares one- and two-electron SO contributions to the ^{13}C and ^{1}H shieldings in $C_{6}H_{5}I$ taken as an example for a somewhat more complex molecule. First of all, the one-electron SO results obtained with EAGLE and with AMFI agree reasonably well (given the small absolute magnitude of some of these values). The two-electron SO terms reduce the overall ^{13}C SO shielding contributions by roughly the same amount as found above for HI or $CH_{3}I$ (ca. 6–7% for the ipso and ortho carbon atoms; the values for the meta and para carbons and for the protons are so small that they probably suffer from significant numerical noise). The one-electron SO corrected shifts for iodobenzene have been previously compared to experiment and were found to agree quite well [6]. As the two-electron SO contributions are significantly smaller than basis set and other errors (in part already in the nonrelativistic calculations), this agreement is not altered appreciably in the present work, and we refer to Ref. [6] for details.

5. Conclusions

Various codes for the calculation of two-electron SO integrals have been interfaced with our program module (within the deMon–NMR code) for the DFT calculation of SO corrections to nuclear shieldings. Both the fully

explicit evaluation of all two-electron SO integrals and a computationally much more expedient mean-field approximation have been compared. The excellent performance found for the latter approximation provides easy access to the evaluation of one- and two-electron SO contributions to NMR chemical shifts for larger systems of chemical interest. We find the two-electron terms to amount to ca. 30% of the one-electron terms for fluorine substituents, much less than this for the overall much larger SO contributions obtained with the heavier halogens (ca. 6–8% for iodine).

The basis set demand for the computation of the FC interactions underlying the SO shifts is significant, such that relatively large basis sets are needed to reach converged results. Due to the dominance and local character of the isotropic hyperfine interactions, we find the use of locally dense basis sets to be a reasonable approximation in this context, allowing even larger systems to be treated with reasonable accuracy.

After completion of the present work, we received a preprint of related work by Vaara et al. [29]. They have implemented a quadratic-response MC–SCF scheme for the calculation of SO corrections to NMR chemical shifts and applied their methods to the same hydrogen halides and methyl halides studied here. Taking these very accurate extended-basis MC–SCF data as benchmark results for our much less expensive DFT calculations (by comparing the largest basis set MC–SCF results of Vaara et al. to our data obtained with the large UP basis), we find the overall agreement to be good. Consistent with the present results, Vaara et al. also find the two-electron contributions to amount to ca. 30% for fluorine substituents, but to drop to ca. 7% with iodine [29].

Acknowledgements

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