

# How Do Spin–Orbit-Induced Heavy-Atom Effects on NMR Chemical Shifts Function? Validation of a Simple Analogy to Spin–Spin Coupling by Density Functional Theory (DFT) Calculations on Some Iodo Compounds

Martin Kaupp,\* Olga L. Malkina, Vladimir G. Malkin, and Pekka Pyykkö

**Abstract:** A simple concept is delineated for the interpretation of spin–orbit-induced heavy-atom effects on NMR chemical shifts. The spin polarization induced by heavy-atom spin–orbit coupling is known to interact with the nuclear magnetic moments of the system mainly by a Fermi-contact mechanism. The rules governing the propagation of these effects through the molecule are thus closely analogous to the well-established mechanisms for indirect Fermi-contact nuclear spin–spin coupling. The scope of this analogy is evaluated by explicit DFT calculations of spin–orbit shifts and of spin–spin coupling con-

stants in some simple iodo-substituted compounds. We find that, for example, the magnitude of the spin–orbit-induced shift on direct neighbor NMR nuclei B of the heavy atom A increases with increasing s-orbital contribution from the NMR atom B to the B–A bond. For the  $\beta$ -hydrogen atoms in iodoethane, a modified Karplus-type relationship is found to hold between the spin–orbit shift and the dihedral

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angle formed by the intervening bonds. The patterns of  $^{13}\text{C}$  and  $^1\text{H}$  shifts in iodobenzene are also significantly affected by spin–orbit coupling, and the variations of the calculated spin–orbit shifts closely follow those of the calculated reduced spin–spin coupling constants. In fact, the observed zigzag  $^1\text{H}$  shift pattern in iodobenzene is due entirely to spin–orbit effects. Typically, a negative reduced coupling constant corresponds to a shielding spin–orbit shift, and a positive coupling to a deshielding spin–orbit contribution. Many further consequences of the described analogy are discussed.

## Introduction

Substituent effects on chemical shifts have been of interest since the early days of NMR spectroscopy. Attempts to explain experimentally observed trends in substituent effects abound, and very different rationalizations have been given by different authors.<sup>[1–3]</sup> While in some cases the relatively recent advent of quantitative ab initio treatments of NMR chemical shifts has led to improved understanding,<sup>[4–6]</sup> many questions are still open owing to the multifaceted nature of the NMR chemical shift.

One of the most heavily debated substituent effects in both organic and inorganic chemistry is that due to heavy halogen

(or e.g. chalcogen) substituents. The term normal halogen dependence (NHD) was coined<sup>[7]</sup> for the frequently observed decrease in the chemical shift  $\delta$  of the nucleus bound directly to the halogen substituent with increasing atomic number of the halogen. This is the predominant behavior in main-group chemistry and for the nuclei of transition metals in low oxidation states. Inverse halogen dependence (IHD),<sup>[7]</sup> that is, an increase of the shifts on going from chlorine to iodine substituents, is often observed for early transition metals in their highest oxidation states, but also occasionally in main-group chemistry (e.g., in lower oxidation states of p block elements).<sup>[1,3,7]</sup> In organic chemistry, halogen substituent effects on nuclei more remote from the substituent have also been of interest.<sup>[2,3a–g,8,9]</sup>

The number of different, sometimes mutually contradictory, explanations suggested for the observed trends is remarkable. Most NMR textbooks explain heavy atom effects in terms of diamagnetic shielding due to the many electrons around the heavy atom.<sup>[2,3,9,10]</sup> Other arguments include electronegativity effects acting via the  $r^{-3}$  dependence of the paramagnetic term.<sup>[7]</sup> However, as early as 1969 Nakagawa et al.<sup>[11]</sup> suggested, in the context of  $^1\text{H}$  shifts of disubstituted benzenes, that the unusual halogen substituent effects observed are due to electronic spin polarization induced by

[\*] Priv. Doz. Dr. M. Kaupp  
Max-Planck-Institut für Festkörperforschung  
Heisenbergstr. 1, D-70569 Stuttgart (Germany)  
Fax: Int. code + 49 711-689-1562  
e-mail: kaupp@vsibm1.mpi-stuttgart.mpg.de  
O. L. Malkina, Prof. Dr. V. G. Malkin  
Institute of Inorganic Chemistry, Slovak Academy of Sciences  
Dubraska Cesta 9, SK-84236 Bratislava (Slovakia)  
Prof. Dr. P. Pyykkö  
Department of Chemistry, P.O.B. 55, University of Helsinki  
FIN-00014 Helsinki (Finland)

spin–orbit coupling. Semiempirical calculations by others<sup>[12]</sup> supported the idea that the NHD of the <sup>13</sup>C shifts in halomethanes and of the <sup>1</sup>H shifts in hydrogen halides may be a relativistic effect, due to increasing spin–orbit contributions for the heavier halogens.

Apparently these results were not appreciated by practising NMR spectroscopists, as explanations based on diamagnetic contributions,  $\pi$  backbonding, steric crowding, or nephelauxetic effects are still widely used.<sup>[13]</sup> Recently, more quantitative ab initio Hartree–Fock<sup>[14]</sup> and density functional theory (DFT)<sup>[15–17]</sup> treatments of spin–orbit corrections to NMR chemical shifts have become available. These approaches have helped to confirm that in main-group chemistry NHD is largely a spin–orbit effect, thus supporting the earlier semiempirical results.

Here we delineate a simple but general model based on the results of DFT calculations, which explains how spin–orbit effects on chemical shifts (referred to as spin–orbit shifts below) propagate within a molecule. The model provides improved understanding of the factors that control the sign and magnitude of the spin–orbit-induced substituent effects on NMR chemical shifts and should provide a general basis for the discussion of halogen or chalcogen dependence and other spin–orbit chemical shift phenomena.

In the following section, we will start by briefly discussing the theoretical background of spin–orbit corrections to chemical shifts, based on triple perturbation theory. We will then relate the Fermi-contact mechanism, which is now known to be the predominant mechanism of interaction between the spin–orbit-induced spin density and the nuclear magnetic moments,<sup>[14,16]</sup> to the analogous Fermi-contact mechanism of scalar spin–spin coupling constants. This allows us to benefit from the vast amount of knowledge (see, e.g., refs. [1–3]) on spin–spin coupling in understanding the factors which control the magnitude of spin–orbit effects on chemical shifts. It is notable that this analogy has also been suggested by Nakagawa et al.<sup>[11]</sup> In the subsequent three sections, we present detailed DFT calculations of spin–orbit shifts and of spin–spin coupling constants in some simple iodine-substituted compounds. The results illustrate the validity and scope of the proposed model. Finally, we will summarize the results and, in particular, indicate related phenomena which may be understood along the same lines.

## Results

### Theoretical background of spin–orbit corrections to chemical shifts:

The most satisfactory approach to include spin–orbit coupling in NMR chemical shift calculations would start from a relativistic four- or two-component wavefunction. Double perturbation theory is then sufficient to account for the perturbations due to the external magnetic field and the nuclear magnetic moment. Such a fully relativistic approach has been outlined earlier,<sup>[18]</sup> and has been used in the framework of the simple extended Hückel model.<sup>[12c,19]</sup> However, to date, methods for a more quantitative treatment of spin–orbit effects on chemical shifts, including the one we employ in the present work, were usually based on non-

relativistic wavefunctions. Thus, triple perturbation theory has to be employed, as the spin–orbit operators are introduced as an additional perturbation.<sup>[20]</sup> This approach has the advantage of providing a simple conceptual link to calculations of spin–spin coupling constants, which will be exploited in the following sections. Thus, the Hamiltonian of a closed-shell molecule in the presence of an external magnetic field, a nuclear magnetic moment, and a spin–orbit operator (spin–spin coupling is excluded) may be written as in Equations (1)–(10).<sup>[11a,12a,12b,16]</sup>

$$\mathbf{H}(\mathbf{B}, \mu_N, \mathbf{SO}) = \mathbf{H}^0 + \mathbf{H}_u^{100} \mathbf{B}_u + \sum_N \mu_{Nu} \mathbf{H}_{Nu}^{010} + \sum_N \mu_{Nu} \mathbf{H}_{Nuv}^{110} \mathbf{B}_v + \sum_i \mu_{eiu} \mathbf{H}_{iu}^{001} + \sum_i \sum_N \mu_{eiu} \mathbf{H}_{iNuv}^{011} \mu_{Nv} \quad (1)$$

$$\mathbf{H}^0 = \frac{1}{2} \sum_i p_i^2 + \sum_{i>j} \frac{1}{r_{ij}} - \sum_N \sum_i \frac{Z_N}{r_{Ni}} \quad (2)$$

$$\mathbf{H}_u^{100} = \beta \sum_i \mathbf{L}_{iu} \quad (3)$$

$$\mathbf{H}_{Nu}^{010} = \frac{e}{mc} \sum_i \frac{\mathbf{L}_{iNu}}{r_{iN}^3} \quad (4)$$

$$\mathbf{H}_{Nuv}^{110} = \frac{e^2}{2mc^2} \sum_i \frac{(\mathbf{r}_i \cdot \mathbf{r}_{iN} \delta_{uv} - r_{iu} r_{iNv})}{r_{iN}^3} \quad (5)$$

$$\mathbf{H}_{iu}^{001} = \beta \left( \sum_N \frac{Z_N \mathbf{L}_{iNu}}{r_{iN}^3} - \sum_{j \neq i} \frac{\mathbf{L}_{ju}}{r_{ij}^3} - 2 \sum_{j \neq i} \frac{\mathbf{L}_{ju}^j}{r_{ij}^3} \right) \quad (6)$$

$$\mathbf{H}_{iNuv}^{011} = \frac{8\pi}{3} \delta(\mathbf{r}_{iN}) - \frac{(\mathbf{r}_{iN} \cdot \mathbf{r}_{iN} \delta_{uv} - 3r_{iNu} r_{iNv})}{r_{iN}^5} \quad (7)$$

$$\mathbf{L}_{iu} = -i(\mathbf{r}_i \times \nabla_i)_u \quad (8)$$

$$\mathbf{L}_{iNu} = -i(\mathbf{r}_{iN} \times \nabla_i)_u \quad (9)$$

$$\mathbf{L}_{ju}^j = -i(\mathbf{r}_{ij} \times \nabla_j)_u \quad (10)$$

In the above expressions,  $\mathbf{B}$  denotes the external magnetic field,  $\mu_N = g_N \beta_N \mathbf{I}_N$  and  $\mu_e = g \beta \mathbf{S}$  the nuclear and electronic magnetic moments,  $g_N$  and  $g$  the nuclear and electronic  $g$  values,  $\beta_N = e\hbar/2m_p c$  and  $\beta = e\hbar/2mc$  the nuclear and Bohr magnetons,  $\mathbf{I}_N$  and  $\mathbf{S}$  the nuclear and electron spin angular momenta, and  $N$  the nucleus of interest. The operator  $\mathbf{H}^{lm}$  has an  $l$ th order dependence on  $\mathbf{B}$ ,  $l$ th order in  $\mu_N$ , and  $m$ th order in  $\mu_e$ . Angular momentum operators are denoted as  $\mathbf{L}$ . For further details, see ref. [16] and references cited therein.

The unperturbed Hamiltonian [Eq. (2)], the interaction of orbital angular momentum with the external magnetic field [Eq. (3)], the interaction of the nuclear magnetic dipole with electronic orbital motion [Eq. (4)], and the electronic–nuclear Zeeman correction [Eq. (5)] are terms which are already present in the absence of the spin–orbit interaction. To this we have to add the spin–orbit operator [one- and two-electron terms, Eq. (6)], as well as a Fermi-contact and a spin-dipolar term [first and second terms in Eq. (7)]. The latter two terms may be interpreted as follows: in the presence of an external magnetic field, spin–orbit coupling induces spin polarization, that is, it mixes some triplet character into the closed-shell singlet ground state.

Early qualitative, semiempirical work employed straightforward Rayleigh–Schrödinger triple perturbation theory.<sup>[12a,b]</sup> This has the disadvantage of being inaccurate in quantitative calculations. Within their finite-perturbation theory (FPT) Hartree–Fock scheme, Nakatsuji et al. included the one-electron spin–orbit operator [first term in Eq. (6)] in the ground-state Hamiltonian by FPT and, based on the perturbed orbitals, employed second-order perturbation theory for the remaining perturbations.<sup>[14]</sup> Alternatively, Malkin et al.,<sup>[16]</sup> within a density-functional framework, include the Fermi-contact term [first term in Eq. (7)] in the ground-state Hamiltonian by FPT and use sum-over-states density-functional perturbation theory (SOS-DFPT)<sup>[15,21]</sup> to compute the expectation value of the spin–orbit operator(s) with the magnetic field dependent, spin-polarized Kohn–Sham orbitals. The spin-dipolar term [second term in Eq. (7)], which is neglected in this approach, was previously found to make negligible contributions.<sup>[14]</sup> This DFT approach<sup>[16]</sup> is simple in implementation, computationally efficient, and allows distributed-gauge methods to be used. It was motivated by the closely related (perturbative, nonrelativistic) treatment of spin–spin coupling constants published earlier.<sup>[22]</sup> The calculations reported below are based on this method (see also ref. [17]). Note that the hyperfine operators in Equation (7) correspond to a nonrelativistic formalism, which is consistent with the nonrelativistic wave functions employed. For very heavy atoms, a relativistic formulation of both wavefunctions and hyperfine operators will have to be employed.<sup>[23]</sup>

**The Fermi-contact mechanism of spin–orbit effects on chemical shifts; analogy to spin–spin coupling constants:** Previous calculations, both at the Hartree–Fock<sup>[14]</sup> and at the DFT<sup>[15–17]</sup> level, have confirmed the early suggestion by Nakagawa et al.<sup>[11]</sup> that it is mainly the Fermi-contact term [first term in Eq. (7)] which is responsible for the interaction of the spin–orbit-induced spin polarization with the nuclear magnetic moments of the system. We will neglect the spin-dipolar term [second term in Eq. (7)] in the following discussion, and in the actual calculations below.

Consider the following physical picture: the nuclear magnetic moment of nucleus B induces electronic spin polarization in the system (Figure 1 a, left) analogous to the Fermi-contact contribution to spin–spin coupling constants (Figure 1 b, left). This spin polarization contributes to the expectation values of the spin–orbit operators in the presence of the external magnetic field (right side of Figure 1 a; this mechanism corresponds to our computational scheme<sup>[16]</sup>). Alternatively (again in the presence of the external magnetic field), the spin–orbit operators may mix singlet and triplet states and thus induce spin polarization (right side of Figure 1 a). This polarized spin density will then interact with the nuclear magnetic moment of nucleus B by a Fermi-contact mechanism (left side of Figure 1 a; this order of perturbations corresponds to the computational scheme of Nakatsuji et al.<sup>[14]</sup>).

The only difference between this overall interaction mechanism (Figure 1 a) and the Fermi-contact mechanism of spin–spin coupling (Figure 1 b) is that in the latter case the spin–orbit operators (plus external magnetic field) in Equa-

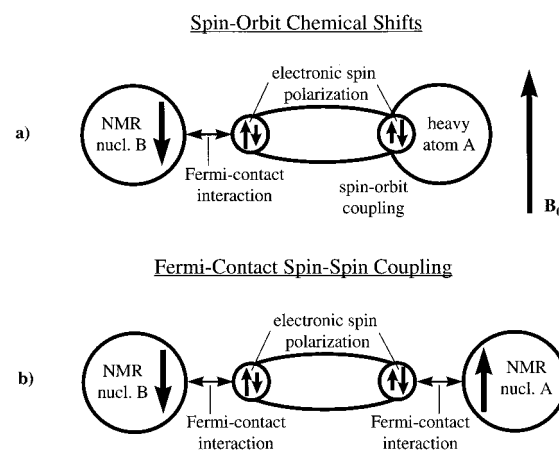


Figure 1. Schematic illustration of the suggested analogy between spin–orbit shifts and the Fermi-contact mechanism of indirect spin–spin coupling. a) Qualitative interaction mechanism for spin–orbit shifts. b) Qualitative Fermi-contact interaction mechanism for spin–spin coupling. The schemes correspond to the simplest situation of a one-bond SO shift (negative  $\sigma_{SO}$ ) and a one-bond coupling (positive  $K_{FC}$ ) in the absence of lone pairs. In the presence of lone pairs (e.g., for A = iodine, as in the examples studied computationally) or for longer-range interactions, both schemes need to be modified.

tion (1) have to be replaced by the magnetic moment of nucleus A (right-hand sides of Figure 1). Thus, we may expect the two mechanisms to be identical with respect to one half of the interaction, namely, the interaction between the electronic spin polarization and nuclear magnetic moment of nucleus B (left-hand sides of Figure 1). This analogy was already assumed by Nakagawa et al.<sup>[11]</sup> If it holds, we should be able to draw from the extensive knowledge available on spin–spin coupling in order to better understand the spin–orbit shifts.

In particular, the analogy between the Fermi-contact mechanisms of spin–spin coupling and of spin–orbit shifts leads us to the following expectations:

a) Predominantly (but not exclusively) in the case of nuclei directly attached to the heavy atom ( $\alpha$  effect), the spin–orbit shift should depend strongly on the involvement of valence s orbitals of the NMR atom B in bonding to the heavy atom A (for a given heavy atom A, for a given magnitude of the atomic spin–orbit splitting, and assuming constant energy denominators of the major terms contributing to the sum-over-states expression).

b) In contrast to spin–spin coupling, the s orbital contribution of the heavy atom A is not a major factor in the spin–orbit shift. On this side (right side of Figure 1 a), it is the occupation of orbitals with  $l \geq 1$ , and the partial charge on the heavy atom [entering via the  $r^{-3}$  factors of the spin–orbit operators, Eq. (6)] which are decisive for the magnitude of the spin–orbit splitting.

c) Owing to the energy denominators in the sum-over-states terms, effects which decrease (increase) the energy difference between the most important excited states and the ground state will enhance (diminish) the spin–orbit effects.

d) For atoms B that are further removed from the heavy atom A, we expect that many of the rules known for spin–spin coupling will also hold. Thus, for example, we expect a Karplus-type relationship for the spin–orbit contribution of

an atom three bonds away as function of the corresponding dihedral angle (see below).

e) Independent of the detailed mechanism, the magnitude of the spin–orbit contribution to chemical shifts of the neighboring atoms will of course depend on the magnitude of the spin–orbit splitting of the heavy atom. For example, the spin–orbit contributions will increase from fluorine to iodine substituents, and from left to right within a given row of the p-block main groups (e.g., from chalcogen to halogen).

**DFT calculations on  $\text{H}_3\text{C}-\text{CH}_2\text{I}$ ,  $\text{H}_2\text{C}=\text{CHI}$ , and  $\text{HC}\equiv\text{CI}$ :** As simple but representative examples of heavy halogen substituent effects, we chose a number of compounds having one iodine substituent. In this section, iodoethane, iodoethylene, and iodoacetylene are used to demonstrate the validity and the consequences of the considerations mentioned above. Uncorrected chemical shifts were calculated at the SOS-DFPT-IGLO level.<sup>[15,21]</sup> Spin–orbit corrections to the chemical shifts were obtained in separate calculations by the methods described in ref. [16]. For reasons discussed in the section Methods of Calculation, the spin–orbit corrections were evaluated with a common gauge origin on iodine. Spin–spin coupling constants were calculated by the closely related DFT method of ref. [22] (see also ref. [24]). These calculations are nonrelativistic. The easiest way to estimate relativistic corrections to the hyperfine integrals are multiplicative correction factors. For iodine this would be 1.4039 or 1.4263 at hydrogen-like<sup>[23a]</sup> and Dirac–Fock<sup>[25]</sup> levels, respectively. Although we have not previously attempted to calculate couplings to iodine, we expect the results to be reasonable for the trends in which we are mainly interested here. Experimental spin–spin coupling constants are not available for comparison (couplings to iodine are difficult to observe because of the large nuclear quadrupole coupling constant of iodine<sup>[26]</sup>).

Tables 1–3 compare calculated and experimental data for iodoethane, iodoethylene, and iodoacetylene. Comparison with experimental chemical shifts was possible in all cases, except for the  $^{13}\text{C}$  shifts of unsubstituted iodoacetylene (experimental  $^{13}\text{C}$  shift data for substituted iodoacetylenes suggest spin–orbit shifts of comparable magnitude). We have tried to minimize discrepancies due to solvent effects by using experimental data obtained in nonpolar solvents, in some

Table 2. Computed spin–orbit shifts and spin–spin coupling constants in iodoethylene.<sup>[a]</sup>

| Atom E | $\sigma$ | $\sigma_{\text{SO}}$ | $\sigma + \sigma_{\text{SO}}$ | $\delta(+\text{SO})$ | $\delta(\text{exptl})$ | $J_{\text{FC}}(\text{I,E})$ | $K_{\text{FC}}(\text{I,E})$ |
|--------|----------|----------------------|-------------------------------|----------------------|------------------------|-----------------------------|-----------------------------|
| C1     | 66.6     | +33.6                | 100.2                         | 87.5 [b]             | 84.1                   | −238.3                      | −391.5                      |
| C2     | 57.0     | −0.7                 | 56.3                          | 131.2 [b]            | 129.2                  | −0.8                        | −1.3                        |
| H1     | 25.0     | +0.1                 | 25.1                          | 5.9 [c]              | 6.48                   | +38.1                       | +15.7                       |
| H2     | 25.3     | −0.3                 | 25.0                          | 6.0 [c]              | 6.18                   | +16.0                       | +6.6                        |
| H3     | 25.2     | −0.4                 | 24.8                          | 6.2 [c]              | 6.45                   | +22.7                       | +9.4                        |

[a] Absolute shieldings  $\sigma$  in ppm, relative shifts  $\delta$  vs. TMS, coupling constants  $J_{\text{FC}}$  in Hz, reduced coupling constants  $K_{\text{FC}}$  in  $10^{19} \text{NA}^{-2} \text{m}^{-3}$ . [b] Ref. [2]. [c] R. E. Mayo, J. H. Goldstein, *J. Mol. Spectrosc.* **1964**, *14*, 173.

Table 3. Computed spin–orbit shifts and spin–spin coupling constants in iodoacetylene.<sup>[a]</sup>

| Atom E | $\sigma$ | $\sigma_{\text{SO}}$ | $\sigma + \sigma_{\text{SO}}$ | $\delta(+\text{SO})$ | $\delta(\text{exptl})$ | $J_{\text{FC}}(\text{I,E})$ | $K_{\text{FC}}(\text{I,E})$ |
|--------|----------|----------------------|-------------------------------|----------------------|------------------------|-----------------------------|-----------------------------|
| C1     | 140.1    | +56.7                | 196.8                         | −9.3                 | −395.5                 | −649.8                      |                             |
| C2     | 104.3    | +1.5                 | 105.8                         | +81.7                | −52.6                  | −86.4                       |                             |
| H1     | 28.6     | −0.5                 | 28.1                          | +2.9                 | +2.23 <sup>b</sup>     | −0.3                        | −0.1                        |

[a] Absolute shieldings  $\sigma$  in ppm, relative shifts  $\delta$  vs. TMS, coupling constants  $J_{\text{FC}}$  in Hz, reduced coupling constants  $K_{\text{FC}}$  in  $10^{19} \text{NA}^{-2} \text{m}^{-3}$ . [b] E. Kloster-Jensen, R. Tabacchi, *Tetrahed. Lett.* **1972**, *39*, 4023.

cases with extrapolation to infinite dilution. Direct comparison of the  $^1\text{H}$  shifts with experiment is further complicated by the neglect of ro-vibrational effects in our calculations, which are expected to be significant.<sup>[27]</sup> However, the major trends of interest will be apparent. Let us first look at the  $^{13}\text{C}$  shifts of the  $\alpha$ -carbon nuclei (C1) in Tables 1–3. After spin–orbit correction, the agreement with experiment is good. The strong shielding of these nuclei is undoubtedly a spin–orbit effect. Figure 2 shows that the calculated spin–orbit shifts  $\sigma_{\text{SO}}$

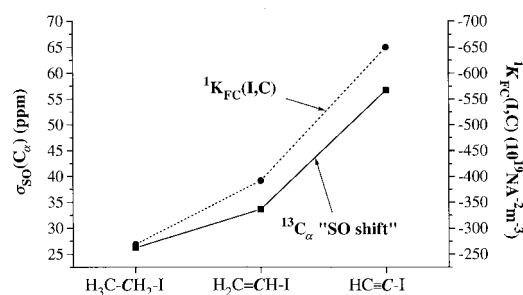


Figure 2. Correlation between  $^{13}\text{C}$  spin–orbit shifts  $\sigma_{\text{SO}}(\text{C})$  and reduced spin–spin coupling constants  $^1K_{\text{FC}}(\text{I,C})$  in iodoethane, iodoethylene, and iodoacetylene.

increase from iodoethane to iodoethylene to iodoacetylene, that is, with increasing s character of the bonding carbon hybrid orbital (formally from  $\text{sp}^3$  to  $\text{sp}^2$  to  $\text{sp}$ ). This is what we would expect from the Fermi-contact interaction mechanism detailed in the previous section. The calculated reduced spin–spin coupling constants  $^1K_{\text{FC}}(\text{I,C})$  do indeed follow the same trend. Notably, an increasingly negative  $K_{\text{FC}}$  corresponds to increasingly shielding  $\sigma_{\text{SO}}$ .

Table 1. Computed spin–orbit shifts and spin–spin coupling constants in iodoethane.<sup>[a]</sup>

| Atom E | $\sigma$ | $\sigma_{\text{SO}}$ | $\sigma + \sigma_{\text{SO}}$ | $\delta(+\text{SO})$ | $\delta(\text{exptl})$ | $J_{\text{FC}}(\text{I,E})$ | $K_{\text{FC}}(\text{I,E})$ |
|--------|----------|----------------------|-------------------------------|----------------------|------------------------|-----------------------------|-----------------------------|
| C1     | 166.0    | +26.2                | 192.2                         | −4.7                 | −2.3 [b]               | −163.4                      | −268.5                      |
| C2     | 165.8    | +0.3                 | 166.1                         | +21.4                | +23.5 [b]              | +4.8                        | +7.9                        |
| H1,H1' | 28.3     | +0.1                 | 28.4                          | +2.6                 | +3.0 [c]               | +19.7                       | +8.1                        |
| H2,H2' | 29.6     | −0.1                 | 29.5                          | +1.5                 | av 1.8 [c]             | +6.5                        | +2.7                        |
| H3     | 29.8     | −0.3                 | 29.5                          | +1.5                 | av 1.8 [c]             | +28.5                       | +11.8                       |

[a] Absolute shieldings  $\sigma$  in ppm, relative shifts  $\delta$  vs. TMS, coupling constants  $J_{\text{FC}}$  in Hz, reduced coupling constants  $K_{\text{FC}}$  in  $10^{19} \text{NA}^{-2} \text{m}^{-3}$ . [b] Ref. [2]. [c] H. Spiess, W. G. Schneider, *J. Chem. Phys.* **1961**, *35*, 722.

Spin-orbit effects on the  $^{13}\text{C}$  shifts of the  $\beta$ -carbon atoms (C2) are considerably smaller, as expected. In fact, for iodoethane and iodoethylene, the contribution appears to be essentially negligible (within the numerical accuracy of the method), whereas  $\sigma_{\text{SO}}$  is still notably shielding in iodoacetylene. Again, the agreement with the available experimental shifts  $\delta$  is good. Only for iodoacetylene are the absolute values of both spin-orbit shift and spin-spin coupling constant sufficiently large to allow a discussion of sign and magnitude. We find a shielding contribution and a negative spin-spin coupling constant, again consistent with the above results for the  $\alpha$ -carbon nuclei. The accuracy of calculated spin-orbit corrections and spin-spin coupling constants is probably not sufficient to discuss this type of relationship for the  $\beta$ -carbon nuclei of iodoethane and iodoethylene.

The  $^1\text{H}$  spin-orbit shifts of the  $\beta$ -hydrogen atoms (H2, H3) of iodoethane and iodoethylene appear to be slightly deshielding, and the calculated coupling constants are small and positive. This type of correlation is not apparent for the  $\alpha$ -hydrogen atoms (H1), and for the  $\beta$ -hydrogen atom of iodoacetylene. The numerical accuracy of the method may again be insufficient for these very small values. The overall agreement with experimental shifts  $\delta$  is reasonable.

The well-known empirical Karplus relationship (often given in the form  $^3K = C \cos 2\phi + B \cos \phi + A$ )<sup>[28]</sup> describes the dependence of three-bond spin-spin coupling constants on the dihedral angle formed by the intervening single bonds. Figure 3 shows that the calculated  $^3K_{\text{FC}}(\text{I,H})$  of iodoethane

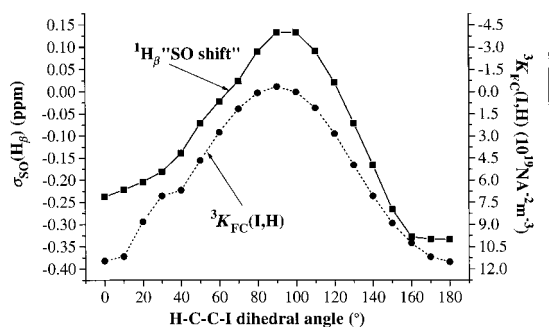


Figure 3. Karplus-type relationship:  $^1\text{H}$  spin-orbit shifts  $\sigma_{\text{SO}}(\text{H}_\beta)$  and reduced spin-spin coupling constants  $^3K_{\text{FC}}(\text{I,H})$  as a function of the H-C-C-I dihedral angle in iodoethane.

approximately follows this type of relation within numerical accuracy (in view of the very small couplings involved, the calculated curve is remarkably smooth). Most interestingly, the same type of behavior is also found for the (small) calculated  $^1\text{H}$  spin-orbit shifts  $\sigma_{\text{SO}}$  of the  $\beta$ -hydrogen nuclei. While the change of sign of the two quantities does not occur at the same angles [the calculated  $^3K_{\text{FC}}(\text{I,H})$  is only slightly negative for  $\phi \approx 90^\circ$ ], the angles for maxima and minima of the two curves almost coincide (coupling constants to halogen calculated at this level are in any case expected to be shifted by a systematic error, even if relativistic corrections are taken into account<sup>[24]</sup>). The overall behavior does again relate increasingly shielding  $\sigma_{\text{SO}}$  to increasingly negative  $K_{\text{FC}}$ , and increasingly deshielding  $\sigma_{\text{SO}}$  to increasingly positive  $K_{\text{FC}}$ . Thus,

Figure 3 indicates that the spin-orbit shift/spin-spin coupling analogy does hold even for such small interactions across three single bonds.

**DFT calculations on  $\text{EH}_3\text{I}$  (E = C, Si, Ge):** Table 4 lists spin-orbit shifts and spin-spin coupling constants of iodomethane and its heavier Group 14 congeners. One-bond spin-orbit effects on the central atom are again strongly shielding (comparable for  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{CH}_2\text{I}$ , cf. Table 1), and they increase for E = Si, Ge (Figure 4). This is the expected

Table 4. Computed spin-orbit shifts and spin-spin coupling constants in  $\text{EH}_3\text{I}$  (E = C, Si, Ge).<sup>[a]</sup>

| Atom E                  | $\sigma$ | $\sigma_{\text{SO}}$ | $\sigma + \sigma_{\text{SO}}$ | $\delta(+\text{SO})$ | $\delta(\text{exptl})$ | $J_{\text{FC}}(\text{I,E})$ | $K_{\text{FC}}(\text{I,E})$ |
|-------------------------|----------|----------------------|-------------------------------|----------------------|------------------------|-----------------------------|-----------------------------|
| <b>CH<sub>3</sub>I</b>  |          |                      |                               |                      |                        |                             |                             |
| C                       | 190.7    | +29.1                | 219.8                         | -33.3                | -21.8 [b]              | -179.5                      | -294.9                      |
| H                       | 29.5     | -0.1                 | 29.4                          | +1.6                 | +1.8 [c]               | +15.2                       | +6.3                        |
| <b>SiH<sub>3</sub>I</b> |          |                      |                               |                      |                        |                             |                             |
| Si                      | 424.3    | +46.0                | 470.3                         | -112.5               | -83.3 [d]              | +408.8                      | -849.6                      |
| H                       | 26.4     | +0.9                 | 27.3                          | +3.7                 | +3.6 [e]               | +23.4                       | +9.7                        |
| <b>GeH<sub>3</sub>I</b> |          |                      |                               |                      |                        |                             |                             |
| Ge                      | 1785.0   | +117.9               | 2002.9                        | -488.9               |                        | +134.2                      | -1585.0                     |
| H                       | 26.3     | +2.2                 | 28.5                          | +2.5                 |                        | +13.4                       | +5.5                        |

[a] Absolute shieldings  $\sigma$  in ppm, relative shifts  $\delta(\text{Ge})$  vs.  $\text{Ge}(\text{CH}_3)_4$ ,  $\delta(\text{H,C,Si})$  vs. TMS, coupling constants  $J_{\text{FC}}$  in Hz, reduced coupling constants  $K_{\text{FC}}$  in  $10^{19} \text{NA}^{-2} \text{m}^{-3}$ . [b] Ref. [2]. [c] H. Spiess, W. G. Schneider, *J. Chem. Phys.* **1961**, 35, 722. [d] M. Vongehr, H. C. Marsmann, *Z. Naturf. B* **1976**, 31, 1423. [e] C. Schumann, H. Dreiskamp, *J. Magn. Reson.* **1970**, 3, 204.

behavior, as the hyperfine integrals become larger for the heavier Group 14 atoms.<sup>[25]</sup> The s orbital involvement also increases down the group, due to hybridization defects.<sup>[29]</sup> For the same reason, the computed<sup>[30]</sup>  $^1K_{\text{FC}}(\text{I,E})$  become increasingly negative along the same series (Figure 4).

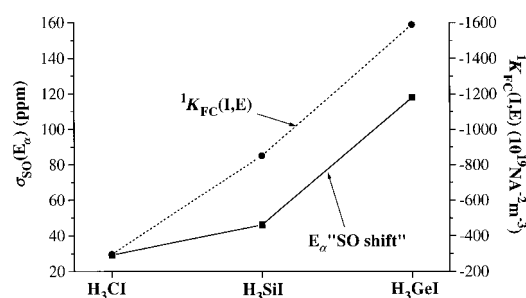


Figure 4. Correlation between central atom (E = C, Si, Ge) spin-orbit shifts  $\sigma_{\text{SO}}(\text{E})$  and reduced spin-spin coupling constants  $^1K_{\text{FC}}(\text{I,E})$  in  $\text{EH}_3\text{I}$ .

Agreement between theory and experiment for E = C, Si is reasonable, both for the central-atom shifts (only after spin-orbit correction), and for the  $^1\text{H}$  shifts. The  $^1\text{H}$  spin-orbit shifts are small, as are the corresponding  $^2K_{\text{FC}}(\text{I,H})$  values. In the case of E = Si, Ge, the calculated  $\sigma_{\text{SO}}(^1\text{H})$  are deshielding, and  $^2K_{\text{FC}}$  is positive. This relationship is consistent with the above discussion. The  $^1\text{H}$  spin-orbit shift of  $\text{CH}_3\text{I}$  is essentially negligible, and  $^2K_{\text{FC}}$  is very small and positive. Note again that we expect systematic errors in the calculated  $K_{\text{FC}}$ . Moreover, part of  $\sigma_{\text{SO}}$  in  $\text{SiH}_3\text{I}$  and  $\text{GeH}_3\text{I}$  is probably due to silicon and germanium spin-orbit coupling, in particular for  $\sigma_{\text{SO}}(\text{H})$ .

**DFT calculations on C<sub>6</sub>H<sub>5</sub>I:** A larger number of nuclei may be investigated for iodobenzene, chosen as a prototype example of an aromatic compound. As long-range spin–spin coupling is known to be particularly significant in such delocalized systems, it was expected that long-range spin–orbit shifts might also be sufficiently large for closer inspection.

Table 5 lists calculated and experimental shieldings and shifts, and spin–spin coupling constants. As in the case of the

Table 5. Computed spin–orbit shifts and spin–spin coupling constants in C<sub>6</sub>H<sub>5</sub>I.<sup>[a]</sup>

| Atom E             | $\sigma$ | $\sigma_{\text{SO}}$ | $\sigma + \sigma_{\text{SO}}$ | $\delta(+\text{SO})$ | $\delta(\text{exptl})$ | $J_{\text{FC}}(\text{I,E})$ | $K_{\text{FC}}(\text{I,E})$ |
|--------------------|----------|----------------------|-------------------------------|----------------------|------------------------|-----------------------------|-----------------------------|
| C <sub>ipso</sub>  | 60.1     | +33.3                | 93.4                          | 94.1                 | 96.2 [b]               | −231.3                      | −380.0                      |
| C <sub>ortho</sub> | 53.7     | −1.5                 | 52.2                          | 135.3                | 138.4 [b]              | +10.6                       | +17.4                       |
| C <sub>meta</sub>  | 60.5     | −0.5                 | 60.0                          | 127.5                | 131.3 [b]              | +0.1                        | +0.2                        |
| C <sub>para</sub>  | 63.5     | +0.2                 | 63.7                          | 123.8                | 128.1 [b]              | −0.9                        | −1.5                        |
| H <sub>ortho</sub> | 23.9     | −0.3                 | 23.6                          | 7.4                  | 7.67 [c]               | +8.3                        | +3.4                        |
| H <sub>meta</sub>  | 23.9     | +0.2                 | 24.1                          | 6.9                  | 7.02 [c]               | +1.0                        | +0.4                        |
| H <sub>para</sub>  | 23.9     | +0.1                 | 24.0                          | 7.0                  | 7.24 [c]               | +2.7                        | +1.1                        |

[a] Absolute shieldings  $\sigma$  in ppm, relative shifts  $\delta$  vs. TMS, coupling constants  $J_{\text{FC}}$  in Hz, reduced coupling constants  $K_{\text{FC}}$  in  $10^{19} \text{ NA}^{-2} \text{ m}^{-3}$ . [b] Ref. [2]. [c] H. Spiess, W. G. Schneider, *J. Chem. Phys.* **1961**, 35, 731.

systems discussed above, the calculated  $\sigma_{\text{SO}}$  of the carbon atom bound directly to the iodo substituent (C<sub>ipso</sub>) is significantly shielding, and  $^1K_{\text{FC}}(\text{I,C})$  is negative and large. Both values are close to those calculated for iodoethylene (cf. Table 2), in which C1 is also approximately sp<sup>2</sup> hybridized. Comparing  $\sigma_{\text{SO}}(\text{C})$  and  $K_{\text{FC}}(\text{I,C})$  for all carbon nuclei (Figure 5), we again find a remarkable correspondence between

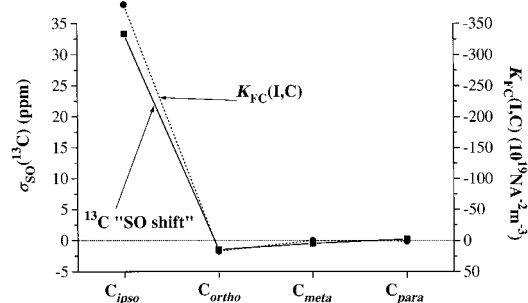


Figure 5. Correlation between <sup>13</sup>C spin–orbit shifts  $\sigma_{\text{SO}}(\text{C})$  and reduced spin–spin coupling constants  $K_{\text{FC}}(\text{I,C})$  in iodobenzene.

these two quantities. They both exhibit the typical damped oscillation well known for H–H and C–H coupling constants in aromatic systems.<sup>[2,3]</sup> Remarkably, even the change of sign for  $\sigma_{\text{SO}}(\text{C})$  and  $K_{\text{FC}}(\text{I,C})$  occurs simultaneously with this test system, although the interactions with C<sub>meta</sub> and C<sub>para</sub> are already very small. Figure 6 shows that only the spin–orbit shift for C<sub>ipso</sub> is essential to reproduce the experimental <sup>13</sup>C shift patterns around the aromatic ring, whereas spin–orbit shifts provide only small contributions to the other carbon shifts (i.e., the observed decrease of  $\delta(^{13}\text{C})$  from C<sub>ortho</sub> to C<sub>para</sub> is not due mainly to spin–orbit coupling). The remaining slight systematic underestimate by about 3–4 ppm with respect to the experimental values may be removed by taking benzene as a secondary reference [ $\delta_{\text{calcd}}(^{13}\text{C}) = 124.6$ ,

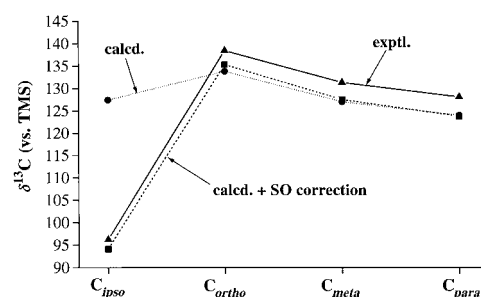


Figure 6. Comparison of calculated and experimental <sup>13</sup>C shifts in iodobenzene.

$\delta_{\text{exptl}}(^{13}\text{C}) = 128.5$  relative to TMS<sup>[2]</sup>). Alternatively, larger basis sets would improve the agreement with experiment by slightly increasing the paramagnetic contributions,<sup>[32]</sup> which are larger for the aromatic systems than for TMS.

The situation is somewhat different for the <sup>1</sup>H shifts. Here the spin–orbit corrections appear to explain the observed differences between H<sub>ortho</sub>, H<sub>meta</sub>, and H<sub>para</sub> shifts (Figure 7).

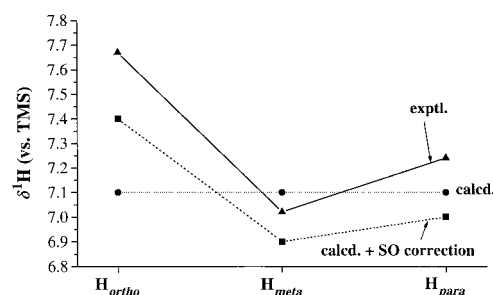


Figure 7. Comparison of calculated and experimental <sup>1</sup>H shifts in iodobenzene.

Uncorrected shifts do not show any position dependence and are almost identical to those calculated at the same level for benzene [ $\delta_{\text{calcd}}(^1\text{H}) = 7.0$ ,  $\delta_{\text{exptl}}(^1\text{H}) = 7.27$  versus TMS<sup>[32]</sup>]. This leads to the interesting conclusion that spin–orbit shifts are the exclusive mechanism by which the iodo substituent affects the <sup>1</sup>H shifts in this system. Our results thus provide strong quantitative support for the early qualitative considerations of Nakagawa et al.<sup>[11]</sup> for disubstituted benzenes.

Figure 8 shows that the <sup>1</sup>H spin–orbit shifts follow  $K_{\text{FC}}(\text{I,H})$  remarkably well (again bearing in mind the very small values

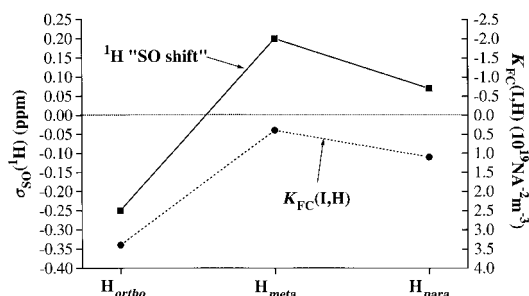


Figure 8. Correlation between <sup>1</sup>H spin–orbit shifts  $\sigma_{\text{SO}}(\text{H})$  and reduced spin–spin coupling constants  $K_{\text{FC}}(\text{I,H})$  in iodobenzene.

obtained for both quantities). The deshielding  $\sigma_{\text{SO}}(\text{H})$  for  $\text{H}_{\text{ortho}}$  corresponds to a positive calculated  ${}^3K_{\text{FC}}(\text{I},\text{H})$ . For  $\text{H}_{\text{meta}}$ , the small shielding effect is paralleled by a very small positive calculated  ${}^4K_{\text{FC}}(\text{I},\text{H})$ . For  $\text{H}_{\text{para}}$ , both spin-orbit shift and  ${}^5K_{\text{FC}}(\text{I},\text{H})$  are very small. Thus, while the trends of  $\sigma_{\text{SO}}$  and  $K_{\text{FC}}$  agree well (Figure 8), the change of sign does not exactly agree. This may partly be due to the known systematic errors in the calculated values (particularly for  $K_{\text{FC}}$ , see discussion above), but of course the change in sign does not necessarily have to coincide.

## Discussion

The computational results given in the preceding section demonstrate that the analogy between spin-orbit shifts and the Fermi-contact mechanism of spin-spin coupling suggested as early as 1969 by Nakagawa et al.<sup>[11]</sup> holds remarkably well. This has considerable consequences for our understanding of spin-orbit-induced heavy-atom substituent effects on NMR chemical shifts, some of which were already apparent from the examples investigated in the preceding sections.

All quantum-chemical calculations carried out to date, including the present work, at various computational levels on the question of normal halogen dependence (NHD), have confirmed spin-orbit shifts to be largely responsible for NHD.<sup>[12,14-17]</sup> The present computational results and consideration of known experimental spin-spin coupling constants suggest that the origin of NHD (shielding one-bond spin-orbit shifts) is connected to negative one-bond reduced spin-spin coupling constants. The latter are thought to be related to the presence of free electron pairs on the halogen substituents,<sup>[33]</sup> and the same apparently holds for the spin-orbit shifts.<sup>[34]</sup> Analogous behavior is expected with other Group 13-18 p-block main-group substituents bearing lone pairs, for example, with chalcogen substituents. For one-bond I-C interactions, it appears from the data in Tables 1-5 (also see Figures 2-5), that the ratio  $\sigma_{\text{SO}}(\text{C})/{}^1K_{\text{FC}}(\text{I},\text{C})$  is consistently on the order of about  $-0.1$  (with  $\sigma_{\text{SO}}$  in ppm and  $K_{\text{FC}}$  in  $10^{-19} \text{ NA}^{-2} \text{ m}^{-3}$ ).

The magnitude of a one-bond spin-orbit shift depends not only on the magnitude of the heavy-atom spin-orbit splitting (and of course on the number of heavy-atom substituents) and on energy denominators of the sum-over-states terms, but to a large extent on the NMR atom valence s-orbital character used for bonding to the heavy substituent. For example, shielding one-bond spin-orbit shifts increase from  $\text{sp}^3$  to  $\text{sp}^2$  to  $\text{sp}$  hybridized carbon. A pronounced s character is always present for hydrogen, and thus we expect  ${}^1\text{H}$  shifts to be particularly sensitive to spin-orbit effects from neighboring heavy atoms. This is indeed found, for example, in the hydrogen halides,<sup>[16]</sup> and for organomercury hydrides.<sup>[35]</sup>

In the case of p-block main-group central atoms in their highest oxidation states, the valence s orbitals are fully involved in bonding (e.g., to halogen substituents), and we thus expect large shielding spin-orbit shifts and therefore NHD. This is in fact the observed behavior.<sup>[1]</sup> In lower oxidation states, the central atom may have (a) free electron

pair(s) with pronounced s character, as in  $\text{P}^{\text{III}}$ ,  $\text{Sn}^{\text{II}}$ , or  $\text{Pb}^{\text{II}}$  compounds, and thus the bonds may involve only very little s character. Indeed, recent solid-state tin and lead NMR experiments on  $\text{Sn}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  halides have indicated significant inverse halogen dependence (IHD).<sup>[36]</sup> Similarly, weak IHD is observed for  ${}^{31}\text{P}$  shifts on going from  $\text{PCl}_3$  to  $\text{PBr}_3$  ( $\delta = 219$  vs.  $227$  ppm).<sup>[37]</sup> Calculations confirm that this trend is related to very small spin-orbit contributions in the  $\text{P}^{\text{III}}$  halides, due to the low s character of phosphorus in the phosphorus-halogen bonds.<sup>[38]</sup>

IHD is also the rule for early transition metals in high oxidation states.<sup>[1,3,7]</sup> Our calculations on the titanium tetrahalides (to be published elsewhere) confirm very small, deshielding titanium spin-orbit shifts, as well as small and positive  ${}^1K_{\text{FC}}(\text{Ti},\text{X})$ . This is also readily understood in the light of the present concept: the Ti-X bonds have very little titanium 4s character and are dominated by the metal 3d orbitals. In the absence of large spin-orbit shifts, the increase in the large paramagnetic contributions (related to low-lying d orbitals) on going from the chloride to the iodide leads to IHD. In contrast, transition metals in lower oxidation states may have significant metal s character in their bonding. Thus, heavy halogen substituents are expected to cause significant shielding spin-orbit shifts and thus NHD, in agreement with observation.<sup>[1,3]</sup>

When neither the heavy atom nor the main-group NMR atom bears lone pairs,  ${}^1K$  is usually large and positive, for example,  ${}^1K(\text{Hg},\text{C})$  in organomercury compounds and  ${}^1K(\text{M},\text{C})$  in Group 14 organometallic compounds ( $\text{M} = \text{Sn}, \text{Pb}$ ).<sup>[33]</sup> In analogy, we would expect the corresponding one-bond  ${}^{13}\text{C}$  spin-orbit shifts due to heavy metal substituents to generally be deshielding. First calculations on organomercury compounds confirm this assumption.<sup>[35]</sup>

As shown in Figure 3,  ${}^1K_{\text{FC}}(\text{I},\text{E})$  becomes increasingly negative and the corresponding spin-orbit shifts increasingly shielding in the series  $\text{E} = \text{C}, \text{Si}, \text{Ge}$ . A similar periodic dependence is expected for other main-group systems, as one-bond couplings frequently increase down a group.<sup>[33]</sup>

It should be possible to transfer other trends known from spin-spin coupling to the spin-orbit shifts. Thus, in main-group chemistry the magnitude of  ${}^1K(\text{A},\text{B})$  for a given pair of atoms A and B increases with increasing electronegativity of the substituents on A or B.<sup>[33]</sup> This is due to increasing s contributions to bonding, caused by increasing hybridization defects<sup>[29]</sup> with increasing positive charge at the central atom (A or B).<sup>[39]</sup> Thus, we also expect the spin-orbit shifts to increase with increasing electronegativity of additional substituents on the NMR atom. Our calculations on  $\text{CF}_3\text{I}$  (IGLO-II basis) give a shielding  $\sigma_{\text{SO}}(\text{C})$  of 52.6 ppm, compared to 29.1 ppm found above for  $\text{CH}_3\text{I}$  (fluorine spin-orbit coupling is expected to account for at most about 3 ppm of this increase<sup>[17]</sup>). This is due to an increased carbon 2s character in the C-I bond. However, the larger (nonrelativistic) paramagnetic contributions will override the larger  $\sigma_{\text{SO}}$ . For instance, the uncorrected  $\delta(^{13}\text{C})$  of  $\text{CF}_3\text{I}$  is +158.8, compared to  $-3.2$  ppm for  $\text{CH}_3\text{I}$ . With spin-orbit corrections, the calculated shifts are +106.2 and  $-33.3$ , in reasonable agreement with the experimental values of +78.2<sup>[40]</sup> and  $-21.8$  ppm, respectively. Changes in spin-orbit shifts from

one compound to a differently substituted one may thus frequently be hidden by other factors.

The increase of *s* character due to electronegative substituents also explains the nonadditivity of spin–orbit shifts<sup>[16]</sup> upon multiple halogen or chalcogen substitution. On going from CH<sub>3</sub>I to CH<sub>2</sub>I<sub>2</sub> to CHI<sub>3</sub> to CI<sub>4</sub>, the positive charge on carbon and thus the 2*s* character of the C–I bonds increase. Therefore, the individual spin–orbit shifts due to each iodine substituent increase along this series. As a consequence, the overall spin–orbit shifts and therefore the total shielding increase considerably more than linearly upon multiple substitution.

Structural effects may alter the hybridization of the NMR atom and should also affect the spin–orbit shifts. We have recently found an example of this in two tin–phosphorus cage compounds, Sn<sub>6</sub>P<sub>6</sub>R<sub>6</sub> and Sn<sub>3</sub>P<sub>2</sub>Cl<sub>2</sub>R<sub>2</sub> (R<sub>exptl</sub> = organosilyl, R<sub>comptl</sub> = H).<sup>[41]</sup> The former compound exhibits an unusually shielded  $\delta(^{31}\text{P})$  of  $-475$ , and calculations suggest large shielding spin–orbit shifts due to the heavy Sn<sup>II</sup> substituents. In contrast, for the latter compound  $\delta(^{31}\text{P}) = -122$ , and the calculated spin–orbit shifts are small, even though in both cases each phosphorus atom is bound to three tin atoms and to one exo substituent R. The explanation is given by the large endocyclic Sn–P–Sn angles in Sn<sub>6</sub>P<sub>6</sub>R<sub>6</sub>, which lead to large phosphorus *s* contributions in two of the P–Sn bonds. This in turn is responsible for significant spin–orbit shifts. In contrast, the endocyclic angles and phosphorus *s* contributions to the P–Sn bonds in Sn<sub>3</sub>P<sub>2</sub>Cl<sub>2</sub>R<sub>2</sub> are small, as is the spin–orbit shift.<sup>[41]</sup> Undoubtedly, many more examples of this kind will be found.

In the systems studied here, spin–orbit shifts decrease very quickly with an increasing number of bonds between the heavy substituent and the NMR nucleus. This is the same behavior as that found for Fermi-contact contributions to spin–spin coupling constants. Nevertheless, the small long-range spin–orbit shifts may be important for an understanding of certain trends, such as the pattern of the <sup>1</sup>H shifts in iodobenzene (see Figure 8). Long-range spin–orbit shifts are expected to occur in delocalized systems, which are known to exhibit significant long-range spin–spin coupling.<sup>[33]</sup> Halogen-substituted allenes might be other interesting examples to investigate.

The present qualitative concept should be useful in many ways. For example, known spin–spin coupling constants in related species may already provide some information on spin–orbit shifts in heavy-atom substituted compounds. In many cases, simple qualitative bonding considerations may even be sufficient to estimate the magnitude and/or sign of heavy-atom substituent effects on NMR chemical shifts. In more complicated cases, suitable population analyses may provide the necessary bonding information. Apart from improved qualitative understanding, such considerations may also help to decide a priori whether spin–orbit corrections have to be considered in quantitative nuclear shielding calculations.

Finally, we point out that the importance of spin–orbit effects on NMR chemical shifts is still widely underestimated by the practical chemists and NMR spectroscopists. We hope that the present computational results, and in particular the

proposed qualitative concept, will increase the appreciation of relativistic effects in NMR spectroscopy.

## Methods of Calculation

All calculations were carried out on experimental gas-phase structures.<sup>[42]</sup> The initial nuclear shielding calculations (uncorrected for spin–orbit coupling) used the sum-over-states density-functional perturbation theory approach (SOS-DFPT),<sup>[15,21]</sup> with individual gauges for localized orbitals (IGLO<sup>[5]</sup>). The underlying Kohn–Sham calculations employed the gradient-corrected PW91<sup>[43]</sup> exchange-correlation functional. A compromise strategy discussed earlier<sup>[15,44]</sup> was applied to obtain accurate Kohn–Sham MOs with moderate effort, by adding an extra iteration with a larger integration grid and without fit of the exchange-correlation potential after initial SCF convergence had been reached. FINE<sup>[44]</sup> angular grids with 32 points of radial quadrature were used. All calculations were carried out with the deMon-NMR code.<sup>[16,44]</sup>

IGLO-II all-electron basis sets<sup>[5]</sup> were used on all atoms (with omission of *f* functions on iodine), with density and exchange-correlation potential fitting auxiliary basis sets of the sizes 5,1 (H), 5,2 (C, F), 5,4 (Si), and 5,5 (Ge, I) (*n,m* denotes *ns* functions and *m*spd shells with shared exponents<sup>[44]</sup>). All six Cartesian components of *d*-basis functions were kept. The IGLO procedure<sup>[5]</sup> employed the Boys localization scheme.<sup>[45]</sup> Core shells of similar energies were grouped together in the localization. Thus, the iodine K shell was localized separately, the iodine L shell with the germanium K shell, the iodine M shell with the silicon K and the germanium L shell, and the iodine N shell with the carbon and/or fluorine K, silicon L or germanium M shells, separate from the valence shell. Calculated absolute shieldings  $\sigma$  were converted to relative shifts  $\delta$  via shieldings  $\sigma$  calculated at the same level for TMS [ $\sigma_{\text{calcd}}(\text{Si}) = 367.6$ ,  $\sigma_{\text{calcd}}(\text{C}) = 187.5$ ,  $\sigma_{\text{calcd}}(\text{H}) = 31.0$  ppm], and for Ge(CH<sub>3</sub>)<sub>4</sub> [ $\sigma_{\text{calcd}}(\text{Ge}) = 1514.0$  ppm].

Spin–orbit corrections to the nuclear shieldings were calculated separately by the combined finite-perturbation/SOS-DFPT approach.<sup>[16]</sup> However, an IGLO choice of gauge origin was found to give significant numerical instabilities for the small longer-range spin–orbit shifts. The necessary separate localization of  $\alpha$  and  $\beta$  MOs<sup>[16]</sup> appears to be the source of errors. Therefore, we used a common gauge origin on iodine in these calculations. This is justified by the fact that we have only one heavy atom in the system, which is a natural choice of gauge origin (see discussion in ref. [16]). The validity of this assumption is borne out by the results given above. For systems with several heavy atoms, the localization problem may possibly be solved by modification of the algorithm.<sup>[46]</sup> An alternative would be to use gauge-including atomic orbitals (GIAO<sup>[47]</sup>). The spin–orbit calculations used the same basis sets described above. However, 64 points of radial quadrature and the PP86 functional<sup>[48]</sup> were employed. The initial finite perturbation (with a perturbation parameter  $\lambda = 10^{-3}$  a.u.) was chosen to be the nuclear magnetic moment of the NMR nucleus of interest. Thus, a separate calculation had to be carried out for each nucleus investigated. Only the one-electron spin–orbit operator was included. We expect some error cancellation, as the neglect of the two-electron contributions should cause some overestimate of the spin–orbit contributions, while the moderate IGLO-II basis sets may not recover all of the one-electron spin–orbit corrections.

Fermi-contact contributions to indirect spin–spin coupling constants were calculated by the finite perturbation method of ref. [22], which is closely analogous to the method used for the computation of the spin–orbit shifts (we do not report the diamagnetic and paramagnetic spin–orbit contributions to the couplings, which are also calculated by the program<sup>[22,24]</sup>). All other computational parameters were also kept identical to the spin–orbit calculations, except that the initial finite perturbation was taken to be the iodine nuclear magnetic moment. This allowed us to obtain couplings to all other atoms in one calculation. Test calculations with other initial perturbations confirmed that, with the large integration grids used, the results are not sensitive to this choice.

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