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Spin–orbit corrections to the indirect nuclear spin–spin coupling constants in XH_4 (X=C, Si, Ge, and Sn)

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Summary. Using the quadratic response function at the *ab initio* SCF level of approximation we have calculated the relativistic corrections from the spin–orbit Hamiltonian, H^{SO}, to the indirect nuclear spin–spin coupling constants of XH_4 (X = C, Si, Ge, and Sn). We find that the spin–orbit contributions to $J_{X\text{-}H}$ are small, amounting only to about 1% for $J_{Sn\text{-}H}$. For the geminal H–H coupling constants the relativistic corrections are numerically smaller than for $J_{X\text{-}H}$, but in some cases relatively larger compared to the actual magnitude of $J_{H\text{-}H}$. We also investigate the use of an effective one-electron spin–orbit Hamiltonian rather than the full H^{SO} in the calculation of these corrections.

Key words: Indirect nuclear spin–spin coupling constants – Spin–orbit corrections

1 Introduction

In a previous study [1] we reported correlated, Multiconfiguration Linear Response (MCLR), nonrelativistic calculations of the indirect nuclear spin–spin coupling constants of CH_4, SiH_4, GeH_4, and SnH_4. These results demonstrated that further investigations are necessary in order to obtain better agreement with experiment, especially for the geminal H–H coupling constants. There are at least two obvious effects that might play an important role in the accurate determination of the coupling constants, namely, relativistic effects and the effect of nuclear motion. Semi-empirical studies of Pyykkö and Wiesenfeld [2] indicate that the relativistic effects particularly for the Sn–H coupling constant may be very large indeed. Using nonrelativistic extended Hückel (EHT) [3] and relativistic extended Hückel (REX) [2, 4, 5] they predicted a relativistic increase in the $J_{Sn\text{-}H}$ coupling constant in SnH_4 of approximately 30%. The corresponding effect in GeH_4 was found to be about 10%.

However, there is, to our knowledge, no *ab initio* determinations of the relativistic corrections to the coupling constants of group IV tetrahydrides. Therefore, we have undertaken a study of one part of the relativistic correction, namely, the one originating from the spin–orbit operator. This electron-spin dependent part of the Dirac–Pauli Hamiltonian [6] is employed in the present calculations to obtain the lowest order spin–orbit corrections to the coupling constants of the series

XH_4, X = C, Si, Ge, and Sn. The spin–orbit operator is included to first order in perturbation theory in conjunction with a nonrelativistic zeroth order wave function. Due to operator divergence, the scalar relativistic effects from another part of the Dirac–Pauli Hamiltonian, the spin-free mass–velocity and Darwin operators (MVD) cannot be incorporated into the present perturbative calculations.

Our primary aim is to estimate the magnitude of the spin–orbit correction to see if it can account for some of the remaining differences between our previous nonrelativistic calculations [1] and experiment. Besides, we wish to investigate how these compare to the relativistic corrections predicted by Pyykkö and Wiesenfeld. Furthermore, we examine if the calculation of the two-electron spin–orbit contribution, which represent the largest bottleneck in this type of calculations, can be omitted. If this is possible one may obtain an inexpensive order-of-magnitude estimate of the spin–orbit correction from the screened one-electron term alone.

2 Theory

2.1 General considerations

In the nonrelativistic limit three of the four contributions to the indirect NMR coupling tensors can be represented as second order energy expressions or as linear response functions. The nonrelativistic coupling constants in this study have been calculated by propagator methods. This theory [7–9], as well as its application to the calculation of coupling constants [10–12], is described elsewhere. Here we only state the form of the four perturbing operators relevant for the calculation of the coupling constant. These operators were first derived by Ramsey [13] and comprise

the paramagnetic spin–orbit Hamiltonian

$$H_{\mathrm{PSO}}(N) = \frac{\mu_0 e h}{8\pi^2 m_e} \sum_j \gamma_N \frac{l_{jN}}{r_{jN}^3} \cdot I_N; \tag{1}$$

the Fermi contact Hamiltonian

$$H_{\mathrm{FC}}(N) = \frac{\mu_0 e g_e h}{6\pi m_e} \sum_j \gamma_N \delta(r_{jN}) s_j \cdot I_N; \tag{2}$$

the spin dipolar Hamiltonian

$$H_{\mathrm{SD}}(N) = \frac{\mu_0 e g_e h}{16\pi^2 m_e} \sum_j \gamma_N \frac{3(s_j \cdot r_{jN})(r_{jN} \cdot I_N) - r_{jN}^2 s_j \cdot I_N}{r_{jN}^5}; \tag{3}$$

and the diamagnetic spin–orbit Hamiltonian

$$H_{\mathrm{DSO}}(N,K) = \frac{\mu_0^2 e^2}{32\pi^2 m_e} \sum_j \gamma_N \gamma_K I_N \left(\frac{r_{jK}}{r_{jK}^3} \cdot \frac{r_{jN}}{r_{jN}^3} 1 - \frac{r_{jK}}{r_{jK}^3} \frac{r_{jN}}{r_{jN}^3} \right) I_K. \tag{4}$$

The contributions from the four operators to the *isotropic coupling constants* are the traces of the following spin–spin coupling tensors:

$$J_{NK}^{\mathrm{PSO}} = \left(\frac{\mu_0 e}{4\pi m_e}\right)^2 \frac{\gamma_N \gamma_K}{h} \sum_{n \neq 0} \frac{\left\langle 0 \middle| \sum_j \frac{l_{jN}}{r_{jN}^3} \middle| n \right\rangle \left\langle n \middle| \sum_j \frac{l_{jK}}{r_{jK}^3} \middle| 0 \right\rangle}{E_0 - E_n}, \tag{5}$$

$$J_{NK}^{\mathrm{FC}} = \left(\frac{\mu g_e e_0}{3 m_e}\right)^2 \frac{\gamma_N \gamma_K}{h} \sum_{n \neq 0} \frac{\langle 0 | \sum_j \delta(r_{jN}) s_j | n \rangle \langle n | \sum_j \delta(r_{jK}) s_j | 0 \rangle}{E_0 - E_n}, \tag{6}$$

$$J_{NK}^{\mathrm{SD}} = \left(\frac{\mu g_0 e_0}{8\pi m_e}\right)^2 \frac{\gamma_N \gamma_K}{h} \sum_{n \neq 0} \times \frac{\left\langle 0 \middle| \sum_j \frac{s_j}{r_N^3} - 3\,\frac{(s_j \cdot r_{jN}) r_{jN}}{r_{jN}^5} \middle| n \right\rangle \left\langle n \middle| \sum_j \frac{s_j}{r_{jK}^3} - 3\,\frac{(s_j \cdot r_{jK}) r_{jK}}{r_{jK}^5} \middle| 0 \right\rangle}{E_0 - E_n}, \tag{7}$$

and

$$J_{NK}^{\mathrm{DSO}} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^2}{2 m_e} \frac{\gamma_N \gamma_K}{h} \left\langle 0 \middle| \sum_j \left(\frac{r_{jK}}{r_{jK}^3} \cdot \frac{r_{jN}}{r_{jN}^3}\,\mathbf{1} - \frac{r_{jK}}{r_{jK}^3} \frac{r_{jN}}{r_{jN}^3}\right) \middle| 0 \right\rangle. \tag{8}$$

As we have assumed a singlet ground state there are no contributions from cross terms such as $J_{NK}^{\mathrm{PSO,SD}}$ involving a mixture of singlet and triplet operators. However, the introduction of the spin–orbit operator, which is a triplet operator, as an additional perturbing operator causes such cross terms to reappear in a third order perturbation expansion. The corrections to the coupling constants can be calculated using quadratic response functions [14–16] in a way similar to the calculations of relativistic corrections to the polarizabilities [17]. Modifying Eq. (5) of Ref. [17] to having only static perturbations we obtain an expression for the quadratic response function (in atomic units):

$$\begin{aligned}
&\lim_{\varepsilon_1, \varepsilon_2 \to 0^+} \langle\langle A; V^{\omega_1=0}, V^{\omega_2=0} \rangle\rangle_{0+i\varepsilon_1 0+i\varepsilon_2} \\
&= \sum_{kn>0} \left[\frac{\langle 0|A|k\rangle (\langle k|V^{\omega_1=0}|n\rangle - \delta_{kn}\langle 0|V^{\omega_1=0}|0\rangle)(n|V^{\omega_2=0}|0\rangle}{\omega_k \omega_n} \right. \\
&\quad + \frac{\langle 0|V^{\omega_2=0}|n\rangle (\langle n|V^{\omega_1=0}|k\rangle - \delta_{kn}\langle 0|V^{\omega_1=0}|0\rangle)(k|A|0\rangle}{\omega_k \omega_n} \\
&\quad + \frac{\langle 0|V^{\omega_1=0}|k\rangle (\langle k|A|n\rangle - \delta_{kn}\langle 0|A|0\rangle)\langle n|V^{\omega_2=0}|0\rangle}{\omega_k \omega_n} \\
&\quad + \frac{\langle 0|A|k\rangle (\langle k|V^{\omega_2=0}|n\rangle - \delta_{kn}\langle 0|V^{\omega_2=0}|0\rangle)(n|V^{\omega_1=0}|0\rangle}{\omega_k \omega_n} \\
&\quad + \frac{\langle 0|V^{\omega_1=0}|n\rangle (\langle n|V^{\omega_2=0}|k\rangle - \delta_{kn}\langle 0|V^{\omega_2=0}|0\rangle)(k|A|0\rangle}{\omega_k \omega_n} \\
&\quad \left. + \frac{\langle 0|V^{\omega_2=0}|k\rangle (\langle k|A|n\rangle - \delta_{kn}\langle 0|A|0\rangle)\langle n|V^{\omega_1=0}|0\rangle}{\omega_k \omega_n} \right],
\end{aligned} \tag{9}$$

where $\omega_n = E_n - E_0$ are excitation energies.

The spin–orbit corrections are then obtained using either of the three operators in Eqs. (1)–(3) as A or $V^{\omega_1=0}$ and the spin–orbit operator, H_{SO}, as $V^{\omega_2=0}$.

2.2 *Corrections to the coupling constants*

Again, having a singlet ground state and using the fact that the quadratic response function in the static limit is symmetric in the perturbing operators we obtain in principle five corrections to the coupling constants. These corrections expressed in terms of the quadratic response functions are given below in expected descending order of importance.

(a) $\langle\langle H_{\mathrm{FC}}(N); H_{\mathrm{FC}}(K), H^{\mathrm{SO}}\rangle\rangle_{0,0}$,

(b) $\langle\langle H_{\mathrm{PSO}}(N); H_{\mathrm{FC}}(K), H^{\mathrm{SO}}\rangle\rangle_{0,0}$,

(c) $\langle\langle H_{\mathrm{FC}}(N); H_{\mathrm{SD}}(K), H^{\mathrm{SO}}\rangle\rangle_{0,0}$,

(d) $\langle\langle H_{\mathrm{PSO}}(N); H_{\mathrm{SD}}(K), H^{\mathrm{SO}}\rangle\rangle_{0,0}$,

(e) $\langle\langle H_{\mathrm{SD}}(N); H_{\mathrm{SD}}(K), H^{\mathrm{SO}}\rangle\rangle_{0,0}$.

Of these five response functions only two were calculated, namely, (b) and (d). The quadratic response function (a), which could be expected to give the largest contribution to the one-bond coupling constants is identically zero. This is shown below by application of the Wigner–Eckart theorem. The corrections (c) and (e) require a combination of three triplet operators, an option not yet implemented in the program. However, we expect (c) to be smaller than (b) as it involves the spin-dipolar operator which only gives a small contribution to the coupling constant. The contribution from the quadratic response function (e), which is quadratic in the spin-dipolar operator, is for the same reason expected to be negligible.

Thus, to assess the importance of the spin–orbit corrections to the coupling constant we argue that it suffices to calculate the terms (b) and (d). They will be denoted as the PSO-FC cross term $J^{\mathrm{PSO\text{-}FC\text{-}SO}}$ and the PSO-SD cross term $J^{\mathrm{PSO\text{-}SD\text{-}SO}}$, respectively.

2.3 *The $\langle\langle H_{\mathrm{FC}}(N); H_{\mathrm{FC}}(K), H^{\mathrm{SO}}\rangle\rangle_{0,0}$ term*

From the sum over states formulation in Eq. (9) we see that the correction term (a) in Sect. 2.2 has products of transition matrix elements of the type

$$\langle S^0|H_{\mathrm{FC}}(N)|T \times T|H_{\mathrm{FC}}(K)|T' \times T'|H^{\mathrm{SO}}|S^0\rangle. \tag{10}$$

As H^{SO} is a vector operator in the electronic spin space with components $S_x, S_y, S_z \propto S_+ + S_-, S_+ - S_-, S_z$ the states $|T\rangle$ and $|T'\rangle$ must be triplet states such that the H^{SO} operator can couple back to the singlet ground state.

The Fermi contact operator, too, is a vector operator in the electronic spin space with components (proportional to)

$$H_x^{\mathrm{FC}} \propto \frac{1}{2}(S_+ + S_-)I_x, \qquad H_y^{\mathrm{FC}} \propto \frac{1}{2i}(S_+ - S_-)I_y, \qquad H_z^{\mathrm{FC}} \propto S_z I_z. \tag{11}$$

Therefore, to obtain, e.g., the diagonal element, $(J_{NK}^{\text{FC-FC-SO}})_{xx}$, of the coupling tensor we must calculate products of the type

$$\begin{aligned} J_{xx} \propto\; & \langle S^0|S_+ + S_-|T\rangle\langle T|S_+ + S_-|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle \\ =\; & \langle S^0|S_+|T\rangle\langle T|S_+|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle \\ & + \langle S^0|S_+|T\rangle\langle T|S_-|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle \\ & + \langle S^0|S_-|T\rangle\langle T|S_+|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle \\ & + \langle S^0|S_-|T\rangle\langle T|S_-|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle. \end{aligned} \tag{12}$$

Since the application of $S_+ (S_-)$ shifts M_s by 1 (-1) the first and last term after the equality sign in Eq. (12) will not contribute to J_{xx} as this would require the state $|T'\rangle$ to be at least a quintet state with $M_s = 2$ (-2), from which the spin–orbit operator cannot couple back to the singlet ground state. The contributions to J_{xx} therefore reduce to

$$\begin{aligned} J_{xx} \propto\; & \langle S^0|S_+|T\rangle\langle T|S_-|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle \\ & + \langle S^0|S_-|T\rangle\langle T|S_+|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle. \end{aligned} \tag{13}$$

Application of the Wigner–Eckart Theorem [18] gives

$$\langle S^0|S_+|T^{-1}\rangle = (S\|S\|T)\sqrt{2} \tag{14}$$

and

$$\langle T^{-1}|S_-|T^0\rangle = (T\|S\|T)\sqrt{2}. \tag{15}$$

Thus the first term in Eq. (13) becomes

$$\langle S^0|S_+|T\rangle\langle T|S_-|T'\rangle\langle T'|H^{\text{SO}}|S^0\rangle = 2(S\|S\|T)(T\|S\|T)\langle T^0|H^{\text{SO}}|S^0\rangle. \tag{16}$$

Similarly, the second term becomes

$$\begin{aligned} & \langle S^0|S_-|T^{+1}\rangle\langle T^{+1}|S_+|T^0\rangle\langle T^0|H^{\text{SO}}|S^0\rangle \\ & = -2(S\|S\|T)(T\|S\|T)\langle T^0|H^{\text{SO}}|S^0\rangle \end{aligned} \tag{17}$$

and the two terms in Eq. (13) which contribute to J_{xx} thus cancel. The same applies to the J_{yy} component of the coupling tensor. By examination of J_{zz} component we find

$$J_{zz} \propto \langle S^0|S_z|T^0\rangle\langle T^0|S_z|T'^0\rangle\langle T'^0|H^{\text{SO}}|S^0\rangle \tag{18}$$

as the S_z operator does not alter the M_s value. The matrix element $\langle T^0|S_z|T'^0\rangle$ is proportional to M_s and thus all contributions to J_{zz} vanish. The same arguments apply to all permutations of these operators in Eq. (9), and therefore the quadratic response function $\langle\langle H_{\text{FC}}(N); H_{\text{FC}}(K), H^{\text{SO}}\rangle\rangle_{0,0}$ vanishes.

2.4 One- and two-electron terms of H^{SO}

The spin–orbit operator including both the one-electron and the two-electron part is

$$H^{\text{SO}} = \frac{g_e h e^2}{32\pi^2 \varepsilon_0 m_e^2 c^2}\left(\sum_N \sum_j \frac{Z_N}{r_{jN}^3} s_j \cdot l_{jN} - \sum_{i<j} \frac{(2s_i + s_j)\cdot l_{ij}}{r_{ij}^3}\right). \tag{19}$$

The first term in Eq. (19) can be viewed as the interaction of electron j's spin magnetic moment with its angular moment due to the motion of the electron relative to the charged nucleus. For this one-electron operator we use the symbol $H^{\mathrm{SO}(1)}$. The last two terms constitute a two-electron operator, $H^{\mathrm{SO}(2)}$, composed of the spin–own–orbit interaction (the last term), i.e. electron j's spin-magnetic moment coupled to its own orbital motion due to its motion relative to electron i, and the spin–other-orbit interaction being electron i's spin-magnetic moment coupled to the orbital magnetic moment of electron j [6].

The effect of the two-electron operator can be construed as a shielding of the actual field from the nucleus felt by electron j thus reducing the one-electron part [19]. This effect may be mimicked by the introduction of an effective nuclear charge, Z_{eff}, such that Eq. (19) is replaced by an *effective one-electron operator*

$$H^{\mathrm{eff}} = \frac{g_e h e^2}{32\pi^2 \varepsilon_0 m_e^2 c^2} \sum_N \sum_j \frac{Z_N(\mathrm{eff})}{r_{jN}^3}\, s_j \cdot l_{jN}. \tag{20}$$

It is assumed that all the electrons in the molecule experience the same effective nuclear charge. Equating (20) and (19) we may now obtain an expression for the effective nuclear charge

$$\sum_N \sum_j \frac{Z_N}{r_{jN}^3} s_j \cdot l_{jN} - \sum_{i<j} \frac{(2s_i + s_j)\cdot l_{ij}}{r_{ij}^3} = \sum_N \sum_j \frac{Z_N(\mathrm{eff})}{r_{jN}^3} s_j \cdot l_{jN} \tag{21}$$

or

$$-\sum_{i<j} \frac{(2s_i + s_j)\cdot l_{ij}}{r_{ij}^3} = \sum_N (Z_N(\mathrm{eff}) - Z_N) \sum_j s_j \cdot \frac{l_{jN}}{r_{jN}^3}. \tag{22}$$

For an atom, the sum over the nuclei reduces to a single term, and the effective nuclear charge, Z_{eff}, can be found from the ratio of the two-electron and one-electron terms. For molecules, however, the sum over N in Eq. (22) does not in general reduce to a single term. Using the assumption [20–22] that the effective nuclear charge for hydrogen equals the nuclear charge, i.e. that hydrogen nuclei are not shielded, we can, for the XH_4 molecules, obtain a reduction and an expression for the effective nuclear charge of the central atom

$$\frac{-\sum_{i<j} \dfrac{(2s_i - s_j)\cdot l_{ij}}{r_{ij}^3}}{\sum_j s_j \cdot \dfrac{l_{jX}}{r_{jX}^3}} = (Z_X(\mathrm{eff}) - Z_X). \tag{23}$$

Dividing by Z_X gives

$$Z_X(\mathrm{eff}) = \left(1 + \frac{H^{\mathrm{SO}(2)}}{H_X^{\mathrm{SO}(1)}}\right) Z_X. \tag{24}$$

In $H_X^{\mathrm{SO}(1)}$ the contributions from the hydrogen nuclei are excluded, whereas in $H^{\mathrm{SO}(1)}$ they are retained. Note, however, that both one-electron operators include a sum over *all* electrons in the molecule.

For computational reasons we have, in the calculations of $Z_X(\mathrm{eff})$, used a slightly modified version of Eq. (24), in which $H_X^{\mathrm{SO}(1)}$ is replaced by $H^{\mathrm{SO}(1)}$ such that $Z_X(\mathrm{eff})$ is calculated as

$$Z_X(\mathrm{eff}) = \left(1 + \frac{H^{\mathrm{SO}(2)}}{H^{\mathrm{SO}(1)}}\right) Z_X. \tag{25}$$

3 Computational details

All calculations were performed with the HERMIT/SIRIUS/RESPONSE MCSCF programs [23–26] at the SCF (RPA) level of approximation. The basis sets and geometries are, except for Si, identical to the ones used in the nonrelativistic calculations on the same molecules [1]. The basis for Si used in the previous calculations turned out to give a poor description of the p-space due to unbalanced contractions. Therefore, we recalculated the non-relativistic coupling constants for SiH_4 as well as the spin–orbit corrections using a basis derived from triple zeta valence basis for Si of Ahlrichs and co-workers [27]. The basis set for Si employed here is given in Appendix 1.

4 Results and discussion

As explained in Sect. 2.2 we have calculated the $J^{\mathrm{PSO\text{-}FC\text{-}SO}}$ and $J^{\mathrm{PSO\text{-}SD\text{-}SO}}$ terms. However, the $J^{\mathrm{PSO\text{-}SD\text{-}SO}}$ term turned out to be insignificant, varying from 0.1–10% (SnH_4–CH_4) of the $J^{\mathrm{PSO\text{-}FC\text{-}SO}}$ term. This could have been anticipated from the knowledge of the relative importance of the nonrelativistic contributions, of which the Fermi contact term is the overall dominant contribution to $J_{X\text{-}H}$ and the spin dipolar term is negligible. Nevertheless, we have included the sum of both correction terms in Tables 1–3.

Tables 1 and 2 show the one-bond and the two-bond geminal coupling constants calculated nonrelativistically [1], as well as the total spin–orbit correction to the coupling constants. Table 3 displays the one-electron and two-electron spin–orbit correction contributions as well as the effective nuclear charge calculated according to Eq. (25).

4.1 One-bond couplings

The spin–orbit correction is only important for SnH_4, yet it is merely 1% of the total coupling constant even in this case. When added to the nonrelativistic RAS B value the spin–orbit correction brings us further away from the experimental value although the agreement is still good. As can be seen from Table 1 the RAS B value is approximately off by 2% compared to the experiment, whereas the spin–orbit corrected value deviates by about 3% from the experimental result. This does leave some room for other corrections, including scalar relativistic effects. The latter are expected to increase the numerical value of the coupling constant.

For the three lightest molecules CH_4–GeH_4 the spin–orbit corrections are very small, though comparable in magnitude to the non-contact terms. At first glance Table 1 seems to show that the spin–orbit correction is larger for CH_4 than for SiH_4. However, taking into account the different g_N-factors for ^{13}C and ^{29}Ge ($g_N(^{13}C) = 1.4048$ and $g_N(^{29}Si) = 1.11058$) we find similar corrections for the two molecules.

Table 1. Nonrelativistic one-bond indirect nuclear spin–spin coupling constants, $J_{\text{X-H}}$, in Hz, and spin–orbit corrections to them

Molecule	Approx.	J^{FC}	J^{SD}	J^{PSO}	J^{DSO}	J^{NRb}	J^{SOc}	$J^{\text{Exp.}}$
CH_4	RPA	157.90	− 0.23	1.39	0.25	159.31	− 0.058	120.8[d]
	CAS B	123.53	0.02	1.48	0.27	125.30		
SiH_4	RPA	− 230.81	0.71	0.33	− 0.02	− 229.79	0.059	−202.5[e]
	CAS B	− 186.80	0.53	0.20	− 0.03	− 186.10		
GeH_4	RPA	− 126.5	0.18	0.23	− 0.01	− 126.10	0.071	−97.6[f]
	RAS B	− 97.86	0.10	0.21	− 0.01	− 97.56		
SnH_4	RPA	− 2184.39	1.21	6.27	− 0.03	− 2176.94	21.173	−1930[e]
	RAS B	− 1897.65	0.87	5.52	− 0.03	− 1891.29		

[a] The nonrelativistic values are taken from Ref. [10] for CH_4 and from Ref. [1] for GeH_4, SiH_4, and SnH_4. The labels CAS B and RAS B for the correlated results refer to the MCSCF wave functions used as references in the calculations; see Ref. [1]

[b] J^{NR} is the sum of the four nonrelativistic Ramsey terms, Eqs. (5)–(8)

[c] J^{RC} is the relativistic correction, calculated as the sum of the two cross terms $J^{\text{PRO-FC-SO}}$ and $J^{\text{PRO-SD-SO}}$

[d] The equilibrium value at $r_e = 1.0858$ Å obtained from an analysis of the temperature dependence of the couplings in CH_4 isotopmers [39]

[e] From Ref. [40]

[f] From Ref. [41]

Table 2. Nonrelativistic geminal proton–proton indirect nuclear spin–spin coupling constants, $J_{\text{H-H}}$, in Hz, and spin–orbit corrections to them

Molecule	Approx.	J^{FC}	J^{SD}	J^{PSO}	J^{DSO}	J^{NRb}	J^{SOc}	$J^{\text{Exp.d}}$
CH_4[a]	RPA	− 27.69	0.44	3.63	− 3.54	− 27.16	0.004	− 12.4
	CAS B	− 15.73	0.35	3.59	− 3.51	− 15.30		
SiH_4	RPA	− 0.81	0.05	1.87	− 2.37	− 1.25	0.006	
	CAS B	− 1.17	0.05	1.85	− 2.34	− 1.63		
GeH_4	RPA	− 0.57	0.06	2.52	− 4.84	− 2.83	0.530	
	RAS B	2.18	0.05	2.50	− 4.82	− 0.09		
SnH_4	RPA	2.45	0.00	2.93	− 4.80	0.58	0.121	15.3
	RAS B	3.38	0.01	2.91	− 4.88	1.42		

[a–c] See corresponding footnotes to Table 1

[d] From Ref. [42]

Relativistic effects and correlation effects are in general not additive [17, 28]. In this connection it is important to note that the spin–orbit corrections are calculated at the RPA level. As it is well established [1, 29, 11, 30] that correlation effects are indeed important for coupling constants, we anticipate that the corrections would change if they were to be calculated at a correlated level. In fact, we have previously seen that inclusion of correlation reduces the magnitude of the

Table 3. One- and two-electron spin–orbit corrections, $J^{\mathrm{PSO-FC+SD-SO}}$, to the one-bond, $J_{\mathrm{X-H}}$, and two-bond, $J_{\mathrm{H-H}}$, coupling constants

Molecule	Coupling constant	$J^{\mathrm{PSO-FC+SD-SO(1)a}}$ [Hz]	$J^{\mathrm{PSO-FC+SD-SO(2)a}}$ [Hz]	$Z_X(\mathrm{eff})^b$	$Z_X(\mathrm{eff, Slater})^c$
CH_4	$J_{\mathrm{X-H}}$	-0.096	0.038	3.63	3.25
	$J_{\mathrm{H-H}}$	6.79×10^{-3}	-3.03×10^{-3}	3.32	
SiH_4	$J_{\mathrm{X-H}}$	0.0876	-0.028	9.53	4.14
	$J_{\mathrm{H-H}}$	7.54×10^{-3}	-1.58×10^{-3}	11.07	
GeH_4	$J_{\mathrm{X-H}}$	0.118	-0.044	20.46	5.65
	$J_{\mathrm{H-H}}$	63.50×10^{-3}	-10.54×10^{-3}	26.69	
SnH_4	$J_{\mathrm{X-H}}$	24.41	-3.261	43.31	5.65
	$J_{\mathrm{H-H}}$	128.25×10^{-3}	-8.21×10^{-3}	46.80	

[a] The sum of the terms $J^{\mathrm{PSO-FC-SO}}$ and $J^{\mathrm{PSO-SD-SO}}$ obtained by using only $H^{\mathrm{SO(1)}}$ or $H^{\mathrm{SO(2)}}$, respectively, in Eq. (9)

[b] The effective nuclear charge is determined from Eq. (25)

[c] $Z_X(\mathrm{eff, Slater}) = Z_X - \sigma_{\mathrm{Slater}}$, where σ_{Slater} is the shielding of the outermost p electron of the central atom

relativistic corrections for another molecular property, the dynamic dipole polarizability [17] by approximately a factor of two. However, we do not expect that inclusion of correlation will significantly change the main conclusion of this study, namely, that the contributions from H_{SO} to the X–H couplings are small.

Pyykkö and Wiesenfeld predicted a total relativistic effect of about 30% [2] for $J_{\mathrm{Sn-H}}$ and approximately 10% for $J_{\mathrm{Ge-H}}$. When comparing their results with the present investigation it must be kept in mind that our calculations do not include scalar relativistic effects and that we only include the effect of H_{SO} perturbatively. It is therefore probably more illuminating to compare the K_{sp} term found by Pyykkö and co-workers [2, 5, 31] to the spin–orbit correction in this work. They found that this term reduces the numerical value of the ${}^1J_{\mathrm{Hg-C}}$ coupling constant in $Hg(CH_3)_4$ by 1.7%, and the ${}^1J_{\mathrm{Pb-H}}$ in PbH_4 by approximately 9%. These numbers are comparable in magnitude and sign to the spin–orbit corrections reported here.

However, our results do not leave room for relativistic corrections of the order of 30% estimated by Pyykkö and Wiesenfeld. This diagreement may be caused by some inconsistency in the comparison of the results obtained with two different semi-empirical methods, namely, EHT and REX. The EHT method used by Pyykkö and co-workers [2, 4, 5] is parametrized to approximate nonrelativistic. Hartree–Fock calculations, for coupling constants to approximate RPA, whereas REX is parametrized to approximate the corresponding relativistic methods. The extended Hückel [2, 5] results are often in poor agreement with RPA calculations employing larger basis sets [1, 32]. It remains to be seen if there is a similar difference between REX results and results of relativistic *ab initio* RPA calculations. Only if this is the case one can attribute differences between EHT and REX couplings to pure relativistic effects. That is, only then can we expect the difference between EHT and REX results to give a cancellation of the errors inherent in the two methods.

4.2 *Geminal couplings*

The absolute magnitude of the corrections to the geminal coupling constants is smaller than the one-bond couplings. Again GeH_4 seems to drop out of line, the spin–orbit corrections being larger than for SnH_4. The importance of the corrections to J(H–H) is, however, more difficult to establish as the question arises with which number we should compare. Comparison with the RPA results gives, for SiH_4 and SnH_4, a smaller relative correction than comparison with the CAS B/RAS B results. For GeH_4 the picture is opposite. Indeed, for GeH_4 the spin–orbit correction is larger than the total nonrelativistic RAS B result. If we compare with the experimental numbers we find yet another conclusion. However, no matter with which of the nonrelativistic results we compare the relative magnitudes of the spin–orbit corrections are larger for the H–H couplings than for the X–H couplings.

4.3 *Comparison of the one- and two-electron contributions, effective nuclear charge*

Calculations of the spin–orbit corrections to the coupling constants using both the full H^{SO} and $H^{SO(1)}$ in Eq. (9) make it possible to estimate the effective nuclear charge, Z_H(eff). Taking the ratio of the corrections computed with H^{SO} and $H^{SO(1)}$, respectively, and multiplying this ratio with Z_X gives according to Eq. (25), an estimate of Z_X(eff). Ideally, both X–H and H–H coupling should give the same effective nuclear charge. From Table 3 we see that the effective nuclear charges obtained from the two coupling constants agree quite well for CH_4 and SnH_4 whereas for SiH_4 and GeH_4 the agreement is less satisfactory. This could indicate that approximating Z_H(eff) with 1 does not hold for the two latter molecules. Another possibility is the obvious: the assumption that one can replace the full spin–orbit operator with an effective one-electron operator does not hold – or at least the simplified version, that all electrons experience the same Z_N(eff) in an atom–molecule is inadequate.

If we compare the effective nuclear charge calculated according to Eq. (25) with the effective nuclear charge calculated from the Slater rules, i.e. $Z_X(\text{eff, Slater}) = Z_N - \sigma_{\text{Slater}}$, where σ_{Slater} is the shielding for the outermost p electron of the central atom, we can see that the Slater effective nuclear charge is much too small for all molecules but CH_4. This is in accordance with the conclusions reached by Abegg [22] who calculated *spin–orbit* coupling constants for a number of molecules containing first row atoms. There is an overall trend, most pronounced in the case of geminal two-bond couplings, indicating that the two-electron term becomes less important with increasing Z_X. Hinkley et al. [33] made the same observation for the *spin–orbit* coupling constants.

5 Conclusions

The results presented here indicate that spin–orbit effects do not make a significant contribution to the isotropic indirect nuclear spin–spin coupling constants of the XH_4 molecules for X = C, Si, Ge and Sn. One may argue that a perturbative treatment of the spin–orbit operator cannot correctly reproduce this effect. However, Nakatsuji and co-workers [34] did *ab initio* calculations of the first order spin–orbit correction to chemical shieldings of methyl and hydrogen halides.

They found large contributions from the one-electron part of the spin–orbit Hamiltonian, which accounted for a major fraction of the differences between experiments and nonrelativistic calculations. It seems unlikely that a perturbative treatment of the spin–orbit correction is justified for one set of NMR parameters but not for the other; so, we believe that the present results are indicative of the magnitude of the spin–orbit corrections. The main reason that a perturbative approach gives large corrections to the shieldings is most likely that the Fermi contact operator, which already contributes to the coupling constant now also contributes to the shieldings via the spin–orbit operator.

One further comment which may be appropriate here is that we only have included one of the possible relativistic correction terms. The mass–velocity and Darwin (MVD) operators give rise to direct as well as indirect corrections to the coupling constants. The indirect effect is related to the relativistic bond length contraction. However, this correction is already included in the present calculations as we report the couplings at experimental geometries. Moreover, it seems that the effect of a bond shortening generally is to reduce the numerical value of the coupling constant [35–37] which is the opposite of the effect expected from the results of Pyykkö and Wiesenfeld [2]. The direct effect of the MVD operator should in principle be calculated in the same way as the spin–orbit correction. Unfortunately, due to the unbounded nature of the MVD operators, we cannot apply the method used here to find the scalar relativistic corrections.

It is not possible *a priori* to predict which of the operators, the MVD or the spin–orbit operator, of the Dirac–Pauli Hamiltonian will give the largest corrections to the coupling constants. Until full relativistic calculations are performed we do not know if the spin–orbit corrections reported here constitute a major part of the total relativistic correction. However, one point supporting that the relativistic corrections, including the spin–orbit corrections, probably are not very large is that we in fact only have room for rather small corrections to $J_{\mathrm{X-H}}$ when we compare the nonrelativistic results with experiments.

From preliminary studies of the geometry dependence of the coupling constants in the XH_4 molecules we have indications that vibrational effects may give nonnegligible corrections especially to geminal H–H couplings. Depending on the size and sign of these corrections we may have room for a larger total relativistic correction. A similar effect could result if we were to use basis sets of even higher quality than those of Ref. [1].

A second conclusion arising from this study is that the use of an effective one-electron spin–orbit operator is possible if only rough estimates of the spin–orbit effects are wanted. The choice of Z_N(eff) is the crucial point in this connection. The values of Z_{X}(eff) found in this study (see Table 3) cannot be reproduced by the use of the Slater rules [38] for the outermost *p*-electron. It is probable that different values of Z_N(eff) must be applied for the same atom, depending on which property one wishes to calculate. However, it seems that Z_N(eff) for a given atom and a given property is roughly the same in all molecules [22, 33]. As the one-electron spin–orbit correction is always larger then the total spin–orbit correction, an inexpensive way to establish the importance of the spin–orbit corrections would be to calculate the one-electron term first. If this term is important one can subsequently add the two-electron term.

Note added in proof

We have recently found that uncontracting the Sn basis set of Ref. [1] for SnH_4 reduces the magnitude of the non-relativistic contribution to the $J_{\mathrm{Sn-H}}$ coupling constant by about 200 Hz at the correlated level of approximation making it equal to about −1700 Hz, thus leaving room for about a 10% relativistic correction (see the discussion in Sect. 5).

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Appendix 1

Basis for Si, derived from Ref. [27], by addition of uncontracted *s* and *d* functions

s-space		*p*-space		*d*-space	
88385228.8200	1.00000000	394.4750363	0.00262857	24.0000000	1.0000000
		93.1376831	0.02055626		
13259852.3243	1.00000000	29.5196087	0.09207026	6.00000000	1.0000000
		10.7816638	0.25565890		
1989288.93753	1.00000000	4.1626575	0.42111707	1.4551006	1.0000000
		1.6247973	0.34401746		
298440.007295	1.00000000			0.48100000	1.0000000
		0.5430666	1.000000000		
44773.3580780	1.00000000			0.15900000	1.0000000
		0.2058207	1.000000000		
6717.1992104	0.00432060			0.04000000	1.0000000
1528.8960325	0.02218710	0.0700535	1.00000000		
432.5474659	0.08648925				
140.6150523	0.24939890				
49.8576367	0.46017197				
18.4349749	0.34250237				
86.5338861	0.02130006				
26.6246068	0.09467614				
4.4953057	−0.32616265				
2.1035046	1.39808039				
1.106095	0.63865787				
0.2370175	1.00000000				
0.0857034	1.00000000				

References

1. Kirpekar S, Jensen HJ Aa, Oddershede J (1994) Chem Phys 188:171
2. Pyykkö P, Wiesenfeld L (1981) Mol Phys 43:557
3. Hoffmann R (1963) J Chem Phys 39:1397
4. Lohr LL Jr, Pyykkö P (1979) Chem Phys Lett 62:333
5. Pyykkö P (1982) J Organometal Chem 232:21
6. See, for example, Moss RE (1973) Advanced molecular quantum mechanics. Chapman & Hall, London; McWeeny R (1992) Methods of molecular quantum mechanics. Academic, San Diego

7. See e.g. Oddershede J, Jørgensen P, Yeager DL (1984) Comp Phys Rep 2
8. Jørgensen P, Jensen HJAa, Olsen J (1988) J Chem Phys 89:3654
9. Olsen J, Yeager DL, Jørgensen P (1989) J Chem Phys 91:381
10. Vahtras O, Ågren H, Jørgensen P, Jensen HJAa, Padkjær SB, Helgaker T (1992) J Chem Phys 96:6120
11. Geertsen J, Oddershede J (1984) Chem Phys 90:301
12. Albertsen P, Jørgensen P, Yeager DL (1980) Chem Phys Lett 76:354
13. Ramsey NF (1953) Phys Rev 91:303
14. Olsen J, Jørgensen P (1985) J Chem Phys 82:3235
15. Hettema H, Jensen HJAa, Jørgensen P, Olsen J (1992) J Chem Phys 97:1174
16. Parkinson WA, Oddershede J (1991) J Chem Phys 94:7251
17. Kirpekar S, Oddershede J, Jensen HJAa (1995) J Chem Phys 103:2983
18. See e.g. Tinkham M (1964) Group theory and quantum mechanics. McGraw-Hill, New York
19. See for example McGlynn SP, Azumi T, Kinoshita M (1969) Molecular spectroscopy of the triplet state. Prentice-Hall, Englewood Cliffs, NJ; Richards WG, Trivedi HP and Copper DL (1981) Spin–orbit coupling in molecules. Clarendon Press, Oxford
20. Ha T, Cimiraglia R (1982) Mol Phys 45:1095
21. Abegg PW, Ha T (1974) Mol Phys 27:763
22. Abegg PW (1975) Mol Phys 30:579
23. Jørgensen P, Jensen HJAa, Olsen J (1989) J Chem Phys 89:3654
24. Olsen J, Yeager DL, Jørgensen P (1989) J Chem Phys 91:381
25. Helgaker T, Taylor PR, Ruud K, Vahtras O, Koch H HERMIT, a molecular integral program.
26. Jensen HJAa, Ågren H, Olsen J (1990) Sirius, a general purpose direct second order MCSCF program. In: Clementi E (ed.) Modern techniques in computational chemistry: MOTECC-90, ESCOM, Leiden
27. Schäfer A, Huber C, Ahlrichs R (1994) J Chem Phys 100:5829
28. Hess BA (1986) Phys Rev A 33:3742
29. Barszczewicz A, Helgaker T, Jaszunski M, Jørgensen P, Ruud K (1994) J Chem Phys 101:6822
30. Perera SA, Sekino H, Bartlett RJ (1994) J Chem Phys 101:2186
31. Pyykkö P (1977) Chem Phys 22:289
32. Guest MF, Overill RE (1980) Chem Phys Lett 73:612
33. Hinkley RK, Walker TEH, Richards WG (1972) Mol Phys 24:1095
34. Nakatsuji H, Takashima H, Hada M (1995) Chem Phys Lett 233:95
35. Geertsen J, Oddershede J, Scuseria GE (1988) J Phys Chem 92:3056
36. Geertsen J, Oddershede J, Scuseria GE (1987) J Chem Phys 87:2138
37. Geertsen J, Oddershede J, Raynes WT, Marwin TL (1994) Mol Phys 82:29
38. See e.g. Atkins PW (1983) Molecular quantum mechanics. Oxford University Press, Oxford
39. Bennett B, Raynes WT, Anderson CT (1989) Spectrochim Acta 45A:821
40. Dreeskamp H (1964) Z Naturforsch 19:139
41. Wilkins AL, Watkinson PJ MacKay KM (1987) J Chem Soc Dalton Trans 2365
42. Brügel W (1979) Handbook of NMR spectral parameters, Vol. 13. Heyden, London