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Relativistic calculation of indirect NMR spin-spin couplings using the Douglas-Kroll-Hess approximation

Juan I. Melo and Martín C. Ruiz de Azúa

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón 1, 1428 Buenos Aires, Argentina

Juan E. Peralta^{a)} and Gustavo E. Scuseria

Department of Chemistry, Rice University, Houston, Texas 77005-1892

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We have employed the Douglas-Kroll-Hess approximation to derive the perturbative Hamiltonians involved in the calculation of NMR spin-spin couplings in molecules containing heavy elements. We have applied this two-component quasirelativistic approach using finite perturbation theory in combination with a generalized Kohn-Sham code that includes the spin-orbit interaction self-consistently and works with Hartree-Fock and both pure and hybrid density functionals. We present numerical results for one-bond spin-spin couplings in the series of tetrahydrides CH_4 , SiH_4 , GeH_4 , and SnH_4 . Our two-component Hartree-Fock results are in good agreement with four-component Dirac-Hartree-Fock calculations, although a density-functional treatment better reproduces the available experimental data. © 2005 American Institute of Physics.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy has been a powerful tool in chemistry since its discovery in 1946.^{1,2} In isotropic phase, the NMR spectrum is determined mainly by two parameters; the nuclear magnetic shieldings (NMSs) and the spin-spin couplings (SSCs). These parameters have been at the center of theoretical research for decades, starting with the pioneer work of Ramsey.^{3,4} Today, modern quantum chemistry provides reliable methods for routinely calculating NMSs and SSCs in molecules bearing hydrogen atoms and first- and second-row elements.⁵⁻⁷

However, this is not the case for NMR parameters involving heavy elements. The main reason for this is that when heavy elements are involved, relativistic effects must be explicitly taken into account. NMR parameters strongly depend on the electronic environment in the vicinity of the nuclei and, thus, they are affected by relativistic effects. Several approaches can be found in the literature incorporating relativistic effects in the calculation of NMR parameters.⁸⁻¹⁵

Most of these works are focused on NMSs, while those reporting calculations of SSCs are less abundant. Full four-component calculations were carried out by Visscher *et al.* in the hydrogen halides HX ($X=\text{F}$, Cl , Br , and I)¹³ and by Enevoldsen *et al.* in the tetrahydrides series XH_4 ($X=\text{C}$, Si , Ge , Sn , and Pb)⁹ using the Dirac-Hartree-Fock (DHF) formalism. Calculations based on two-component (quasirelativistic) approximations are more attractive in terms of computational cost. Autschbach and Ziegler employed the zeroth-order regular approximation (ZORA) to calculate SSCs using Slater functions in the framework of density-functional theory (DFT).^{11,16} Recently, Filatov and Cremer developed a

code for the calculation of SSCs in molecules containing heavy atoms based on the infinite-order regular approximation with modified metric (IORAMM) and Gaussian basis sets (GBS).¹⁰

In this work we investigate the suitability of the Douglas-Kroll-Hess (DKH) approach¹⁷⁻²⁰ for the calculation of SSCs. The DKH method for decoupling the large and small components of the Dirac Hamiltonian has been widely used for the incorporation of relativistic effects in quantum chemistry calculations.²¹⁻²³ The main attractives of the DKH method are that it is variationally stable and it can be systematically improved by increasing the order of the transformation.²⁴ In particular, the calculation of NMSs was discussed in this context by Baba and Fukui²⁵ and by Fukuda *et al.*^{26,27} In our derivation of the magnetic operators in the DKH context we follow below steps similar to those of Fukuda *et al.*,²⁶ although our final expressions for the second-order perturbative Hamiltonians are more compact, simplifying its implementation. The formal theory of electric and magnetic perturbations in the DKH formalism was presented by Dyall.²⁸ However, no previous computational studies on SSCs using the DKH formalism were performed. SSCs critically test the behavior of the wave function near the nuclei, making its calculation very difficult. In this paper, we investigate the performance of the DKH approach within the point-nucleus model taking XH_4 ($X=\text{C}$, Si , Ge , and Sn) as model compounds.

The organization of this paper is as follows. We first describe in Sec. II the theoretical background related to the standard Ramsey's theory and DKH theory. In Sec. III we outline our implementation and the computational details, and in Sec. IV, we present benchmark results for the XH_4 ($X=\text{C}$, Si , Ge , and Sn) series, where accurate four-component Dirac-Hartree-Fock calculations are available.⁹

^{a)}Electronic mail: juanp@rice.edu

II. THEORY

The indirect NMR spin-spin coupling tensor $\mathbf{J}(N, M)$ can be calculated from the second derivative of the electronic energy $E(N, M)$ in the presence of two nuclear magnetic moments $\boldsymbol{\mu}_N$ and $\boldsymbol{\mu}_M$ (atomic units are used throughout this paper),

$$\mathbf{J}(N, M) = \frac{\hbar \gamma_N \gamma_M}{2\pi} \frac{\partial^2 E(N, M)}{\partial \boldsymbol{\mu}_N \partial \boldsymbol{\mu}_M} \Big|_{\boldsymbol{\mu}_N = \boldsymbol{\mu}_M = 0}, \quad (1)$$

where γ_N and γ_M are the nuclear gyromagnetic ratios of nuclei N and M , respectively. This energy derivative can be obtained considering the perturbative magnetic Hamiltonians arising from the presence of the nuclear magnetic moments. In the point-nucleus model, the nuclear magnetic potential \mathbf{A} (such that the magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$) is given by

$$\mathbf{A} = \sum_K \mathbf{A}_K = \sum_K \boldsymbol{\mu}_K \times \frac{\mathbf{r}_K}{r_K^3}, \quad (2)$$

with $\mathbf{r}_K = \mathbf{r} - \mathbf{R}_K$, and c is the speed of light in vacuum.

A. Ramsey's theory

The lowest-order (in c^{-1}) magnetic interaction perturbative Hamiltonian can be obtained by expressing the mechanical momentum $\boldsymbol{\pi}$ in terms of the canonical momentum $\mathbf{p} = -i\nabla$ as $\boldsymbol{\pi} = \mathbf{p} + (1/c)\mathbf{A}$ ($e = -1$ a.u.) and writing down the kinetic-energy operator of the Pauli Hamiltonian $(1/2) \times (\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2$ (where $\boldsymbol{\sigma}$ is the Pauli spin matrix vector). In this way it is possible to identify four perturbative Hamiltonians: the Fermi contact (FC)

$$\mathbf{h}_K^{\text{FC}} = \frac{4\pi}{3c} \delta(\mathbf{r}_K) \boldsymbol{\sigma}, \quad (3)$$

the spin dipolar (SD)

$$\mathbf{h}_K^{\text{SD}} = \frac{1}{2c} \left(\frac{3(\mathbf{r}_K \cdot \boldsymbol{\sigma}) \cdot \mathbf{r}_K - r_K^2 \boldsymbol{\sigma}}{r_K^5} \right), \quad (4)$$

the paramagnetic spin orbital (PSO)

$$\mathbf{h}_K^{\text{PSO}} = \frac{1}{c} \frac{\mathbf{r}_K}{r_K^3} \times \mathbf{p}, \quad (5)$$

and the diamagnetic spin orbital (DSO)

$$\mathbf{h}_{KL}^{\text{DSO}} = \frac{1}{2c^2} \frac{\mathbf{r}_K \cdot \mathbf{r}_L - \mathbf{r}_K \mathbf{r}_L}{r_K^3 r_L^3}. \quad (6)$$

The first three hyperfine operators, Eqs. (3)–(5), are linear in $\boldsymbol{\mu}_K$ (also called paramagnetic terms), while the last one, Eq. (6), is linear in $\boldsymbol{\mu}_K$ and $\boldsymbol{\mu}_L$ (diamagnetic term).

B. First-order Douglas-Kroll-Hess theory

In the relativistic framework, the magnetic interaction perturbative Hamiltonian is obtained by introducing the mechanical momentum $\boldsymbol{\pi} = \mathbf{p} + \mathbf{A}/c$ in the Dirac Hamiltonian:

$$\mathcal{H}_D = V_N + \beta c^2 + c \boldsymbol{\alpha} \cdot \left(\mathbf{p} + \frac{\mathbf{A}}{c} \right), \quad (7)$$

where V_N represents the nucleus-electron interaction, c is the speed of light, and β and $\boldsymbol{\alpha}$ are the four Dirac matrices. In what follows, we shall consider a general vector potential \mathbf{A} , although we are interested in the vector potential of the nuclear magnetic moments. In order to obtain the expression for the operators involved in the calculation of SSCs in the DKH theory, successive DKH transformations are applied to the Dirac Hamiltonian, Eq. (7).

The first step to decouple the large and small components of \mathcal{H}_D is to apply the free particle Foldy-Wouthuysen transformation²⁹ by means of the unitary operator

$$U_0 = K(1 + \beta R \boldsymbol{\alpha} \cdot \mathbf{p}) \quad (8)$$

with the following operators diagonal in p space:

$$K = \sqrt{\frac{E_p + c^2}{2E_p}}, \quad R = \frac{c}{E_p + c^2}, \quad (9)$$

where

$$E_p = c \sqrt{p^2 + c^2}. \quad (10)$$

The unitary transformation U_0 fully decouples the free particle Dirac Hamiltonian. However, in the presence of external fields, the transformed Hamiltonian contains both *even* (i.e., 2×2 block-diagonal) and *odd* (i.e., off-diagonal) terms,

$$\mathcal{H}_1 = U_0 \mathcal{H}_D U_0^\dagger = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1, \quad (11)$$

where the even terms are given by

$$\mathcal{E}_0 = \beta E_p, \quad (12)$$

$$\mathcal{E}_1 = \mathcal{E}_1^V + \mathcal{E}_1^A, \quad (13)$$

$$\mathcal{E}_1^V = K \{ V_N + R(\boldsymbol{\alpha} \cdot \mathbf{p}) V_N (\boldsymbol{\alpha} \cdot \mathbf{p}) R \} K, \quad (14)$$

and

$$\mathcal{E}_1^A = \beta K \{ R(\boldsymbol{\alpha} \cdot \mathbf{p})(\boldsymbol{\alpha} \cdot \mathbf{A}) + (\boldsymbol{\alpha} \cdot \mathbf{A})(\boldsymbol{\alpha} \cdot \mathbf{p}) R \} K, \quad (15)$$

while the odd terms can be expressed as

$$\mathcal{O}_1 = \mathcal{O}_1^V + \mathcal{O}_1^A, \quad (16)$$

$$\mathcal{O}_1^V = \beta K \{ R(\boldsymbol{\alpha} \cdot \mathbf{p}) V_N - V_N (\boldsymbol{\alpha} \cdot \mathbf{p}) R \} K, \quad (17)$$

and

$$\mathcal{O}_1^A = K \{ (\boldsymbol{\alpha} \cdot \mathbf{A}) - R(\boldsymbol{\alpha} \cdot \mathbf{p})(\boldsymbol{\alpha} \cdot \mathbf{A})(\boldsymbol{\alpha} \cdot \mathbf{p}) R \} K. \quad (18)$$

Restricting the Hamiltonian to the upper 2×2 block (corresponding to $\beta = +1$) gives place to the first-order DKH approximation (DKH1). At this level of approximation, all terms containing V_N and \mathbf{A} are decoupled. The spin-orbit (SO) operator appears in \mathcal{E}_1^V . The sum $\mathcal{E}_0 + \mathcal{E}_1^V$ leads to the DKH1 Hamiltonian in the absence of the external magnetic field, while \mathcal{E}_1^A is the perturbative Hamiltonian. At this point, it is important to stress that we are interested in the expression for the perturbative Hamiltonian, and therefore only those terms which are at most quadratic in \mathbf{A} should be considered. The perturbative Hamiltonian \mathcal{E}_1^A is linear in \mathbf{A} , and

as a consequence, no diamagnetic contribution arises at this level of theory. \mathcal{E}_1^A can be splitted into spin-dependent and orbital (spin-free) contributions using the relation

$$(\boldsymbol{\alpha} \cdot \mathbf{a})(\boldsymbol{\alpha} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i\boldsymbol{\alpha} \cdot (\mathbf{a} \times \mathbf{b}). \quad (19)$$

In terms of two-component Pauli matrices, a working equation for the DKH1 magnetic perturbation is obtained:

$$h_1 = i\boldsymbol{\sigma} \cdot \mathbf{h}_1^S + h_1^O, \quad (20)$$

where

$$\mathbf{h}_1^S = K(R\mathbf{p} \times \mathbf{A} + \mathbf{p} \times \mathbf{A}R)K, \quad (21)$$

and

$$h_1^O = K(R\mathbf{p} \cdot \mathbf{A} + \mathbf{p} \cdot \mathbf{A}R)K, \quad (22)$$

are the first-order paramagnetic spin-dependent and orbital perturbations, respectively. It is easy to show that in the non-relativistic limit ($c \rightarrow \infty$), the kinetic factors $K \rightarrow 1$ and $R \rightarrow (2c)^{-1}$. Therefore, the nonrelativistic limit [keeping $\mathcal{O}(c^{-2})$ terms] of h_1^S corresponds to the FC and SD operators in Ramsey's theory, Eqs. (3) and (4), while h_1^O maps into the PSO operator, Eq. (5).

It is worth mentioning that another approach has been suggested by Fukuda *et al.* to introduce the vector potential \mathbf{A} in the DKH approximation.²⁶ This approach consists in replacing the momentum operator \mathbf{p} in the field-free DKH expressions by the mechanical momentum $\mathbf{p} + \mathbf{A}$ and expanding in powers of \mathbf{A}/c . However, it was pointed out that up to second order in \mathbf{A}/c the same final result is obtained.²⁶

C. Second-order Douglas-Kroll-Hess theory

In the DKH2 approximation, a second unitary transformation U_1 is introduced:

$$U_1 = e^{\mathcal{W}}, \quad (23)$$

with \mathcal{W} satisfying the condition $\mathcal{W}^\dagger = -\mathcal{W}$. Expansion of $U_1 U_0 \mathcal{H}_D U_0^\dagger U_1^\dagger$ leads to

$$\begin{aligned} \mathcal{H}_2 = & \beta E_p + \mathcal{E}_1 + \mathcal{O}_1 + [\mathcal{W}, \beta E_p] + [\mathcal{W}, \mathcal{O}_1] \\ & + \frac{1}{2}[\mathcal{W}, [\mathcal{W}, \beta E_p]] + [\mathcal{W}, \mathcal{E}_1] + \dots, \end{aligned} \quad (24)$$

where $[A, B]$ represents the commutator of A and B . The operator \mathcal{W} is defined such that the first-order odd terms in Eq. (24) cancel, i.e.,

$$[\mathcal{W}, \beta E_p] = -\mathcal{O}_1 = -(\mathcal{O}_1^A + \mathcal{O}_1^V). \quad (25)$$

Therefore, \mathcal{W} is an odd operator and the only remaining odd term in Eq. (24) is $[\mathcal{W}, \mathcal{E}_1]$. The even part of \mathcal{H}_2 , provided that Eq. (25) is satisfied, can be expressed as

$$\mathcal{H}_2 = \beta E_p + \mathcal{E}_1^A + \mathcal{E}_1^V + \frac{1}{2}[\mathcal{W}, \mathcal{O}_1^A + \mathcal{O}_1^V]. \quad (26)$$

For the present purpose of obtaining a perturbative expansion in \mathbf{A} , it is convenient to split \mathcal{W} up into two contributions, \mathcal{W}^A and \mathcal{W}^V , satisfying the following conditions:²⁶

$$[\mathcal{W}^V, \beta E_p] = -\mathcal{O}_1^V \quad (27)$$

and

$$[\mathcal{W}^A, \beta E_p] = -\mathcal{O}_1^A. \quad (28)$$

The condition given by Eq. (27) leads to the standard second-order DKH Hamiltonian for the unperturbed system,

$$\mathcal{H}_2^{(0)} = \beta E_p + \mathcal{E}_1^V + \frac{1}{2}[\mathcal{W}^V, \mathcal{O}_1^V]. \quad (29)$$

The second condition, Eq. (28), yields to operators which are linear and quadratic in the magnetic potential,

$$\mathcal{H}_2^{(1)} = \mathcal{E}_1^A + \frac{1}{2}[\mathcal{W}^V, \mathcal{O}_1^A] + \frac{1}{2}[\mathcal{W}^A, \mathcal{O}_1^V] \quad (30)$$

and

$$\mathcal{H}_2^{(2)} = +\frac{1}{2}[\mathcal{W}^A, \mathcal{O}_1^A], \quad (31)$$

which are the perturbative operators.

The reduction from four-component spinors to electronic two-component spinors is carried out by keeping the upper diagonal block of all operators in Eqs. (30) and (31). As a result, the magnetic perturbative Hamiltonians acting on two-component electronic spinors can be separated into those arising from the DKH1 transformation, Eq. (20), and those arising from the DKH2 transformation,

$$h_2^{(1)} = \frac{1}{2}[\mathcal{O}^V, \tilde{\mathcal{O}}^A] + \frac{1}{2}[\tilde{\mathcal{O}}^V, \mathcal{O}^A] \quad (32)$$

and

$$h_2^{(2)} = \frac{1}{2}[\mathcal{O}^A, \tilde{\mathcal{O}}^A]_+, \quad (33)$$

where the superscripts (1) and (2) refer to the order of the magnetic potential involved in each case, $[A, B]_+$ is the anti-commutator of A and B , and the following operators are defined in terms of two-component electronic spinors:

$$\mathcal{O}^V = K(R(\boldsymbol{\sigma} \cdot \mathbf{p})V - V(\boldsymbol{\sigma} \cdot \mathbf{p})R)K, \quad (34)$$

$$\mathcal{O}^A = K[(\boldsymbol{\sigma} \cdot \mathbf{A}) - R(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{p})R]K, \quad (35)$$

and, in p space,

$$(\tilde{\mathcal{O}}^V)_{pp'} = \frac{\mathcal{O}_{pp'}^V}{E_p + E_{p'}} \quad (36)$$

and

$$(\tilde{\mathcal{O}}^A)_{pp'} = \frac{\mathcal{O}_{pp'}^A}{E_p + E_{p'}}. \quad (37)$$

It is interesting to remark that the leading order in c of the second term in the right-hand side of Eq. (35) is c^{-2} , while for the first term it is c^0 . Therefore, in the nonrelativistic limit only the first term of \mathcal{O}^A remains as $\mathcal{O}(c^0)$, and the $\mathcal{O}(c^{-2})$ diamagnetic Ramsey term is recovered in $h_2^{(2)}$. Explicit working expressions for the second-order perturbative operators $h_2^{(1)}$ are given in the Appendix. The second-order paramagnetic Hamiltonian $h_2^{(1)}$ can be splitted into spin-dependent and spin-free contributions analogously to h_1 (see the Appendix).

Using the FC operator [Eq. (3)] with a nonrelativistic wave function leads to the evaluation of the wave function at the nuclear positions (provided that a pointlike nuclear model is used). This is not a problem since the nonrelativistic wave function remains finite at the nuclei. However, the rela-

tivistic (and quasirelativistic) wave function shows a logarithmic divergence at the Coulomb singularities' centers. Therefore, Ramsey's theory *cannot* be employed in a quasirelativistic framework since the value of the wave function at the nuclei is ill defined. If a Gaussian basis-set expansion is used, this problem will manifest in the lack of basis-set convergence for the FC term. Unlike the ZORA, the regularization of the FC operator in the DKH1 approximation is done *only* through kinetic factors, while in second order, the terms arising from $h_2^{(1)}$ contain products of the nuclear potential V and the vector potential \mathbf{A} .

III. IMPLEMENTATION AND COMPUTATIONAL DETAILS

The matrix elements of $\mathbf{A}_K \cdot \mathbf{p}$ and $\mathbf{A}_K \times \mathbf{p}$ are obtained using standard integration routines. To evaluate the perturbative Hamiltonians, we proceed in the same way as in the standard DKH transformation. First, the nonrelativistic kinetic-energy matrix (in the atomic basis-set expansion) is diagonalized to obtain a unitary transformation to a p^2 representation where all the kinetic factors are diagonal, and therefore straightforwardly evaluated. Second, all matrix elements involving the external potentials (nuclei-electron interaction and vector potential) are transformed to this representation. Third, the matrix elements of the operators in Eqs. (20) and (32) are evaluated and back transformed to the r representation. The diamagnetic (second order in \mathbf{A}) contribution is kept nonrelativistic.

Relativistic calculations were carried out using the generalized Kohn-Sham (GKS) and generalized Hartree-Fock (GHF) approaches. In these schemes, the electronic ground state is described by means of the set of occupied two-component spinors. To guarantee the rotational invariance of the total energy in the GKS case, we employed a noncollinear generalization of the spin-density functional energy and potential.³⁰ The first-order response is obtained by including the matrix elements of the perturbative Hamiltonian in the self-consistent-field (SCF) procedure multiplied by an appropriate constant. In all cases, a tight convergence criterion was imposed. We note in passing that our GKS and GHF codes allow us to handle Hamiltonians with any arbitrary spin dependence. Therefore, only three SCF calculations *per perturbed nucleus* are needed to obtain the spin-dependent response, in contrast to six in standard unrestricted codes. Moreover, as spin and orbital perturbed states do not mix at first order, it is possible to obtain the complete linear response (spin plus orbital) with only three SCF calculations per perturbed nucleus, instead of nine needed in a standard calculation (six for spin and three for orbital perturbations). However, the lack of analytical linear response^{31,32} in our relativistic code is subject to all the well-known shortcomings of numerical differentiation.

Nonrelativistic calculations were carried out using the coupled-perturbed Kohn-Sham (CPKS) scheme or coupled-perturbed Hartree-Fock (CPHF). We have checked the accuracy of our numerical differentiation procedure by using the nonrelativistic Hamiltonian in the GHF code and comparing it with the CPHF results.

An interesting feature of our approach is that the SO operator is variationally included in the Hamiltonian. Thus, we can choose to include SO *not* as a perturbation but fully self-consistently. It is also possible to "turn SO off" to analyze its effect on the calculated SSCs.

Relativistic effects are included in the one-electron Hamiltonian, while the electron-electron Coulomb, the portion of Hartree-Fock exchange, and DFT exchange-correlation potential remain nonrelativistic.

IV. BENCHMARK RESULTS

All calculations were carried out using modified versions of the GAUSSIAN (Ref. 33) suite of codes. SSC values reported in this paper are referred to the isotopic species with nonzero nuclear magnetic moment and the largest natural abundance, i.e., ^1H , ^{13}C , ^{29}Si , ^{73}Ge , and ^{119}Sn . In all calculations, nuclear g factors are $g(^1\text{H})=5.585\,692$, $g(^{13}\text{C})=1.404\,822$, $g(^{29}\text{Si})=-1.110\,580$, $g(^{73}\text{Ge})=-0.195\,438$, and $g(^{119}\text{Sn})=-2.094\,560$, and the electronic g factor is $g_e=2$. For comparison, all XH_4 geometrical structures were chosen to be identical to those in Ref. 9, i.e., tetrahedral T_h symmetry with $R(\text{C}-\text{H})=1.09\text{ \AA}$, $R(\text{Si}-\text{H})=1.48\text{ \AA}$, $R(\text{Ge}-\text{H})=1.52\text{ \AA}$, and $R(\text{Sn}-\text{H})=1.70\text{ \AA}$.

It is known that a good description of the core electrons is needed to achieve reliable results for calculated SSCs, mainly due to the presence of the Fermi contact operator. In the case of the DKH operators, there is an additional basis-set dependence since the transformation to p^2 representation is carried out using the same basis-set expansion. Therefore, the election of the basis set is critical for our calculations.

An extensive analysis of the basis-set dependence of nonrelativistic SSCs can be found in Refs. 34 and 35. We have first analyzed the basis-set requirements for the calculation of SSCs using the DKH method starting from Dunning's aug-cc-pVTZ (Ref. 36–38) in fully uncontracted form for H, C, Si, and Ge. For Ge, we have progressively added s -type functions at the tight end of these basis sets using a geometric progression with the ratio of the two steepest s -type orbitals. For Sn, we have proceeded in the same way

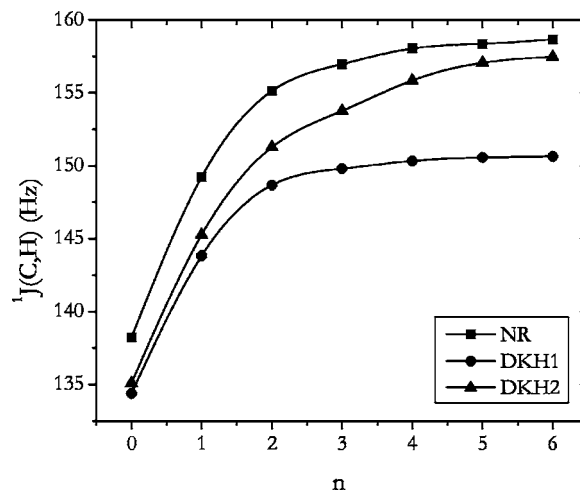


FIG. 1. Dependence of the calculated $^1J(\text{C},\text{H})$ coupling in CH_4 with the number of additional tight functions added to the fully uncontracted cc-pVTZ basis set.

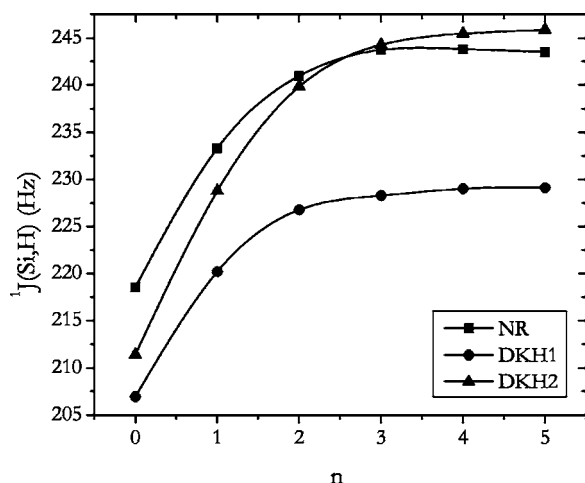


FIG. 2. Dependence of the calculated $^1J(\text{Si,H})$ coupling in SiH_4 with the number of additional tight functions added to the fully uncontracted cc-pVTZ basis set.

but starting from the universal Gaussian basis set developed by Malli *et al.*,³⁹ which consists in a fully uncontracted (22s18p12d) basis set. In Figs. 1 and 2 we show the convergence behavior of calculated $^1J(X,\text{H})$ in CH_4 and SiH_4 with the number of s -type functions added (for a given n , n steep functions were added to both H and X). For $^1J(\text{C,H})$, the nonrelativistic (NR) value (Ramsey's theory) saturates for $n=4$, while DKH1 shows a slightly better convergence. On the other hand, DKH2 seems to be converged with five tight s -type functions added. A similar trend is observed for the series $^1J(\text{Si,H})$, $^1J(\text{Ge,H})$, and $^1J(\text{Sn,H})$, although the number of s -type functions that needs to be added to achieve a good basis-set convergence is different in each case. In view of these results, we have decided to include five tight s -type functions for $^1J(\text{C,H})$, five for $^1J(\text{Si,H})$, four for $^1J(\text{Ge,H})$, and six for $^1J(\text{Sn,H})$ for the benchmark calculations reported in this paper.

In Table I we present our calculated $^1J(X,\text{H})$ for the series of XH_4 molecules with Hartree-Fock and different levels of the DKH approximation. For comparison, four-component Dirac-Hartree-Fock and IORamm results taken from the literature are also shown. In all cases, DKH1 gives a too large relativistic correction, while this trend is reverted by using the DKH2 Hamiltonian. A similar behavior was

TABLE I. Calculated one-bond $^1J(X,\text{H})$ SSCs for the series of tetrahydrides XH_4 using the Hartree-Fock approximation. For comparison, four-component random-phase approximation (4-c RPA) and IORamm calculations are also included (values in Hz).

Method	CH_4	SiH_4	GeH_4	SnH_4
Nonrelativistic	158.4	-243.5	-108.2	-1930.6
DKH1-scalar	150.6	-229.1	-110.3	-2371.0
DKH1-SO	150.6	-229.1	-109.9	-2392.3
DKH2-scalar	157.1	-245.9	-122.5	-2616.0
DKH2-SO	157.1	-245.9	-121.9	-2629.3
4-c RPA ^a	159.1	-250.1	-123.9	-2650.2
IORamm ^b	160.1	-248.7	-125.8	-2704.6

^aReference 9.

^bReference 10.

TABLE II. Calculated spin-dependent (S) and orbital (O) contributions to $^1J(X,\text{H})$ and total relativistic correction (ΔJ , defined as $J_{\text{rel}} - J_{\text{non-rel}}$) of one-bond $^1J(X,\text{H})$ SSCs for the series of tetrahydrides XH_4 . In all cases the Hartree-Fock approximation has been employed. All values are in Hz.

	CH_4	SiH_4	GeH_4	SnH_4
$^1J(S)$	155.4	-246.3	-122.1	-2635.0
$^1J(O)$	2.1	0.4	0.2	5.7
$\Delta J(\text{DKH2-SO})$	-1.3	-2.4	-13.7	-698.7
$\Delta J(4\text{-c RPA})^a$	0.6	-4.8	-13.5	-719.6
IORamm ^b	0.6	-5.1	-15.0	-766.0

^aReference 9.

^bReference 10.

found in Ref. 40 for hyperfine coupling tensors. The SO effect is negligible for the one-bond couplings of CH_4 , SiH_4 , and GeH_4 , while for $^1J(\text{Sn,H})$ in SnH_4 the SO corrections are -21.3 and -13.3 Hz for DKH1 and DKH2, respectively.

In Table II we present the (Hartree-Fock) calculated spin-dependent (S) and orbital (O) contributions to $^1J(X,\text{H})$ for the series of XH_4 hydrides, as well as the total relativistic correction for these couplings (ΔJ). Comparing the magnitude of spin-dependent and orbital contributions, these $^1J(X,\text{H})$ couplings are dominated by the spin-dependent term, mainly due to the fact that they include the FC contribution. Moreover, the relativistic correction is dominated by its spin-dependent contribution. With the exception of CH_4 , where the relativistic correction reported using four-component random-phase approximation (4-c RPA) is about 0.6 Hz, the DKH2 approximation reproduces the relativistic effects for these couplings. For $^1J(\text{Sn,H})$, the total DKH2 calculated correction is about -698.7 Hz, in good agreement with the 4-c RPA calculation, -719.6 Hz.

It is known that DFT can deliver SSCs with reasonable accuracy.^{31,32,41,42} Therefore, it is wise to test the performance of DFT in this case. To this end, we have employed three representative functionals: PBE (Ref. 43) (based on the generalized-gradient approximation), PBEh (Refs. 44 and 45) (hybrid PBE, also referred to as PBE0 and PBE1PBE in the literature), and the widely used hybrid B3LYP.⁴⁶ We have chosen not to use functionals from the local-spin density approximation family since they were shown to perform poorly for nonrelativistic SSCs.^{40,42} Table III summarizes our DFT results using the DKH2 approximation for the calculation of one-bond $^1J(X,\text{H})$ SSCs in the series of tetrahydrides XH_4 . The three functionals employed here tend to correct the

TABLE III. Calculated one-bond $^1J(X,\text{H})$ SSCs for the series of tetrahydrides XH_4 using different density functionals. All values were obtained using the DKH2-SO approximation (in Hz).

Molecule	CH_4	SiH_4	GeH_4	SnH_4
PBE	117.8	-186.3	-86.8	-1883.3
PBEh	121.9	-194.1	-92.5	-1727.0
B3LYP	131.2	-209.6	-99.6	-1922.6
Expt.	120.1 ^a	-201.1 ^b	-97.6 ^c	-1933.3 ^d

^aReference 47.

^bReference 48.

^cReference 49.

^dReference 50.

overestimation of the magnitude of the coupling given by the Hartree-Fock approximation, and therefore the agreement with experiment is better. However, the trend is not uniform along the series of molecules studied here: the hybrid B3LYP functional seems to work better for GeH₄ and SnH₄ molecules, while PBE and PBEh reproduce fairly well the one-bond coupling in CH₄. Although a comparison of SSCs calculated with the ZORA method for this series of tetrahydrides would be interesting, we could not find such results in the literature.

V. CONCLUSIONS

We have implemented and tested the DKH approximation for the calculation of NMR spin-spin couplings in the series of tetrahydrides CH₄, SiH₄, GeH₄, and SnH₄. We show that the basis-set dependence is slightly different than that found for Ramsey's theory, probably due to the transformation to p^2 space. It is worth mentioning that the results are stable and consistent as the Gaussian basis set is enlarged. The first-order DKH1 gives unexpectedly large relativistic corrections to $^1J(X,H)$ even for light nuclei, while DKH2 considerably improves the agreement with relativistic corrections given by four-component DHF calculations.⁹

In our approach, the SO operator is variationally included in the calculation. Although for the molecules tested in this work a perturbative treatment of SO could be adequate, our approach is more suitable for other systems with a stronger SO coupling. The results obtained for the XH₄ series are promising and suggest that DKH2 is a worthy al-

ternative for the quasirelativistic calculation of SSCs. However, a deeper analysis of its performance for different couplings should be carried out. Work along these lines is being carried out in our group.

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APPENDIX: SECOND-ORDER PERTURBATIVE TERMS

Second-order magnetic perturbation operators are defined in Eqs. (32) and (33),

$$h_2^{\text{mag}} = h_2^{(1)} + h_2^{(2)} = \frac{1}{2}[O^V, \tilde{O}^A] + \frac{1}{2}[\tilde{O}^V, O^A] + \frac{1}{2}[\tilde{O}^A, O^A]_+, \quad (\text{A1})$$

where O^V and O^A are defined in Eqs. (34) and (35). The first two terms in Eq. (A1) refer to second-order paramagnetic contributions, while the last term represents a diamagnetic contribution.

Expanding the commutators and using shorthand notation defined in Eqs. (36) and (37), $h_2^{(1)}$ can be expressed in terms of its spin and orbital contributions:

$$h_2^{(1)} = h_2^{(1)}(O) + h_2^{(1)}(S) = (X^O + X^{O^\dagger}) + (X^S + X^{S^\dagger}), \quad (\text{A2})$$

where

$$\begin{aligned} X^O = & M(\widetilde{\mathbf{pVp}})K\frac{1}{p^2}K(\mathbf{p} \cdot \mathbf{A})K - K(\mathbf{A} \cdot \mathbf{p})KM(\tilde{V})K - M(\widetilde{\mathbf{p} \times \mathbf{Vp}})K\frac{1}{p^2}K(\mathbf{p} \times \mathbf{A})K - M(\widetilde{\mathbf{pVp}})MK(\mathbf{A} \cdot \mathbf{p})M \\ & + M(\mathbf{p} \cdot \mathbf{A})M\frac{1}{p^2}M(\tilde{V})K + M(\widetilde{\mathbf{p} \times \mathbf{Vp}})MK(\mathbf{A} \times \mathbf{p})M + M(\mathbf{pVp})K\frac{1}{p^2}K(\mathbf{p} \cdot \mathbf{A})K - K(\mathbf{A} \cdot \mathbf{p})KM(V)K \\ & - M(\mathbf{p} \times \mathbf{Vp})K\frac{1}{p^2}K(\mathbf{p} \times \mathbf{A})K - M(\mathbf{pVp})MK(\mathbf{A} \cdot \mathbf{p})M + M(\mathbf{p} \cdot \mathbf{A})M\frac{1}{p^2}M(V)K + M(\mathbf{p} \times \mathbf{Vp})MK(\mathbf{A} \times \mathbf{p})M \end{aligned} \quad (\text{A3})$$

and

$$\begin{aligned} X^S = & i\sigma \cdot \left(M(\widetilde{\mathbf{p} \times \mathbf{Vp}})K\frac{1}{p^2}K(\mathbf{p} \cdot \mathbf{A})K + M(\widetilde{\mathbf{p} \cdot \mathbf{Vp}})K\frac{1}{p^2}K(\mathbf{p} \times \mathbf{A})K - K(\mathbf{A} \times \mathbf{p})MK(\tilde{V})K - M(\widetilde{\mathbf{p} \times \mathbf{Vp}})K\frac{1}{p^2}K(\mathbf{p} \times \mathbf{A})K \right. \\ & - M(\widetilde{\mathbf{p} \cdot \mathbf{Vp}})MK(\mathbf{A} \times \mathbf{p})K - M(\widetilde{\mathbf{p} \times \mathbf{Vp}})MK(\mathbf{A} \cdot \mathbf{p})M + M(\mathbf{p} \times \mathbf{A})Mp^2M(\tilde{V})K + M(\widetilde{\mathbf{p} \times \mathbf{Vp}})MK(\mathbf{A} \times \mathbf{p})M \\ & + M(\mathbf{p} \times \mathbf{Vp})K\frac{1}{p^2}K(\mathbf{p} \cdot \mathbf{A})K + M(\mathbf{p} \cdot \mathbf{Vp})K\frac{1}{p^2}K(\mathbf{p} \times \mathbf{A})K - K(\mathbf{A} \times \mathbf{p})MK(V)K - M(\mathbf{p} \times \mathbf{Vp})K\frac{1}{p^2}K(\mathbf{p} \times \mathbf{A})K \\ & \left. - M(\mathbf{p} \cdot \mathbf{Vp})MK(\mathbf{A} \cdot \mathbf{p})K - M(\mathbf{p} \times \mathbf{Vp})MK(\mathbf{A} \cdot \mathbf{p})M + M(\mathbf{p} \times \mathbf{A})Mp^2M(V)K + M(\mathbf{p} \times \mathbf{Vp})MK(\mathbf{A} \times \mathbf{p})M \right), \end{aligned} \quad (\text{A4})$$

and $M=KR$ was used for brevity.

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