

Calculation of indirect nuclear spin–spin coupling constants within the regular approximation for relativistic effects

Michael Filatov^{a)} and Dieter Cremer

Department of Theoretical Chemistry, Göteborg University, Reutersgatan 2, S-41320 Göteborg, Sweden

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A new method for calculating the indirect nuclear spin–spin coupling constant within the regular approximation to the exact relativistic Hamiltonian is presented. The method is completely analytic in the sense that it does not employ numeric integration for the evaluation of relativistic corrections to the molecular Hamiltonian. It can be applied at the level of conventional wave function theory or density functional theory. In the latter case, both pure and hybrid density functionals can be used for the calculation of the quasirelativistic spin–spin coupling constants. The new method is used in connection with the infinite-order regular approximation with modified metric (IORAmm) to calculate the spin–spin coupling constants for molecules containing heavy elements. The importance of including exact exchange into the density functional calculations is demonstrated.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is one of the most important experimental tools in chemistry as is documented in dozens of monographs and review articles.^{1–3} During the last ten years, quantum chemistry has taken this into account by focusing on the development of methods for calculating NMR parameters such as chemical shieldings^{3,4} or spin–spin coupling constants (SSCCs).^{5–11} The reliable prediction of SSCCs on a routine basis represented for many years a major obstacle, however this has been solved in the last decade. Quantum chemistry can offer now a spectrum of reliable methods that make it possible to predict the indirect isotropic SSCCs for nontrivial molecules with satisfying accuracy. These methods range from MCSCF,⁶ second order polarization propagator approximation (SOPPA),⁷ equation of motion coupled cluster (EOM–CC)⁸ to projected coupled cluster theory with all single and double excitations (CCSD).⁹ Even more important than the wave function theory (WFT)-based methods for calculating SSCCs are the density functional theory (DFT)-based methods.^{10,11} Whereas earlier DFT work^{12,13} was based on finite perturbation theory, which led to a number of calculational problems,¹⁴ the more recent work focuses on coupled perturbed DFT (CP–DFT) and a completely analytical formulation of the SSCC.^{10,11} CP–DFT predictions of SSCCs have proven in many cases to be reliable and, because of its favorable cost/efficiency ratio, CP–DFT is the method of choice for calculating SSCCs of larger molecules.¹⁵

There are four basic ingredients, which have to be considered for obtaining reliable SSCCs: (a) The method used must account for a considerable amount of long-range electron correlation to lead to reasonable singlet–triplet splittings essential for the calculation of the Fermi contact (FC) term of the SSCC. A lack of long-range correlation could lead to singlet–triplet instabilities or quasi-instabilities, which cause an artificial exaggeration of the FC term and by this also of

the total SSCC.¹⁰ (b) Spin–spin coupling information is transferred between the coupled nuclei essentially by exchange interactions. A satisfactory description of exchange interactions is therefore essential for a reliable calculation of the SSCCs.^{10,16} (c) A correct description of the FC term requires basis sets with steep *s* functions having a maximum in the core region to describe the contact interactions, which lead to spin polarization at the surface of the nucleus.^{17,18} (d) In the case of spin–spin coupling involving one or two heavy nuclei, there is a need for relativistic corrections especially of the FC term to obtain a reasonable description of spin polarization at the contact surface of the nuclei.^{19–23}

Additional requirements concern (e) the use of basis sets with augmented basis functions to obtain reliable paramagnetic spin–orbit (PSO) and spin–dipole (SD) terms [the fourth Ramsay term, the diamagnetic spin–orbit (DSO) depends on the zeroth rather than the first order density distribution and is computationally not so demanding]; (f) the vibrational corrections of the SSCC,²⁴ and (g) the consideration of solvent effects.²⁵ The latter two requirements concern the comparison of calculated and measured SSCCs.

Recent quantum chemical work on SSCCs has focused on requirements (a), (b), (c), (e), (f), and (g). However, if one is concerned with the inclusion of relativistic effects into the SSCC calculations, only a few quantum-chemical methods are available. First principles SSCC calculations were carried out for tetrahydrides MH₄ (M=C, Si, Ge, Sn, and Pb) by Enevoldsen *et al.*²² employing the four-component relativistic Dirac–Hartree–Fock (DHF) approach. Because no electron correlation is included within this approach, the calculated values of the SSCCs are far from the experimentally measured ones.²² Furthermore, because this is a four-component method, the computational demands are very high and the application of this approach is limited to relatively small molecules. A quasirelativistic computational scheme, which incorporates electron correlation by means of DFT was developed by Autschbach and Ziegler²³ within the zeroth-order regular approximation (ZORA)²⁶ to the exact

^{a)}Electronic mail: filatov@theoc.gu.se

relativistic Hamiltonian. Although this computational scheme has been successfully applied to study the SSCCs in molecules containing heavy atoms,²⁷ the implementation of the ZORA method is based on the use of numeric integration for the calculation of the Hamiltonian matrix elements.^{23,26} Although such a procedure is acceptable for the use of pure density functionals, it precludes the inclusion of HF exchange (such as in hybrid HF/DFT functionals) into the ZORA SSCC calculations because the inclusion of the HF exchange would require the development of analytic techniques for the calculation of the Hamiltonian matrix elements. In view of the fact that the spin–spin coupling mechanism strongly depends on exchange interactions,^{10,16} it is desirable that a DFT method for calculating relativistic SSCCs is able to use both pure and hybrid exchange functionals.

Recently, we have developed^{28,29} a new computational procedure for the calculation of the Hamiltonian matrix elements within the regular approximation for relativistic effects. The new procedure is fully analytic and thus it can be applied in the context of both WFT and DFT calculations. With the use of the new procedure, quasirelativistic computational schemes more accurate than ZORA, such as infinite-order regular approximation (IORA)³⁰ and infinite-order regular approximation with modified metric (IORAmm),²⁸ can be installed easily within the standard quantum-chemical codes designed for nonrelativistic calculations. This is possible, because the new approach does not employ any new molecular integrals besides those already available in the nonrelativistic calculation.^{28,29} Currently, the calculation of the analytic gradient (derivative of the total energy with respect to nuclear coordinates)²⁹ for geometry optimizations and the analytic calculation of static electric properties³¹ is possible. The IORAmm method has much weaker gauge dependence than IORA and is the method of choice in these calculations.^{28,29,31,32}

In the present work, the formalism presented in our earlier investigations^{28,29,31} will be extended to the calculation of NMR SSCCs. The derivation will be carried out in a general way so that the corresponding formalism can be applied both within WFT and within DFT. Results of the current work will be presented in the following way: In Sec. II, the theory of calculating the indirect isotropic SSCCs is briefly presented. Then, the IORA/IORAmm formalism is described and extended to the calculation of SSCCs. The working formulas for calculating the quasirelativistic SSCCs are given for both WFT and DFT. In Sec. III, the implementation of the algorithm for calculating the quasirelativistic SSCCs will be described. Finally, in Sec. IV the results of benchmark SSCC calculations will be discussed where special emphasis is given to a balanced use of exact and DFT exchange.

II. THEORY OF NMR SPIN–SPIN COUPLING CONSTANTS

The nuclear magnetic moment μ_N is related to the nuclear spin \mathbf{I}_N via Eq. (1),

$$\mu_N = \hbar \gamma_N \mathbf{I}_N, \quad (1)$$

where γ_N is the nuclear gyromagnetic ratio. The reduced indirect nuclear SSCCs \mathbf{K}_{AB} can be calculated as the derivative of the total molecular energy with respect to the nuclear magnetic moments μ_A and μ_B [see Eq. (2)],

$$\mathbf{K}_{AB} = \frac{\partial}{\partial \mu_A} \circ \frac{\partial}{\partial \mu_B} E(\mu_A, \mu_B, \dots) \Big|_{\mu_A = \mu_B = \dots = 0}. \quad (2)$$

The symbol \circ denotes a tensor product and \mathbf{K}_{AB} is the reduced spin–spin coupling tensor. For the purpose of relating the tensor property \mathbf{K}_{AB} to the measured indirect isotropic SSCC J_{AB} , the tensor \mathbf{J}_{AB} is defined

$$\mathbf{J}_{AB} = \frac{\hbar}{2\pi} \gamma_A \gamma_B \mathbf{K}_{AB}. \quad (3)$$

If the NMR spectrum of a compound is measured in solution or the gas phase, rapid rotations about arbitrarily oriented molecular rotation axes lead to an averaging over the different components of \mathbf{J}_{AB} with the result that only the isotropic part (4) of the second rank tensor (3) can be determined from the measured NMR spectra,

$$J_{AB} = \frac{1}{3} \text{tr} \mathbf{J}_{AB}, \quad (4a)$$

$$K_{AB} = \frac{1}{3} \text{tr} \mathbf{K}_{AB}. \quad (4b)$$

A. Nonrelativistic theory of spin–spin coupling constants: Ramsey's theory

Consider N independent electrons moving in the external electrostatic potential $V(\mathbf{r})$. The nonrelativistic quantum motion of these electrons is described by the Schrödinger equation, which for convenience can be represented according to the following:³³

$$\hat{H}\Psi = (\hat{T} + V(\mathbf{r}))\Psi = \left(\sum_i \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}_i)^2 + V(\mathbf{r}) \right) \Psi = E\Psi, \quad (5)$$

where $\mathbf{p}_i = -i\nabla_i$ is the linear momentum operator of the i th electron and $\boldsymbol{\sigma}$ is the vector of the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$.³⁴

The external magnetic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ due to the vector potential $\mathbf{A}(\mathbf{r})$ couples to the linear momentum of the electrons through

$$\boldsymbol{\pi}_i = \mathbf{p}_i + \mathbf{A}(\mathbf{r}_i). \quad (6)$$

The vector potential $\mathbf{A}(\mathbf{r})$ caused by the magnetic nuclei is given by

$$\mathbf{A}(\mathbf{r}) = \frac{1}{c^2} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3}, \quad (7)$$

where $\mathbf{r}_N = \mathbf{r} - \mathbf{R}_N$ is the position of an electron with respect to the N th nucleus and c is the velocity of light. Substituting (6) and (7) into the Hamiltonian of Eq. (5), the Schrödinger–Pauli equation for the electrons in a magnetic field is derived.³³ According to Eq. (2), one obtains the reduced indirect spin–spin coupling tensor (8) by differentiating with respect to the nuclear magnetic moments of the coupled nuclei,

$$\begin{aligned}
(K_{AB})_{\beta\alpha} &= \frac{\partial^2}{\partial(\mu_A)_\beta \partial(\mu_B)_\alpha} \langle \Psi(\mu_A, \mu_B, \dots) | \hat{H}(\mu_A, \mu_B, \dots) | \Psi(\mu_A, \mu_B, \dots) \rangle \Big|_{\mu_A=\mu_B=\dots=0} \\
&= \langle \Psi^{(0)} | \frac{\partial^2 \hat{H}(\mu_A, \mu_B, \dots)}{\partial(\mu_A)_\beta \partial(\mu_B)_\alpha} \Big|_{\mu_A=\mu_B=\dots=0} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | \frac{\partial \hat{H}(\mu_A, \mu_B, \dots)}{\partial(\mu_A)_\beta} \Big|_{\mu_A=\mu_B=\dots=0} | \Psi_\alpha^{(\mu_B)} \rangle \\
&= \langle \Psi^{(0)} | \sum_i (\hat{\mathbf{h}}_{AB}^{\text{DSO}}(\mathbf{r}_i))_{\beta\alpha} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | \sum_i (i(\hat{\mathbf{h}}_A^{\text{PSO}}(\mathbf{r}_i))_\beta + (\hat{\mathbf{h}}_A^{\text{FC}}(\mathbf{r}_i))_\beta + (\hat{\mathbf{h}}_A^{\text{SD}}(\mathbf{r}_i))_\beta) | \Psi_\alpha^{(\mu_B)} \rangle. \quad (8)
\end{aligned}$$

In Eq. (8), the one-electron operators $\hat{\mathbf{h}}_{AB}^{\text{DSO}}(\mathbf{r})$, $\hat{\mathbf{h}}_A^{\text{PSO}}(\mathbf{r})$, $\hat{\mathbf{h}}_A^{\text{FC}}(\mathbf{r})$ and $\hat{\mathbf{h}}_A^{\text{SD}}(\mathbf{r})$ correspond to the four Ramsey terms DSO, PSO, FC, and SD of the SSCC,³⁵ which are defined in Eq. (9),

$$(\hat{\mathbf{h}}_{AB}^{\text{DSO}}(\mathbf{r}))_{\beta\alpha} = \frac{1}{c^4} \frac{\delta_{\beta\alpha}(\mathbf{r}_A \cdot \mathbf{r}_B) - (r_A)_\alpha (r_B)_\beta}{r_A^3 r_B^3}, \quad (9a)$$

$$(\hat{\mathbf{h}}_A^{\text{PSO}}(\mathbf{r}))_\beta = -\frac{1}{c^2} \frac{(\mathbf{r}_A \times \nabla)_\beta}{r_A^3}, \quad (9b)$$

$$(\hat{\mathbf{h}}_A^{\text{FC}}(\mathbf{r}))_\beta = \frac{4\pi}{3} \frac{1}{c^2} \delta(\mathbf{r}_A) \sigma_\beta, \quad (9c)$$

$$(\hat{\mathbf{h}}_A^{\text{SD}}(\mathbf{r}))_\beta = \frac{1}{2c^2} \left(3 \frac{(\sigma \cdot \mathbf{r}_A)(r_{iA})_\beta}{r_A^5} - \frac{\sigma_\beta}{r_A^3} \right), \quad (9d)$$

where the subscripts α and β denote the Cartesian components of a tensor or a vector.

Wave function $\Psi^{(0)}$ is a solution of the field-free Schrödinger equation and the first order perturbed wave function $\Psi^{(\mu_B)}$ contains the response of the many-body wave function to the different perturbations generated by the presence of the magnetic moment of nucleus B ,

$$\begin{aligned}
\Psi^{(\mu_B)} &= \frac{\partial}{\partial \mu_B} \Psi(\mu_A, \mu_B, \dots) \Big|_{\mu_A=\mu_B=\dots=0} \\
&= i\Psi^{(\mu_B),\text{PSO}} + \Psi^{(\mu_B),\text{FC}} + \Psi^{(\mu_B),\text{SD}}. \quad (10)
\end{aligned}$$

Within the Kohn–Sham (KS) DFT,³⁶ the M -electron wave function is represented by a single Slater determinant (11),

$$\Psi_{\text{KS}} = (M!)^{-1/2} \det[\dots \psi_{i,\sigma}(\mathbf{r}_i) \psi_{i,\sigma'}(\mathbf{r}_i) \dots], \quad (11)$$

where functions $\psi_{i,\sigma}(\mathbf{r}_i)$ are the spin–orbitals, which depend on the position \mathbf{r}_i and the spin σ of the i th electron. The KS wave function Ψ_{KS} is the solution of a Schrödinger-type equation with the electrostatic potential defined in Eq. (12),

$$V(\mathbf{r}) = V_n(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) \quad (12)$$

where $V_n(\mathbf{r})$ is the potential due to the nuclei, $\rho(\mathbf{r})$ is the electron density (13) at the position \mathbf{r} ,

$$\rho(\mathbf{r}) = \sum_{j,\sigma} |\psi_{j,\sigma}(\mathbf{r})|^2 \quad (13)$$

and $V_{xc}(\mathbf{r})$ is the so-called exchange–correlation potential.³⁶ For the standard exchange–correlation density functionals, $V_{xc}(\mathbf{r})$ does not depend on the external magnetic field explicitly. Thus, the first-order perturbed wave function $\Psi^{(\mu_B)}$ can be constructed from the perturbed spin–orbitals $\psi_{i,\sigma}^{(\mu_B),X}(\mathbf{r})$, which are the solutions of Eq. (14),

$$(\hat{\mathbf{h}}_A^X + \mathbf{V}_A^X(\mathbf{r}) - \epsilon_A^X) \psi_{i,\sigma}^{(0)}(\mathbf{r}) + (\hat{h}_0 + V(\mathbf{r}) - \epsilon^{(0)}) \psi_{i,\sigma}^{(\mu_B),X}(\mathbf{r}) = 0. \quad (14)$$

In Eq. (14), X denotes the Ramsey perturbation ($X = \text{PSO, FC, SD}$) and $\mathbf{V}_A^X(\mathbf{r})$ is the first-order variation of the potential $V(\mathbf{r})$ due to the distortion of the spin–orbitals by perturbation X .

$$(\mathbf{V}_A^X(\mathbf{r}))_\beta = \sum_{j,\sigma}^{\text{occ}} \int (\psi_{j,\sigma}^{(\mu_A),X}(\mathbf{r}'))_\beta \frac{\delta V(\mathbf{r})}{\delta (\psi_{j,\sigma}^{(\mu_A),X}(\mathbf{r}'))_\beta} d\mathbf{r}'. \quad (15)$$

Since the PSO term generates purely imaginary variations of the spin–orbitals, there is no net change of the density due to perturbation $X = \text{PSO}$. When pure density functionals are used, $\mathbf{V}_A^{\text{PSO}}(\mathbf{r}) = 0$ and Eq. (14) is solved in one step. The FC and SD perturbation generate spin-polarization and, by this, a nonzero potential $\mathbf{V}_A^X(\mathbf{r})$. Accordingly, Eq. (15) is solved iteratively even when pure density functionals are employed. In the case of hybrid density functionals, which blend a fraction of Hartree–Fock (HF) exchange with DFT exchange,³⁷ Eq. (15) must be solved iteratively for all three perturbations. A more detailed description of the nonrelativistic KS formalism for the calculation of SSCCs can be found elsewhere.¹⁰

B. Methodology of the quasirelativistic methods IORA and IORAm

The matrix IORAm (or IORA) Kohn–Sham equations in the one-electron ($1\bar{e}$) approximation³⁸ are given by Eq. (16),^{28,29}

$$\begin{aligned}
&((\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger (\mathbf{V}_n + \mathbf{T} + \mathbf{W}) (\mathbf{U}^{-1/2}) (\mathbf{S}^{1/2}) + \mathbf{J} + \mathbf{V}_{xc}) \mathbf{C}_{i,\sigma} \\
&= \mathbf{S} \mathbf{C}_{i,\sigma} \epsilon_{i,\sigma}, \quad (16)
\end{aligned}$$

where \mathbf{V}_n is the matrix of the electron–nuclear attraction integrals $\langle \chi_\mu | V_n(\mathbf{r}) | \chi_\nu \rangle$ (χ_μ , basis functions; $\mathbf{C}_{i,\sigma}$, column vector of expansion coefficients of the spin–orbital $\psi_{i,\sigma}$), \mathbf{J} is the matrix of the classical Coulomb repulsion operator

[second term in Eq. (12)], and \mathbf{V}_{xc} is the matrix of the exchange-correlation potential V_{xc} . The matrix \mathbf{U} (quasi-relativistic wave function normalization) is given by

$$\mathbf{U} = \mathbf{S} + \frac{1}{2mc^2} (\mathbf{T} + a\mathbf{W} + b\mathbf{W}\mathbf{T}^{-1}\mathbf{W}) \quad (17)$$

(parameters a and b for IORA: $a=2$, $b=1$; for IORAm: $a=\frac{3}{2}$, $b=\frac{1}{2}$).^{28,29} \mathbf{T} is the matrix of the kinetic energy operator $(2m)^{-1}(\boldsymbol{\sigma} \cdot \mathbf{p})^2$, \mathbf{S} the overlap matrix, and matrix \mathbf{W} in Eqs. (16) and (17) the solution of Eq. (18),

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0\mathbf{T}^{-1}\mathbf{W}, \quad (18)$$

which is given in

$$\mathbf{W}^{-1} = \mathbf{W}_0^{-1} - \mathbf{T}^{-1}. \quad (19)$$

The matrix \mathbf{W}_0 in Eqs. (18) and (19) is calculated in the $1\bar{c}$ approximation according to

$$(\mathbf{W}_0)_{\mu\nu} = \frac{1}{4m^2c^2} \langle \chi_\mu | (\boldsymbol{\sigma} \cdot \mathbf{p}) V_n (\boldsymbol{\sigma} \cdot \mathbf{p}) | \chi_\nu \rangle. \quad (20)$$

Note that only the electron–nuclear attraction potential V_n is used in Eq. (20). Although in the actual IORA/IOAm calculations, the scalar relativistic (SR) approximation is used, i.e., all spin-dependent relativistic corrections are neglected, the spin-dependence is retained in Eq. (20) for the purpose of introducing the magnetic field due to the nuclear

magnetic moments. The dependence on the magnetic field due to the vector potential (7) is introduced into matrices \mathbf{T} and \mathbf{W}_0 via the minimal coupling prescription (6).

The total IORA/IOAm DFT energy is given by

$$E_{\text{DFT}}^{\text{IORA/IOAm}} = \text{tr}(\mathbf{P}((\mathbf{S}^{1/2})^\dagger(\mathbf{U}^{-1/2})^\dagger(\mathbf{V}_n + \mathbf{T} + \mathbf{W}) \times (\mathbf{U}^{-1/2})(\mathbf{S}^{1/2}))) + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}, \quad (21)$$

where \mathbf{P} is the density matrix in the basis of functions χ_μ ,

$$\mathbf{P} = \mathbf{C}\mathbf{n}\mathbf{C}^\dagger. \quad (22)$$

In Eq. (22), \mathbf{n} is the diagonal matrix of spin–orbital occupation numbers and \mathbf{C} is the (orthogonal) matrix constructed from the column vectors $\mathbf{C}_{i,\sigma}$. Equation (21) differs from the corresponding nonrelativistic DFT expression only in the use of the relativistically corrected one-electron Hamiltonian for the calculation of the one-electron part of the total DFT energy [first term on the right-hand side of Eq. (21)].

With the use of the standard density functionals, the KS exchange–correlation energy does not depend explicitly on the magnetic field of the nuclei. Thus, differentiating the total energy (21) with respect to the nuclear magnetic moments yields Eq. (23) for the reduced indirect spin–spin coupling tensor,

$$\begin{aligned} (K_{AB})_{\beta\alpha} &= \left. \frac{\partial E_{\text{DFT}}^{\text{IORA/IOAm}}(\mu_A, \mu_B, \dots)}{\partial(\mu_A)_\beta \partial(\mu_B)_\alpha} \right|_{\mu_A = \mu_B = \dots = 0} \\ &= \text{tr} \left(\left(\frac{\partial \mathbf{P}}{\partial(\mu_A)_\beta} \right) \left(\mathbf{G}^\dagger \left(\frac{\partial \mathbf{H}}{\partial(\mu_B)_\alpha} \right) \mathbf{G} \right) \right) + \text{tr} \left(\mathbf{P} \left(\mathbf{G}^\dagger \left(\frac{\partial^2 \mathbf{H}}{\partial(\mu_A)_\beta \partial(\mu_B)_\alpha} \right) \mathbf{G} \right) \right) + \text{tr} \left(\left(\frac{\partial \mathbf{P}}{\partial(\mu_A)_\beta} \right) \left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial(\mu_B)_\alpha} \right) \mathbf{H} \mathbf{G} \right. \right. \\ &\quad \left. \left. + \mathbf{G}^\dagger \mathbf{H} \left(\frac{\partial \mathbf{G}}{\partial(\mu_B)_\alpha} \right) \right) \right) + \text{tr} \left(\mathbf{P} \left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial(\mu_A)_\beta} \right) \left(\frac{\partial \mathbf{H}}{\partial(\mu_B)_\alpha} \right) + \left(\frac{\partial \mathbf{G}^\dagger}{\partial(\mu_B)_\alpha} \right) \left(\frac{\partial \mathbf{H}}{\partial(\mu_A)_\beta} \right) \right) \mathbf{G} \right) + \text{tr} \left(\mathbf{P} \mathbf{G}^\dagger \left(\left(\frac{\partial \mathbf{H}}{\partial(\mu_A)_\beta} \right) \left(\frac{\partial \mathbf{G}}{\partial(\mu_B)_\alpha} \right) \right. \right. \\ &\quad \left. \left. + \left(\frac{\partial \mathbf{H}}{\partial(\mu_B)_\alpha} \right) \left(\frac{\partial \mathbf{G}}{\partial(\mu_A)_\beta} \right) \right) \right) + \text{tr} \left(\mathbf{P} \left(\left(\frac{\partial^2 \mathbf{G}^\dagger}{\partial(\mu_A)_\beta \partial(\mu_B)_\alpha} \right) \mathbf{H} \mathbf{G} + \mathbf{G}^\dagger \mathbf{H} \left(\frac{\partial^2 \mathbf{G}}{\partial(\mu_A)_\beta \partial(\mu_B)_\alpha} \right) \right) \right) \\ &\quad \left. + \text{tr} \left(\mathbf{P} \left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial(\mu_A)_\beta} \right) \mathbf{H} \left(\frac{\partial \mathbf{G}}{\partial(\mu_B)_\alpha} \right) + \left(\frac{\partial \mathbf{G}^\dagger}{\partial(\mu_B)_\alpha} \right) \mathbf{H} \left(\frac{\partial \mathbf{G}}{\partial(\mu_A)_\beta} \right) \right) \right), \quad (23) \end{aligned}$$

where the matrices \mathbf{G} (renormalization on the nonrelativistic metric) and \mathbf{H} (unrenormalized regular Hamiltonian) are defined in Eqs. (24) and (25), respectively,

$$\mathbf{G} = \mathbf{U}^{-1/2} \mathbf{S}^{1/2}, \quad (24)$$

$$\mathbf{H} = \mathbf{V}_n + \mathbf{T} + \mathbf{W}. \quad (25)$$

With the use of Eq. (33) from Ref. 29, the derivative of the matrix \mathbf{H} with respect to a component of the nuclear magnetic moment $(\mu_A)_\beta$ is given by

$$\begin{aligned} \frac{\partial \mathbf{H}}{\partial(\mu_A)_\beta} &= \frac{\partial \mathbf{T}}{\partial(\mu_A)_\beta} - \mathbf{W}\mathbf{T}^{-1} \frac{\partial \mathbf{T}}{\partial(\mu_A)_\beta} \mathbf{T}^{-1}\mathbf{W} \\ &\quad + \mathbf{W}\mathbf{W}_0^{-1} \frac{\partial \mathbf{W}_0}{\partial(\mu_A)_\beta} \mathbf{W}_0^{-1}\mathbf{W}. \quad (26) \end{aligned}$$

The derivative of the kinetic energy matrix \mathbf{T} is merely the sum of the matrices of the operators $i\hat{\mathbf{h}}_A^{\text{PSO}}$, $\hat{\mathbf{h}}_A^{\text{FC}}$, and $\hat{\mathbf{h}}_A^{\text{SD}}$ in Eqs. (9b)–(9d). The corresponding integrals are readily

available in any nonrelativistic code designed for the nonrelativistic SSCC calculation.¹⁰ The derivatives of the \mathbf{W}_0 matrix are derived in Appendix A. Substituting the respective derivatives into Eq. (26), one obtains Eq. (27) for the first derivative of the matrix \mathbf{H} with respect to component $(\mu_A)_\beta$ of the nuclear magnetic moment,

$$\begin{aligned} \frac{\partial \mathbf{H}}{\partial (\mu_A)_\beta} &= i\mathbf{H}_{A,\beta}^{\text{PSO}} + \mathbf{H}_{A,\beta}^{\text{FC}} + \mathbf{H}_{A,\beta}^{\text{SD}} - \mathbf{W}\mathbf{T}^{-1}(i\mathbf{H}_{A,\beta}^{\text{PSO}} + \mathbf{H}_{A,\beta}^{\text{FC}} + \mathbf{H}_{A,\beta}^{\text{SD}})\mathbf{T}^{-1}\mathbf{W} + \frac{i}{2m}(\mathbf{W}\mathbf{T}^{-1}\mathbf{H}_{A,\beta}^{\text{PSO}}\mathbf{W}_0^{-1}\mathbf{W} + \mathbf{W}\mathbf{W}_0^{-1}\mathbf{H}_{A,\beta}^{\text{PSO}}\mathbf{T}^{-1}\mathbf{W}) \\ &+ \frac{3}{4m}(\mathbf{W}\mathbf{T}^{-1}\mathbf{H}_{A,\beta}^{\text{FC}}\mathbf{W}_0^{-1}\mathbf{W} + \mathbf{W}\mathbf{W}_0^{-1}\mathbf{H}_{A,\beta}^{\text{FC}}\mathbf{T}^{-1}\mathbf{W}) + \frac{1}{2m}(\mathbf{W}\mathbf{T}^{-1}\mathbf{H}_{A,\beta}^{\text{X}}\mathbf{W}_0^{-1}\mathbf{W} - \mathbf{W}\mathbf{W}_0^{-1}\mathbf{H}_{A,\beta}^{\text{X}}\mathbf{T}^{-1}\mathbf{W}) \\ &+ \mathbf{W}\mathbf{W}_0^{-1}(\mathbf{W}_0^{\text{SD}})_{A,\beta}\mathbf{W}_0^{-1}\mathbf{W}. \end{aligned} \quad (27)$$

In Eq. (27), $\mathbf{H}_{A,\beta}^{\text{PSO}}$, $\mathbf{H}_{A,\beta}^{\text{FC}}$, and $\mathbf{H}_{A,\beta}^{\text{SD}}$ are the matrices of the operators (9b), (9c), and (9d), respectively, and the matrices $(\mathbf{W}_0^{\text{SD}})_{A,\beta}$ and $(\mathbf{H}^{\text{X}})_{A,\beta}$ are defined in Eqs. (A8) and (A10) of Appendix A.

For the second derivative, $\partial^2\mathbf{H}/\partial(\mu_A)_\beta\partial(\mu_B)_\alpha$, Eq. (28) can be derived,

$$\begin{aligned} \frac{\partial^2 \mathbf{H}}{\partial (\mu_A)_\beta \partial (\mu_B)_\alpha} &= \frac{\partial^2 \mathbf{T}}{\partial (\mu_A)_\beta \partial (\mu_B)_\alpha} - \mathbf{W}\mathbf{T}^{-1} \frac{\partial^2 \mathbf{T}}{\partial (\mu_A)_\beta \partial (\mu_B)_\alpha} \mathbf{T}^{-1}\mathbf{W} + \mathbf{W}\mathbf{W}_0^{-1} \frac{\partial^2 \mathbf{W}_0}{\partial (\mu_A)_\beta \partial (\mu_B)_\alpha} \mathbf{W}_0^{-1}\mathbf{W} \\ &+ \mathbf{W}\mathbf{T}^{-1} \left[\frac{\partial \mathbf{T}}{\partial (\mu_B)_\alpha} \mathbf{T}^{-1} \frac{\partial \mathbf{T}}{\partial (\mu_A)_\beta} + \frac{\partial \mathbf{T}}{\partial (\mu_A)_\beta} \mathbf{T}^{-1} \frac{\partial \mathbf{T}}{\partial (\mu_B)_\alpha} + \frac{\partial \mathbf{T}}{\partial (\mu_B)_\alpha} \mathbf{T}^{-1} \mathbf{W}\mathbf{T}^{-1} \frac{\partial \mathbf{T}}{\partial (\mu_A)_\beta} \right. \\ &+ \left. \frac{\partial \mathbf{T}}{\partial (\mu_A)_\beta} \mathbf{T}^{-1} \mathbf{W}\mathbf{T}^{-1} \frac{\partial \mathbf{T}}{\partial (\mu_B)_\alpha} \right] \mathbf{T}^{-1}\mathbf{W} - \mathbf{W}\mathbf{W}_0^{-1} \left[\frac{\partial \mathbf{W}_0}{\partial (\mu_B)_\alpha} \mathbf{W}_0^{-1} \frac{\partial \mathbf{W}_0}{\partial (\mu_A)_\beta} + \frac{\partial \mathbf{W}_0}{\partial (\mu_A)_\beta} \mathbf{W}_0^{-1} \frac{\partial \mathbf{W}_0}{\partial (\mu_B)_\alpha} \right. \\ &- \left. \frac{\partial \mathbf{W}_0}{\partial (\mu_B)_\alpha} \mathbf{W}_0^{-1} \mathbf{W}\mathbf{W}_0^{-1} \frac{\partial \mathbf{W}_0}{\partial (\mu_A)_\beta} - \frac{\partial \mathbf{W}_0}{\partial (\mu_A)_\beta} \mathbf{W}_0^{-1} \mathbf{W}\mathbf{W}_0^{-1} \frac{\partial \mathbf{W}_0}{\partial (\mu_B)_\alpha} \right] \mathbf{W}_0^{-1}\mathbf{W} \\ &- \mathbf{W}\mathbf{W}_0^{-1} \left[\frac{\partial \mathbf{W}_0}{\partial (\mu_B)_\alpha} \mathbf{W}_0^{-1} \mathbf{W}\mathbf{T}^{-1} \frac{\partial \mathbf{T}}{\partial (\mu_A)_\beta} + \frac{\partial \mathbf{W}_0}{\partial (\mu_A)_\beta} \mathbf{W}_0^{-1} \mathbf{W}\mathbf{T}^{-1} \frac{\partial \mathbf{T}}{\partial (\mu_B)_\alpha} \right] \mathbf{T}^{-1}\mathbf{W} \\ &- \mathbf{W}\mathbf{T}^{-1} \left[\frac{\partial \mathbf{T}}{\partial (\mu_B)_\alpha} \mathbf{T}^{-1} \mathbf{W}\mathbf{W}_0^{-1} \frac{\partial \mathbf{W}_0}{\partial (\mu_A)_\beta} + \frac{\partial \mathbf{T}}{\partial (\mu_A)_\beta} \mathbf{T}^{-1} \mathbf{W}\mathbf{W}_0^{-1} \frac{\partial \mathbf{W}_0}{\partial (\mu_B)_\alpha} \right] \mathbf{W}_0^{-1}\mathbf{W}, \end{aligned} \quad (28)$$

where the second derivative of the kinetic energy matrix is merely $\mathbf{H}_{AB,\beta\alpha}^{\text{DSO}}$ and the second derivative of the \mathbf{W}_0 matrix is $(\mathbf{W}_0^{\text{DSO}})_{AB}$ defined in Eq. (A6) of Appendix A.

The derivative of the renormalization matrix \mathbf{G} is given in Eq. (29) [cf. Eq. (36) in Ref. 29],

$$\frac{\partial}{\partial (\mu_B)_\alpha} \mathbf{G} = -\mathbf{U}^{-1/2} \left(\frac{\partial}{\partial (\mu_B)_\alpha} \mathbf{U}^{1/2} \right) \mathbf{G}, \quad (29)$$

where the derivatives of the square-root matrix $\mathbf{U}^{1/2}$ are calculated via Eq. (B1) in Appendix B. Differentiating Eq. (29) with respect to $(\mu_A)_\beta$ leads to Eq. (30) for the second derivative of the renormalization matrix \mathbf{G} ,

$$\begin{aligned} \frac{\partial^2}{\partial (\mu_B)_\alpha \partial (\mu_A)_\beta} \mathbf{G} &= - \left[\mathbf{U}^{-1/2} \left(\frac{\partial^2}{\partial (\mu_B)_\alpha \partial (\mu_A)_\beta} \mathbf{U}^{1/2} \right) \right. \\ &- \mathbf{U}^{-1/2} \left(\frac{\partial}{\partial (\mu_B)_\alpha} \mathbf{U}^{1/2} \right) \mathbf{U}^{-1/2} \left(\frac{\partial}{\partial (\mu_A)_\beta} \mathbf{U}^{1/2} \right) \\ &- \left. \mathbf{U}^{-1/2} \left(\frac{\partial}{\partial (\mu_A)_\beta} \mathbf{U}^{1/2} \right) \mathbf{U}^{-1/2} \left(\frac{\partial}{\partial (\mu_B)_\alpha} \mathbf{U}^{1/2} \right) \right] \mathbf{G}, \end{aligned} \quad (30)$$

where the second derivatives of the square-root matrix $\mathbf{U}^{1/2}$ are calculated via Eq. (B9) derived in Appendix B.

Next, we consider the magnitude of the terms in the IORA/IORamm expression (23) for the SSCC. The deriva-

tive of the density matrix, which is obtained by solving the matrix version of Eq. (14), is of the same order of magnitude (in powers of $1/c^2$) as the corresponding perturbation operator. Thus, the first two terms in Eq. (23) are of the order of $1/c^4$. Because the derivative of the relativistic normalization matrix \mathbf{U} defined in Eq. (17) with respect to the nuclear magnetic moment is of the order $1/c^4$, the third, fourth, and fifth term in Eq. (23) are of the order $1/c^6$ and the last term is of the order $1/c^8$. The second derivative of the renormalization matrix \mathbf{G} , Eq. (30), is of the order $1/c^6$, because the second derivative of the matrix \mathbf{U} is of the order of $1/c^2$ multiplied by the order of the second derivative of the matrix $\mathbf{H}(1/c^4)$. This establishes a hierarchy of terms in the quasirelativistic indirect nuclear SSCC (23) and reveals that the first two terms in Eq. (23) should be sufficient for an accurate calculation of this property.

Although nearly all molecular integrals necessary to calculate the first and the second derivatives of the matrix \mathbf{H} are readily available in the standard nonrelativistic quantum-chemical codes designed for the SSCC calculation,¹⁰ a further simplification of Eqs. (27) and (28) is possible. Note, that nearly all terms in these equations contain factors $\mathbf{W}\mathbf{T}^{-1}$ or $\mathbf{W}\mathbf{W}_0^{-1}$. Inspection of Eq. (19) for matrix \mathbf{W} shows that in those cases where the elements of the matrix \mathbf{W}_0 are larger than the elements of the kinetic energy matrix \mathbf{T} , matrix \mathbf{W} is dominated by the kinetic energy, that is

$$\mathbf{W} \rightarrow -\mathbf{T} \quad \text{for } |\mathbf{W}_0| \gg |\mathbf{T}|. \quad (31)$$

This situation occurs for tight basis functions which determine the shape of the atomic and molecular orbitals in the vicinity of the nuclei. Thus, in the deep core regions of atoms, Eqs. (32) apply,

$$\mathbf{W}\mathbf{T}^{-1} \rightarrow -\mathbf{I} \quad \text{for } |\mathbf{W}_0| \gg |\mathbf{T}|, \quad (32a)$$

$$\mathbf{W}\mathbf{W}_0^{-1} \rightarrow \mathbf{0} \quad \text{for } |\mathbf{W}_0| \gg |\mathbf{T}|. \quad (32b)$$

For diffuse basis functions, the elements of the \mathbf{W}_0 matrix are small compared to the elements of the kinetic energy matrix. Consequently, the \mathbf{W} matrix is dominated by the \mathbf{W}_0 matrix and the following relationships hold:

$$\mathbf{W}\mathbf{T}^{-1} \rightarrow \mathbf{0} \quad \text{for } |\mathbf{W}_0| \ll |\mathbf{T}|, \quad (33a)$$

$$\mathbf{W}\mathbf{W}_0^{-1} \rightarrow \mathbf{I} \quad \text{for } |\mathbf{W}_0| \ll |\mathbf{T}|. \quad (33b)$$

With the use of the Gaussian-type functions (GTF), the switching between these two regimes, (32) and (33), occurs when the exponential parameter α is of the order $\alpha \sim (9\pi/8)(c^4/Z^2)$, where Z is the charge of the atomic nucleus. That is, for heavy nuclei ($Z \geq 50$), the switching to (32) occurs already for moderately tight basis set functions ($\alpha \leq 5 \times 10^5$).

For the first derivative of the quasirelativistic Hamiltonian, Eqs. (27), (32), and (33) have important implications. First of all, for tight basis functions, which are used to describe the behavior of the wave function close to the nucleus, the second term in Eq. (27) compensates the first term exactly. Second, the third term on the right-hand side must

vanish at the two extremes (a) tight and (b) diffuse basis functions because one of the prefactors $\mathbf{W}\mathbf{T}^{-1}$ or $\mathbf{W}\mathbf{W}_0^{-1}$ vanishes at these extremes. Third, the fifth term in Eq. (27) vanishes at both extremes (a) and (b) because in such a case one of the factors $\mathbf{W}\mathbf{T}^{-1}$ or $\mathbf{W}\mathbf{W}_0^{-1}$ turns to a unit matrix and another converges to zero. Consequently, this term can be neglected in the final expression. Fourth, the contribution of the last term, $(\mathbf{W}_0^{\text{SD}})_{A,\beta}$, is dominated by the matrix elements with steep basis functions and because of the prefactors $\mathbf{W}\mathbf{W}_0^{-1}$ should vanish. Although, the fourth term contains these prefactors as well, this term should be retained in the final formula, because the divergent FC operator compensates for the vanishing prefactor $\mathbf{W}\mathbf{W}_0^{-1}$ and this term makes a finite contribution to the derivative. Considering all simplifications, we obtain Eq. (34) for the first derivative of the matrix \mathbf{H} with respect to a component of the nuclear magnetic moment,

$$\begin{aligned} \frac{\partial \mathbf{H}}{\partial (\mu_A)_\beta} = & \mathbf{H}_{A,\beta}^{\text{FC}} - \mathbf{W}\mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{FC}} \mathbf{T}^{-1} \mathbf{W} \\ & + \frac{3}{4m} (\mathbf{W}\mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{FC}} \mathbf{W}_0^{-1} \mathbf{W} \\ & + \mathbf{W}\mathbf{W}_0^{-1} \mathbf{H}_{A,\beta}^{\text{FC}} \mathbf{T}^{-1} \mathbf{W}) \\ & + i(\mathbf{H}_{A,\beta}^{\text{PSO}} - \mathbf{W}\mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{PSO}} \mathbf{T}^{-1} \mathbf{W}) \\ & + \mathbf{H}_{A,\beta}^{\text{SD}} - \mathbf{W}\mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{SD}} \mathbf{T}^{-1} \mathbf{W}, \end{aligned} \quad (34)$$

where we separated the FC, PSO, and SD contributions.

In the case of the second derivative of the quasirelativistic Hamiltonian as given by Eq. (28), all terms after the third one can be neglected. Indeed, the fourth and the fifth terms vanish for both tight and diffuse basis set functions, because the prefactors $\mathbf{W}\mathbf{T}^{-1}$ and $\mathbf{W}\mathbf{W}_0^{-1}$ converge to a unit matrix or vanish. Thus, the terms in the square brackets either compensate one another or vanish due to the vanishing prefactors. The last two terms will vanish because one of the prefactors, $\mathbf{W}\mathbf{T}^{-1}$ or $\mathbf{W}\mathbf{W}_0^{-1}$, vanishes for tight or diffuse basis functions. As is known,¹⁰ the major contribution to the DSO term results from the core densities at the coupling nuclei. The third term in Eq. (28) is large only when $\mathbf{W}\mathbf{W}_0^{-1} \rightarrow \mathbf{I}$, i.e., for the diffuse basis set functions. Consequently, the third term can also be neglected and only the first two terms survive in the final formula,

$$\frac{\partial^2 \mathbf{H}}{\partial (\mu_A)_\beta \partial (\mu_B)_\alpha} = \mathbf{H}_{AB,\beta\alpha}^{\text{DSO}} - \mathbf{W}\mathbf{T}^{-1} \mathbf{H}_{AB,\beta\alpha}^{\text{DSO}} \mathbf{T}^{-1} \mathbf{W}. \quad (35)$$

In this connection it has to be stressed that the DSO term is more important for the anisotropic rather than isotropic SSCC and rarely contributes more than 1 SI unit ($10^{19} \text{ T}^2 \text{ J}^{-1}$) to the latter.¹⁰

Equations (34) and (35) can be combined to yield Eq. (36), which represents our final working equation for the calculation of relativistically corrected indirect nuclear SSCC,

$$\begin{aligned}
(K_{AB})_{\beta\alpha} &= \text{tr} \left(\left(\frac{\partial \mathbf{P}}{\partial (\mu_A)_\beta} \right) \left(\mathbf{G}^\dagger \left(\frac{\partial \mathbf{H}}{\partial (\mu_B)_\alpha} \right) \mathbf{G} \right) \right) + \text{tr} \left(\mathbf{P} \left(\mathbf{G}^\dagger \left(\frac{\partial^2 \mathbf{H}}{\partial (\mu_A)_\beta \partial (\mu_B)_\alpha} \right) \mathbf{G} \right) \right) \\
&= \text{tr} \left(\left(\frac{\partial \mathbf{P}}{\partial (\mu_A)_\beta} \right) \mathbf{G}^\dagger \left(\mathbf{H}_{A,\beta}^{\text{FC}} - \mathbf{W} \mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{FC}} \mathbf{T}^{-1} \mathbf{W} + \frac{3}{4m} (\mathbf{W} \mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{FC}} \mathbf{W}_0^{-1} \mathbf{W} + \mathbf{W} \mathbf{W}_0^{-1} \mathbf{H}_{A,\beta}^{\text{FC}} \mathbf{T}^{-1} \mathbf{W}) \right. \right. \\
&\quad \left. \left. + i(\mathbf{H}_{A,\beta}^{\text{PSO}} - \mathbf{W} \mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{PSO}} \mathbf{T}^{-1} \mathbf{W}) + \mathbf{H}_{A,\beta}^{\text{SD}} - \mathbf{W} \mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{SD}} \mathbf{T}^{-1} \mathbf{W} \right) \mathbf{G} \right) + \text{tr} (\mathbf{P} \mathbf{G}^\dagger (\mathbf{H}_{AB,\beta\alpha}^{\text{DSO}} - \mathbf{W} \mathbf{T}^{-1} \mathbf{H}_{AB,\beta\alpha}^{\text{DSO}} \mathbf{T}^{-1} \mathbf{W}) \mathbf{G}).
\end{aligned}
\tag{36}$$

The final equation (36) takes into account the effect of relativity on the corresponding nonrelativistic operators, but neglects changes of the quasirelativistic wave function metric under the influence of the external field (magnetic field due to the nuclear magnetic moment). In the nonrelativistic limit, that is in the limit of $c \rightarrow \infty$, the factor $\mathbf{W} \mathbf{T}^{-1}$ in Eq. (36) vanishes and the standard non-relativistic formalism is recovered in Eq. (36).

The formulas derived for the SSCC tensor are applicable to both WFT and DFT. Indeed, the effect of relativity (i.e., finite velocity of light) is incorporated into the one-electron part of the Hamiltonian only. Thus, Eq. (36) as well as its complete version Eq. (23) can be used in the standard WFT calculations provided that the derivative of the density matrix $\partial \mathbf{P} / \partial (\mu_A)_\beta$ is available.

III. IMPLEMENTATION AND DETAILS OF CALCULATIONS

The computational scheme described in the preceding section was programmed and implemented into the COLOGNE 2004 suite of quantum-chemical programs.³⁹ The implementation is straightforward because all molecular integrals needed for the quasirelativistic calculation of SSCCs are already available from the nonrelativistic formalism implemented earlier.¹⁰ Since only the one-electron part of the molecular Hamiltonian is modified in the IORamm calculations, the cost of these calculations is essentially the same as the cost of the corresponding nonrelativistic calculations. The quasirelativistic formalism implemented can be employed at the HF and DFT level of theory using in the latter case pure or hybrid exchange–correlation functionals.

To the best of our knowledge this is the first implementation of a quasirelativistic computational scheme for the calculation of indirect nuclear SSCCs, which can apply hybrid functionals within the framework of DFT. Because of this, the role of the exchange functional and its influence on the quasirelativistic value of the SSCC in dependence of the mixing of DFT and exact exchange can be studied in this work for the first time. We coin the new methods IORamm/CP–HF/SSCC and IORamm/CP–DFT/SSCC (IORamm with coupled perturbed HF or coupled perturbed DFT for SSCC calculations) to simplify the notation.

In the present work, we report the results of pilot IORamm/CP–HF/SSCC and IORamm/CP–DFT/SSCC calculations. The quasirelativistic wave function was optimized at the scalar-relativistic IORamm level, i.e., excluding the

effect of spin–orbit interactions. Pointlike nuclei were used in the calculation of the electron–nuclear attraction potential during the wave function optimization. As was pointed out by Autschbach and Ziegler,²³ this leads to an artificial increase of the electron density at the nuclear position and, therefore, more realistic models of a finite-size nucleus should be employed. Note, that all relativistic four-component calculations cited here²² employ extended nuclear models, simulated, e.g., by a Gaussian-type distribution of nuclear charge. However, the calculation of the electron–nuclear attraction based on the potential of extended nuclei is currently not implemented in our program.

The benchmark calculations with the IORamm/CP–HF/SSCC and IORamm/CP–DFT/SSCC methods summarized in Sec. IV are organized as follows. First, the results of quasirelativistic IORamm and nonrelativistic calculations of ${}^1K_{M-H}$ carried out at the HF level for tetrahydrides MH_4 of the group IV elements $M = \text{C}, \text{Si}, \text{Ge}, \text{Sn},$ and Pb are presented and compared with the available results of the full four-component DHF and nonrelativistic HF calculations.²²

Next, one-bond SSCCs are calculated for the following set of molecules: $\text{CH}_4, \text{SiH}_4, \text{GeH}_4, \text{SnH}_4, \text{PbH}_4, \text{PbH}(\text{CH}_3)_3, \text{Pb}(\text{CH}_3)_4, \text{Cd}(\text{CH}_3)_2, \text{Hg}(\text{CH}_3)_2, \text{Hg}(\text{CH}_3)\text{Cl}, \text{Hg}(\text{CH}_3)\text{Br}, \text{Hg}(\text{CH}_3)\text{I},$ and $\text{Hg}(\text{CN})_2$. For these molecules measured values of SSCCs are available.^{40–48} The calculations are carried out within the framework of DFT with different density functionals employed. The density functionals vary from pure functionals such as BLYP⁴⁹ to hybrid functionals with increasing fractions of the HF exchange such as B3LYP (20% of HF exchange)⁵⁰ and BHLYP (50% of HF exchange).³⁷

For light elements, the following Huzinaga basis sets were used: Hydrogen ($5s1p$)/[$3s1p$], carbon and nitrogen ($9s5p1d$)/[$5s4p1d$], silicon and chlorine ($11s6p2d$)/[$7s6p2d$].⁵¹ For bromine and iodine atoms, the cc-pVDZ basis set of Dunning⁵² and the TZVpp basis set of Ahlrichs and May⁵³ were employed. These basis sets were reconstructed (see below) similar to the Huzinaga basis sets into [$9s8p4d$] and [$10s10p7d1f$] basis sets. Since we do not calculate the SSCCs between bromine/iodine and other elements, the use of these basis sets is acceptable.

Since the Huzinaga basis sets are not specifically designed for the calculation of SSCCs, they were adjusted for this purpose in the following way: For hydrogen, two steep s -type primitive GTFs were added in geometric progression using the ratio of the two steepest s -type GTFs from the original basis set. For carbon and silicon, one tight s -type

TABLE I. Spin–spin coupling constants ${}^1K(\text{M,H})$ calculated for a series of MH_4 molecules at the nonrelativistic CP–HF/SSCC and IORAm/CP–HF/SSCC levels of theory.^a

Molecule	Contribution	IORAm	4-RPA ^b	Nonrel.	RPA ^c
CH_4	DSO	0.05		0.05	
	PSO	0.40		0.40	
	FC	52.54		52.34	
	SD	−0.04		−0.04	
	Total	52.95	52.6	52.74	52.4
SiH_4	DSO	0.02		0.02	
	PSO	−0.21		−0.21	
	FC	104.05		101.90	
	SD	−0.06		−0.06	
	Total	103.80	104.4	101.65	102.4
GeH_4	DSO	0.02		0.02	
	PSO	−0.70		−0.70	
	FC	300.07		264.44	
	SD	−0.15		−0.12	
	Total	299.24	294.8	263.63	262.7
SnH_4	DSO	−0.01		−0.01	
	PSO	−1.28		−1.30	
	FC	601.89		431.75	
	SD	−0.23		−0.12	
	Total	600.37	588.3	430.33	430.5
PbH_4	DSO	0.03		0.02	
	PSO	−2.17		−2.38	
	FC	2083.17		719.54	
	SD	−1.27		−0.40	
	Total	2079.76	1819.0	716.78	711.4

^aAll values in SI units ($10^{19} \text{T}^2 \text{J}^{-1}$). See text for details on basis sets and geometries used in the calculations.

^bFour-component RPA results from Ref. 22.

^cNonrelativistic RPA results from Ref. 22.

primitive GTF was added and the two steepest s -type primitive GTFs were split off from the most tight s -type contracted GTF of the original set. This amended Huzinaga basis set enables one to reproduce the results of the large basis nonrelativistic HF calculations of SSCCs in tetrahydrides CH_4 and SiH_4 with reasonable accuracy (see Table I).

For germanium, the cc-pVDZ basis set of Dunning⁵² was recontracted and amended as follows: The original basis set was decontracted completely. The most tight primitive s -type GTF was left uncontracted. The s -type primitive GTFs #2 to #5 were contracted to one GTF and the same was done for the primitive GTFs #6 and #7. The remaining s -type primitive GTFs were left uncontracted. The p -type primitive GTFs #1 to #3 and #4 and #5 were contracted to two GTFs. The remaining p -type primitive functions remained uncontracted. The three first d -type primitive functions were contracted into one GTF and the remaining three were left uncontracted. This contraction scheme is similar to that of the Huzinaga basis and was also used for the bromine basis set (with the only difference that the most tight s -type primitive function was not split off for the latter). Finally, one tight s -type primitive function with the exponential parameter obtained in a geometric progression was added. The resulting [11s8p4d] Ge basis set reproduces the nonrelativistic HF values for the SSCCs of GeH_4 (Ref. 22) in a reasonable way.

For tin, the TZVpp basis set of Ahlrichs and May⁵³ was employed. The original basis set was completely recontracted and amended to become a [13s10p6d1f] basis set: The s -type primitive functions #2 to #5, #6 to #8, #9 and #10, and #11 and #12 were contracted into four GTFs. The

rest of s -type primitive GTFs, including the most tight s -function, remained uncontracted. The p -type primitive GTFs #1 to #4, #5 and #6, and #7 and #8 were contracted into three GTFs, with the rest of the functions remaining uncontracted. The first five d -type primitives were contracted to one GTF. The most diffuse polarizing d -type primitive function was dropped from the tin basis set due to the linear dependence problem. A similar contraction pattern was used for iodine with the difference that the most tight s -type primitive function was contracted with the first GTF. Finally, one steep s -type primitive function was added to the tin basis set. The described basis set enables one to reproduce the SSCC between Sn and H in SnH_4 obtained by a large basis set nonrelativistic HF calculation²² with reasonable accuracy (see Table I).

For cadmium, a [15s10p6d1f] basis set was derived from the Cd basis set of Gropen⁵⁴ by again first decontracting the original basis set. The s -type primitive functions #4 and #5, and #6 to #8 were contracted to two GTFs. The rest of the s -type primitive GTFs remained uncontracted including the three most tight s -functions. The p -type primitive functions #1 to #4, #5 and #6, and #7 and #8 were contracted to three GTFs. The d -type primitive functions #1 to #3 and #4 and #5 were contracted to two GTFs. The basis set obtained was augmented with one diffuse s -type function, three diffuse p -type functions and one diffuse d -type function, where the exponential factors follow an even-tempered sequence with the ratio 2.5. Finally, one f -type primitive GTF was added and its exponential factor set equal to 7/5 of the exponential factor of the most diffuse d -GTF.

For mercury and lead, $[17s11p7d3f]$ basis sets were constructed again using the basis sets of Gropen as starting points.⁵⁴ The original basis sets were decontracted to $(19s14p10d5f)$ and $(19s16p10d5f)$ sets, respectively. For both elements, the s -type primitives #4 and #5, and #6 to #8 were contracted to two GTFs. The remaining s -type primitive GTFs remained uncontracted. The p -type primitive GTFs #1 to #4, #5 to #7, and #8 and #9 were contracted to three p -GTFs. The d -type primitives #1 to #3, #4 and #5, and #7 and #8 were contracted to three d -GTFs. The first four f -type primitives were contracted into one f -function. For both atoms, the most diffuse d -type primitive function was removed due to orthogonality problems. The basis sets obtained were augmented with one diffuse s - and f -type function, two diffuse d -type functions, and for lead (mercury) one (three) diffuse p -type function(s), thus yielding a $[17s11p7d3f]$ basis set for both elements. When combined with the $[5s1p]$ basis set for hydrogen (see above), the $[17s11p7d3f]$ basis set reproduced the nonrelativistic HF value²² of the Pb-H SSCC in PbH_4 with reasonable accuracy (see Table I).

The molecular geometries were taken for MH_4 and trimethyl plumbane from Ref. 22, for dimethylmercury from Ref. 55, for methylmercury(II) halides from Ref. 56, and for mercury(II) dicyanide from Ref. 57. The molecular geometries of dimethylcadmium and tetramethyllead were optimized using the IORAm/B3LYP method. In these optimizations, the aug-cc-pVDZ basis sets⁵² were used for the light atoms and the basis sets described above were used for the heavy atoms. All calculations employed basis set with Cartesian rather than spherical functions.

IV. RESULTS AND DISCUSSION

In this section, the results of IORAm/CP-HF/SSCC and IORAm/CP-DFT/SSCC calculations of the indirect nuclear SSCCs for a set of molecules containing heavy atoms are presented and discussed. First, the ${}^1K_{\text{M-H}}$ constants in tetrahydrides MH_4 of group IV elements $\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn},$ and Pb are calculated with the nonrelativistic HF and quasirelativistic IORAm/HF methods. The results are compared in Table I with the corresponding values of nonrelativistic and full four-component relativistic DHF calculations carried out by Enevoldsen *et al.*²² using large basis sets.

The nonrelativistic CP-HF SSCCs ${}^1K_{\text{M-H}}$ are in good agreement with the nonrelativistic RPA (random phase approximation: synonym for CP-HF) results confirming that the basis set decontraction/contraction pattern used in this work is both economic and effective. The FC contribution completely dominates the SSCC in all cases so that the discussion can focus on this Ramsey term.

The FC contribution experiences the largest influence of relativity. Because our quasirelativistic calculations are carried out at the scalar-relativistic level of approximation (i.e., all spin-dependent relativistic effects such as spin-orbit interactions are neglected), the contraction of the atomic s -shells is the main reason for the enhanced FC coupling term in the total SSCC. The same conclusion was drawn by Enevoldsen *et al.*²² on the basis of the four-component RPA (4-RPA, i.e., coupled-perturbed DHF) calculations.

The quasirelativistic IORAm/CP-HF/SSCC results also agree reasonably with the 4-RPA SSCC values of Enevoldsen *et al.*²² for the light elements C, Si, and Ge. The deviation from the 4-RPA values is larger for the heavier atoms Sn and Pb (12 and 261 SI units, Table I) because of the following reasons: First, the effect of spin-orbit coupling, which leads to a FC-PSO correction, is not included in the IORAm values. Although for SnH_4 , this correction is small,⁵⁸ ca. 1% (4.7 SI units) of the total nonrelativistic SSCC, for lead tetrahydride the FC-PSO correction constitutes ca. 10% (79.3 SI units) of the total nonrelativistic SSCC⁵⁹ making the total SSCC substantially smaller. Second, in the relativistic four-component calculations,²² the wave function was optimized using nuclei of finite size whereas in the IORAm/CP-HF/SSCC calculations point nuclei are employed. The use of the pointlike nucleus artificially increases the electron density at the nucleus thus leading to larger values of the SSCCs.²³ Given these factors, the agreement of the IORAm/CP-HF/SSCC one-bond values with the reference values is satisfactory even for the heaviest element in Table I.

Table II summarizes the results of DFT calculations carried out with the use of pure (BLYP) and hybrid (B3LYP and BHHLYP) density functionals. In all molecules presented in Table II, the FC contribution dominates the SSCC. The DSO term is extremely small and never exceeds 0.2 SI unit. The PSO and SD terms are also small. For the molecules in Table II, the PSO and SD term do not contribute more than 10% to the total SSCC.

Similar to the molecules of Table I, relativity has the largest impact on the FC coupling term. The FC coupling is mediated by spin polarization of s -type electrons. These are the electrons that experience the largest relativistic effect. Relativity results in the contraction of the atomic s -shells and a subsequent stabilization of the energies of the atomic s -orbitals. This leads to an enhancement of the weight of the valence s -type orbitals in the molecular orbitals and consequently to an increase in the FC coupling term. The atomic orbitals with nonzero orbital angular momentum l experience a much weaker relativistic influence. Accordingly, the PSO and SD coupling terms, which both depend on the orbitals with nonzero l , vary only slightly as a result of relativity where one has to consider that the SSCCs of saturated molecules have anyway rather small noncontact terms.

Apart from relativity, electron correlation plays an important role for the accurate calculation of NMR SSCCs. For instance, at the nonrelativistic level, the inclusion of correlation leads to a 16% to 24% reduction (as compared to the HF calculation) of the absolute value of the SSCC.⁵⁹ To the best of our knowledge, relativistic four-component correlated calculations of nuclear SSCCs were not carried out so far. The only attempt to incorporate the effect of electron correlation into four-component relativistic calculations of SSCCs was the scaling of the 4-RPA values²² with the ratio of the SSCCs calculated at the nonrelativistic RPA level and at the level of the correlated method SOPPA (second order polarization propagator approach). The SSCCs obtained in this way by Enevoldsen *et al.*²² for tetrahydrides of the group IV elements are reported in the last column of Table II. Compari-

TABLE II. One-bond indirect nuclear spin–spin coupling constants K for molecules with and without heavy atoms calculated at the CP–DFT/SSCC and IORamm/CP–DFT/SSCC levels of theory.^a

Molecule	Coupling	Expt.	IORamm/CP–DFT/SSCC			CP–DFT/SSCC			Ref. value
			BHLYP	B3LYP	BLYP	BHLYP	B3LYP	BLYP	
CH ₄	C–H	41.5 ^b	47.4	44.2	44.5	47.3	44.1	44.4	43.5 ^c
SiH ₄	Si–H	84.3 ^d	93.2	87.9	87.5	91.4	86.2	85.9	88.2 ^c
GeH ₄	Ge–H	232 ^e	261	240	235	232	215	211	237 ^c
SnH ₄	Sn–H	429 ^f	499	448	430	367	335	325	459 ^c
PbH ₄	Pb–H	(1035;1115) ^g	1601	1370	1272	603	546	519	1383 ^c ; 1318 ^h
Pb(CH ₃) ₃ H	Pb–H	949 ^f	1469	1210	1089	614	543	521	1668 ⁱ ; 978 ^h
Pb(CH ₃) ₄	Pb–C	39 ^j	863	357	78	560	363	268	–198 ^c
Cd(CH ₃) ₂	Cd–C	798 ^k	909	701	581	736	584	494	
Hg(CH ₃) ₂	Hg–C	1287 ^l	1690	1176	935	1038	802	683	827 ^h
Hg(CH ₃)Cl	Hg–C	2631 ^m	3269	2307	1899	1755	1382	1224	1955 ^h
Hg(CH ₃)Br	Hg–C	2563 ^m	3324	2301	1876	1775	1388	1226	1978 ^h
Hg(CH ₃)I	Hg–C	2393 ^m	3195	2179	1759	1714	1338	1180	1827 ^h
Hg(CN) ₂	Hg–C	5778 ⁿ	6074	4886	4149	2773	2439	2233	4408 ^h

^aAll values in SI units ($10^{19} \text{ T}^2 \text{ J}^{-1}$). See text for details on basis sets and geometries used in the calculations.

^bTaken from Ref. 40.

^cScaled relativistic four-component RPA results from Ref. 22.

^dTaken from Ref. 41.

^eTaken from Ref. 42.

^fTaken from Ref. 43.

^gThe values estimated in Refs. 22 and 23 on the basis of the experimental SSCCs for methyl-substituted plumbanes.

^hZORA/GGA results from Ref. 23.

ⁱUnscaled relativistic four-component RPA results from Ref. 22.

^jTaken from Ref. 44.

^kTaken from Ref. 45.

^lTaken from Ref. 46.

^mTaken from Ref. 47.

ⁿTaken from Refs. 46 and 48.

son of these scaled 4-RPA values with the 4-RPA values²² cited in Table I suggests increased importance of electron correlation for the relativistic SSCCs.

DFT takes electron correlation into account via the density functionals. It has been demonstrated that electron correlation enters the DFT calculation not only via the correlation functional, but also (and probably more effectively) via the exchange functional. In the latter, the self-interaction error (SIE; incomplete cancellation of the electron self-interaction energy as contained in the Coulomb term by the self-exchange energy provided by the exchange functional) mimics long-range correlation.^{60–62} Because the HF exchange energy is perfectly self-interaction-free, mixing in some HF exchange as in hybrid functionals, reduces the SIE in the KS calculation and enables one to tune (albeit in a nonspecific way) the amount of long-range electron correlation covered by the KS calculation.

The calculations reported in Table II were carried out with the BLYP, B3LYP, and BHLYP functional thus increasing exact exchange from 0 to 20 and 50%. The results of the DFT calculations carried out with these functionals at the IORamm/CP–DFT/SSCC and at the nonrelativistic CP–DFT/SSCC level of theory are reported in columns four through nine of Table II. Figure 1 shows these results in graphic form giving calculated SSCCs as a function of measured ones for each of the methods employed.

As becomes obvious from Table II and Fig. 1, the nonrelativistic calculations are not able to reproduce correct nu-

meric values of the SSCCs. Although an increase of the fraction of exact exchange improves the agreement of the nonrelativistic SSCCs with measured ones, the match between the BHLYP results and the experimental SSCCs is far from being satisfactory. At the quasirelativistic IORamm/CP–DFT/SSCC level, the match between the calculated and the experimental SSCCs is considerably improved. On average, BLYP underestimates the experimental SSCCs (the slope of the BLYP linear regression line is 0.712), B3LYP approaches the ideal (statistical) correlation with the experimental SSCCs better (slope 0.844), and BHLYP overestimates the measured SSCCs (slope 1.084). Obviously, there exists an optimal HF/DFT mixing parameter, slightly larger than that in B3LYP as can be inferred from Fig. 1 and Table II. However, since the data base of the SSCCs compared in the present work is too small and, more importantly, because the experimental SSCCs are not corrected for rovibrational and environmental effects, we did not take any attempt to determine such an optimal mixing parameter for hybrid density functionals. Nevertheless, the possibility of defining such a parameter does exist as is evidenced by the analysis presented in Fig. 1.

V. CONCLUSIONS

A simple and computationally inexpensive quasirelativistic method for calculating nuclear SSCCs in mol-

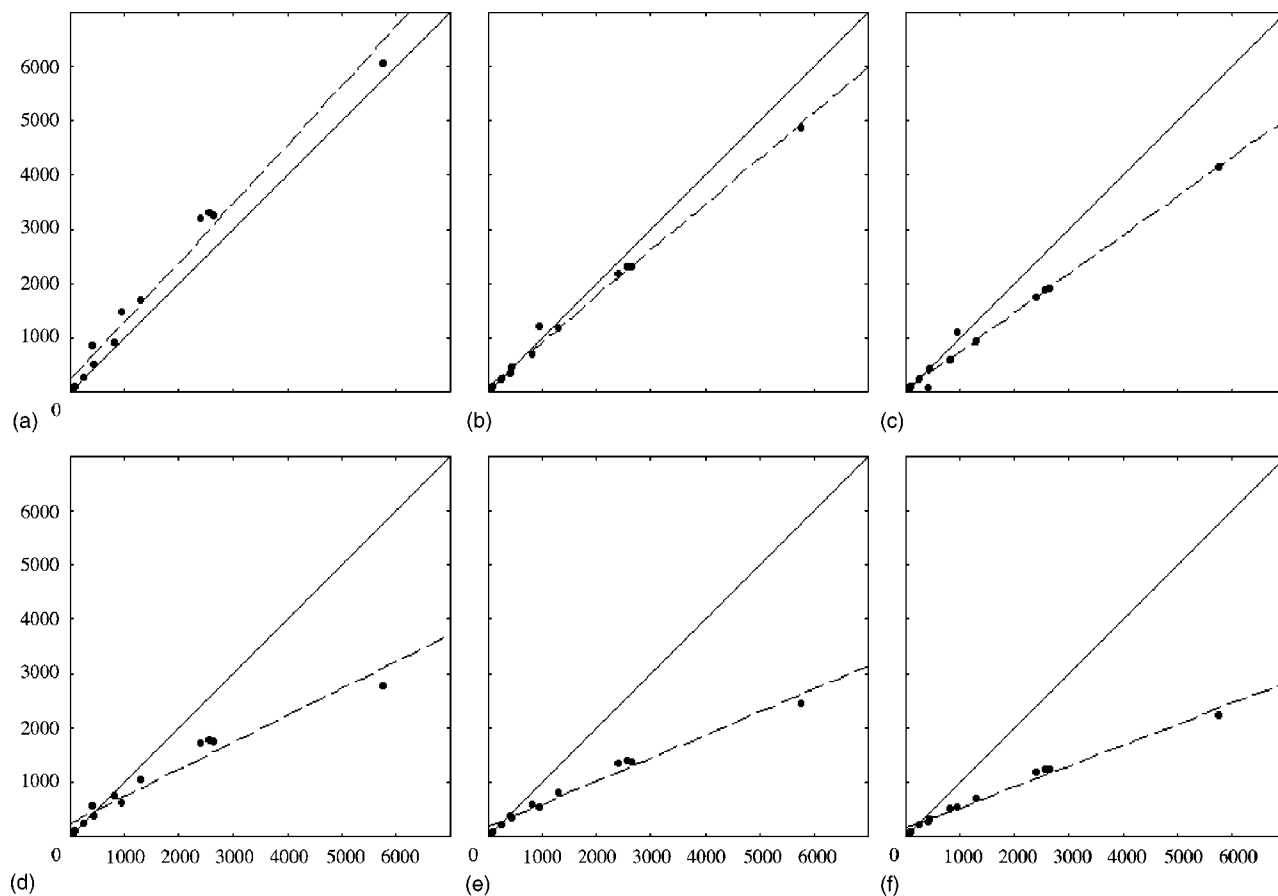


FIG. 1. Linear regression analysis (dashed lines) between calculated and measured SSCCs: (a) IORAm/BHHLYP, (b) IORAm/B3LYP, (c) IORAm/BLYP, (d) nonrelativistic BHHLYP, (e) nonrelativistic B3LYP, and (f) nonrelativistic BLYP results. The solid line bisecting the angle between the axes denotes the ideal correlation between calculated and measured SSCC values. Calculated SSCCs from Table II are indicated by filled circles.

olecules containing heavy elements is presented. The method is based on the IORAm approximation, which enables one to carry out either conventional WFT or DFT calculations to determine molecular equilibrium geometries and electric response properties of heavy atom molecules. The present work extends the IORAm formalism to the SSCC as new second-order response property thus extending the applicability of the method. This extension of IORAm comprises the IORAm/CP-HF/SSCC and IORAm/CP-DFT/SSCC methods. The formalism presented can also be applied to ZORA and IORA, which however suffer from an erroneous gauge dependence much more than IORAm does.

An important feature of the IORAm method, in general, and the IORAm/CP-HF/SSCC and IORAm/CP-DFT/SSCC methods presented in this paper especially is that they all can be easily implemented into existing nonrelativistic quantum-chemical codes. Indeed, there are no new molecular integrals that must be calculated in the IORAm calculation. The method employs only those integrals already available from the nonrelativistic calculation. Furthermore, the IORAm calculation is as fast as the corresponding nonrelativistic one. This opens up a possibility of investigating relatively large molecular systems with the help of the IORAm methods.

The investigation of the one-bond nuclear SSCCs carried

out in this paper reveals that the IORAm/CP-HF/SSCC formalism is suitable for the calculation of SSCCs. Although the present implementation employs the scalar-relativistic approximation (i.e., spin-orbit interaction is neglected) thus missing certain terms such as FC-PSO coupling term in the expression for the SSCC, the overall agreement with the results of the four-component relativistic calculations is good. The inclusion of relativistic effects via the IORAm Hamiltonian leads to a substantial increase (up to 100%) in FC coupling. The other contributions (DSO, PSO, and SD) to the total SSCC undergo only minor variations due to relativity.

At the IORAm/CP-DFT/SSCC level, the agreement between calculated and measured SSCCs depends on the density functional used. On average, BLYP tends to underestimate the calculated SSCCs, BHHLYP overestimates them, and B3LYP leads to an improved (albeit nonperfect) performance. The agreement with the experiment can be improved further by a slight increase in the HF/DFT exchange mixing parameter that is used in the B3LYP functional (probably from 20% to 30%). However, making any reparametrization of the existing density functionals on these grounds would require the knowledge of the rovibrational and environmental corrections to the measured SSCCs. Therefore, such a reparametrization was not attempted in the present work, however is subject of work in progress.

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APPENDIX A: DERIVATIVES OF THE \mathbf{W}_0 MATRIX

In the presence of a magnetic field caused by the nuclear magnetic moments, the elements of the \mathbf{W}_0 matrix (20) change as in Eq. (A1),

$$\begin{aligned}
 (\mathbf{W}_0^{(\mu)})_{\mu\nu} &= \langle \chi_\mu | \frac{1}{4m^2c^2} (\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) V_n (\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) | \chi_\nu \rangle \\
 &= (\hat{W}_0^{(0)})_{\mu\nu} + \langle \chi_\mu | \mathbf{p} \cdot \frac{V_n}{4m^2c^4} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} | \chi_\nu \rangle + \langle \chi_\mu | \frac{V_n}{4m^2c^4} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} \cdot \mathbf{p} | \chi_\nu \rangle \\
 &\quad + \langle \chi_\mu | \frac{V_n}{4m^2c^6} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} \cdot \sum_M \frac{\boldsymbol{\mu}_M \times \mathbf{r}_M}{r_M^3} | \chi_\nu \rangle + \langle \chi_\mu | \boldsymbol{\sigma} \cdot \mathbf{p} \times \frac{iV_n}{4m^2c^4} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} | \chi_\nu \rangle \\
 &\quad + \langle \chi_\mu | \frac{iV_n}{4m^2c^4} \boldsymbol{\sigma} \cdot \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} \times \mathbf{p} | \chi_\nu \rangle + \langle \chi_\mu | \frac{iV_n}{4m^2c^6} \boldsymbol{\sigma} \cdot \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} \times \sum_M \frac{\boldsymbol{\mu}_M \times \mathbf{r}_M}{r_M^3} | \chi_\nu \rangle, \tag{A1}
 \end{aligned}$$

where Eqs. (6) and (7) and the Dirac relationship (A2) were used,

$$(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\boldsymbol{\sigma} \cdot \mathbf{A} \times \mathbf{B}. \tag{A2}$$

The first term on the right-hand side of Eq. (A1) is the field-free matrix (20). The next two terms make contributions to PSO coupling as is obvious from Eq. (A3),

$$\begin{aligned}
 &\langle \chi_\mu | \mathbf{p} \cdot \frac{V_n}{4m^2c^4} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} | \chi_\nu \rangle + \langle \chi_\mu | \frac{V_n}{4m^2c^4} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} \cdot \mathbf{p} | \chi_\nu \rangle \\
 &= \langle \chi_\mu | \mathbf{p} \cdot \frac{V_n}{4m^2c^4} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} | \chi_\nu \rangle + \langle \chi_\nu | \mathbf{p} \cdot \frac{V_n}{4m^2c^4} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} | \chi_\mu \rangle \\
 &= \frac{1}{2m} \sum_{\rho,\tau} \langle \chi_\mu | \mathbf{p} \cdot \frac{V_n}{4m^2c^2} \cdot \mathbf{p} | \chi_\rho \rangle (\mathbf{T}^{-1})_{\rho\tau} \langle (\mathbf{p} \chi_\tau) | \cdot \frac{1}{c^2} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} | \chi_\nu \rangle \\
 &\quad + \frac{1}{2m} \sum_{\rho,\tau} \langle \chi_\nu | \mathbf{p} \cdot \frac{V_n}{4m^2c^2} \cdot \mathbf{p} | \chi_\tau \rangle (\mathbf{T}^{-1})_{\tau\rho} \langle (\mathbf{p} \chi_\rho) | \cdot \frac{1}{c^2} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} | \chi_\mu \rangle \\
 &= \frac{1}{2m} \sum_{\rho,\tau} (\mathbf{W}_0)_{\mu\rho} (\mathbf{T}^{-1})_{\rho\tau} \langle \chi_\tau | \frac{1}{c^2} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} \cdot \mathbf{p} | \chi_\nu \rangle + \frac{1}{2m} \sum_{\rho,\tau} (\mathbf{W}_0)_{\nu\tau} (\mathbf{T}^{-1})_{\tau\rho} \langle \chi_\rho | \frac{1}{c^2} \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_N}{r_N^3} \cdot \mathbf{p} | \chi_\mu \rangle \\
 &= \frac{1}{2m} \sum_{\rho,\tau} (\mathbf{W}_0)_{\mu\rho} (\mathbf{T}^{-1})_{\rho\tau} \langle \chi_\tau | \frac{1}{c^2} \sum_N \boldsymbol{\mu}_N \cdot \frac{\mathbf{r}_N \times \mathbf{p}}{r_N^3} | \chi_\nu \rangle + \frac{1}{2m} \sum_{\rho,\tau} (\mathbf{W}_0)_{\nu\tau} (\mathbf{T}^{-1})_{\tau\rho} \langle \chi_\rho | \frac{1}{c^2} \sum_N \boldsymbol{\mu}_N \cdot \frac{\mathbf{r}_N \times \mathbf{p}}{r_N^3} | \chi_\mu \rangle, \tag{A3}
 \end{aligned}$$

where the hermiticity property of the linear momentum operator, resolution of the identity $\hat{I} = (2m)^{-1} \sum_{\rho,\tau} |\nabla \chi_\rho\rangle (\mathbf{T}^{-1})_{\rho\tau} \langle \nabla \chi_\tau|$, and vector algebra relationship $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$ were used. Substituting $-i\nabla$ for the linear momentum operator and differentiating with respect to a component of the nuclear magnetic moment $(\boldsymbol{\mu}_A)_\beta$ yields Eq. (A4),

$$(\mathbf{W}_0^{\text{PSO}})_{A,\beta} = \frac{i}{2m} (\mathbf{W}_0 \mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{PSO}} + \mathbf{H}_{A,\beta}^{\text{PSO}} \mathbf{T}^{-1} \mathbf{W}_0), \tag{A4}$$

where $\mathbf{H}_{A,\beta}^{\text{PSO}}$ is the matrix of the operator (9b).

The next term in Eq. (A1) vanishes in the first derivative (note, that the magnetic moments are set to zero upon differentiation) and contributes only to DSO coupling. Using the relationship $(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d}) = (\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d}) - (\mathbf{a} \cdot \mathbf{d})(\mathbf{b} \cdot \mathbf{c})$ this term can be transformed as in Eq. (A5),

$$\langle \chi_\mu | \frac{V_n}{4m^2c^6} \sum_N \frac{\mu_N \times \mathbf{r}_N}{r_N^3} \cdot \sum_M \frac{\mu_M \times \mathbf{r}_M}{r_M^3} | \chi_\nu \rangle = \langle \chi_\mu | \frac{V_n}{4m^2c^6} \sum_N \sum_M \left(\frac{(\mu_N \cdot \mu_M)(\mathbf{r}_N \cdot \mathbf{r}_M)}{r_N^3 r_M^3} - \frac{(\mu_N \cdot \mathbf{r}_M)(\mathbf{r}_N \cdot \mu_M)}{r_N^3 r_M^3} \right) | \chi_\nu \rangle \quad (\text{A5})$$

which, upon differentiation with respect to $(\mu_A)_\beta$ and $(\mu_B)_\alpha$ and use of the resolution of the identity $\hat{1} = \sum_{\rho\tau} |\chi_\rho\rangle \langle \mathbf{S}^{-1} |_{\rho\tau} \langle \chi_\tau|$, leads to Eq. (A6) for the contribution into the second derivative of the IORamm/IORA Hamiltonian.

$$(\mathbf{W}_0^{\text{DSO}})_{AB,\beta\alpha} = -\frac{1}{8m^2c^2} (\mathbf{V}_n \mathbf{S}^{-1} \mathbf{H}_{AB,\beta\alpha}^{\text{DSO}} + \mathbf{H}_{AB,\beta\alpha}^{\text{DSO}} \mathbf{S}^{-1} \mathbf{V}_n). \quad (\text{A6})$$

In Eq. (A6), $\mathbf{H}_{AB,\beta\alpha}^{\text{DSO}}$ is the matrix of the DSO coupling operator (9a) and \mathbf{V}_n is the matrix of the electron–nuclear attraction integrals.

The next two terms can be transformed according to Eq. (A7) noting that the following relationship holds for the nabla operator $\nabla \times \mathbf{A} = (\nabla \times \mathbf{A}) - \mathbf{A} \times \nabla$ and using the standard vector algebra relationships,

$$\begin{aligned} \langle \chi_\mu | \sigma \cdot \mathbf{p} \times \frac{iV_n}{4m^2c^4} \sum_N \frac{\mu_N \times \mathbf{r}_N}{r_N^3} | \chi_\nu \rangle + \langle \chi_\mu | \frac{iV_n}{4m^2c^4} \sigma \cdot \sum_N \frac{\mu_N \times \mathbf{r}_N}{r_N^3} \times \mathbf{p} | \chi_\nu \rangle \\ = \langle \chi_\mu | \sigma \cdot \left(\mathbf{p} \times \frac{iV_n}{4m^2c^4} \sum_N \frac{\mu_N \times \mathbf{r}_N}{r_N^3} \right) | \chi_\nu \rangle - \langle \chi_\mu | \frac{iV_n}{4m^2c^4} \sigma \cdot \sum_N \frac{\mu_N \times \mathbf{r}_N}{r_N^3} \times \mathbf{p} | \chi_\nu \rangle + \langle \chi_\mu | \frac{iV_n}{4m^2c^4} \sigma \cdot \sum_N \frac{\mu_N \times \mathbf{r}_N}{r_N^3} \times \mathbf{p} | \chi_\nu \rangle \\ = \langle \chi_\mu | \frac{1}{4m^2c^4} \left((\sigma \times \nabla) \cdot \left(V_n \sum_N \frac{\mu_N \times \mathbf{r}_N}{r_N^3} \right) \right) | \chi_\nu \rangle \\ = \langle \chi_\mu | \frac{1}{4m^2c^4} \sum_N (\mu_N \cdot \sigma) \left(\nabla \cdot \left(V_n \frac{\mathbf{r}_N}{r_N^3} \right) \right) | \chi_\nu \rangle - \langle \chi_\mu | \frac{1}{4m^2c^4} \sum_N \left(\mu_N \cdot \nabla \left(V_n \frac{(\sigma \cdot \mathbf{r}_N)}{r_N^3} \right) \right) | \chi_\nu \rangle. \end{aligned} \quad (\text{A7})$$

Differentiation of (A7) with respect to $(\mu_A)_\beta$ yields Eq. (A8),

$$\begin{aligned} ((\mathbf{W}_0^{\text{FC}+\text{SD}})_{A,\beta})_{\mu\nu} = ((\mathbf{W}_0^{\text{FC}})_{A,\beta})_{\mu\nu} + ((\mathbf{W}_0^{\text{SD}})_{A,\beta})_{\mu\nu} = \frac{1}{4m^2c^4} \langle \chi_\mu | \sigma_\beta \left(\nabla \cdot \left(V_n \frac{\mathbf{r}_A}{r_A^3} \right) \right) | \chi_\nu \rangle \\ - \frac{1}{4m^2c^4} \langle \chi_\mu | \nabla_\beta \left(V_n \frac{(\sigma \cdot \mathbf{r}_A)}{r_A^3} \right) | \chi_\nu \rangle. \end{aligned} \quad (\text{A8})$$

The first term in Eq. (A8), which makes correction to the Fermi-contact interaction, $((\mathbf{W}_0^{\text{FC}})_{A,\beta})_{\mu\nu}$, can be transformed further as in Eq. (A9),

$$\begin{aligned}
((\mathbf{W}_0^{\text{FC}})_{A,\beta})_{\mu\nu} &= \frac{1}{4m^2c^4} \langle \chi_\mu | \sigma_\beta \left(\nabla \cdot \left(V_n \frac{\mathbf{r}_A}{r_A^3} \right) \right) | \chi_\nu \rangle \\
&= -\frac{1}{4m^2c^4} \langle (\nabla \chi_\mu) | \cdot \left(V_n \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} \right) | \chi_\nu \rangle - \frac{1}{4m^2c^4} \langle \chi_\mu | \left(V_n \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} \right) \cdot | (\nabla \chi_\nu) \rangle \\
&= -\frac{1}{2m} \sum_{\rho\tau} \langle (\nabla \chi_\mu) | \frac{V_n}{4m^2c^2} \cdot | (\nabla \chi_\rho) \rangle (\mathbf{T}^{-1})_{\rho\tau} \langle (\nabla \chi_\tau) | \cdot \frac{1}{c^2} \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} | \chi_\nu \rangle - \frac{1}{2m} \sum_{\rho\tau} \langle \chi_\mu | \frac{1}{c^2} \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} \\
&\quad \cdot | (\nabla \chi_\tau) \rangle (\mathbf{T}^{-1})_{\tau\rho} \langle (\nabla \chi_\rho) | \frac{V_n}{4m^2c^2} \cdot | (\nabla \chi_\nu) \rangle \\
&= \frac{1}{2m} \sum_{\rho\tau} (\mathbf{W}_0)_{\mu\rho} (\mathbf{T}^{-1})_{\rho\tau} \frac{1}{c^2} \left(\langle \chi_\tau | \left(\nabla \cdot \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} \right) | \chi_\nu \rangle + \langle \chi_\tau | \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} \cdot | (\nabla \chi_\nu) \rangle \right) - \frac{1}{2m} \sum_{\rho\tau} \frac{1}{c^2} \langle \chi_\mu | \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} \\
&\quad \cdot | (\nabla \chi_\tau) \rangle (\mathbf{T}^{-1})_{\tau\rho} (\mathbf{W}_0)_{\rho\nu} \\
&= \frac{3}{4m} (\mathbf{W}_0 \mathbf{T}^{-1} \mathbf{H}_{A,\beta}^{\text{FC}} + \mathbf{H}_{A,\beta}^{\text{FC}} \mathbf{T}^{-1} \mathbf{W}_0)_{\mu\nu} + \frac{1}{2m} (\mathbf{W}_0 \mathbf{T}^{-1} \mathbf{H}_{A,\beta}^X - \mathbf{H}_{A,\beta}^X \mathbf{T}^{-1} \mathbf{W}_0)_{\mu\nu}, \tag{A9}
\end{aligned}$$

where integration by parts, Gauss theorem and the resolution of the identity $\hat{I} = (2m)^{-1} \sum_{\rho\tau} |\nabla \chi_\rho\rangle (\mathbf{T}^{-1})_{\rho\tau} \langle \nabla \chi_\tau|$ were used. In Eq. (A9), $\mathbf{H}_{A,\beta}^{\text{FC}}$ is the matrix of the FC operator (9c) and the matrix $\mathbf{H}_{A,\beta}^X$ has the following elements:

$$(\mathbf{H}_{A,\beta}^X)_{\mu\nu} = \frac{1}{c^2} \langle \chi_\mu | \sigma_\beta \frac{\mathbf{r}_A}{r_A^3} \cdot | (\nabla \chi_\nu) \rangle. \tag{A10}$$

The last term in Eq. (A1) vanishes because $\mathbf{A} \times \mathbf{A} = 0$ for any constant vector \mathbf{A} .

APPENDIX B: SECOND DERIVATIVES OF THE SQUARE-ROOT MATRIX

Let us consider a real symmetric matrix \mathbf{A} with its elements depending on two parameters α and β . We assume that the elements of the matrix \mathbf{A} are differentiable with respect

to these parameters at least through second order. The problem is to obtain an algebraic expressions for the second derivative of the square-root matrix $\mathbf{A}^{1/2}$.

The first derivative of the elements of the square-root matrix with respect to a parameter α has been obtained in Ref. 29 and reads [cf. Eq. (43) there]

$$\left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \alpha} \mathbf{A}^{1/2} \right) \mathcal{C} \right)_{ij} = (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \alpha} \mathbf{A} \right) \mathcal{C} \right)_{ij}, \tag{B1}$$

where \mathbf{a}_{ii} are the eigenvalues of the matrix \mathbf{A} and \mathcal{C} are its eigenvectors, see Eq. (B2).

$$\mathbf{a} = \mathcal{C}^\dagger \mathbf{A} \mathcal{C}. \tag{B2}$$

Differentiating Eq. (B1) with respect to a parameter β one has Eq. (B3),

$$\begin{aligned}
&\left(\mathcal{C}^\dagger \left(\frac{\partial^2}{\partial \beta \partial \alpha} \mathbf{A}^{1/2} \right) \mathcal{C} \right)_{ij} + \left(\left(\frac{\partial}{\partial \beta} \mathcal{C}^\dagger \right) \left(\frac{\partial}{\partial \alpha} \mathbf{A}^{1/2} \right) \mathcal{C} \right)_{ij} + \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \alpha} \mathbf{A}^{1/2} \right) \left(\frac{\partial}{\partial \beta} \mathcal{C} \right) \right)_{ij} \\
&= (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} \left[\left(\mathcal{C}^\dagger \left(\frac{\partial^2}{\partial \beta \partial \alpha} \mathbf{A} \right) \mathcal{C} \right)_{ij} + \left(\left(\frac{\partial}{\partial \beta} \mathcal{C}^\dagger \right) \left(\frac{\partial}{\partial \alpha} \mathbf{A} \right) \mathcal{C} \right)_{ij} + \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \alpha} \mathbf{A} \right) \left(\frac{\partial}{\partial \beta} \mathcal{C} \right) \right)_{ij} \right] \\
&\quad - (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-2} \left[\frac{1}{2} \mathbf{a}_{ii}^{-1/2} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \beta} \mathbf{A} \right) \mathcal{C} \right)_{ii} + \frac{1}{2} \mathbf{a}_{jj}^{-1/2} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \beta} \mathbf{A} \right) \mathcal{C} \right)_{jj} \right] \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \alpha} \mathbf{A} \right) \mathcal{C} \right)_{ij}, \tag{B3}
\end{aligned}$$

where we used Eq. (42) from Ref. 29 for the derivative of the eigenvalue \mathbf{a}_{ii} . Introducing the following notations:

$$\tilde{\mathbf{A}}_{\beta\alpha} = \mathcal{C}^\dagger \left(\frac{\partial^2}{\partial \beta \partial \alpha} \mathbf{A} \right) \mathcal{C}, \tag{B4b}$$

$$\tilde{\mathbf{A}}_\alpha = \mathcal{C}^\dagger \left(\frac{\partial}{\partial \alpha} \mathbf{A} \right) \mathcal{C}, \tag{B4a}$$

$$\mathbf{R}_\alpha = \mathcal{C}^\dagger \left(\frac{\partial}{\partial \alpha} \mathcal{C} \right), \tag{B4c}$$

where \mathbf{R}_α is an antisymmetric matrix (i.e., $\mathbf{R}_\alpha = -\mathbf{R}_\alpha^\dagger$) and using the orthogonality of the eigenvectors \mathcal{C} (i.e., $\mathcal{C}\mathcal{C}^\dagger = \mathcal{C}^\dagger\mathcal{C} = \mathbf{I}$), Eq. (B3) can be transformed into Eq. (B5),

$$\begin{aligned} (\tilde{\mathbf{A}}_{\beta\alpha}^{1/2})_{ij} = & (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} (\tilde{\mathbf{A}}_{\beta\alpha})_{ij} - (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} [(\mathbf{R}_\beta \tilde{\mathbf{A}}_\alpha)_{ij} - (\tilde{\mathbf{A}}_\alpha \mathbf{R}_\beta)_{ij}] + [(\mathbf{R}_\beta \tilde{\mathbf{A}}_\alpha^{1/2})_{ij} - (\tilde{\mathbf{A}}_\alpha^{1/2} \mathbf{R}_\beta)_{ij}] \\ & - (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-2} \left[\frac{1}{2} \mathbf{a}_{jj}^{-1/2} (\tilde{\mathbf{A}}_\beta)_{jj} (\tilde{\mathbf{A}}_\alpha)_{ij} + \frac{1}{2} \mathbf{a}_{ii}^{-1/2} (\tilde{\mathbf{A}}_\beta)_{ii} (\tilde{\mathbf{A}}_\alpha)_{ij} \right]. \end{aligned} \quad (\text{B5})$$

Using Eq. (B1) and Eq. (B6) for the elements of the matrix \mathbf{R}_α [cf. Eq. (40) in Ref. 29],

$$(\mathbf{R}_\alpha)_{ij} = (1 - \delta_{ij})(\mathbf{a}_{jj} - \mathbf{a}_{ii})^{-1} (\tilde{\mathbf{A}}_\alpha)_{ij} \quad (\text{B6})$$

(δ_{ij} denotes the Kronecker delta), the following relationships can be obtained:

$$\begin{aligned} (\mathbf{R}_\beta \tilde{\mathbf{A}}_\alpha^{1/2})_{ij} - (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} (\mathbf{R}_\beta \tilde{\mathbf{A}}_\alpha)_{ij} &= \sum_k (1 - \delta_{ik})(\mathbf{a}_{kk} - \mathbf{a}_{ii})^{-1} (\tilde{\mathbf{A}}_\beta)_{ik} (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} (\tilde{\mathbf{A}}_\alpha)_{kj} \\ &= \sum_l (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} (1 - \delta_{il})(\mathbf{a}_{ll} - \mathbf{a}_{ii})^{-1} (\tilde{\mathbf{A}}_\beta)_{il} (\tilde{\mathbf{A}}_\alpha)_{lj} \\ &= \frac{1}{2} \mathbf{a}_{ii}^{-1/2} (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-2} (\tilde{\mathbf{A}}_\beta)_{ii} (\tilde{\mathbf{A}}_\alpha)_{ij} - (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} \\ &\quad \times \sum_k (\mathbf{a}_{ii}^{1/2} + \mathbf{a}_{kk}^{1/2})^{-1} (\mathbf{a}_{kk}^{1/2} + \mathbf{a}_{jj}^{1/2})^{-1} (\tilde{\mathbf{A}}_\beta)_{ik} (\tilde{\mathbf{A}}_\alpha)_{kj} \end{aligned} \quad (\text{B7})$$

and

$$\begin{aligned} (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} (\tilde{\mathbf{A}}_\alpha \mathbf{R}_\beta)_{ij} - (\tilde{\mathbf{A}}_\alpha^{1/2} \mathbf{R}_\beta)_{ij} &= \frac{1}{2} \mathbf{a}_{jj}^{-1/2} (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-2} (\tilde{\mathbf{A}}_\beta)_{jj} (\tilde{\mathbf{A}}_\alpha)_{ij} - (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} \sum_k (\mathbf{a}_{ii}^{1/2} + \mathbf{a}_{kk}^{1/2})^{-1} \\ &\quad \times (\mathbf{a}_{kk}^{1/2} + \mathbf{a}_{jj}^{1/2})^{-1} (\tilde{\mathbf{A}}_\alpha)_{ik} (\tilde{\mathbf{A}}_\beta)_{kj}. \end{aligned} \quad (\text{B8})$$

Substituting (B7) and (B8) into (B5) one arrives at the final formula for the second derivatives of the square-root matrix, Eq. (B9),

$$(\tilde{\mathbf{A}}_{\beta\alpha}^{1/2})_{ij} = (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} \left[(\tilde{\mathbf{A}}_{\beta\alpha})_{ij} - \sum_k (\mathbf{a}_{ii}^{1/2} + \mathbf{a}_{kk}^{1/2})^{-1} (\mathbf{a}_{kk}^{1/2} + \mathbf{a}_{jj}^{1/2})^{-1} ((\tilde{\mathbf{A}}_\alpha)_{ik} (\tilde{\mathbf{A}}_\beta)_{kj} + (\tilde{\mathbf{A}}_\beta)_{ik} (\tilde{\mathbf{A}}_\alpha)_{kj}) \right]. \quad (\text{B9})$$

Provided that the matrix \mathbf{A} is symmetric, the second derivative from Eq. (B9) is symmetric with respect to the permutation of parameters α and β and the permutation of indices i and j .

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