

Nuclear magnetic resonance spin–spin coupling constants from coupled perturbed density functional theory

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For the first time, a complete implementation of coupled perturbed density functional theory (CPDFT) for the calculation of NMR spin–spin coupling constants (SSCCs) with pure and hybrid DFT is presented. By applying this method to several hydrides, hydrocarbons, and molecules with multiple bonds, the performance of DFT for the calculation of SSCCs is analyzed in dependence of the XC functional used. The importance of electron correlation effects is demonstrated and it is shown that the hybrid functional B3LYP leads to the best accuracy of calculated SSCCs. Also, CPDFT is compared with sum-over-states (SOS) DFT where it turns out that the former method is superior to the latter because it explicitly considers the dependence of the Kohn–Sham operator on the perturbed orbitals in DFT when calculating SSCCs. The four different coupling mechanisms contributing to the SSCC are discussed in connection with the electronic structure of the molecule.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is an indispensable tool for the determination of molecular structure and conformation since the nuclear shielding constants and the scalar spin–spin coupling constants (SSCCs) provide sensitive probes for the electronic structure of a molecule, as has been demonstrated in many review articles and research books.¹ Quantum chemists have predominantly focused on the calculation and interpretation of nuclear shielding constants and the chemical shifts derived from the former as they are both easier to calculate and easier to analyze in connection with structural features.^{2–9} However, the complete description of an NMR spectrum implies the determination and the understanding of the NMR SSCCs. The SSCC between two nuclei depends on the distribution of electrons in a bond or a chain of bonds and, therefore, it represents an important source of information on the bonding situation of the molecule under investigation. An efficient quantum chemical method for reliably predicting NMR SSCCs will be a prerequisite for a detailed understanding of the results of the NMR experiment and the routine determination of molecular geometry and molecular shape with the help of the NMR experiment.

The coupling of nuclear magnetic moments is provided by a direct (through-space) mechanism and an indirect (through-electrons) mechanism where for the NMR measurement in gas or solution phase only the latter mechanism is relevant. The first consistent formulation of the electronic theory of indirect spin–spin coupling was given by Ramsey,¹⁰ who expressed NMR SSCCs in terms of second-order perturbation theory (which implies that the SSCC can be represented as the mixed derivative of the molecular energy with respect to the two spin angular momentums of the coupling nuclei). There are four electronic mechanisms that

contribute to the magnitude of the SSCCs, namely the diamagnetic spin-orbit (DSO) and the paramagnetic spin-orbit (PSO) interactions, which represent the interactions of the magnetic field of the nuclei mediated by the orbital motion of the electrons where the diamagnetic part reflects the dependence of the molecular Hamiltonian on the nuclear magnetic moments (Hellmann–Feynman term) and the paramagnetic part reflects the response of the molecular orbitals to the nuclear magnetic field. The Fermi-contact (FC) interaction is also a response property reflecting the interaction between the spin magnetic moment of the electrons close to the nucleus and the magnetic field inside the nucleus. Finally, the spin-dipole (SD) interaction represents the interaction between the nuclear magnetic moments as mediated by the spin angular momentums of the electrons. For an accurate quantum chemical description of SSCCs all four terms have to be considered.¹¹

The calculation of SSCCs in form of a derivative of the total energy was originally done numerically using finite-perturbation (FP) theory, which can be implemented into an existing quantum chemical method with little additional programming effort because it requires just the consideration of the magnetic field produced by a nuclear magnetic moment.¹² For example, FP theory was applied to calculate SSCCs at MP2,¹³ MCSCF,¹⁴ CI,¹⁵ and CC.¹⁶ The first attempts to calculate SSCCs with density-functional theory (DFT) used FP theory as well,¹⁷ and most current DFT calculations of SSCCs employ FP theory for the calculation of the FC term.^{18–21} However, FP methods suffer from numerical inaccuracy; besides, the interpretation of the results, e.g., the decomposition of the total SSCCs into orbital contributions, is problematic.

Since the calculation of SSCCs with the help of analytical schemes avoids the disadvantages of FP methods, the former were first developed for Hartree–Fock (HF)²² using Coupled Perturbed HF (CPHF).²³ Later the development of

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various correlation corrected *ab initio* methods^{24,25} including the second-order polarization propagator approach (SOPPA),²⁶ and the equation-of-motion (EOM) coupled-cluster (CC) method²⁷ followed where these methods are based on sum-over-states (SOS) rather than second derivative formulations of the SSCC. DFT represents an attractive method for the calculation of SSCCs since the availability of improved (though still approximate) exchange-correlation (XC) functionals has made DFT to a relative accurate but economical routine method for calculating many different molecular properties.^{28,29} So far, the calculation of SSCCs with analytical schemes was implemented only partially. For example, Bouř and Buděšínský calculated DFT SSCCs using SOS density-functional perturbation theory (DFPT), which evaluates the analytic derivatives in an approximative way, thus circumventing the iterative Coupled Perturbed DFT (CPDFT) procedure by a simpler, noniterative procedure.³⁰ In Refs. 18–21, SOS DFPT was used to evaluate the PSO contribution and FP theory for calculating the FC term while the SD term was neglected at all as this contribution is the most expensive one to calculate, but probably negligible in most cases.

In the present paper, we describe the complete DFT calculation of all four spin-spin coupling terms within the CPDFT formalism where the theory is developed for both pure and hybrid XC functionals. By applying the CPDFT method to a number of representative examples, we will first investigate the performance of DFT for the calculation of SSCCs. Second, we will compare the performance of difference XC functionals and investigate the dependence of the results on the basis set employed. Then, a comparison of CPDFT and SOS DFPT results will show which of these methods is better suited to calculate SSCCs. Finally, we will focus on the four coupling mechanisms described by the DSO, PSO, FC, and SD terms and draw a connection between electronic structure and the information provided by the SSCCs. Since the latter aspect has been considered in modern quantum chemical investigations of indirect SSCCs only in a limited way, although it should be of major importance for the interpretation of NMR parameters, it will find special attention in this work.

Our work will be presented (apart from the introduction) in four parts. In Sec. II, the CPDFT formalism for the calculation of SSCCs will be developed, starting from the corresponding many-body formalism. Section III gives a description of the implementation of CPDFT in a computer program for routine calculations. In Sec. IV, the performance of CPDFT is discussed for a number of representative calculations. Also, the four contributions to SSCC values will be analyzed in dependence of the electronic structure of the molecules investigated where the discussion is supported by two Appendices. Section V gives conclusions and an outlook to future work.

II. THEORY OF NMR SPIN-SPIN COUPLING CONSTANTS

The basic theory for the *ab initio* calculation of the indirect SSCCs¹⁰ requires that the magnetic field generated by the nuclear magnetic moments

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

is considered in the Hamiltonian of the molecule, where \mathbf{M}_N is the magnetic moment of nucleus N , γ_N the gyromagnetic ratio, and \mathbf{I}_N the spin angular momentum (in units of \hbar) of nucleus N . Quantities \mathbf{M}_N and \mathbf{I}_N are treated in a classical manner in the present derivation; consequently, the ground state energy of the system parametrically depends on all nuclear magnetic moments \mathbf{M}_N or the corresponding nuclear spin angular momenta \mathbf{I}_N . The indirect SSCC between nuclei A and B is given as the mixed partial derivative of the total energy with respect to the spin angular moments of these two nuclei,

$$\underline{J}_{AB} = \frac{1}{\hbar} \frac{\partial}{\partial \mathbf{I}_A} \circ \frac{\partial}{\partial \mathbf{I}_B} E(\mathbf{I}_A, \mathbf{I}_B, \dots) \Big|_{\mathbf{I}_A = \mathbf{I}_B = \dots = 0}, \quad (2)$$

where \circ denotes the tensor product. For a rapidly rotating molecule with arbitrarily oriented rotation axes as is the case in the gas phase or in solution, only the scalar (isotropic) SSCC given by the trace (Tr) of tensor \underline{J}_{AB}

$$J_{AB} = \frac{1}{3} \text{Tr} \underline{J}_{AB}, \quad (3)$$

is relevant, which is determined from the measured NMR spectrum.

The SSCCs as defined in Eqs. (2), (3) are in units of frequencies and thus directly related to the frequency shifts observed in NMR experiments. They depend on the gyromagnetic ratios γ_A, γ_B of nuclei A, B . For investigations that concentrate on the electronic nature of the spin-spin coupling, a quantity that is independent of the γ_A, γ_B would be more appropriate. Therefore, one defines the reduced SSCC K_{AB} according to

$$\begin{aligned} \underline{K}_{AB} &= \frac{\partial}{\partial \mathbf{M}_A} \circ \frac{\partial}{\partial \mathbf{M}_B} E(\mathbf{M}_A, \mathbf{M}_B, \dots) \Big|_{\mathbf{M}_A = \mathbf{M}_B = \dots = 0} \\ &= \frac{2\pi}{\hbar} \frac{1}{\gamma_A \gamma_B} \underline{J}_{AB}. \end{aligned} \quad (4)$$

In the same way as for the \underline{J}_{AB} , the isotropic average $K_{AB} = \frac{1}{3} \text{Tr} \underline{K}_{AB}$ is of particular interest.

A. Many-body Schrödinger theory

The magnetic field generated by the \mathbf{M}_N enters the Hamiltonian in two ways: (i) The momentum \mathbf{p} has to be replaced by $\mathbf{p} - e\mathbf{A}(\mathbf{r})$, where the vector potential $\mathbf{A}(\mathbf{r})$ is given by

$$\mathbf{A}(\mathbf{r}) = \sum_N \frac{\mu_0}{4\pi} \mathbf{M}_N \times \frac{\mathbf{r} - \mathbf{R}_N}{|\mathbf{r} - \mathbf{R}_N|^3}, \quad (5)$$

where \mathbf{R}_N is the position of nucleus N and μ_0 the magnetic permeability of the vacuum. (ii) A term covering the interaction between the magnetic field $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$ and the spin polarization density of the electrons has to be added to the Hamiltonian. Points (i) and (ii) lead to four additional terms in the Hamiltonian, corresponding to different coupling mechanisms. The interaction between the nuclear magnetic moments and the orbital magnetic moments is de-

scribed by DSO and PSO terms while the interaction between nuclear and electronic spin magnetic moments leads to the FC and SD terms:¹⁰

$$\hat{H}_M = \hat{H}^{\text{DSO}} + \hat{H}^{\text{PSO}} + \hat{H}^{\text{FC}} + \hat{H}^{\text{SD}}, \quad (6a)$$

$$\hat{H}_M = \sum_{A < B} \mathbf{M}_A \hat{H}_{AB}^{\text{DSO}} \mathbf{M}_B + \sum_A \mathbf{M}_A (i \hat{\mathbf{H}}_A^{\text{PSO}} + \hat{\mathbf{H}}_A^{\text{FC}} + \hat{\mathbf{H}}_A^{\text{SD}}). \quad (6b)$$

The DSO term is bilinear in the \mathbf{M}_A and leads thus to the tensor operator $\hat{H}_{AB}^{\text{DSO}}$ while the remaining terms are linear in the \mathbf{M}_A and are expressed by vector operators $\hat{\mathbf{H}}_A^{\text{PSO}}$, $\hat{\mathbf{H}}_A^{\text{FC}}$, and $\hat{\mathbf{H}}_A^{\text{SD}}$. The factor of i in front of $\hat{\mathbf{H}}_A^{\text{PSO}}$ has been introduced to make the operator and the resulting first-order wave function real. In second quantization \hat{H}_M can be expressed in terms of the one-particle operators $\underline{h}_{AB}^{\text{DSO}}$, $\mathbf{h}_A^{\text{PSO}}$, \mathbf{h}_A^{FC} , and \mathbf{h}_A^{SD} according to

$$\hat{H}_M = \int d^3r \Psi^\dagger(\mathbf{r}) \left[\sum_{A < B} \mathbf{M}_A \underline{h}_{AB}^{\text{DSO}} \mathbf{M}_B + \sum_A \mathbf{M}_A (i \mathbf{h}_A^{\text{PSO}} + \mathbf{h}_A^{\text{FC}} + \mathbf{h}_A^{\text{SD}}) \right] \Psi(\mathbf{r}), \quad (6c)$$

$$\underline{h}_{AB}^{\text{DSO}} = \left\{ \frac{1}{m} \left(\frac{4\pi\epsilon_0\hbar^2}{e} \right)^2 \right\} \alpha^4 \left(\frac{\mathbf{r}_A}{r_A^3} \cdot \frac{\mathbf{r}_B}{r_B^3} \mathbb{1} - \frac{\mathbf{r}_A}{r_A^3} \circ \frac{\mathbf{r}_B}{r_B^3} \right), \quad (6d)$$

$$\mathbf{h}_A^{\text{PSO}} = \left\{ \frac{4\pi\epsilon_0\hbar^3}{em} \right\} \alpha^2 \frac{\mathbf{r}_A}{r_A^3} \times \nabla, \quad (6e)$$

$$\mathbf{h}_A^{\text{FC}} = \left\{ \frac{4\pi\epsilon_0\hbar^3}{em} \right\} \frac{8\pi}{3} \alpha^2 \delta(\mathbf{r}_N) \mathbf{s}, \quad (6f)$$

$$\mathbf{h}_A^{\text{SD}} = \left\{ \frac{4\pi\epsilon_0\hbar^3}{em} \right\} \alpha^2 \left[3 \frac{(\mathbf{s} \cdot \mathbf{r}_N) \mathbf{r}_N}{r_N^5} - \frac{\mathbf{s}}{r_N^3} \right], \quad (6g)$$

where $\mathbf{r}_N = \mathbf{r} - \mathbf{R}_N$, ϵ_0 is the dielectric constant of the vacuum, α is Sommerfeld's fine structure constant, $\mathbb{1}$ is the unit tensor, and \mathbf{s} is the electron spin in units of \hbar . The prefactors enclosed in braces in Eqs. (6d)–(6g) become equal to one in atomic units. Note that \mathbf{h}_A^{FC} and \mathbf{h}_A^{SD} are 2×2 matrices with respect to the electron spin variables.

The DSO term is of second order, and the PSO, FC, and SD terms are of first order in the magnetic moments \mathbf{M}_N . Second-order perturbation theory yields thus the following expression for the SSCCs:

$$(K_{AB})_{ij} = \langle \Psi^{(0)} | \hat{H}_{AB,ij}^{\text{DSO}} | \Psi^{(0)} \rangle + 2 \langle \Psi^{(0)} | i \hat{H}_{A,i}^{\text{PSO}} + \hat{H}_{A,i}^{\text{FC}} + \hat{H}_{A,i}^{\text{SD}} | \Psi_j^{(B)} \rangle, \quad (7)$$

where i, j are indices for Cartesian components, $\Psi^{(0)}$ is the ground-state wave function for $\mathbf{M}_A = \mathbf{M}_B = \dots = \mathbf{0}$ and vector Eq. (8)

$$| \Psi^{(B)} \rangle = \frac{\partial}{\partial \mathbf{M}_B} | \Psi \rangle_{\mathbf{M}_A = \mathbf{M}_B = \dots = \mathbf{0}} \quad (8)$$

represents the perturbed wave function, which summarizes the response of the wave function to the three Cartesian components of the magnetic moment of nucleus B .

From standard perturbation theory it follows

$$| \Psi^{(B)} \rangle = i | \Psi^{(B),\text{PSO}} \rangle + | \Psi^{(B),\text{FC}} \rangle + | \Psi^{(B),\text{SD}} \rangle, \quad (9a)$$

$$| \Psi^{(B),X} \rangle = \sum_{m \neq 0} \frac{\langle \Psi_m^{(0)} | \hat{\mathbf{H}}_B^X | \Psi_0^{(0)} \rangle}{E_0 - E_m} | \Psi_m^{(0)} \rangle, \quad (9b)$$

where $X = \text{PSO, FC, SD}$ and E_m and $\Psi_m^{(0)}$ are the eigenvalues and eigenvectors of the unperturbed Hamiltonian. The subscript 0 for the ground state is suppressed in the following. With the decomposition Eq. (9a) of the perturbed wave function, the last term at the r.h.s. of Eq. (7) can be decomposed into nine components related to the different coupling mechanisms. As pointed out by Ramsey,¹⁰ of these components those containing the combinations $\hat{H}^{\text{PSO}} - \Psi^{\text{FC}}$, $\hat{H}^{\text{PSO}} - \Psi^{\text{SD}}$, $\hat{H}^{\text{FC}} - \Psi^{\text{PSO}}$, and $\hat{H}^{\text{SD}} - \Psi^{\text{PSO}}$ do not contribute to K_{AB} , and those containing the combinations $\hat{H}^{\text{FC}} - \Psi^{\text{SD}}$ and $\hat{H}^{\text{SD}} - \Psi^{\text{FC}}$ contribute to K_{AB} but not to K_{AB} . Therefore, the isotropic reduced coupling constant can be decomposed into components related to the four coupling mechanisms and represented as

$$K_{AB} = K_{AB}^{\text{DSO}} + K_{AB}^{\text{PSO}} + K_{AB}^{\text{FC}} + K_{AB}^{\text{SD}}, \quad (10a)$$

$$K_{AB}^{\text{DSO}} = \frac{1}{3} \int d^3r \varrho^{(0)}(\mathbf{r}) \text{Tr} \underline{h}_{AB}^{\text{DSO}}, \quad (10b)$$

$$K_{AB}^{\text{PSO}} = -\frac{2}{3} \langle \Psi^{(0)} | \hat{\mathbf{H}}_A^{\text{PSO}} | \Psi^{(B),\text{PSO}} \rangle, \quad (10c)$$

$$K_{AB}^{\text{FC}} = \frac{2}{3} \langle \Psi^{(0)} | \hat{\mathbf{H}}_A^{\text{FC}} | \Psi^{(B),\text{FC}} \rangle, \quad (10d)$$

$$K_{AB}^{\text{SD}} = \frac{2}{3} \langle \Psi^{(0)} | \hat{\mathbf{H}}_A^{\text{SD}} | \Psi^{(B),\text{SD}} \rangle, \quad (10e)$$

where the DSO term has been expressed as a weighted integral over the density $\varrho^{(0)}$ of the unperturbed state.

B. Density-functional theory

For the calculation of K_{AB} within DFT,^{28,29} the representation of the SSCCs as energy derivatives in Eq. (2) is an appropriate starting point. The total energy of the molecule in the absence of the magnetic fields generated by the nuclear magnetic moments is given in Kohn–Sham (KS) DFT by Eq. (11):

$$E = T + V_H + V_{en} + V_{nn} + E_{XC}, \quad (11a)$$

$$T = \left\{ \frac{1}{m} \right\} \sum_{k\sigma}^{\text{occ}} \langle \psi_{k\sigma} | \frac{\mathbf{p}^2}{2} | \psi_{k\sigma} \rangle, \quad (11b)$$

$$V_H = \frac{1}{2} \left\{ \frac{e^2}{4\pi\epsilon_0} \right\} \int d^3r \int d^3r' \frac{\varrho(\mathbf{r})\varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (11c)$$

$$V_{en} = - \left\{ \frac{e^2}{4\pi\epsilon_0} \right\} \sum_A \int d^3r \frac{Z_A \varrho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_A|}, \quad (11d)$$

$$V_{nn} = \frac{1}{2} \left\{ \frac{e^2}{4\pi\epsilon_0} \right\} \sum_{A \neq A'} \frac{Z_A Z_{A'}}{|\mathbf{R}_A - \mathbf{R}_{A'}|}, \quad (11e)$$

where T is the KS kinetic energy, V_H , V_{en} , and V_{nn} are the electron–electron (Hartree), electron–nucleus, and nucleus–

nucleus part of the electrostatic interaction energy, $|\psi_{k\sigma}\rangle$ are the occupied KS spin orbitals, and Z_A is the atomic number of nucleus A . Index $\sigma = \pm 1$ labels α and β spin orbitals. E_{XC} is the XC energy, which depends as a functional on the eigenvalues of the 2×2 spin density matrix

$$\varrho_{ss'}(\mathbf{r}) = \sum_{k\sigma}^{\text{occ}} \psi_{k\sigma}^*(\mathbf{r}, s') \psi_{k\sigma}(\mathbf{r}, s), \quad (12)$$

where $s, s' = \pm 1$ are spin coordinates. If the spin polarization is parallel to the spin quantization axis these eigenvalues are just the spin-resolved densities $\varrho_\alpha(\mathbf{r}), \varrho_\beta(\mathbf{r})$. The prefactors enclosed in braces in Eqs. (11) become equal to one in atomic units and will be omitted in the following. For closed-shell molecules, the spin-free parts of the unperturbed α and β KS orbitals are pairwise identical, i.e., $|\psi_{k\sigma}\rangle = |\phi_k\rangle\sigma(s)$ where ϕ_k denotes space orbitals and $\sigma(s)$ represents two-dimensional spinors.

The magnetic field of \mathbf{M}_N leads to four additional terms in the DFT energy corresponding to the four additional terms in the Hamiltonian of Eqs. (6), which can be expressed with the one-particle operators introduced in Eqs. (6c)–6(g):

$$E(\mathbf{M}_N) = E^{\text{DSO}} + E^{\text{PSO}} + E^{\text{FC}} + E^{\text{SD}}, \quad (13a)$$

$$E^{\text{DSO}} = \sum_{A < B} \mathbf{M}_A \sum_{k\sigma}^{\text{occ}} \langle \psi_{k\sigma} | \underline{h}_{AB}^{\text{DSO}} | \psi_{k\sigma} \rangle \mathbf{M}_B, \quad (13b)$$

$$E^{\text{PSO}} = \sum_A \mathbf{M}_A \sum_{k\sigma}^{\text{occ}} \langle \psi_{k\sigma} | i\mathbf{h}_A^{\text{PSO}} | \psi_{k\sigma} \rangle, \quad (13c)$$

$$E^{\text{FC}} = \sum_A \mathbf{M}_A \sum_{k\sigma}^{\text{occ}} \langle \psi_{k\sigma} | \mathbf{h}_A^{\text{FC}} | \psi_{k\sigma} \rangle, \quad (13d)$$

$$E^{\text{SD}} = \sum_A \mathbf{M}_A \sum_{k\sigma}^{\text{occ}} \langle \psi_{k\sigma} | \mathbf{h}_A^{\text{SD}} | \psi_{k\sigma} \rangle. \quad (13e)$$

Evaluating the energy derivative of Eq. (4) for the DFT energy and the related KS equations, the contributions to the isotropic SSCCs result as

$$K_{AB}^{\text{DSO}} = \frac{2}{3} \sum_k^{\text{occ}} \langle \phi_k^{(0)} | \text{Tr} \underline{h}_{AB}^{\text{DSO}} | \phi_k^{(0)} \rangle, \quad (14a)$$

$$K_{AB}^{\text{PSO}} = -\frac{4}{3} \sum_k^{\text{occ}} \langle \phi_k^{(0)} | \mathbf{h}_A^{\text{PSO}} | \phi_k^{(B),\text{PSO}} \rangle, \quad (14b)$$

$$K_{AB}^{\text{FC}} = \frac{2}{3} \sum_{k\sigma}^{\text{occ}} \langle \psi_{k\sigma}^{(0)} | \mathbf{h}_A^{\text{FC}} | \psi_{k\sigma}^{(B),\text{FC}} \rangle, \quad (14c)$$

$$K_{AB}^{\text{SD}} = \frac{2}{3} \sum_{k\sigma}^{\text{occ}} \langle \psi_{k\sigma}^{(0)} | \mathbf{h}_A^{\text{SD}} | \psi_{k\sigma}^{(B),\text{SD}} \rangle, \quad (14d)$$

where the prefactors are a result of (a) the isotropic averaging (factor 1/3), (b) the expression for the mixed energy derivative in perturbation theory (factor 2 for PSC, FC, and SD term), and (c) the fact that DSO and PSO terms are expressed in terms of the spin-free orbitals ϕ_k while FC and SD term are written in terms of the spin-dependent orbitals $\psi_{k\sigma}$ (factor 2). The first-order spin orbitals $\psi_{k\sigma}^{(B),X}$ are given by

$$|\psi_{k\sigma}^{(B),X}\rangle = \sum_{a\sigma'}^{\text{virt}} \frac{\langle \psi_{a\sigma'}^{(0)} | \mathbf{F}_B^X | \psi_{k\sigma}^{(0)} \rangle}{\epsilon_k - \epsilon_a} |\psi_{a\sigma'}^{(0)}\rangle, \quad (15)$$

where \mathbf{F}_B^X is the first-order term of the perturbed KS operator. Equation (14a) for the DSO part can easily be rewritten to yield Eq. (10b), i.e., Eq. (10b) is valid both within the many-body and the KS formalism. In analogy to \mathbf{h}_A^{FC} and \mathbf{h}_A^{SD} , \mathbf{F}_A^{FC} and \mathbf{F}_A^{SD} are 2×2 matrices with respect to the electron spin while for the PSO term Eq. (15) can be reduced to an equation for the space orbitals $|\phi_k^{(B),\text{PSO}}\rangle$ occurring in Eq. (14b).

As the KS operator F depends on the KS orbitals through the electron density, \mathbf{F}_A^X depends on the $|\psi_{k\sigma}^{(A),X}\rangle$:

$$\mathbf{F}_A^X = \mathbf{h}_A^X + \tilde{\mathbf{F}}_A^X, \quad (16a)$$

$$\tilde{\mathbf{F}}_A^X = \sum_{k\sigma}^{\text{occ}} \int d^3r \frac{\delta F}{\delta \psi_{k\sigma}(\mathbf{r})} \psi_{k\sigma}^{(A),X}(\mathbf{r}), \quad (16b)$$

hence, Eq. (15) is no explicit equation for the $|\psi_{k\sigma}^{(A),X}\rangle$ [as Eq. (9b) is for the $|\Psi^{(A),X}\rangle$] but has to be solved simultaneously with Eqs. (16) in a self-consistent fashion by CPDFT. This self-consistent procedure is avoided in SOS DFPT,³¹ where concepts from DFT and wave function theory are combined to Eq. (15) by a noniterative equation similar to Eqs. (9). In its simplest form, SOS DFPT is tantamount to the approximation $\mathbf{F}_A^X \approx \mathbf{h}_A^X$. However, there are no reasons to justify this approximation *a priori*. More elaborate versions of SOS DFPT use corrections to the energy denominators $\epsilon_k - \epsilon_a$ in Eq. (15) to approximately account for the coupling, i.e., the one-electron operator $\tilde{\mathbf{F}}_A^X$ (see, e.g., Ref. 31). In general, $\tilde{\mathbf{F}}_A^X$ may contain contributions from the Hartree potential v_H and from the XC potential v_{XC} . For a closed-shell molecule, a magnetic field can lead to first-order changes in the KS orbitals but not in the total density (see, e.g., Ref. 2). Therefore, any contribution to $\tilde{\mathbf{F}}_A^X$ resulting from the Hartree potential vanishes, and $\tilde{\mathbf{F}}_A^X$ consists of changes in v_{XC} solely. The first-order changes of the KS orbitals may influence v_{XC} in different ways:

- (i) As a result of the coupling with the electron spins, the nuclear magnetic field leads to spin polarization of the electron system, which in turn changes v_{XC} . This effect is relevant for the FC and SD terms.
- (ii) In the presence of a magnetic field, the XC energy functional depends not only on the electron density but also on the electronic current density $\mathbf{j}(\mathbf{r})$.³² A magnetic field will change $\mathbf{j}(\mathbf{r})$ in first order and thus influence v_{XC} . However, the currently available approximations for such a current-dependent XC energy functional³³ are problematic to apply; besides, test calculations for NMR shieldings by Lee *et al.*³⁴ indicate that the current dependence of the XC functional has generally little influence on the results. Therefore, DFT calculations of magnetic properties are usually done with the common, \mathbf{j} -independent expressions for the XC energy. This means that the first-order changes of $\mathbf{j}(\mathbf{r})$ do not contribute to $\tilde{\mathbf{F}}_A^X$.
- (iii) If the exchange energy is described by a hybrid functional, the first-order changes of the KS orbitals will

result in a first-order change in the HF part of the exchange operator thus affecting the calculation of PSO, FC, and SD term.

In the following, the evaluation of the individual contributions to K_{AB} within DFT is discussed in more detail.

1. The DSO term

The DSO term depends on the unperturbed KS orbitals only. It can be evaluated either by numerically determining the integral in Eq. (10b) or evaluating Eq. (14a). The latter approach gives the possibility of analyzing orbital contributions to the DSO term. Use of Eq. (14a) requires the calculation of one-electron integrals of the type

$$(D_{AB,pq})_{ij} = \left\langle b_p \left| \frac{r_{A,i}}{r_A^3} \frac{r_{B,j}}{r_B^3} \right| b_q \right\rangle, \quad (17)$$

where $|b_p\rangle, |b_q\rangle$ are basis functions and indices i, j denote Cartesian coordinates. Integrals $(D_{AB,pq})_{ij}$ have to be evaluated by some approximate numerical method.

2. The PSO term

The calculation of the PSO term can be reduced to the calculation of the matrix elements $\langle \phi_k^{(0)} | h_{A,i}^{\text{PSO}} | \phi_a^{(0)} \rangle$ and $\langle \phi_k^{(0)} | \tilde{F}_{A,i}^{\text{PSO}} | \phi_a^{(0)} \rangle$. The matrix elements containing $\mathbf{h}_A^{\text{PSO}}$ eventually lead to vectors $\mathbf{d}_{A,pq}$ with elements

$$(d_{A,pq})_i = \left\langle b_p \left| \frac{r_{A,i}}{r_A^3} \right| b_q \right\rangle. \quad (18)$$

The orbitals $|\psi_{k\sigma}^{(A),\text{PSO}}\rangle$ are not spin polarized. Hence, as discussed under (iii) above, $\mathbf{F}_A^{\text{PSO}}$ is a nonzero operator only when a hybrid exchange functional is used. For a pure DFT functional, integral operator $\mathbf{F}_A^{\text{PSO}}$ vanishes, and the orbitals $|\psi_{k\sigma}^{(A),\text{PSO}}\rangle$ can be determined from Eq. (15) noniteratively.

For a hybrid exchange functional, $\tilde{\mathbf{F}}_A^{\text{PSO}}$ is equal to the first-order HF exchange operator scaled by the weight of HF exchange in the hybrid functional. To calculate $\tilde{\mathbf{F}}_A^{\text{PSO}}$ in this case, one constructs the first-order KS density matrix from orbitals $|\phi_k\rangle$ and $|\phi_k^{(A),\text{PSO}}\rangle$ and calculates the HF exchange operator from this first-order density matrix.

3. The FC term

The contribution of the FC interaction to the spin–spin coupling tensor is isotropic, hence $K_{AB}^{\text{FC}} = K_{AB,zz}^{\text{FC}}$, i.e., it suffices to calculate one diagonal component of \underline{K}_{AB} . The matrix element of the operator $h_{A,z}^{\text{FC}}$ is given by Eq. (19):

$$\langle \psi_{k\sigma}^{(0)} | h_{A,z}^{\text{FC}} | \psi_{a\sigma'}^{(0)} \rangle = \alpha^2 \sigma \delta_{\sigma\sigma'} \phi_k(\mathbf{R}_A) \phi_a(\mathbf{R}_A). \quad (19)$$

Equation (19) is easy to evaluate, however, an accurate determination of the FC term requires basis sets that accurately reproduce the KS orbitals close to the nucleus since the KS orbitals are probed at the nuclear position. The one-particle operator $\tilde{F}_{A,z}^{\text{FC}}$ is determined by the first-order spin polarization as discussed under (i) above and, provided a hybrid XC functional is used, by the exact exchange portion as discussed under (iii). As can be seen from Eq. (19), the perturbation does not mix α and β orbitals, and it is

$$|\psi_{k,\sigma}^{(A),\text{FC}}\rangle = \sigma |\phi_k^{(A),\text{FC}}\rangle |\chi_\sigma\rangle. \quad (20)$$

4. The SD term

The computationally most demanding contribution to K_{AB} is the SD term, which is the reason why this term was neglected in many previous DFT calculations of SSCCs.^{18–21} If Eq. (15) is evaluated directly, the spin orbitals $|\psi^{(A),\text{SD}}\rangle$ will possess two independent complex components. One can, however, simplify the calculation by decomposing the components of $h_{A,i}^{\text{SD}}$ according to

$$h_{A,i}^{\text{SD}} = \sum_j \sigma_j h_{A,ij}^{\text{SD}}, \quad (21a)$$

$$h_{A,ij}^{\text{SD}} = \alpha^2 \left[3 \frac{r_{A,i}}{r_A} \frac{r_{A,j}}{r_A} - \delta_{ij} \right] \frac{1}{r_A^3}, \quad (21b)$$

where σ_j denotes a Pauli spin matrix. Each term $\sigma_j h_{ij}$ is calculated separately, with the spin quantization axis being rotated into the direction i for each of the perturbation calculations. This rotation makes the operator $h_{A,ij}^{\text{SD}} \sigma_j$ real and diagonal in spin space, and the perturbed orbitals can be expressed by real spin-free first-order orbitals $|\phi_{k,i}^{(A),\text{SD}}\rangle$ analogously as for the FC term. The final result for the SD term becomes

$$K_{AB}^{\text{SD}} = \frac{2}{3} \sum_k^{\text{occ}} [\langle \phi_k | h_{A,xx}^{\text{SD}} | \phi_{k,xx}^{(B),\text{SD}} \rangle + \langle \phi_k | h_{A,yy}^{\text{SD}} | \phi_{k,yy}^{(B),\text{SD}} \rangle + \langle \phi_k | h_{A,zz}^{\text{SD}} | \phi_{k,zz}^{(B),\text{SD}} \rangle + 2(\langle \phi_k | h_{A,xy}^{\text{SD}} | \phi_{k,xy}^{(B),\text{SD}} \rangle + \langle \phi_k | h_{A,xz}^{\text{SD}} | \phi_{k,xz}^{(B),\text{SD}} \rangle + \langle \phi_k | h_{A,yz}^{\text{SD}} | \phi_{k,yz}^{(B),\text{SD}} \rangle)]. \quad (22)$$

Equations (12)–(22) form a set of working equations for the DFT calculation of NMR SSCCs.

The calculations of K_{AB} according to Eqs. (10) with the orbitals from Eq. (9) or according to Eq. (14) with the orbitals from Eq. (15) implies perturbing the molecule by adding a magnetic moment at nucleus B (“perturbing nucleus”) and monitoring the effect of this perturbation onto a magnetic moment at nucleus A (“responding nucleus”). As mixed second derivatives with respect to \mathbf{M}_A and \mathbf{M}_B , the K_{AB} are symmetric by definition, hence perturbing and responding nucleus may be interchanged in the calculation. Within the many-body Schrödinger formalism, this interchange leaves the equations for K_{AB} unchanged, as one sees by inserting Eqs. (9) into Eqs. (10). In contrast, for DFT the difference between the operators \mathbf{h}_A^X and \mathbf{F}_A^X leads to a change in the form of the equations. In connection with numerical limitations, especially the use of finite basis sets, the result for K_{AB} may change due to an interchange of perturbed and responding nuclei, as was shown by Dickson and Ziegler.²⁰ We note in this connection that this numerical error can be reduced when Eq. (10) or Eq. (14), respectively, is replaced by an expression symmetric in perturbed and responding nucleus,³⁵ which, however, leads to an undesirable increase in computational cost.

TABLE I. Reduced nuclear spin–spin coupling constants of H₂O and CH₄ calculated at the CPHF level of theory.^a

Molecule	Coupling	K^{DSO} Lit. ^b	K^{tot} Lit. ^b	K^{DSO} This work	ΔK^{DSO} This work
H ₂ O	¹ K(O, H)	0.067	52.116	−0.004	0.063
	² K(H, H)	−0.596	−1.863	−0.665	0.069
CH ₄	¹ K(C, H)	0.082	52.139	0.218	0.136
	² K(H, H)	−0.294	−2.278	−0.276	0.018

^aAll values in SI units ($10^{19} \text{ kg m}^{-2} \text{ s}^{-2} \text{ \AA}^{-2}$) obtained with the 6-311G(*d,p*) basis set (Ref. 40) for H₂O and the BS8 basis set of Ref. 39 for CH₄.

^bTaken from Refs. 27a (H₂O) and 39 (CH₄).

III. IMPLEMENTATION AND COMPUTATIONAL DETAILS

The formalism described in Sec. II B was implemented into the program package COLOGNE99³⁶ in the way that SSCCs can be calculated at both the HF, the pure DFT, and the hybrid DFT levels of theory. A procedure similar to the direct inversion of the iterative subspace (DIIS)³⁷ was applied to accelerate the convergence of the CPDFT or CPHF procedures. The integrals $(d_{A,pr})_i$ were calculated by the McMurchie–Davidson algorithm.³⁸

For the calculation of integrals $(D_{AB,pq})_{ij}$, we applied the resolution of the identity to relate the D integrals to integrals $(d_{A,pr})_i$ according to Eq. (23):

$$(D_{AB,pq})_{ij} \approx \sum_{rr'} (d_{A,pr})_i (S^{-1})_{rr'} (d_{B,r'q})_j, \quad (23a)$$

$$S_{rr'} = \langle b_r | b_{r'} \rangle. \quad (23b)$$

Equation (23a) is exact for a complete (and thus infinite) basis set while it will not necessarily provide accurate results for a given finite basis set. However, it appears justified to use Eq. (23a) for the calculation of the DSO term since: (i) calculations of magnetic properties generally require extended basis sets; (ii) the DSO term is not the dominating contribution to the indirect SSCC values. If the results calculated with Eqs. (23) are not sufficiently accurate, one may insert the identity by using an auxiliary basis that is larger than the basis formed by the functions b_n .

For two molecules, namely CH₄ and H₂O, for which reference values for the DSO term are available in the literature,^{27(a),39} HF coupling constants were calculated to check whether the use of Eq. (23) is justified. Pople's 6-311G(*d,p*) basis set⁴⁰ was used for H₂O and the (17*s*,8*p*,3*d*/13*s*,2*p*)[9*s*,5*p*,3*d*/6*s*,2*p*] basis referred to in Ref. 39 as BS8 for CH₄ to comply with the details given in the literature. In Refs. 27a and 39, the DSO term had been evaluated with the help of an approximate numerical integration scheme described in Ref. 41. Results of the comparison are given in Table I where in this and all following tables the values of reduced coupling constants K_{AB} are given in SI units [$10^{19} \text{ m}^{-2} \text{ kg s}^{-2} \text{ \AA}^{-2}$]. In some cases, SSCC values are also given in Hz and refer to J coupling constants for the isotopes ¹H, ¹³C, ¹⁵N, ¹⁷O, and ¹⁹F, respectively, where the conversion factors given in Ref. 12 were used for the calculation of J values.

The maximum deviation between the DSO terms calculated utilizing Eq. (23) and with the integration scheme from Ref. 41 is 0.136 SI units (0.41 Hz) for the ¹K(C, H) coupling constant in CH₄, which is equal to 52.139 SI units.³⁹ For the ²K(H, H)SSCCs, the maximum deviation is 0.069 SI units (0.83 Hz) for H₂O, for which ²K(H, H) = −1.863 SI units.^{27a} Hence, deviations are negligible, which supports the validity of using Eq. (23) based on assumptions (i) and (ii).

The cpu time for calculating all SSCCs of a molecule scales linearly with the number of perturbing nuclei. If the calculation of the SSCCs of a molecule is arranged in such a way that just those values of interest are determined with as few different perturbing nuclei as possible, the numerical expenses can be decreased considerably, in particular for molecules with high symmetry. For instance, all SSCCs of benzene are calculated with one perturbed C nucleus and one perturbed H nucleus thus effectively exploiting the symmetry of the molecule. Ten different types of one-electron integrals have to be calculated, which requires only a small amount of the total computing time. The latter is dominated by the time used for the solution of the CP equations. Hence, the computing time of NMR SSCCs scales in a similar way as the time for calculating the vibrational frequencies for the same molecule.

HF and DFT coupling constants were calculated for 12 molecules, for which accurate experimental SSCC values are known or for which *ab initio* SSCC values were published. Molecules are grouped for the discussion of results in three classes. Class A contains the hydrides FH, H₂O, NH₃, and CH₄. In class B, all hydrocarbons investigated in this work are collected (CH₄, C₂H₆, C₂H₄, C₂H₂, C₆H₆, CH₃F), while in class C molecules with double and triple bonds (CO, CO₂, and N₂) are discussed separately.

For the DFT calculations, we used the Becke (B) exchange functional⁴² in connection with the Lee–Yang–Parr (LYP)⁴³ and Perdew–Wang 91 (PW91)⁴⁴ correlation functionals. The influence of exact exchange versus DFT exchange was studied by employing the Becke-3 (B3) hybrid exchange functional⁴⁵ with both the PW91 and LYP correlation functionals. In connection with the investigation of correlation effects, calculations were carried out with hybrid functionals constructed from the exact HF exchange, the B exchange functional, and the LYP correlation functional corresponding thus leading to the XC energy of Eq. (24)

$$E_{\text{XC}}(m,n) = \frac{m}{100} (E_X^{\text{B}} + E_C^{\text{LYP}}) + \frac{n}{100} E_X^{\text{HF}}, \quad (24)$$

where E_X^{HF} , E_X^{B} , and E_C^{LYP} represent HF exchange energy, Becke exchange energy, and the LYP correlation energy, respectively, while prefactors m and n can vary from 0 to 100. Hence, $E_{\text{XC}}(100,0)$ is identical with the BLYP XC energy and $E_{\text{XC}}(0,100)$ leads to the HF energy. In this work, the BLYP(m,n) hybrid functionals BLYP (90,10), BLYP (50,50), and BLYP (10,90) were used.

All calculations were done for experimental geometries⁴⁶ with basis sets originally developed by Huzinaga⁴⁷ and later modified by Kutzelnigg and co-workers.² Preliminary calculations were performed with the (9*s*,5*p*,1*d*/5*s*,1*p*)[6*s*,4*p*,1*d*/3*s*,1*p*] basis (basis II in Ref.

TABLE II. Reduced nuclear spin-spin coupling constants for some hydrides calculated with different DFT methods and HF.^a

Molecule	Coupling	Method	DSO	PSO	FC	SD	Total
H ₂	¹ K(H, H) 23.3	BLYP	-0.26	0.39	23.63	0.25	24.01
		BPW91	-0.25	0.39	21.02	0.25	21.41
		B3LYP	-0.26	0.39	22.63	0.25	23.01
		B3PW91	-0.25	0.39	20.69	0.25	21.08
		BLYP (90,10)	-0.26	0.39	23.71	0.25	24.09
		BLYP (50,50)	-0.26	0.39	24.16	0.26	24.55
		BLYP (10,90)	-0.26	0.39	24.94	0.28	25.35
		HF	-0.26	0.39	25.04	0.28	25.45
		FH	¹ K(H, F) 46.8±2	BLYP	0.00	18.0	14.96
BPW91	0.00			17.8	11.83	0.25	29.88
B3LYP	0.00			17.81	19.39	0.11	37.31
B3PW91	0.00			17.64	16.80	0.07	34.51
BLYP (90,10)	0.00			17.94	17.13	0.19	35.26
BLYP (50,50)	0.00			17.69	26.41	-0.24	43.86
BLYP (10,90)	0.00			17.43	36.96	-0.72	53.67
HF	0.00			17.33	39.74	-0.83	56.24
H ₂ O	¹ K(O, H) 48			BLYP	0.09	7.69	33.19
		BPW91	0.10	7.61	29.14	0.48	37.33
		B3LYP	0.09	7.68	35.83	0.43	44.03
		B3PW91	0.09	7.61	32.57	0.41	40.68
		BLYP (90,10)	0.09	7.69	34.79	0.47	43.04
		BLYP (50,50)	0.09	7.67	41.72	0.29	49.77
		BLYP (10,90)	0.09	7.61	49.89	0.10	57.69
		HF	0.09	7.59	52.01	0.05	59.74
		H ₂ O	² K(H, H) -0.6	BLYP	-0.58	0.72	-0.64
BPW91	-0.58			0.72	-0.60	0.08	-0.38
B3LYP	-0.58			0.72	-0.76	0.08	-0.54
B3PW91	-0.58			0.71	-0.73	0.08	-0.52
BLYP (90,10)	-0.58			0.72	-0.74	0.08	-0.52
BLYP (50,50)	-0.58			0.71	-1.19	0.09	-0.97
BLYP (10,90)	-0.59			0.69	-1.77	0.11	-1.56
HF	-0.59			0.69	-1.89	0.11	-1.68
NH ₃	¹ K(N, H) 50			BLYP	0.11	2.62	44.66
		BPW91	0.11	2.59	40.02	0.19	42.91
		B3LYP	0.11	2.59	45.44	0.17	48.31
		B3PW91	0.11	2.58	41.78	0.16	44.63
		BLYP (90,10)	0.11	2.60	45.67	0.19	48.57
		BLYP (50,50)	0.10	2.55	50.09	0.02	52.76
		BLYP (10,90)	0.10	2.48	55.57	-0.02	58.13
		HF	0.09	2.46	56.87	-0.05	59.37
		NH ₃	² K(H, H) -0.87	BLYP	-0.41	0.49	-0.73
BPW91	-0.41			0.49	-0.71	0.05	-0.58
B3LYP	-0.41			0.49	-0.84	0.05	-0.71
B3PW91	-0.41			0.49	-0.82	0.05	-0.69
BLYP (90,10)	-0.41			0.49	-0.83	0.05	-0.70
BLYP (50,50)	-0.41			0.49	-1.27	0.06	-1.13
BLYP (10,90)	-0.42			0.48	-1.82	0.07	-1.69
HF	-0.42			0.48	-1.93	0.07	-1.80

^aAll values in SI units. BLYP (*m,n*) denotes the BLYP-HF hybrid XC functionals described in Eq. (24). Experimental SSCC values are taken from Ref. 12 (exception FH: Ref. 50) and are given below the notation of the corresponding reduced SSCC in the second column. Calculations with the basis (11*s*,7*p*,2*d*/6*s*,2*p*)[7*s*,6*p*,4*s*,2*p*] (basis III in Ref. 2) at experimental geometries (Ref. 46): H₂: *r*(H-H)=0.741 Å; FH: *r*(F-H)=0.9169 Å; H₂O: *r*(O-H)=0.9572 Å, α(HOH)=104.52°; NH₃: *r*(N-H)=1.0124 Å, α(HNH)=106.67°.

2), while the actual calculations discussed in this work are done with the (11*s*,7*p*,2*d*/6*s*,2*p*)[7*s*,6*p*,2*d*/4*s*,2*p*] (basis III in Ref. 2). Actually, these basis sets were developed for the calculation of NMR shielding constants and magnetic susceptibilities rather than NMR SSCCs, which require a more accurate description of regions close to the nucleus (for a discussion of the basis set dependence of calculated coupling constants, see, e.g., Ref. 48). However, since basis sets II and III contain 6*s* and 7*s* descriptions, respectively, of the region close to the nucleus and since parallel calculations for NMR

chemical shifts were carried out with these basis sets, it appeared reasonable to use (basis II and) basis III in calculations of SSCCs.

IV. RESULTS AND DISCUSSION

Calculated reduced SSCC *K*(*A,B*) are summarized in Tables II, III, and IV where just values obtained with the [7*s*,6*p*,2*d*/4*s*,2*p*] are reported. The mean absolute deviation μ of calculated SSCC values from the corresponding experi-

TABLE III. NMR spin-spin coupling constants for some hydrocarbons calculated with different DFT methods and HF.^a

Molecule	Coupling	Method	K^{DSO}	K^{PSO}	K^{FC}	K^{SD}	K^{total}	J^{total}
CH ₄	¹ $K(\text{C}, \text{H})$ 41.5 (125.3 Hz)	BLYP	0.10	0.57	40.39	0.02	41.08	124.0
		BPW91	0.10	0.56	36.32	0.02	37.00	111.7
		B3LYP	0.09	0.55	40.25	0.00	40.89	123.5
		B3PW91	0.10	0.55	37.09	0.00	37.74	114.0
		BLYP (90,10)	0.10	0.56	41.01	0.00	41.67	125.8
		BLYP (50,50)	0.09	0.52	43.81	-0.05	44.37	134.0
		BLYP (10,90)	0.09	0.48	47.43	-0.11	47.89	144.6
		HF	0.09	0.48	48.19	-0.13	48.63	146.9
CH ₄	² $K(\text{H}, \text{H})$ -1.05 (-12.6 Hz)	BLYP	-0.27	0.31	-0.89	0.03	-0.82	-9.8
		BPW91	-0.27	0.31	-0.91	0.03	-0.84	-10.1
		B3LYP	-0.28	0.31	-0.97	0.03	-0.91	-10.9
		B3PW91	-0.28	0.31	-0.99	0.03	-0.93	-11.2
		BLYP (90,10)	-0.28	0.31	-0.99	0.03	-0.93	-11.2
		BLYP (50,50)	-0.28	0.31	-1.42	0.03	-1.36	-16.3
		BLYP (10,90)	-0.28	0.30	-1.94	0.04	-1.88	-22.6
		HF	-0.28	0.30	-2.02	0.04	-1.96	-23.5
C ₂ H ₆	¹ $K(\text{C}, \text{C})$ 45.6 (34.6 Hz)	BLYP	0.16	0.34	25.46	1.67	27.63	21.0
		BPW91	0.16	0.31	20.27	1.63	22.37	17.0
		B3LYP	0.16	0.35	29.03	1.67	31.21	23.7
		B3PW91	0.16	0.33	24.73	1.63	26.85	20.4
		BLYP (90,10)	0.16	0.33	28.31	1.68	30.48	23.2
		BLYP (50,50)	0.16	0.29	41.43	1.71	43.59	33.1
		BLYP (10,90)	0.16	0.25	58.48	1.74	60.63	46.1
		HF	0.16	0.25	62.29	1.74	64.44	49.0
C ₂ H ₆	¹ $K(\text{C}, \text{H})$ 41.3 (124.9 Hz)	BLYP	0.17	0.43	41.66	0.01	42.27	127.7
		BPW91	0.18	0.42	37.75	0.01	38.36	115.8
		B3LYP	0.17	0.42	41.63	-0.01	42.21	127.5
		B3PW91	0.17	0.41	38.59	-0.01	39.16	118.3
		BLYP (90,10)	0.17	0.42	42.34	0.00	42.93	129.7
		BLYP (50,50)	0.17	0.39	45.39	-0.07	45.88	138.6
		BLYP (10,90)	0.17	0.36	49.31	-0.13	49.71	150.1
		HF	0.17	0.36	50.13	-0.15	50.51	152.5
C ₂ H ₆	² $K(\text{C}, \text{H})$ -1.5 (-4.5 Hz)	BLYP	-0.09	0.11	-1.14	0.02	-1.1	-3.3
		BPW91	-0.09	0.11	-1.22	0.02	-1.18	-3.6
		B3LYP	-0.09	0.11	-1.39	0.02	-1.35	-4.1
		B3PW91	-0.09	0.12	-1.47	0.02	-1.42	-4.3
		BLYP (90,10)	-0.09	0.11	-1.37	0.02	-1.33	-4.0
		BLYP (50,50)	-0.09	0.11	-2.42	0.02	-2.38	-7.2
		BLYP (10,90)	-0.09	0.11	-3.86	0.02	-3.82	-11.5
		HF	-0.09	0.11	-4.11	0.02	-4.07	-12.3
C ₂ H ₆	² $K(\text{H}, \text{H})$	BLYP	-0.25	0.28	-0.65	0.03	-0.59	-7.1
		BPW91	-0.25	0.28	-0.69	0.03	-0.63	-7.6
		B3LYP	-0.25	0.28	-0.74	0.03	-0.68	-8.2
		B3PW91	-0.25	0.28	-0.77	0.03	-0.71	-8.5
		BLYP (90,10)	-0.25	0.28	-0.75	0.03	-0.69	-8.3
		BLYP (50,50)	-0.25	0.28	-1.14	0.03	-1.08	-13.0
		BLYP (10,90)	-0.25	0.28	-1.64	0.03	-1.58	-19.0
		HF	-0.26	0.28	-1.71	0.03	-1.66	-19.9
C ₂ H ₆	³ $K(\text{H}, \text{H})$ <i>trans</i> 0.67 (8.0 Hz)	BLYP	-0.26	0.26	1.18	0.00	1.18	14.2
		BPW91	-0.26	0.26	1.07	0.00	1.07	12.8
		B3LYP	-0.26	0.26	1.15	0.00	1.15	13.8
		B3PW91	-0.26	0.26	1.07	0.00	1.07	12.8
		BLYP (90,10)	-0.26	0.26	1.19	0.00	1.19	14.3
		BLYP (50,50)	-0.26	0.26	1.24	0.00	1.24	14.9
		BLYP (10,90)	-0.26	0.26	1.32	0.00	1.32	15.8
		HF	-0.26	0.26	1.34	0.00	1.34	16.1
C ₂ H ₆	³ $K(\text{H}, \text{H})$ <i>gauche</i> 0.67 ^b (8.0 Hz)	BLYP	-0.06	0.05	0.33	0.01	0.33	4.0
		BPW91	-0.06	0.05	0.30	0.01	0.30	3.6
		B3LYP	-0.06	0.05	0.33	0.01	0.33	4.0
		B3PW91	-0.06	0.05	0.31	0.01	0.31	3.7
		BLYP (90,10)	-0.06	0.05	0.34	0.01	0.34	4.1
		BLYP (50,50)	-0.06	0.05	0.38	0.01	0.38	4.6
		BLYP (10,90)	-0.06	0.05	0.45	0.01	0.45	5.4
		HF	-0.06	0.05	0.46	0.01	0.46	5.5
C ₂ H ₄	¹ $K(\text{C}, \text{C})$ 89.1	BLYP	0.10	-14.11	81.39	4.01	71.39	54.3
		BPW91	0.11	-13.89	72.72	4.30	66.24	48.1

TABLE III. (Continued).

Molecule	Coupling	Method	K^{DSO}	K^{PSO}	K^{FC}	K^{SD}	K^{total}	J^{total}
	(67.6 Hz)	B3LYP	0.10	-14.30	86.23	4.88	76.91	58.4
		B3PW91	0.10	-14.15	79.12	5.28	70.35	53.5
		BLYP (90,10)	0.10	-14.16	85.45	4.62	76.01	57.8
		BLYP (50,50)	0.09	-14.28	110.83	9.46	106.1	80.6
		BLYP (10,90)					n.c. ^c	
		HF					n.c. ^c	
C ₂ H ₄	¹ K(C, H)	BLYP	0.13	0.16	53.61	0.07	53.97	163.0
	51.8	BPW91	0.14	0.14	48.87	0.06	49.21	148.6
	(156.4 Hz)	B3LYP	0.13	0.13	53.71	0.04	54.01	163.1
		B3PW91	0.14	0.11	50.05	0.03	50.33	152.0
		BLYP (90,10)	0.13	0.14	54.54	0.05	54.86	165.7
		BLYP (50,50)	0.13	0.08	59.65	-0.04	59.82	180.7
		BLYP (10,90)					n.c. ^c	
		HF					n.c. ^c	
C ₂ H ₄	² K(C, H)	BLYP	-0.21	-0.46	0.03	0.01	-0.63	-1.9
	-0.8	BPW91	-0.21	-0.46	-0.15	0.02	-0.80	-2.4
	(-2.4 Hz)	B3LYP	-0.21	-0.47	-0.48	0.02	-1.14	-3.4
		B3PW91	-0.21	-0.47	-0.66	0.02	-1.32	-4.0
		BLYP (90,10)	-0.21	-0.46	-0.39	0.01	-1.05	-3.2
		BLYP (50,50)	-0.21	-0.47	-3.38	0.04	-4.02	-12.1
		BLYP (10,90)					n.c. ^c	
		HF					n.c. ^c	
C ₂ H ₄	² K(H, H)	BLYP	-0.37	0.38	1.11	0.00	1.12	13.4
	0.21	BPW91	-0.37	0.38	0.91	0.00	0.92	11.0
	(2.5 Hz)	B3LYP	-0.37	0.38	0.97	0.00	0.98	11.8
		B3PW91	-0.37	0.38	0.80	0.00	0.81	9.7
		BLYP (90,10)	-0.37	0.38	1.03	0.00	1.04	12.5
		BLYP (50,50)	-0.37	0.38	0.50	0.00	0.51	6.1
		BLYP (10,90)					n.c. ^c	
		HF					n.c. ^c	
C ₂ H ₄	³ K(H, H) <i>cis</i>	BLYP	-0.06	0.02	0.89	0.00	0.85	10.2
	0.97	BPW91	-0.06	0.02	0.83	0.00	0.79	9.5
	(11.7 Hz)	B3LYP	-0.06	0.02	0.89	0.01	0.86	10.3
		B3PW91	-0.06	0.02	0.87	0.01	0.84	10.1
		BLYP (90,10)	-0.06	0.02	0.92	0.00	0.88	10.6
		BLYP (50,50)	-0.06	0.02	1.25	0.01	1.22	14.6
		BLYP (10,90)					n.c. ^c	
		HF					n.c. ^c	
C ₂ H ₄	³ K(H, H) <i>trans</i>	BLYP	-0.29	0.26	1.28	0.02	1.27	15.2
	1.59	BPW91	-0.29	0.26	1.22	0.02	1.21	14.5
	(19.1 Hz)	B3LYP	-0.29	0.26	1.27	0.03	1.27	15.2
		B3PW91	-0.29	0.26	1.24	0.02	1.23	14.8
		BLYP (90,10)	-0.29	0.26	1.31	0.02	1.30	15.6
		BLYP (50,50)	-0.29	0.26	1.64	0.06	1.67	20.1
		BLYP (10,90)					n.c. ^c	
		HF					n.c. ^c	
C ₂ H ₂	¹ K(C, C)	BLYP	0.10	9.32	236.09	14.12	259.63	197.3
	226.0	BPW91	0.11	9.07	221.38	14.39	244.94	186.1
	(171.5 Hz)	B3LYP	0.09	11.03	238.99	15.27	265.38	201.7
		B3PW91	0.10	10.75	226.96	15.62	253.43	192.6
		BLYP (90,10)	0.09	10.09	239.26	15.02	264.46	201.0
		BLYP (50,50)	0.09	13.84	264.76	20.07	298.76	227.1
		BLYP (10,90)					n.c. ^c	
		HF	0.09	20.49	492.28	40.21	553.07	420.3
C ₂ H ₂	¹ K(C, H)	BLYP	0.07	-0.20	84.71	0.21	84.79	256.1
	82.4	BPW91	0.08	-0.21	77.84	0.20	77.91	235.3
	(248.7 Hz)	B3LYP	0.07	-0.39	84.39	0.17	84.24	254.4
		B3PW91	0.07	-0.39	79.11	0.17	78.96	238.5
		BLYP (90,10)	0.07	-0.29	85.87	0.19	85.84	259.2
		BLYP (50,50)	0.07	-0.67	92.53	0.19	92.12	278.2
		BLYP (10,90)					n.c. ^c	
		HF	0.06	-1.27	130.17	1.29	130.25	393.4
C ₂ H ₂	² K(C, H)	BLYP	-0.45	1.91	15.66	0.29	17.41	52.6
	16.3	BPW91	-0.45	1.89	14.88	0.31	16.63	50.2
	(49.3 Hz)	B3LYP	-0.45	2.05	15.15	0.31	17.06	51.5
		B3PW91	-0.45	2.04	14.51	0.31	16.41	49.6
		BLYP (90,10)	-0.45	1.97	15.47	0.3	17.29	52.2

TABLE III. (Continued).

Molecule	Coupling	HF Method	-0.45 K^{DSO}	2.77 K^{PSO}	-20.21 K^{FC}	-0.89 K^{SD}	-18.78 K^{total}	-56.7 J^{total}
C ₂ H ₂	² <i>K</i> (H, H) 0.8 (9.6 Hz)	BLYP (50,50)	-0.45	2.27	12.64	0.26	14.72	44.4
		BLYP (10,90)					n.c. ^c	
		HF	-0.45	2.77	-20.21	-0.89	-18.78	-56.7
		BLYP	-0.30	0.39	0.65	0.04	0.78	9.4
		BPW91	-0.30	0.39	0.68	0.05	0.82	9.8
		B3LYP	-0.30	0.41	0.69	0.05	0.85	10.2
		B3PW91	-0.30	0.41	0.73	0.05	0.89	10.7
		BLYP (90,10)	-0.30	0.40	0.71	0.05	0.86	10.3
BLYP (50,50)	-0.30	0.42	1.27	0.08	1.47	17.6		
BLYP (10,90)						n.c. ^c		
CH ₃ F	¹ <i>K</i> (C, F) -57.0 (161.9 Hz)	HF	-0.30	0.46	6.34	0.26	6.76	81.2
		BLYP	0.14	11.4	-108.05	7.73	-88.78	-252.1
		BPW91	0.14	11.5	-107.59	7.63	-88.32	-250.8
		B3LYP	0.14	11.84	-99.77	7.81	-79.98	-227.1
		B3PW91	0.14	11.88	-99.88	7.74	-80.12	-227.5
		BLYP (90,10)	0.14	11.45	-104.38	7.76	-85.03	-241.5
		BLYP (50,50)	0.13	11.49	-87.96	7.87	-68.56	-194.7
		BLYP (10,90)	0.13	11.19	-68.71	7.94	-49.45	-140.4
CH ₃ F	¹ <i>K</i> (C, H) 49.4 (149.1 Hz)	HF	0.13	11.21	-63.69	7.97	-44.56	-126.6
		BLYP	0.22	-0.04	47.58	0.01	47.77	144.3
		BPW91	0.23	-0.04	43.15	0.01	43.35	130.9
		B3LYP	0.23	-0.03	47.79	-0.01	47.98	144.9
		B3PW91	0.22	-0.04	44.32	-0.01	44.49	134.4
		BLYP (90,10)	0.22	-0.03	48.49	-0.01	48.67	147.0
		BLYP (50,50)	0.22	-0.03	52.53	-0.07	52.65	159.0
		BLYP (10,90)	0.21	-0.03	57.48	-0.15	57.51	173.7
CH ₃ F	² <i>K</i> (H, F) 4.11 (46.4 Hz)	HF	0.21	-0.03	58.51	-0.16	58.53	176.8
		BLYP	-0.16	1.19	3.60	-0.25	4.38	49.5
		BPW91	-0.16	1.22	3.28	-0.26	4.08	46.1
		B3LYP	-0.16	1.16	3.76	-0.26	4.50	50.8
		B3PW91	-0.16	1.18	3.49	-0.27	4.24	47.9
		BLYP (90,10)	-0.16	1.17	3.77	-0.26	4.52	51.1
		BLYP (50,50)	-0.16	1.09	4.33	-0.30	4.96	56.0
		BLYP (10,90)	-0.16	1.03	4.64	-0.35	5.16	58.3
CH ₃ F	² <i>K</i> (H, H) -0.8 (-9.6 Hz)	HF	-0.16	1.01	4.69	-0.36	5.18	58.5
		BLYP	-0.23	0.24	-0.59	0.04	-0.54	-6.5
		BPW91	-0.23	0.24	-0.62	0.04	-0.57	-6.9
		B3LYP	-0.23	0.24	-0.69	0.04	-0.64	-7.7
		B3PW91	-0.23	0.24	-0.72	0.04	-0.67	-8.0
		BLYP (90,10)	-0.23	0.24	-0.69	0.04	-0.64	-7.7
		BLYP (50,50)	-0.23	0.24	-1.11	0.04	-1.06	-12.7
		BLYP (10,90)	-0.23	0.24	-1.61	0.05	-1.55	-18.6
HF	-0.24	0.25	-1.68	0.05	-1.62	-19.5		

^a*K* values in SI units, *J* values in Hz. BLYP (*m,n*) denotes the BLYP-HF hybrid XC functionals described in Eq. (24). Experimental SSCC values are taken from Ref. 12 (exception CH₃: ¹*K*(C, H), Ref. 51; ²*K*(H, H), Ref. 52) and are given below the notation of the corresponding reduced SSCC in the second column. Calculations with the basis (11*s*,7*p*,2*d*/6*s*,2*p*)[7*s*,6*p*,2*d*/4*s*,2*p*] (basis III in Ref. 2) at experimental geometries (Ref. 46): CH₄: *r*(C-H) = 1.086 Å; C₂H₆: *r*(C-C) = 1.526 Å, *r*(C-H) = 1.088 Å, α(HCH) = 107.4°; C₂H₄: *r*(C-C) = 1.339 Å, *r*(C-H) = 1.088 Å, α(HCH) = 117.4°; C₂H₂: *r*(C-C) = 1.203 Å, *r*(C-H) = 1.061 Å; CH₃F: *r*(C-F) = 1.383 Å, *r*(C-H) = 1.094 Å, α(FCH) = 108.6°.

^bAverage value for *trans* and *gauche* ³*K*(H, H) SSCC for the staggered conformation.

^cNot converged.

mental values⁴⁹⁻⁵⁵ is $\mu = 5.0$ SI units for the [7*s*,6*p*,2*d*/4*s*,2*p*] basis set and 8.3 SI units for the smaller [6*s*,4*p*,1*d*/3*s*,1*p*] basis at the B3LYP level of theory. Relatively large differences between SSCC values obtained with the two basis sets are in most cases dominated by a large difference in the FC contribution. For all molecules considered in this work, the value of μ for calculated *K* values (relative to the experimentally based *K*) is 5.8 at BLYP (90, 10), 6.3 at B3PW91, 6.8 at BLYP, 7.4 at BLYP (50, 50), 8.5 at BPW91, 17.1 at BLYP (10, 90), and 36.9 SI units at HF,

which means that the B3LYP functional provides the best overall performance with regard to SSCCs.

A. AH_{*n*} molecules (class A)

For class A (Table II), the BLYP (50, 50) functional leads to the smallest deviations of calculated SSCCs from experimental values (mean absolute error $\mu = 1.5$ SI units) although B3LYP also provides reasonable values [μ (B3LYP) = 2.1 SI units]. In the following, we will refer to the latter if not otherwise noted. Both ¹*K*(A-H) and

TABLE IV. NMR spin–spin coupling constants for benzene calculated with the B3LYP functional.^a

Coupling	Method	K^{DSO}	K^{PSO}	K^{FC}	K^{SD}	K^{total}	J^{total}
¹ $K(\text{C}, \text{C})$	0.30	-9.49	84.58	1.78	77.17	58.6	56.0
² $K(\text{C}, \text{C})$	-0.03	0.09	-1.47	-1.17	-2.58	-2.0	2.5 ^b
³ $K(\text{C}, \text{C})$	-0.01	0.69	11.09	2.52	14.29	10.9	10.0
¹ $K(\text{C}, \text{H})$	0.25	0.09	52.09	0.04	52.47	158.5	158.4
² $K(\text{C}, \text{H})$	-0.12	-0.28	1.02	0.01	0.63	1.9	1.1
³ $K(\text{C}, \text{H})$	-0.16	0.13	2.58	-0.02	2.53	7.6	7.6
⁴ $K(\text{C}, \text{H})$	-0.15	0.14	-0.41	0.01	-0.41	-1.2	-1.3
³ $K(\text{H}, \text{H})$	-0.03	0.02	0.62	0.00	0.61	7.3	7.7 ^c
⁴ $K(\text{H}, \text{H})$	-0.15	0.15	0.11	0.00	0.11	1.3	1.4 ^c
⁵ $K(\text{H}, \text{H})$	-0.15	0.15	0.05	0.01	0.06	0.7	0.6 ^c

^a K values in SI units, J values in Hz. Experimental SSCC values are taken if not otherwise noted from Ref. 49. Calculations with the basis $(11s, 7p, 2d/6s, 2p)[7s, 6p, 2d/4s, 2p]$ (basis III in Ref. 2) at the experimental geometry (Ref. 46): $r(\text{C}-\text{C}) = 1.399 \text{ \AA}$, $r(\text{C}-\text{H}) = 1.101 \text{ \AA}$.

^bSign unknown.

^cReference 53.

² $K(\text{H}-\text{A}-\text{H})$ SSCCs increase in absolute value with decreasing atomic number of the heavy atom A (FH: 37.3; H₂O: 44.0; NH₃: 48.3 SI units, Table II). These trends are dominated, with a few exceptions found for ² $K(\text{H}-\text{A}-\text{H})$, by the FC term (FH: 19.4; H₂O: 35.8; NH₃: 45.4 SI units, Table II).

The FC interaction is mediated by spin polarization of the s -type valence electrons. According to Eq. (19) spin polarization will be large if there are both occupied and low-lying virtual orbitals present that have distinct s character at both of the coupling nuclei. There is always a relatively large rather spherically electron maximum of the density at the nucleus of heavy atom A due to the s -electrons, however, depending on the electronegativity of A and the polarity of the bond A–H the density maximum at nucleus H and the FC contribution will vary thus explaining the trends in calculated FC and ¹ $K(\text{A}-\text{H})$ values in the series FH, H₂O, NH₃ (Table II). Different XC functionals will differ in the description of the nuclear region and the s -electron density, which explains the sensitivity of the FC contributions to the XC functional (Table II).

The PSO term is important for the ¹ K values of the hydrides where it decreases (opposite to the FC contribution) in the order: FH: 17.8, H₂O: 7.7, NH₃: 2.6, CH₄: 0.6 SI units. For H₂ and the ² $K(\text{H}-\text{A}-\text{H})$ SSCCs, the PSO contributions are all < 1 SI unit, but reveal a similar trend as observed for the PSO contribution to ¹ K . The PSO interactions result from paramagnetic electron currents in the valence orbitals, which become significant when occupied and low-lying virtual orbitals are present that have distinct non- s -character (p -, d -orbitals) at the two coupled nuclei. In the series CH₄ to FH, the increase of the electronegativity of the heavy atom A leads to a polarization of the A–H bond density so that the electron density at the H atom becomes more anisotropic, which is described by the inclusion of more p -type polarization functions at the H atom into the A–H bonding orbital. Accordingly, the electron density at the H atom determines the increase of the PSO term with increasing electronegativity of A.

The electronegativity of A leads to a lowering of the energy of the $\sigma^*(\text{AH})$ orbital, which in connection with the increased p -character at H also influences the magnitude of

the PSO term. Matrix elements including the angular momentum operator as in the case of the PSO term will be relatively large if they involve a high-lying lone pair orbital with p_x or p_y character and a low-lying $\sigma^*(\text{AH})$ orbital with considerable p_z character at both coupling nuclei, which is the situation for H₂O and FH. Since s orbitals do not contribute to the PSO term (the PSO matrix elements become zero), the PSO interaction does not probe the electron density distribution in the immediate vicinity of the nucleus, which is the reason why the choice of the method (XC functional, basis set) influences the PSO term less strongly than the FC term.

The DSO term is smaller than 1 SI unit for all molecules considered (Table II) and nearly independent of the XC functional. The (absolutely seen) largest DSO terms are found for the ² $K(\text{H}-\text{A}-\text{H})$ coupling constants in H₂O (-0.58 SI units) and NH₃ (-0.41 SI units) where they lead to a canceling of the PSO contribution of opposite sign. The DSO contribution for H₂ is -0.26 SI units (PSO: 0.39, Table II) and, by this, it is smaller than for the ² $K(\text{H}-\text{A}-\text{H})$ coupling constants but larger than for the ¹ $K(\text{A}-\text{H})$ coupling constants in FH, H₂O, and NH₃ (Table II). In distinction to the other SSCC terms, the DSO term is determined by the electron density of the unperturbed state of the molecule. This implies that the magnitude of the DSO contribution is less dependent on the chemical environment of the coupling nuclei than the other terms. The choice of the XC functional, or more generally the choice of the calculational method, will be of little influence for the value of the DSO contribution as long as the electron density is described reasonably.

Although the calculated DSO contributions are all rather small, it pays out to get a better understanding of the DSO term so that unusual DSO values for larger molecules can be better understood. The major contributions to the DSO part of the tensor \underline{K} result from the core densities at the two coupled nuclei. These contributions are mainly anisotropic (see Appendix A) and, therefore, add only little to the isotropic average K , which explains the relatively small absolute magnitude of the DSO contributions to K . For instance, the principal values of the DSO contribution to \underline{K} for FH are 1.57 and -3.14 SI units, respectively, while the isotropic

average is 1.1×10^{-3} SI units. If there are third atoms in the molecule that are close to both coupling nuclei, then the core electron densities of these atoms will be responsible for the main contribution to K . This explains why the DSO contributions to the 2K coupling constants are generally higher than those to the 1K coupling constants. The larger DSO contribution in H_2 in comparison with the 1K coupling constants in FH, H_2O , and NH_3 is due to the shorter bond length in H_2 (see Appendix A).

The SD term makes no significant contribution to K for the molecules in class A, its absolute value being below 1 SI unit in all cases. The values are sensitive to the calculations method employed.

B. Hydrocarbon molecules (class B)

For the molecules of this class, the B3LYP values provide the best agreement with experiment as reflected by $\mu = 4.5$ SI units (Table III). Calculated SSCC values show the same trends as the corresponding experimental values and, since the latter were discussed in the literature in detail, we refrain from analyzing these trends and consider instead some typical relationships between the electronic structure of a molecule and its SSCCs.

The calculated ${}^1K(C-H)$ SSCCs increase in the order CH_4 (40.9 SI units; ${}^1J = 123.5$ Hz), C_2H_6 (42.2; 127.5), CH_3F (48.0; 144.9), C_2H_4 (54.0; 163.1), C_2H_2 (84.2; 204.9). Again, this trend is dominated by the value of the FC part, which in turn reflects the different electronic situations. The ${}^2K(H-C-H)$ SSCCs ($\mu = 4.3$ Hz) are all smaller than 1 SI unit while the ${}^2K(C-C-H)$ SSCCs are in the order of 1 SI unit except for C_2H_2 , where the calculated value is 17.06 SI units (51.5 Hz) in good agreement with the experimental value of 49.2 Hz.¹² The ${}^3K(H-C-C-H)$ SSCCs are all below 1 SI unit with the known trend of *trans*-SSCCs being higher than the corresponding *cis*- or *gauche*-SSCCs values.¹² The calculated ${}^1K(C-C)$ SSCCs ($\mu = 4.2$ Hz) increase in the order C_2H_6 (31.2 SI units, 23.7 Hz), C_2H_4 (76.9, 58.4), and C_2H_2 (265.4, 201.4, Table III) where again the FC term dominates (29.0; 86.2; 239.0 SI units). In contrast to the ${}^1K(C-H)$ SSCCs the PSO (0.35; -14.30; 11.03 SI units) and SD terms (1.67; 4.88; 15.27 SI units) make nonnegligible contributions to the ${}^1K(C-O)$ values.

The increase of the FC(C-C) term with increasing bond multiplicity is usually explained by the increasing s character of the bonding C-C σ orbital in the series C_2H_6 (sp^3 hybridization), C_2H_4 (sp^2), and C_2H_2 (sp). In addition, the FC and SD interactions are mediated by changes in the orbitals that give rise to spin polarization, i.e., that kind of changes that are described by triplet (T) excitations in wave function theory (see, e.g., Ref. 25 and Appendix B). Such changes are easier to induce the larger the gain in XC energy caused by the spin polarization is. One can test the tendency of a given molecule to spin polarize by calculating its magnetic susceptibility or, simpler, by determining the stability of the restricted DFT (RDFT) of the molecule: The lower the external stability of the RDFT description, the larger is the tendency of mixing in a T wave function into the DFT state function of the molecule and thus yielding an unrestricted DFT (UDFT)

description. Accordingly, the spin polarizability of the molecule is larger as is the gain in XC energy. Hence, the external stability of the RDFT description can be directly related to the magnitude of the two response terms FC and SD.

The external stability of the RDFT description^{56,57} decreases with increasing bond multiplicity, the lowest eigenvalues for singlet-triplet (S-T) transitions of the Hessian matrix being 0.31, 0.31, 0.31 for C_2H_6 , 0.10, 0.26, 0.26 for C_2H_4 , and 0.13, 0.17, 0.17 for C_2H_2 . The decrease of external stability in a closed-shell molecule is in turn an indication for the onset of nondynamic (static) electron correlation. Hence, the increase in the FC and SD contributions with increasing bond multiplicity within class B is related to the nondynamic electron correlation effects occurring in multiply bonded systems. Generally, DFT is poor at describing static electron correlation effects. The error caused by this shortcoming is larger for the unperturbed nonspin polarized state than for the perturbed spin polarized one, thus leading to an unbalanced description of perturbed and unperturbed states and inaccurate values for the FC and SD terms. The same problem occurs at the HF level of theory where it is more serious as HF does not cover (dynamic or static) correlation effects at all. This is responsible, e.g., for the large exaggeration of the FC and SD terms and, consequently, the total coupling constants of C_2H_2 at HF and is probably also the reason why the CPHF iterations did not converge for C_2H_4 (see Table III).

For the SD mechanism to be effective, either a pair of an occupied $s(d)$ and a low-lying virtual $d(s)$ orbital or a pair of an occupied p and a low-lying unoccupied p orbital are necessary. This becomes obvious when considering the form of the one-electron SD operator Eq. (21b) (components: xx, xy , etc.) and the expression for the SD part in Eq. (22). Accordingly, the $\pi - \pi^*$ pairs in multiple C-C bonds are important for an effective SD interaction as well as an effective PSO interaction mechanism.

Similarly as for the molecules of class A, the DSO contribution is always smaller than 1 SI unit for class B molecules. The effect of a third nucleus in the vicinity of the coupling nuclei can be observed in the same way as for class 1; for instance, the DSO contribution to the ${}^2K(H-C-H)$ coupling constant in CH_4 is -0.27 SI units as compared to 0.09 SI units for the ${}^1K(C-H)$ coupling constant.

Table IV gives K and J SSCCs for benzene calculated with the B3LYP functional. Agreement between calculated and measured SSCCs^{49,53} for $J(C,H)$, $J(C,H)$, and $J(H,H)$ are satisfactory as reflected by μ values of 2.7 Hz, 0.3 Hz, and 0.2 Hz, respectively, for basis set III. It is noteworthy that the ${}^1J(C-C)$, ${}^1J(C-H)$, and ${}^3J(H-C-C-H)$ coupling constants for benzene are close to their counterparts in C_2H_4 whereas the ${}^2J(C-C-H)$ coupling constants have different signs in C_2H_4 and C_6H_6 .

Most of the coupling constants for the molecules of class B follow the general rule that the sign of the SSCCs alternates with the number of bonds separating the coupling nuclei, i.e., that 1K coupling constants are positive, 2K coupling constants negative, 3K coupling constants positive, etc. However, substituent or geometrical effects can lead to a change sign as for example in the case of the ${}^2K(H-C-H)$ SSCC of

TABLE V. Reduced nuclear spin–spin coupling constants for CO, CO₂, and N₂ calculated with different DFT methods and HF.^a

Molecule	Coupling	Method	DSO	PSO	FC	SD	Total
CO	¹ K(C, C) −41.1 ^b	BLYP	−0.22	−35.51	−33.41	13.97	−55.17
		BPW91	−0.21	−35.95	−40.96	13.60	−63.52
		B3LYP	−0.22	−34.88	−27.02	14.97	−47.15
		B3PW91	−0.22	−35.26	−33.79	14.72	−54.55
		BLYP 90/10	−0.22	−35.05	−29.85	14.70	−50.42
		BLYP 50/50	−0.23	−32.88	−12.31	17.96	−27.46
		BLYP 10/90	−0.24	−30.24	12.89	22.12	4.53
		HF	−0.24	−29.65	19.93	22.91	12.95
		CO ₂	¹ K(C, O) −39.4 ^b	BLYP	0.19	−11.41	−63.13
BPW91	0.20			−11.14	−70.66	6.99	−74.61
B3LYP	0.19			−12.38	−50.24	6.88	−55.55
B3PW91	0.19			−12.16	−56.85	6.80	−62.01
BLYP 90/10	0.19			−11.89	−56.74	7.06	−61.38
BLYP 50/50	0.19			−13.58	−29.46	6.75	−36.10
BLYP 10/90	0.18			−14.87	2.36	6.34	−5.99
HF	0.17			−15.15	10.39	6.17	1.58
CO ₂	² K(O, O)			BLYP	−0.41	12.39	−38.65
		BPW91	−0.41	11.04	−38.51	25.23	−2.65
		B3LYP	−0.41	14.73	−33.12	28.21	9.41
		B3PW91	−0.41	13.52	−33.57	27.54	7.08
		BLYP 90/10	−0.41	13.48	−36.09	27.42	4.40
		BLYP 50/50	−0.41	17.43	−21.25	32.84	28.61
		BLYP 10/90	−0.41	20.24	2.05	37.94	59.82
		HF	−0.41	20.83	13.52	38.84	72.78
		N ₂	¹ K(N, N) −20 ± 7 ^c	BLYP	−0.26	−34.49	−22.08
BPW91	−0.26			−35.27	−30.22	24.14	−41.61
B3LYP	−0.27			−31.37	−15.03	28.74	−17.93
B3PW91	−0.27			−32.14	−22.61	28.38	−26.64
BLYP 90/10	−0.27			−32.90	−18.16	27.21	−24.12
BLYP 50/50	−0.28			−24.03	3.53	42.15	21.37
BLYP 10/90	−0.29			−9.26	59.57	79.69	129.71
HF	−0.29			−4.14	91.85	97.26	184.68

^aReduced SSCCs in SI units. BLYP (*m,n*) denotes the BLYP–HF hybrid XC functionals described in Eq. (24). Experimental SSCC values are given below the notation of the corresponding reduced SSCC in the second column. Calculations with the basis (11*s*,7*p*,2*d*/6*s*,2*p*)[7*s*,6*p*,2*d*/4*s*,2*p*] (basis III in Ref. 2) at experimental geometries (Ref. 46): CO: *r*(C–O) = 1.128 Å; CO₂: *r*(C–O) = 1.162 Å; N₂: *r*(N–N) = 1.0977 Å.

^bReference 54.

^cReference 55. Sign is unknown.

C₂H₄ and the ²K(C–C–H)SSCC of C₂H₂ (Table III). Theory can be used to verify the sign of the SSCC as in the case of the ²K(C–C–C) coupling constant of C₆H₆, which should be negative.

C. Molecules with multiple bonds (class C)

The SSCC of molecules CO, CO₂, and N₂ are more difficult to calculate than those of class A and class B molecules, which is reflected by the *K* values listed in Table V, and therefore, we discuss these molecules separately. At B3LYP, absolute SSCC values deviate by $\mu = 8.1$ SI units the average, which is small compared to HF results ($\mu = 91.3$ SI units). The latter result confirms that HF performs poorly when calculating SSCCs of multiple-bonded molecules.²⁵ Both PSO and SD terms are nonnegligible in comparison to the FC term while the DSO term is negligible contributing less than 1 SI units to the total *K* value. The FC and SD terms depend on the choice of the XC functional more strongly than the PSO term. As discussed in connection with multiple-bonded molecules of class B, the FC and SD terms are sensitive to the balanced treatment of electron cor-

relation in the unperturbed and perturbed states, which is different for different XC functionals as well as between DFT and HF theory.

D. Comparison of CPDFT and SOS DFT

In Table VI, SSCCs calculated at the CPDFT and at the SOS DFT level of theory are compared for molecules of classes A, B, and C. The mean absolute deviation for all SSCCs considered is $\mu = 5.0$ SI units for CPDFT but 12.8 SI units for SOS DFT. This confirms that the dependence of $\tilde{\mathbf{F}}_A^X$ in Eqs. (16) on the perturbed orbitals, thus requiring an iterative determination of this operator, significantly influences the value of the SSCCs and improves its accuracy. This *coupling*, which enters into the CPDFT description, tends to increase the PSO, FC, and SD terms. For the FC and SD terms, SOS DFT does not account for the possible energy gain caused by spin polarization and accordingly underestimates the response of the orbitals to the perturbation by the magnetic fields of the nuclei, i.e., *T* and *S* excitations in the sense of Appendix B are treated in the same way.

TABLE VI. Comparison of reduced NMR spin-spin coupling constants calculated with CPDFT and SOS DFT using the B3LYP functional.^a

Molecule	Coupling	Method	DSO	PSO	FC	SD	Total
H ₂	¹ K(H, H)	CPDFT	-0.26	0.39	22.63	0.25	23.01
	23.3	SOS DFT		0.36	9.78	0.16	10.04
FH	¹ K(H, F)	CPDFT	0.00	17.81	19.39	0.11	37.31
	46.8±2	SOS DFT		14.22	15.05	0.39	29.66
H ₂ O	¹ K(O, H)	CPDFT	0.09	7.68	35.83	0.43	44.03
	48	SOS DFT		6.36	23.47	0.39	30.31
	² K(H, H)	CPDFT	-0.58	0.72	-0.76	0.08	-0.54
	-0.6	SOS DFT		0.64	0.11	0.04	0.21
NH ₃	¹ K(N, H)	CPDFT	0.11	2.59	45.44	0.17	48.31
	50	SOS DFT		2.26	26.82	0.17	29.36
	² K(H, H)	CPDFT	-0.41	0.49	-0.84	0.05	-0.71
CH ₄	-0.87	SOS DFT		0.45	0.05	0.03	0.12
	¹ K(C, H)	CPDFT	0.09	0.55	40.25	0.00	40.89
	41.5	SOS DFT		0.49	22.41	0.04	23.03
C ₂ H ₆	² K(H, H)	CPDFT	-0.28	0.31	-0.97	0.03	-0.91
	-1.05	SOS DFT		0.29	-0.02	0.02	0.01
	¹ K(C, C)	CPDFT	0.16	0.35	29.03	1.67	31.21
	45.6	SOS DFT		0.27	9.67	1.08	11.18
	¹ K(C, H)	CPDFT	0.17	0.42	41.63	-0.01	42.21
	41.3	SOS DFT		0.37	23.01	0.03	23.58
	² K(C, H)	CPDFT	-0.09	0.11	-1.39	0.02	-1.35
	-1.5	SOS DFT		0.11	0.36	0.01	0.39
	² K(H, H)	CPDFT	-0.25	0.28	-0.74	0.03	-0.71
		SOS DFT		0.26	0.08	0.02	0.11
C ₂ H ₄	³ K(H, H) <i>trans</i>	CPDFT	-0.26	0.26	1.15	0.00	1.15
	(0.67) ^b	SOS DFT		0.24	0.53	0.00	0.51
	³ K(H, H) <i>gauche</i>	CPDFT	-0.06	0.05	0.33	0.01	0.33
	(0.67) ^b	SOS DFT		0.05	0.14	0.00	0.13
	¹ K(C, C)	CPDFT	0.10	-14.34	86.23	4.88	76.87
	89.1	SOS DFT		-10.70	50.75	1.08	41.23
	¹ K(C, H)	CPDFT	0.13	0.13	53.71	0.04	54.01
	51.8	SOS DFT		0.17	29.08	0.06	29.44
	² K(C, H)	CPDFT	-0.21	-0.47	-0.48	0.00	-1.16
	-0.8	SOS DFT		-0.33	1.56	0.02	1.04
C ₂ H ₂	² K(H, H)	CPDFT	-0.37	0.38	0.97	0.00	0.98
	0.21	SOS DFT		0.35	0.82	0.00	0.80
	³ K(H, H) <i>cis</i>	CPDFT	-0.06	0.02	0.89	0.01	0.86
	0.97	SOS DFT		0.02	0.35	0.00	0.31
	³ K(H, H) <i>trans</i>	CPDFT	-0.29	0.26	1.27	0.03	1.27
	1.59	SOS DFT		0.25	0.54	0.0	0.50
	¹ K(C, C)	CPDFT	0.01	11.03	238.99	15.26	265.29
	226.0	SOS DFT		5.38	173.09	5.64	184.12
	¹ K(C, H)	CPDFT	0.07	-0.38	84.39	0.17	84.25
	82.4	SOS DFT		-0.07	46.91	0.12	47.03
CH ₃ F	² K(C, H)	CPDFT	-0.45	2.05	15.15	0.31	17.06
	16.3	SOS DFT		1.51	9.37	0.21	10.64
	² K(H, H)	CPDFT	-0.30	0.41	0.69	0.05	0.85
	0.8	SOS DFT		0.36	0.22	0.02	0.30
	¹ K(C, F)	CPDFT	0.14	11.84	-99.77	7.81	-79.98
	-57.0	SOS DFT		8.23	-66.97	5.05	-53.05
	² K(C, H)	CPDFT	0.23	-0.03	47.79	-0.01	47.98
	49.4	SOS DFT		-0.02	26.18	0.03	26.42
	¹ K(H, F)	CPDFT	-0.16	1.16	3.76	-0.26	4.50
	4.11	SOS DFT		0.92	1.54	-0.11	2.19
CO	² K(H, H)	CPDFT	-0.23	0.24	-0.69	0.04	-0.64
	-0.8	SOS DFT		0.23	0.12	0.02	0.14
	¹ K(C, O)	CPDFT	-0.22	-34.88	-27.02	14.97	-47.15
	-41.1	SOS DFT		-26.83	-25.27	7.17	-45.15
CO ₂	¹ K(C, O)	CPDFT	0.19	-12.38	-50.24	6.88	-55.55
	-39.4	SOS DFT		-10.22	-23.56	4.03	-29.56
	² K(O, O)	CPDFT	-0.41	14.73	-33.12	28.21	9.41
N ₂		SOS DFT		6.94	-22.19	11.85	-3.81
	¹ K(N, N)	CPDFT	-0.27	-31.37	-15.03	28.74	-17.93
	-20.0 ^c	SOS DFT		-26.17	-17.91	10.97	-33.38

^aAll values in SI units. Experimental SSCC values (see Tables II, III, and IV) are given below the notation of the corresponding reduced SSCC in the second column. Calculations with the basis (11s,7p,2d/6s,2p)[7s,6p,2d/4s,2p] (basis III in Ref. 2) at experimental geometries (Ref. 46) (see Tables II, III, and V).

^bAverage value for *trans* and *gauche* ³K(H, H) SSCC for the staggered conformation.

^cSign is unknown.

V. CONCLUSIONS

For the first time, the CPDFT formalism for the calculation of NMR spin–spin coupling constants was implemented completely. We calculated coupling constants for several classes of molecules and investigated the influence of the XC functional, the basis set, and the coupling in the CPDFT equations on the results. The following conclusions can be drawn from this work:

- (1) DFT is useful to calculate SSCC with a reasonable accuracy at reasonable cost. In this way, the calculation of SSCC for larger molecules becomes possible.
- (2) The inclusion of electron correlation effects via the XC functional makes DFT clearly superior to HF when calculating SSCCs. Especially for molecules that are close to an external instability (see Sec. IV), DFT still yields SSCCs of reasonable accuracy while HF completely fails as was pointed out before by other authors (see, e.g., Ref. 25).
- (3) The SD contribution to the coupling constants is significant in systems with multiple bonds. Calculating the SD contribution to the SSCC increases its accuracy.
- (4) Of all XC functionals considered in this work, B3LYP leads to the highest accuracy for the set of molecules investigated. This is in line with the general experience that B3LYP performs well for the calculation of electronic properties. We therefore recommend the use of B3LYP for the calculation of SSCCs.
- (5) The DFT values for coupling constants are sensitive to the basis set. Hence, care has to be taken with the choice of the basis set.
- (6) It is important to treat the dependence of the DFT operator $\tilde{\mathbf{F}}_A^X$ [Eq. (16)] on the perturbed orbitals (*coupling*)

within the CPDFT formalism in an appropriate way. The application of SOS DFPT^{21,30} is not justified in general.

- (7) The dependence of the FC, DSO, PSO, and SD term on the electronic structure of a molecule was analyzed and in each case predictions were made under which conditions a particular contribution becomes large.

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APPENDIX A

In this Appendix, it is shown that the contribution to K_{AB}^{DSO} from the *s*-type densities at atoms *A* and *B* is essentially anisotropic. For this purpose, we express K_{AB}^{DSO} in terms of the auxiliary quantity $\tilde{K}_{AB}^{\text{DSO}}$ for a charge distribution $\varrho(r_A)$ that is rotationally symmetric at the position \mathbf{R}_A of nucleus *A*:

$$\tilde{K}_{AB}^{\text{DSO}} = \int d^3r \varrho(r_A) \frac{\mathbf{r}_A}{r_A^3} \circ \frac{\mathbf{r}_B}{r_B^3}. \quad (\text{A1})$$

The components \mathbf{r}_A/r_A^3 are spherical harmonics with $l=1$ at \mathbf{R}_A . Hence, if one expands the term \mathbf{r}_B/r_B^3 in the integral in Eq. (A1) into spherical harmonics at \mathbf{R}_A , only the $l=1$ term of this expansion will contribute to $\tilde{K}_{AB}^{\text{DSO}}$. The spherical-harmonics (von Neumann) expansion of \mathbf{r}_B/r_B^3 reads⁵⁸

$$\frac{\mathbf{r}_B}{r_B^3} = \begin{cases} -\frac{1}{R_{AB}^2} \frac{\mathbf{R}_{AB}}{R_{AB}} + \frac{1}{R_{AB}^3} \left[-3 \frac{\mathbf{R}_{AB}}{R_{AB}} \circ \frac{\mathbf{R}_{AB}}{R_{AB}} + \frac{1}{3} \right] \mathbf{r}_A + \dots & \text{for } r_A < R_{AB} \\ \frac{1}{r_A^3} \mathbf{r}_A + \dots & \text{for } r_A > R_{AB} \end{cases}, \quad (\text{A2})$$

where $\mathbf{R}_{AB} = \mathbf{R}_B - \mathbf{R}_A$, $R_{AB} = |\mathbf{R}_{AB}|$, and the underbraces mark the $l=1$ terms of the expansion. This leads to

$$\begin{aligned} \tilde{K}_{AB}^{\text{DSO}} &= \frac{1}{R_{AB}^3} \left[-3 \frac{\mathbf{R}_{AB}}{R_{AB}} \circ \frac{\mathbf{R}_{AB}}{R_{AB}} + \frac{1}{3} \right] \int_{r_A < R_{AB}} d^3r \varrho(r_A) \frac{\mathbf{r}_A \circ \mathbf{r}_A}{r_A^3} + \int_{r_A > R_{AB}} d^3r \varrho(r_A) \frac{\mathbf{r}_A \circ \mathbf{r}_A}{r_A^6} \\ &= \frac{1}{R_{AB}^4} \left(\underbrace{\int_{r_A < R_{AB}} d^3r \frac{R_{AB}}{r_A} \varrho(r_A)}_{=Q_{<}} \left[-3 \frac{\mathbf{R}_{AB}}{R_{AB}} \circ \frac{\mathbf{R}_{AB}}{R_{AB}} + \frac{1}{3} \right] + \underbrace{\int_{r_A > R_{AB}} d^3r \left(\frac{R_{AB}}{r_A} \right)^4 \varrho(r_A)}_{=Q_{>}} \right). \end{aligned} \quad (\text{A3})$$

In the last expression, $Q_{<}$ is the part of the density ϱ inside a sphere with radius R_{AB} centered at \mathbf{R}_A and weighted with the factor $R_{AB}/r_A > 1$ while $Q_{>}$ is the part of ϱ outside this sphere, weighted with the factor $(R_{AB}/r_A)^4 < 1$. As the density is concentrated close to \mathbf{R}_A , $Q_{<}$ will in general be large compared to $Q_{>}$. In atomic units it is

$$\underline{K}_{AB}^{\text{DSO}} = \alpha^4 (\text{Tr} \underline{\tilde{K}}_{AB}^{\text{DSO}} \underline{1} - \underline{\tilde{K}}_{AB}^{\text{DSO}}), \quad (\text{A4})$$

hence

$$\underline{K}_{AB}^{\text{DSO}} = \alpha^4 \frac{1}{R_{AB}^4} \left(Q_{<} \left[3 \frac{\mathbf{R}_{AB}}{R_{AB}} \circ \frac{\mathbf{R}_{AB}}{R_{AB}} - \underline{1} \right] + 2Q_{>} \underline{1} \right),$$

$$K_{AB}^{\text{DSO}} = \alpha^4 \frac{2}{R_{AB}^4} Q_{>} \underline{1}. \quad (\text{A5})$$

The tensor $\underline{K}_{AB}^{\text{DSO}}$ is dominated by contributions due to $Q_{<}$. These contributions are completely anisotropic and only $Q_{>}$ makes a contribution to the isotropic average K_{AB}^{DSO} .

For comparison, we estimate the magnitude of the contribution to K_{AB}^{DSO} resulting from the core charge of a third nucleus C . In lowest order one can assume that the total amount Q_C of this charge is concentrated at \mathbf{R}_C . Then it is

$$K_{AB}^{\text{DSO}} \approx 2\alpha^4 Q_C \frac{\mathbf{R}_{AC} \mathbf{R}_{BC}}{R_{AC}^3 R_{BC}^3}. \quad (\text{A6})$$

As Q_C is the total charge at nucleus C , it is in general large compared to $Q_{>}$. The prefactor $\mathbf{R}_{AC}\mathbf{R}_{BC}/(R_{AC}R_{BC})^3$ decays rapidly with R_{AC} and R_{BC} . Hence, the contributions from nucleus C will be most important if C is bonded with both A and B , i.e., if K_{AB} is a geminal coupling constant. This explains why the DSO contributions are larger for geminal 2K rather than for bond coupling constants 1K . In addition, Eq. (A6) shows that the contribution of Q_C to K_{AB}^{DSO} will be positive if $\angle ACB$ is pointed and negative if this angle is blunt. According to Thales' theorem, this means that Q_C in leading order will make a negative contribution to the coupling constant if nucleus C lies within the sphere with diameter AB and a positive contribution for C outside this sphere as has been pointed out, e.g., in Ref. 30.

APPENDIX B

In wave-function-oriented methods, the behavior of the PSO term on the one hand and the FC and SD terms on the other hand can be discussed by decomposing the one-particle excitations of the system into S and T excitations (see, e.g., Ref. 25). The notion of S and T excitations makes no immediate sense for DFT as the KS determinant must not be regarded as an approximation to the real wave function. However, one can represent the first-order changes of the KS orbitals in a way that is formally analogous to S and T excitations and allows to discuss the effect on the coupling, i.e., the operator $\tilde{\mathbf{F}}_A^X$, on the first-order KS orbitals.

In this Appendix, we shall assume that the perturbation operator $h_{ss'}$ is either isotropic in spin space, i.e., $h_{ss'}$ can be written as

$$h_{ss'}^S = h^S \delta_{ss'}, \quad (\text{B1a})$$

where h^S is a spin-free operator, or proportional to the σ_z spin matrix in spin space, i.e., $h_{ss'}$ can be represented as

$$h_{ss'}^T = h^T \delta_{ss'}, \quad (\text{B1b})$$

where h^T is a spin-free operator. Operators that are of the form of Eq. (B1a) or (B1b) will be called S or T operators, respectively. The operators $h_{A,j}^{\text{PSO}}$ from Eq. (6e) are S opera-

tors. The operators $h_{A,j}^{\text{FC}}$ from Eq. (6f) and the $h_{A,j}^{\text{SD}}\sigma_j$ from Eq. (21a) are T operators in this sense provided that the spin quantization axis is rotated to the j axis as is tacitly assumed in the following. S and T operators according to this definition do not mix α and β orbitals. The first-order perturbed KS orbitals can therefore be expanded in the zeroth-order virtual KS orbitals as

$$|\psi_{k\sigma}^A\rangle = \sum_a^{\text{virt}} c_{ka}^\sigma |\psi_{a\sigma}^{(0)}\rangle. \quad (\text{B2})$$

We consider here one component of the vector $|\psi^A\rangle$; the indices i for the Cartesian coordinate and A for the nucleus are omitted in the following.

The coefficients c_{ka}^σ describe the α and β perturbed orbitals separately. Instead of the c_{ka}^σ , one can introduce expansion coefficients C_{ka}^S, C_{ka}^T according to

$$C_{ka}^S = \frac{1}{\sqrt{2}} (c_{ka}^\alpha + c_{ka}^\beta), \quad (\text{B3a})$$

$$C_{ka}^T = \frac{1}{\sqrt{2}} (c_{ka}^\alpha - c_{ka}^\beta). \quad (\text{B3b})$$

The C_{ka}^S describe rotations of the KS orbitals that leave the system spin-unpolarized. If $\text{Re } C_{ka}^S$ is nonzero, these orbital rotations result in a first-order change of the total electron density. These changes of the orbitals correspond to S excitations in wave function theory. The C_{ka}^T describe infinitesimal rotations of the orbitals that leave the total density unchanged but result into spin polarization, i.e., lead to an open-shell system. These orbital rotations correspond to T excitations in wave function theory.

The transformation of the c_{ka}^σ into S and T contributions allows a transparent discussion of the relation between the coupling (dependence of the operator $\tilde{\mathbf{F}}_A^X$ on the perturbed orbitals) in CPDFT and the stability of the KS solution. For this purpose, we write down the change of the total energy to second order in the C_{ka}^S, C_{ka}^T :

$$\delta E = \delta E(A) + \delta E(\bar{A}) + \delta E(B) + \delta E(\bar{B}), \quad (\text{B4a})$$

$$\delta E(A) = \frac{1}{2} \sum_{ka,k'a'} A_{ka,k'a'} \text{Re } C_{ka}^S \text{Re } C_{k'a'}^S, \quad (\text{B4b})$$

$$\delta E(\bar{A}) = \frac{1}{2} \sum_{ka,k'a'} \bar{A}_{ka,k'a'} \text{Im } C_{ka}^S \text{Im } C_{k'a'}^S, \quad (\text{B4c})$$

$$\delta E(B) = \frac{1}{2} \sum_{ka,k'a'} B_{ka,k'a'} \text{Re } C_{ka}^T \text{Re } C_{k'a'}^T, \quad (\text{B4d})$$

$$\delta E(\bar{B}) = \frac{1}{2} \sum_{ka,k'a'} \bar{B}_{ka,k'a'} \text{Im } C_{ka}^T \text{Im } C_{k'a'}^T. \quad (\text{B4e})$$

Here, the $A_{ka,k'a'}$, $\bar{A}_{ka,k'a'}$, $B_{ka,k'a'}$, and $\bar{B}_{ka,k'a'}$ are the stability matrices for real internal stability, complex internal stability, real external instability, and complex external instability.^{56,57} The eigenvalues of the stability matrices determine the stability of the solution against the corresponding kind of perturbations. If one of the matrices has one or more

negative eigenvalues, the solution is unstable with respect to the corresponding types of orbital relaxations; if the smallest eigenvalue is positive but close to zero then the system is close to an instability. If the KS operator were independent of the KS orbitals, the stability matrices would get the form

$$A_{ka,k'a'} = \bar{A}_{ka,k'a'} = B_{ka,k'a'} = \bar{B}_{ka,k'a'} = 2\delta_{kk'}\delta_{aa'}(\varepsilon_a - \varepsilon_k), \quad (\text{B5})$$

and the lowest eigenvalue of all stability matrices were twice the difference between the orbital energies for LUMO and HOMO. The dependence of the KS operator on the KS orbitals leads to additional terms in the stability matrices. Reference 56 gives the explicit form of the stability matrices for HF, Ref. 57 the form of A , \bar{A} , and B for DFT in local-density and generalized-gradient approximations. Consequently, the lowest eigenvalues of the stability matrices can become smaller than twice the HOMO–LUMO energy difference and in particular negative. Hence, instabilities or near-instabilities of the KS solution are caused by a small HOMO–LUMO energy difference in connection with a strong dependence of the KS operator on the orbitals.

If a S or T perturbation is switched on then the total energy change up to second order consists of δE from Eqs. (B4) and the energy change

$$\begin{aligned} \delta E^Y = & \sqrt{2} \sum_{ka} \text{Re} C_{ka}^Y \langle \phi_a^{(0)} | \text{Re} h^Y | \phi_k^{(0)} \rangle \\ & + \sqrt{2} \sum_{ka} \text{Im} C_{ka}^Y \langle \phi_a^{(0)} | \text{Im} h^Y | \phi_k^{(0)} \rangle \end{aligned} \quad (\text{B6})$$

with $Y=S$ or $Y=T$ for a S or T operator, respectively. The CPDFT equation can be found from the requirement that $\delta E + \delta E^X$ has to be stationary under orbital rotations, i.e., changes of the C_{ka}^X . This leads to linear equation systems for the C_{ka}^X . The operators $h_{A,i}^{\text{PSO}}$ are purely imaginary-valued S operators, the operators $h_{A,i}^{\text{FC}}$ and $h_{A,ij}^{\text{SD}}\sigma_j$ are purely real-valued T operators. For these two cases, the CPDFT equations take the form

$$\sum_{k'a'} \bar{A}_{ka,k'a'} \text{Im} C_{k'a'}^S = \sqrt{2} \langle \phi_a^{(0)} | \text{Im} h^S | \phi_k^{(0)} \rangle, \quad (\text{B7a})$$

$$\sum_{k'a'} B_{ka,k'a'} \text{Re} C_{k'a'}^T = \sqrt{2} \langle \phi_a^{(0)} | \text{Re} h^T | \phi_k^{(0)} \rangle. \quad (\text{B7b})$$

These equations are equivalent to the CPDFT set of Eqs. (15), (16). While the coupling is incorporated in the operator \mathbf{F}_B^X in Eq. (15), it is accounted for in the coefficient matrices on the l.h.s. in Eqs. (B7a). If the coupling is neglected, i.e., Eq. (B5) is used for the stability matrices, then Eqs. (B7) will be equivalent to the SOS DFPT equations. Equations (B7) will yield large values for the $C_{k'a'}^Y$ relative to the matrix elements of the h^Y indicating a strong response of the KS orbitals to the perturbation if the corresponding stability matrix has one or more small eigenvalues. That is, for systems that are close to a complex internal instability the PSO contribution to the coupling constants can be expected to become large with large differences between SOS DFPT and CPDFT values. The same holds for the FC and SD terms in a system close to a S – T instability, as was discussed in Sec.

IV. For systems close to some instability, only one or a few of the eigenvalues of the corresponding stability matrix become small. The ratio of the largest and smallest eigenvalue of the equation system becomes therefore large, and the equation system becomes ill-conditioned. This explains the convergence problems that occur for the CPHF and CPDFT procedures for systems that are close to an instability.

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