

Vibrational corrections to indirect nuclear spin–spin coupling constants calculated by density-functional theory

Torgeir A. Ruden, Ola B. Lutnæs, and Trygve Helgaker^{a)}

Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo, Norway

Kenneth Ruud

Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway

(Received 18 November 2002; accepted 5 March 2003)

At the present level of electronic-structure theory, the differences between calculated and experimental indirect nuclear spin–spin coupling constants are typically as large as the vibrational contributions to these constants. For a meaningful comparison with experiment, it is therefore necessary to include vibrational corrections in the calculated spin–spin coupling constants. In the present paper, such corrections have been calculated for a number of small molecular systems by using hybrid density-functional theory (DFT), yielding results in good agreement with previous wave-function calculations. A set of empirical equilibrium spin–spin coupling constants has been compiled from the experimentally observed constants and the calculated vibrational corrections. A comparison of these empirical constants with calculations suggests that the restricted-active-space self-consistent field method is the best approach for calculating the indirect spin–spin coupling constants of small molecules, and that the second-order polarization propagator approach and DFT are similar in performance. To illustrate the usefulness of the presented method, the vibrational corrections to the indirect spin–spin coupling constants of the benzene molecule have been calculated. © 2003 American Institute of Physics. [DOI: 10.1063/1.1569846]

I. INTRODUCTION

The indirect nuclear spin–spin coupling constants of nuclear magnetic resonance (NMR) spectroscopy may nowadays be calculated by a variety of electronic-structure methods.¹ Until recently, the most popular methods for such calculations were multiconfigurational self-consistent field (MCSCF) theory^{2–12} and the second-order polarization propagator approach (SOPPA),^{13–24} although some work has been carried out using coupled-cluster theory.^{25–29} Lately, density-functional theory (DFT) has become a popular tool for the calculation of spin–spin coupling constants. The first successful implementations are those by Malkin, Malkina, and Salahub from 1994³⁰ and by Dickson and Ziegler from 1996.³¹ In 2000, Sychrovsky, Gräfenstein and Cremer³² and Helgaker, Watson and Handy³³ independently presented fully analytical spin–spin implementations at the hybrid level of DFT, demonstrating that hybrid theory represents a reliable and inexpensive method for the calculation of such constants.

The current status of the theory for the calculation of spin–spin coupling constants is now such that the difference between theory and experiment is often no larger than the vibrational corrections to the couplings, which may constitute as much as 10% of the coupling.^{17,34} Therefore, to make further progress towards the accurate description of indirect nuclear spin–spin coupling constants, it has become important to develop efficient methods for the calculation of vibrational corrections.

The vibrational corrections to molecular properties can be calculated in several ways. For polyatomic molecules, the most common techniques are based on perturbation theory.^{35–40} Although the details may vary, these methods all require the calculation of the geometrical derivatives of the molecular property itself as well as of the potential-energy surface. Usually, no implementation exists for the analytical evaluation of property derivatives, which are instead obtained numerically by, for example, finite-difference techniques, making the calculation of vibrational corrections expensive. Therefore, to calculate vibrational corrections for systems containing 10–15 atoms, we must reduce as much as possible the cost of evaluating the molecular property at each geometry. This is particularly true for indirect nuclear spin–spin coupling constants, whose evaluation in general is very expensive.

In view of the low cost and the high accuracy achieved by hybrid DFT for the calculation of indirect spin–spin couplings constants, here we shall apply this theory to the calculation of the vibrational corrections to these constants. Provided DFT yields good results compared to wave-function methods for small molecules, it will represent a very useful method for the calculation of vibrationally corrected indirect spin–spin coupling constants in large molecules. Here we therefore first apply DFT to the calculation of vibrational corrections to the nuclear spin–spin coupling constants of small molecules, comparing these corrections with those previously obtained using wave-function methods. Next, we apply DFT to the calculation of the vibrationally averaged indirect nuclear spin–spin couplings of benzene, a molecule too big to be treated accurately by non-DFT methods.

^{a)}Electronic mail: trygve.helgaker@kjemi.uio.no

II. THEORY AND IMPLEMENTATION

In this section, we discuss in some detail the calculation of vibrationally averaged indirect nuclear spin–spin coupling constants. After a review of Ramsey’s theory of spin–spin coupling constants in Sec. II A, we describe in Sec. II B the calculation of vibrational corrections to the spin–spin coupling constants as implemented in DALTON.⁴¹

A. Ramsey’s theory

The indirect nuclear spin–spin coupling constants can be calculated as derivatives of the electronic energy. We first recall that the nuclear magnetic moments \mathbf{M}_K are related to the nuclear spins \mathbf{I}_K as

$$\mathbf{M}_K = \gamma_K \hbar \mathbf{I}_K, \quad (1)$$

where γ_K is the nuclear magnetogyric ratio of nucleus K . The normal and reduced indirect nuclear spin–spin coupling constants \mathbf{J}_{KL} and \mathbf{K}_{KL} may then be calculated as the total derivatives of the energy with respect to the nuclear magnetic moments,

$$\mathbf{J}_{KL} = \hbar \frac{\gamma_K}{2\pi} \frac{\gamma_L}{2\pi} \mathbf{K}_{KL} = \hbar \frac{\gamma_K}{2\pi} \frac{\gamma_L}{2\pi} \frac{d^2 E}{d\mathbf{M}_K d\mathbf{M}_L}. \quad (2)$$

In the Born–Oppenheimer approximation, Ramsey’s nonrelativistic expression for the reduced spin–spin coupling constants \mathbf{K}_{KL} of a closed-shell molecule is given by⁴²

$$\begin{aligned} \mathbf{K}_{KL} = & \langle 0 | \mathbf{h}_{KL}^{\text{DSO}} | 0 \rangle + 2 \sum_{s \neq 0} \frac{\langle 0 | \mathbf{h}_K^{\text{PSO}} | s \rangle \langle s | \mathbf{h}_L^{\text{PSOT}} | 0 \rangle}{E_0 - E_s} \\ & + 2 \sum_t \frac{\langle 0 | \mathbf{h}_K^{\text{FC}} + \mathbf{h}_K^{\text{SD}} | t \rangle \langle t | \mathbf{h}_K^{\text{FCT}} + \mathbf{h}_K^{\text{SDT}} | 0 \rangle}{E_0 - E_t}. \end{aligned} \quad (3)$$

While the first summation is over all singlet states $|s\rangle$ different from the ground state $|0\rangle$, the second is over all triplet states $|t\rangle$. The energies E_0 , E_s , and E_t are those of the ground state, of the singlet excited states, and of the triplet excited states, respectively. In atomic units, the operators occurring in Eq. (3) are, respectively, the diamagnetic spin–orbit (DSO) operator, the paramagnetic spin–orbit (PSO) operator, the Fermi-contact (FC) operator, and the spin–dipole (SD) operator:

$$\mathbf{h}_{KL}^{\text{DSO}} = \alpha^4 \sum_i \frac{(\mathbf{r}_{iK}^T \mathbf{r}_{iL}) \mathbf{I}_3 - \mathbf{r}_{iK} \mathbf{r}_{iL}^T}{r_{iK}^3 r_{iL}^3}, \quad (4)$$

$$\mathbf{h}_K^{\text{PSO}} = \alpha^2 \sum_i \frac{\mathbf{r}_{iK} \times \mathbf{p}_i}{r_{iK}^3}, \quad (5)$$

$$\mathbf{h}_K^{\text{FC}} = \frac{8\pi\alpha^2}{3} \sum_i \delta(\mathbf{r}_{iK}) \mathbf{s}_i, \quad (6)$$

$$\mathbf{h}_K^{\text{SD}} = \alpha^2 \sum_i \frac{3(\mathbf{s}_i^T \mathbf{r}_{iK}) \mathbf{r}_{iK} - r_{iK}^2 \mathbf{s}_i}{r_{iK}^5}. \quad (7)$$

Here, α is the fine-structure constant, \mathbf{I}_3 is the three-dimensional unit matrix, \mathbf{r}_{iL}^T is the transpose of the \mathbf{r}_{iL} vector, and the summations are over the electrons.

Although Eq. (3) clearly displays the different mechanisms that contribute to the total spin–spin coupling con-

stants in the conventional formalism of time-independent perturbation theory, it is not useful for practical calculations.³³ Instead, the nuclear spin–spin coupling constants are evaluated as second-order properties according to Eq. (2), using the standard techniques of linear response theory.⁴³ In this approach, the closed-shell Kohn–Sham energy is written as $E(\mathbf{M}_K, \boldsymbol{\lambda}_S, \boldsymbol{\lambda}_T)$, where $\boldsymbol{\lambda}_S$ and $\boldsymbol{\lambda}_T$ contain, respectively, the parameters that represent the singlet and triplet variations of the ground state. The reduced spin–spin coupling constants can then be calculated as

$$\begin{aligned} \mathbf{K}_{KL} = & \frac{d^2 E}{d\mathbf{M}_K d\mathbf{M}_L} = \frac{\partial^2 E}{\partial \mathbf{M}_K \partial \mathbf{M}_L} + \frac{\partial^2 E}{\partial \mathbf{M}_K \partial \boldsymbol{\lambda}_S} \frac{\partial \boldsymbol{\lambda}_S}{\partial \mathbf{M}_L} \\ & + \frac{\partial^2 E}{\partial \mathbf{M}_K \partial \boldsymbol{\lambda}_T} \frac{\partial \boldsymbol{\lambda}_T}{\partial \mathbf{M}_L}, \end{aligned} \quad (8)$$

where all derivatives are evaluated for the optimized energy, for which $\boldsymbol{\lambda}_S$ and $\boldsymbol{\lambda}_T$ are zero. The derivatives of $\boldsymbol{\lambda}_S$ and $\boldsymbol{\lambda}_T$ with respect to \mathbf{M}_K are obtained by solving the first-order response equations:

$$\frac{\partial^2 E}{\partial \boldsymbol{\lambda}_S \partial \boldsymbol{\lambda}_S} \frac{\partial \boldsymbol{\lambda}_S}{\partial \mathbf{M}_L} = - \frac{\partial^2 E}{\partial \boldsymbol{\lambda}_S \partial \mathbf{M}_L}, \quad (9)$$

$$\frac{\partial^2 E}{\partial \boldsymbol{\lambda}_T \partial \boldsymbol{\lambda}_T} \frac{\partial \boldsymbol{\lambda}_T}{\partial \mathbf{M}_L} = - \frac{\partial^2 E}{\partial \boldsymbol{\lambda}_T \partial \mathbf{M}_L}, \quad (10)$$

where the symmetric matrices on the left-hand sides are the singlet and triplet electronic Hessians, respectively.⁴³ The solutions to Eqs. (9) and (10) represent the first-order perturbed wave functions due to the imaginary singlet PSO operator Eq. (5) and due to the combined real triplet FC and SD operators, Eqs. (6) and (7), respectively. By spin symmetry, there is no coupling between the singlet and triplet perturbations. We finally note that the real singlet DSO operator, Eq. (4), enters the reduced coupling constant in the first term of Eq. (8), which represents an expectation value of the unperturbed reference state.

B. Vibrational corrections to molecular properties

The theory for the calculation of vibrational corrections to molecular properties by second-order perturbation theory is well documented.^{35–40} Here we evaluate the vibrational correction to the indirect nuclear spin–spin coupling constants as the zero-point vibrational (ZPV) correction, using the approach of Kern *et al.*^{35–37}

In this approach, the zeroth-order ground-state vibrational wave function is written as a product of harmonic-oscillator functions in normal coordinates:

$$X^{(0)}(\mathbf{Q}) = \Phi_0(\mathbf{Q}) = \prod_{K=1}^{3N-6} \phi_0^K(Q_K), \quad (11)$$

where ϕ_n^K is the n ’th excited harmonic-oscillator state of the K ’th vibrational normal mode. Next, the first-order ground-state vibrational wave function is expanded in the full set of virtual excitations from $X^{(0)}(\mathbf{Q})$. Assuming a fourth-order Taylor expansion of the potential energy-surface about equi-

librium, the only contributions are from single and triple excitations. The ground-state wave function may then be written in the form³⁵

$$X^{(1)}(\mathbf{Q}) = \sum_{K=1}^{3N-6} [a_K^1 \Phi_K^1(\mathbf{Q}) + a_K^3 \Phi_K^3(\mathbf{Q})] \\ + \sum_{K,L=1}^{3N-6} b_{KL}^{21} \Phi_{KL}^{21}(\mathbf{Q}) \\ + \sum_{K,L,M=1}^{3N-6} c_{KLM}^{111} \Phi_{KLM}^{111}(\mathbf{Q}), \quad (12)$$

where $\Phi_{KLM}^{klm}(\mathbf{Q})$, for example, has been obtained from $\Phi_0(\mathbf{Q})$ by exciting the K 'th, L 'th, and M 'th modes to the k 'th, l 'th, and m 'th harmonic-oscillator states, respectively. The expansion coefficients in Eq. (12) may be calculated from the cubic force constants,

$$F_{KLM} = \frac{d^3 E}{dQ_K dQ_L dQ_M}, \quad (13)$$

and the harmonic frequencies ω_K as follows:

$$a_K^1 = -\frac{1}{4\sqrt{2}\omega_K^{3/2}} \sum_{L=1}^{3N-6} \frac{F_{KLL}}{\omega_L}, \quad (14)$$

$$a_K^3 = -\frac{\sqrt{3}}{36\omega_K^{5/2}} F_{KKK}, \quad (15)$$

$$b_{KL}^{21} = -\frac{1}{4\omega_K \sqrt{\omega_L}} \frac{F_{KKL}}{2\omega_K + \omega_L}, \quad (16)$$

$$c_{KLM}^{111} = -\frac{1}{12\sqrt{2}\omega_K \omega_L \omega_M} \frac{F_{KLM}}{\omega_K + \omega_L + \omega_M}. \quad (17)$$

To determine the ZPV correction to the equilibrium value P_{eq} of some molecular property P , we consider the expectation value

$$\langle P \rangle = \langle X^{(0)} + X^{(1)} | P | X^{(0)} + X^{(1)} \rangle, \quad (18)$$

where $X^{(0)}$ and $X^{(1)}$ are given by Eqs. (11) and (12), respectively. Expanding P in Eq. (18) in a Taylor series about the equilibrium geometry,

$$P = P_{\text{eq}} + \sum_{K=1}^{3N-6} \frac{dP}{dQ_K} Q_K + \frac{1}{2} \sum_{K,L=1}^{3N-6} \frac{d^2 P}{dQ_K dQ_L} Q_K Q_L + \dots, \quad (19)$$

and collecting terms, we obtain the following expression for the expectation value:

$$\langle P \rangle = P_{\text{eq}} + \frac{1}{4} \sum_{K=1}^{3N-6} \frac{1}{\omega_K} \frac{d^2 P}{dQ_K^2} + \sqrt{2} \sum_K \frac{dP_{\text{exp}}}{dQ_K} \frac{a_K^1}{\sqrt{\omega_K}} + \dots \\ = P_{\text{eq}} + \frac{1}{4} \sum_{K=1}^{3N-6} \frac{1}{\omega_K} \frac{d^2 P}{dQ_K^2} \\ - \frac{1}{4} \sum_{K=1}^{3N-6} \frac{1}{\omega_K^2} \frac{dP}{dQ_K} \sum_{L=1}^{3N-6} \frac{F_{KLL}}{\omega_L} + \dots. \quad (20)$$

To second order in perturbation theory, the ZPV correction to the property can then be written as

$$P_{\text{ZPV}} = \frac{1}{4} \sum_{K=1}^{3N-6} \frac{1}{\omega_K} \frac{d^2 P}{dQ_K^2} - \frac{1}{4} \sum_{K=1}^{3N-6} \frac{1}{\omega_K^2} \frac{dP}{dQ_K} \sum_{L=1}^{3N-6} \frac{F_{KLL}}{\omega_L}. \quad (21)$$

Thus, to calculate the ZPV correction, we need the first and diagonal second derivatives of the property, as well as the harmonic frequencies and the semi-diagonal part of the cubic force field. As pointed out in the Introduction, no analytical implementation exists for the evaluation of these derivatives for the indirect nuclear spin–spin coupling constants, so some numerical procedure must be used instead. There are several ways that derivatives can be found numerically.

One approach is to fit an analytic hypersurface to the property and energy calculated at different geometries. The derivatives can then be obtained by differentiation of the fitted surface.^{14–19,44–48} A disadvantage of this approach is that it is difficult to automate and that it becomes expensive for large systems. Alternatively, the necessary derivatives may be calculated numerically, relying as much as possible on available analytical derivatives.⁴⁹ Unlike the fitting approach, this approach is easily automated, making the calculation of vibrational corrections straightforward, and at most equally expensive, even for polyatomic systems.

In this paper, we calculate the indirect nuclear spin–spin coupling constants using the DFT implementation in DALTON.³³ Applying the technique described in Ref. 49, the property and energy derivatives are calculated numerically from the highest available analytical derivatives. With respect to geometrical derivatives, only molecular gradients have been implemented analytically at the DFT level—in particular, no analytical geometry derivatives are available for the spin–spin coupling constants in DALTON.

Assuming that the number of normal modes is $3N-6$, we therefore need to carry out $6N-11$ property and gradient calculations to determine the ZPV correction to each indirect nuclear spin–spin coupling constant. Since the calculation of spin–spin coupling constants is much more demanding than the calculation of molecular gradients, the calculation of the ZPV corrections will be completely dominated by the calculation of the property derivatives.

III. CALCULATIONS

In this section, we discuss the calculation of ZPV corrections to the indirect nuclear spin–spin coupling constants for a number of small molecules. As advocated by Helgaker *et al.*, all calculations have been carried out with the Becke 3-parameter Lee–Yang–Parr (B3LYP) functional.³³

Having briefly introduced the basis sets in Sec. III A, we examine in Sec. III B the force fields that are used in our calculations of vibrationally averaged spin–spin coupling constants. After an investigation of the basis-set dependence of the ZPV contribution to the indirect spin–spin coupling constants in Sec. III C, we compare in Sec. III D the calculated ZPV corrections with previously published results. These ZPV corrections are then in Sec. III E subtracted from experimentally observed constants to yield a set of empirical

TABLE I. B3LYP and valence-electron CCSD(T) harmonic frequencies compared with experiment (cm^{-1}).

		B3LYP						CCSD(T)	Exp.
		HII	HIII	HIV	sHII	sHIII	sHIV	cc-pVQZ	
H ₂	ω	4407	4410	4409	4406	4410	4409	4404	4401
HF	ω	4083	4076	4074	4077	4077	4074	4162	4138
CO	ω	2220	2208	2210	2219	2208	2210	2164	2170
N ₂	ω	2437	2444	2445	2436	2444	2445	2356	2359
H ₂ O	ω_1	3903	3904	3899	3896	3904	3900	3952	3942
	ω_2	3796	3800	3798	3789	3801	3798	3945	3832
	ω_3	1635	1633	1625	1637	1633	1625	1659	1648
HCN	ω_1	3449	3435	3440	3448	3436	3440	3436	3443
	ω_2	2204	2197	2200	2203	2197	2200	2123	2127
	ω_3	785	735	760	786	733	760	722	727
NH ₃	ω_1	3576	3582	3583	3571	3582	3583	3609	3597
	ω_2	3457	3464	3463	3453	3464	3463	3481	3478
	ω_3	1679	1670	1660	1681	1670	1660	1680	1684
CH ₄	ω_4	1054	1042	1024	1060	1042	1024	1084	≈ 1030
	ω_1	3121	3129	3126	3121	3129	3126	3157	3157
	ω_2	3020	3028	3023	3019	3028	3023	3036	3026
	ω_3	1558	1561	1555	1559	1561	1555	1570	1583
C ₂ H ₂	ω_4	1342	1343	1338	1343	1343	1339	1345	1367
	ω_1	3509	3506	3510	3509	3507	3510	3502	3495
	ω_2	3407	3410	3411	3407	3410	3411	3410	3415
	ω_3	2072	2063	2067	2072	2063	2067	2006	2008
	ω_4	772	750	766	774	749	766	746	747
	ω_5	673	632	667	673	629	667	595	624
Δ		32	25	30	33	25	30	15	

equilibrium spin–spin coupling constants, which are subsequently used to benchmark the coupling constants calculated by different theoretical methods. Finally, the vibrationally averaged spin–spin coupling constants of benzene are discussed in Sec. III F.

A. Basis sets

The ZPV corrections have been calculated using two sequences of basis sets. The first sequence consists of the Huzinaga sets HII, HIII, and HIV^{50,51} with the polarization functions and contraction patterns of van Wüllen and Kutzelnigg *et al.*⁵² These basis sets have been widely used for the calculation of nuclear shielding constants and indirect spin–spin coupling constants.

However, for an accurate calculation of the FC contribution to the spin–spin coupling constants, it is essential to use basis sets with a flexible inner core.^{2,20,33} To ensure a flexible core description, we have used the basis sets HII-su2, HIII-su3, and HIV-su4. The postfix “-sun” indicates that the *s* functions in the original basis have been decontracted, and that an additional set of *n* tight *s* functions have been added in an even-tempered manner.³³ For brevity of notation, we shall here abandon the general notation HX-sun and instead refer to these basis sets as sHII, sHIII, and sHIV, respectively. The performance of the different basis sets is examined in Sec. III C.

B. Quality of the B3LYP force field

For an accurate description of vibrational corrections, it is necessary to ensure that the quadratic and cubic force fields are calculated to sufficient accuracy. Several studies of

DFT harmonic and anharmonic force fields have shown that, in a sufficiently large basis, B3LYP provides a good description of harmonic and anharmonic force fields.^{53–55} In particular, Martin *et al.* found that, for 13 small molecules, the B3LYP harmonic frequencies have a mean absolute error of only 30 cm^{-1} relative to experimental harmonic frequencies.⁵⁴

In Table I, we have listed the B3LYP harmonic frequencies for all molecules included in this study except for ethene and benzene, calculated using the same basis sets as in the subsequent spin–spin calculations. For comparison, we have included experimental harmonic frequencies as well as the harmonic vibrational frequencies of Martin *et al.*,⁵⁴ obtained using the valence-correlated coupled-cluster singles-and-doubles (CCSD) method with a perturbative triples correction [CCSD(T)]. In their study, Martin *et al.* found that, relative to experiment, the mean absolute error of the CCSD(T) frequencies are 8 cm^{-1} for the 13 molecules.

Clearly, in the Huzinaga-type basis sets, the DFT/B3LYP model provides a good representation of the harmonic force field, with mean absolute errors relative to experiment of about 30 cm^{-1} . The B3LYP model also compares favorably with the more expensive CCSD(T)/cc-pVQZ model, whose mean absolute errors are 15 cm^{-1} relative to experiment.

Also, the cubic force field is important for the calculation of ZPV corrections to properties. To examine the quality of the cubic force field, we here compare the calculated ZPV correction to the molecular geometry with available theoretical data. To second order in the perturbation, the ZPV correction to the geometry can be calculated using the following formula:^{35,38}

TABLE II. B3LYP ZPV corrections to bond distances (pm) and bond angles (°) compared with MCSCF corrections.

		B3LYP				MCSCF
		HII	sHII	sHIII	sHIV	
HF	r	1.6	1.6	1.5	1.6	1.5 ^a
H ₂ O	r	1.5	1.5	1.5	1.4	1.5 ^b
	θ	-0.1	-0.1	-0.1	-0.0	-0.1 ^b
H ₂ CO	r_{CO}	0.3	0.3	0.3	0.3	0.4 ^b
	r_{CH}	1.4	1.4	1.4	1.4	1.4 ^b
	θ_{HCH}	-0.1	-0.2	-0.1	-0.1	-0.1 ^b
C ₂ HD	r_{CC}	0.4	0.4	0.4	0.4	0.5 ^c
	r_{CD}	-0.1	-0.1	-0.2	-0.1	-0.2 ^c
	r_{CH}	-0.4	-0.4	-0.5	-0.5	-0.5 ^c
	θ_{DCC}	0.0	0.0	0.0	0.0	0.0 ^c
	θ_{CCH}	0.0	0.0	0.0	0.0	0.0 ^c

^aReference 5.^bReference 38.^cReference 63.

$$Q_K^{\text{ZPV}} = -\frac{1}{4\omega_K^2} \sum_{L=1}^N \frac{F_{KLL}}{\omega_L}. \quad (22)$$

Since this expression resembles the term in Eq. (21) that contains the cubic force constants, it should give a good indication of the error arising from the cubic force field in the calculated ZPV corrections to other molecular properties. As seen from Table II, the ZPV corrections to the geometry calculated at the B3LYP level agree well with previously calculated MCSCF corrections.

C. Basis-set dependence of the ZPV contribution to indirect nuclear spin–spin coupling constants

As seen from Table III, the vibrational corrections to the indirect nuclear spin–spin coupling constants depend noticeably on the basis set—both when the valence description is improved from HII to HIV and when the inner-core description is improved from, say, HIII to sHII. However, although the couplings change by 5% to 10% in both cases, the

TABLE III. ZPV corrections to the indirect nuclear spin–spin coupling constants calculated at the B3LYP level of theory (Hz).

		HII	HIII	HIV	sHII	sHIII	sHIV
HD	$^1J_{\text{HH}}$	2.8	2.7	2.6	2.7	2.8	2.8
HF	$^1J_{\text{HF}}$	-36.1	-36.0	-34.9	-41.9	-38.1	-37.7
CO	$^1J_{\text{CO}}$	0.7	0.7	0.7	0.7	0.7	0.7
N ₂	$^1J_{\text{NN}}$	0.1	0.1	0.1	0.1	0.1	0.1
H ₂ O	$^1J_{\text{OH}}$	5.5	5.1	4.9	6.0	5.4	5.2
	$^2J_{\text{HH}}$	0.8	0.7	0.7	0.8	0.9	0.9
HCN	$^1J_{\text{CN}}$	2.1	1.9	1.9	2.0	2.0	2.0
	$^1J_{\text{CH}}$	4.0	4.6	4.4	4.9	5.1	5.1
	$^2J_{\text{NH}}$	0.8	0.7	0.8	0.8	0.8	0.8
NH ₃	$^1J_{\text{NH}}$	-0.3	-0.4	-0.3	-0.5	-0.3	-0.3
	$^2J_{\text{HH}}$	0.7	0.6	0.6	0.7	0.7	0.8
CH ₄	$^1J_{\text{CH}}$	5.1	4.8	4.8	5.2	5.3	5.3
	$^2J_{\text{HH}}$	-0.5	-0.6	-0.6	-0.6	-0.7	-0.6
C ₂ H ₂	$^1J_{\text{CC}}$	-9.6	-9.8	-8.8	-9.1	-10.0	-9.3
	$^1J_{\text{CH}}$	4.4	4.4	4.2	5.0	4.6	4.7
	$^2J_{\text{CH}}$	-2.7	-2.7	-2.7	-2.7	-3.0	-2.8
	$^3J_{\text{HH}}$	-0.1	-0.5	-0.1	0.0	-0.1	-0.1

TABLE IV. B3LYP harmonic vibrational contribution to the indirect nuclear spin–spin coupling constants (Hz).

		HII	HIII	HIV	sHII	sHIII	sHIV
HD	$^1J_{\text{HH}}$	1.3	0.2	0.3	0.0	0.1	0.0
HF	$^1J_{\text{HF}}$	14.9	13.9	13.5	13.8	14.6	14.8
CO	$^1J_{\text{CO}}$	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4
N ₂	$^1J_{\text{NN}}$	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1
H ₂ O	$^1J_{\text{OH}}$	-0.3	0.0	0.0	0.1	0.0	-0.1
	$^2J_{\text{HH}}$	1.0	0.8	0.9	0.9	1.0	1.0
HCN	$^1J_{\text{CN}}$	1.5	1.5	1.4	1.5	1.5	1.5
	$^1J_{\text{CH}}$	3.7	4.8	4.4	4.6	5.2	5.0
	$^2J_{\text{NH}}$	0.7	0.6	0.7	0.6	0.7	0.7
NH ₃	$^1J_{\text{NH}}$	0.2	-0.1	-0.1	-0.2	-0.1	-0.1
	$^2J_{\text{HH}}$	0.2	0.2	0.2	0.3	0.3	0.3
CH ₄	$^1J_{\text{CH}}$	3.1	2.6	2.5	2.8	2.9	2.9
	$^2J_{\text{HH}}$	-0.7	-0.7	-0.6	-0.7	-0.8	-0.7
C ₂ H ₂	$^1J_{\text{CC}}$	-9.0	-9.1	-8.3	-8.6	-9.3	-8.7
	$^1J_{\text{CH}}$	3.8	4.2	3.9	4.4	4.4	4.3
	$^2J_{\text{CH}}$	-2.5	-2.5	-2.5	-2.5	-2.8	-2.6
	$^3J_{\text{HH}}$	-0.3	-0.7	-0.3	-0.2	-0.3	-0.3

changes are in opposite directions. As a result, the HII constants are usually closer to the sHIV results than to the HIV results. An exception is $^1J_{\text{CH}}$ in HCN, where the changes upon the addition of valence and inner-core s orbitals are in the same direction, giving an sHIV vibrational correction (5.1 Hz) that is about one third larger than the HII correction (4.0 Hz)—in all other cases, the differences between the HII and sHIV corrections are less than 5%. Clearly, in calculations of ZPV corrections to indirect nuclear spin–spin coupling constants, we should not improve the valence description without simultaneously improving the inner-core description.

In spite of its good performance, the HII basis should be used with some care as it sometimes gives good results by error cancellation. For $^1J_{\text{HD}}$, for example, the HII and sHIV vibrational corrections are similar. However, whereas the sHIV correction is dominated by the anharmonic contribution, the harmonic and anharmonic contributions are both large in the HII basis—see Tables IV and V, where we have

TABLE V. B3LYP anharmonic vibrational contribution to the indirect nuclear spin–spin coupling constants (Hz).

		HII	HIII	HIV	sHII	sHIII	sHIV
HD	$^1J_{\text{HH}}$	1.5	2.5	2.4	2.7	2.8	2.8
HF	$^1J_{\text{HF}}$	-51.0	-49.8	-48.4	-55.7	-52.8	-52.4
CO	$^1J_{\text{CO}}$	1.1	1.1	1.1	1.1	1.1	1.1
N ₂	$^1J_{\text{NN}}$	0.2	0.2	0.2	0.2	0.2	0.2
H ₂ O	$^1J_{\text{OH}}$	5.8	5.1	4.9	5.8	5.4	5.3
	$^2J_{\text{HH}}$	-0.1	0.0	-0.2	-0.2	-0.1	-0.1
HCN	$^1J_{\text{CN}}$	0.6	0.4	0.5	0.5	0.4	0.5
	$^1J_{\text{CH}}$	0.3	-0.1	0.1	0.3	-0.2	0.1
	$^2J_{\text{NH}}$	0.2	0.1	0.1	0.2	0.1	0.1
NH ₃	$^1J_{\text{NH}}$	-0.5	-0.3	-0.2	-0.3	-0.2	-0.2
	$^2J_{\text{HH}}$	0.5	0.5	0.4	0.5	0.5	0.5
CH ₄	$^1J_{\text{CH}}$	2.0	2.2	2.2	2.4	2.5	2.5
	$^2J_{\text{HH}}$	0.2	0.1	0.1	0.1	0.1	0.1
C ₂ H ₂	$^1J_{\text{CC}}$	-0.6	-0.6	-0.6	-0.5	-0.6	-0.6
	$^1J_{\text{CH}}$	0.6	0.2	0.3	0.6	0.2	0.4
	$^2J_{\text{CH}}$	-0.2	-0.2	-0.2	-0.2	-0.3	-0.2
	$^3J_{\text{HH}}$	0.2	0.2	0.2	0.2	0.2	0.2

TABLE VI. Changes in the vibrational corrections to the spin–spin couplings going from the HX basis to the sHX basis at the DFT/B3LYP level of theory (Hz).

		HII→sHII		HIII→sHIII		HIV→sHIV	
		ΔJ_{FC}	ΔJ_{tot}	ΔJ_{FC}	ΔJ_{tot}	ΔJ_{FC}	ΔJ_{tot}
HD	$^1J_{HH}$	-0.05	-0.05	0.11	0.10	0.23	0.23
HF	$^1J_{HF}$	-6.12	-5.87	-2.11	-2.18	-2.81	-2.82
CO	$^1J_{CO}$	-0.01	-0.01	0.02	0.02	0.03	0.03
N ₂	$^1J_{NN}$	-0.01	-0.01	0.00	0.00	0.01	0.01
H ₂ O	$^1J_{OH}$	0.44	0.43	0.31	0.31	0.34	0.34
	$^2J_{HH}$	-0.06	-0.06	0.16	0.16	0.17	0.17
HCN	$^1J_{CN}$	-0.10	-0.10	0.03	0.03	0.09	0.09
	$^1J_{CH}$	0.89	0.90	0.42	0.43	0.64	0.64
	$^2J_{NH}$	-0.02	-0.02	0.04	0.04	0.04	0.03

listed separately the harmonic and anharmonic contributions to the ZPV corrections, respectively. Clearly, as we go from HII to sHIV, the harmonic and anharmonic contributions change in opposite directions, leading to an overall small change in the total vibrational correction.

It is noteworthy that, as we go from sHIII to sHIV, the vibrational corrections change very little—in fact, only in three cases does the vibrational correction change by more than 0.1 Hz. This observation indicates that, in most cases, the sHIV basis gives vibrational corrections to the nuclear spin–spin coupling constants that are within 0.1 Hz of the basis-set limit of DFT, and that the vibrational corrections obtained with the sHIII basis are also good.

As expected, the change in the vibrational correction upon the addition of tight *s* functions is caused almost entirely by the FC contribution. Indeed, from Table VI, we see that the FC contribution usually accounts for more than 99% of the change in the vibrational correction (in all cases more than 95%). Since the calculation of the FC contribution is much cheaper than the calculation of the remaining contributions and since the force-field calculation is essentially free, we suggest the following approach for large molecules: for the FC contribution, we use sHII, sHIII or sHIV, depending on molecule size; for the SD, PSO, and DSO contributions, we use HII or HIII.

In conclusion, we recommend the sHIV basis for small systems since it gives vibrational corrections close to the DFT basis-set limit. However, very good estimates of the vibrational corrections are obtained also with the sHIII basis, which we advocate for larger systems. For large systems such as benzene, accurate vibrational corrections to the indirect nuclear spin–spin coupling constants are obtained by using sHIII for the FC term and HII for the remaining terms.

D. Comparison with previously calculated vibrational corrections

As seen from Table VII, the B3LYP vibrational corrections to the indirect nuclear spin–spin coupling constants agree well with previous calculations.^{5,13–19,34,45} However, there are two cases of striking differences—the $^1J_{NN}$ coupling in N₂ and the $^3J_{HH}$ in C₂H₂. In both cases, the DFT vibrational correction does not change with the basis set,

TABLE VII. ZPV corrections to indirect nuclear spin–spin coupling constants (Hz).

		B3LYP			Other calculations	
		sHII	sHIII	sHIV		
HD	$^1J_{HD}$	2.7	2.8	2.8	1.8, ^a	2.0 ^b
HF	$^1J_{FH}$	-41.9	-38.2	-37.7	-26.9, ^c	-40 ^d
CO	$^1J_{CO}$	0.7	0.7	0.7	0.8 ^e	
N ₂	$^1J_{NN}$	0.1	0.1	0.1	0.4 ^e	
H ₂ O	$^1J_{OH}$	6.0	5.4	5.2	4.0, ^f	4.2 ^g
	$^2J_{HH}$	0.8	0.9	0.9	0.7, ^f	0.8 ^g
CH ₄	$^1J_{CH}$	5.2	5.3	5.3	5.0, ^h	4.4 ⁱ
	$^2J_{HH}$	-0.6	-0.7	-0.6	-0.7, ^h	-0.6 ⁱ
C ₂ H ₂	$^1J_{CC}$	-9.1	-10.0	-9.3	-9.2 ^j	
	$^1J_{CH}$	5.0	4.6	4.7	4.8 ^j	
	$^2J_{CH}$	-2.7	-3.0	-2.8	-3.2 ^j	
	$^3J_{HH}$	-0.0	-0.1	-0.1	-1.2 ^j	

^aReference 23.

^bReference 9.

^cReference 5.

^dReference 34.

^eReference 13.

^fReference 14.

^gCalculated using the rovibrational numbers from Ref. 10, and correcting it with the temperature dependent part from Ref. 14.

^hReference 15.

ⁱReference 45.

^jReference 17.

indicating that the correction is close to the basis-set limit. We also note that, for N₂, the calculated SOPPA value constitutes as much as one fourth of the total spin–spin coupling constant. For $^3J_{HH}$ in C₂H₂, the difference is even larger—in fact, the SOPPA(CCSD) correction is an order of magnitude larger than the B3LYP correction. As the individual contributions to the vibrational corrections have not been reported for C₂H₂ in Ref. 17, a comparison of the individual contributions is not possible but we note that the other vibrational corrections to the spin–spin coupling constants in C₂H₂ agree well with the SOPPA(CCSD) values.

For the remaining spin–spin coupling constants in Table VII, the DFT corrections are similar to the literature values. The largest discrepancies occur for H₂O, where $^1J_{OH}$ differs from SOPPA by 24% and from MCSCF by 20%, and for the HF molecule, where the B3LYP vibrational correction of -38 Hz is bracketed by the MCSCF correction of -27 Hz and the experimental correction -40 Hz. Although the B3LYP result for HF is close to experiment, we do not attach much significance to this result since, for this particular system, B3LYP predicts a much too low equilibrium coupling constant.

E. Experimental equilibrium values

Once the vibrational corrections to the indirect nuclear spin–spin coupling constants have been calculated theoretically, we can extract a set of empirical equilibrium coupling constants from experiment by subtracting the calculated ZPV corrections from the experimentally observed couplings:

$$J_{eq}^{emp} = J_{tot}^{exp} - J_{vib}^{cal}. \quad (23)$$

TABLE VIII. Calculated and experimental indirect nuclear spin–spin coupling constants (Hz). The ZPV correction has been calculated at the B3LYP/sHIII level and the empirical coupling constants have been obtained using Eq. (23).

		$J_{\text{eq}}^{\text{CAS}}$	$J_{\text{eq}}^{\text{RAS}}$	$J_{\text{eq}}^{\text{SOPPA}}$	$J_{\text{eq}}^{\text{CCSD}}$	$J_{\text{eq}}^{\text{B3LYP}}$	$J_{\text{eq}}^{\text{CC3}}$	$J_{\text{eq}}^{\text{emp}}$	$J_{\text{vib}}^{\text{B3LYP}}$	$J_{\text{tot}}^{\text{exp}}$
HF	$^1J_{\text{HF}}$	542.6 ^a	544.2 ^f	529.4 ^l	521.6 ^p	416.6	521.5 ^p	538	−38	500 ^t
CO	$^1J_{\text{CO}}$	11.5 ^b	16.1 ^b	18.6 ^l	15.7 ^p	18.4	15.3 ^p	15.7	0.7	16.4 ^u
N ₂	$^1J_{\text{NN}}$	0.5 ^b	0.8 ^b	2.1 ^l	1.8 ^p	1.4	1.8 ^p	1.7	0.1	1.8 ^v
H ₂ O	$^1J_{\text{OH}}$	−83.9 ^c	−76.7 ^g	−80.6 ^l	−78.9 ^p	−75.9	−78.5 ^p	−86.0	5.4	−80.6 ^w
	$^2J_{\text{HH}}$	−9.6 ^c	−7.8 ^g	−8.8 ^l	−7.8 ^p	−7.5	−7.4 ^p	−8.2	0.9	−7.3 ^w
HCN	$^1J_{\text{CN}}$		−19.8 ^a		−18.2 ^p	−19.2	−17.9 ^p	−20.5	2.0	−18.5 ^x
	$^1J_{\text{CH}}$		258.9 ^a		245.8 ^p	283.5	242.1 ^p	262.2	5.1	267.3 ^y
	$^2J_{\text{NH}}$		−6.8 ^a		−7.7 ^p	−7.8	−7.7 ^p	−8.2	0.8	−7.4 ^y
NH ₃	$^1J_{\text{NH}}$	42.3 ^d	43.6 ^h	44.3 ^m	41.8 ^q	45.7		44.1	−0.3	43.8 ^z
	$^2J_{\text{HH}}$	−9.8 ^d	−11.3 ^h	−11.3 ^m	−12.1 ^q	−10.1		−10.3	0.7	−9.6 ^z
CH ₄	$^1J_{\text{CH}}$	116.7 ^d	120.6 ⁱ	122.3 ^l		132.6		120.0	5.3	125.3 ^{aa}
	$^2J_{\text{HH}}$	−13.2 ^d	−13.2 ⁱ	−14.0 ^l		−13.3		−12.1	−0.7	−12.8 ^{aa}
C ₂ H ₂	$^1J_{\text{CC}}$	187.7 ^e	184.7 ^j	190.0 ⁿ		205.1		184.8	−10.0	174.8 ^{ab}
	$^1J_{\text{CH}}$	238.5 ^e	244.3 ^j	254.9 ⁿ		271.9		243.0	4.6	247.6 ^{ab}
	$^2J_{\text{CH}}$	47.0 ^e	53.1 ^j	51.7 ⁿ		56.0		53.1	−3.0	50.1 ^{ab}
	$^3J_{\text{HH}}$	12.1 ^e	10.8 ^j	11.3 ⁿ		10.6		9.7	−0.1	9.6 ^{ab}
C ₂ H ₄	$^1J_{\text{CC}}$	75.7 ^d	68.8 ^k	70.3 ^o	70.1 ^r	74.7		66.7	0.9	67.6 ^{ac}
	$^1J_{\text{CH}}$	155.7 ^d	151.6 ^k	157.2 ^o	153.2 ^s	165.3		151.2	5.1	156.3 ^{ac}
	$^2J_{\text{CH}}$	−5.8 ^d	−1.6 ^k	−3.1 ^o	−3.0 ^s	−1.3		−1.2	−1.2	−2.4 ^{ac}
	$^2J_{\text{HH}}$	−2.4 ^d	1.1 ^k	1.0 ^o	0.4 ^s	2.9		2.0	0.3	2.3 ^{ac}
	$^3J_{\text{cis}}$	12.4 ^d	11.5 ^k	11.8 ^o	11.6 ^s	13.5		10.5	1.2	11.7 ^{ac}
	$^3J_{\text{trans}}$	18.4 ^d	17.8 ^k	18.4 ^o	17.8 ^s	20.7		16.7	2.3	19.0 ^{ac}

^aReference 2.^bReference 3.^cReference 14.^dReference 1.^eReference 4.^fReference 11. Extrapolated in the excitation limit to be 536.6 Hz.^gReference 10.^hReference 6.ⁱReference 7.^jReference 8.^kReference 12.^lReference 20.^mReference 21.ⁿReference 17.^oReference 22.^pReference 25.^qReference 26.^rReference 28.^sReference 27.^tReference 34.^uReference 64.^vReference 65.^wReference 66.^xReference 67.^yReference 68.^zReference 69.^{aa}Reference 45.^{ab}Reference 70.^{ac}Reference 71.

Such empirical equilibrium coupling constants are listed in Table VIII, together with the equilibrium coupling constants calculated by different theoretical methods. The empirical equilibrium values have been obtained by subtracting the B3LYP/sHIII vibrational corrections from the experimental values listed in the table.

In Table IX, we have made a statistical analysis of the errors of the different theoretical methods relative to the experimental total spin–spin coupling constants and to the empirical equilibrium constants. Somewhat surprisingly, the mean absolute relative error increases for all methods except

RAS after the vibrational contributions to the coupling constants have been accounted for. The relative error found for RAS decreases slightly from 11% to 10%.

By contrast, the mean absolute errors and standard deviations decrease for all methods except DFT/B3LYP. The reduction in the error is particularly pronounced for the MCSCF model—from 5.8 to 3.3 Hz for the complete active-space self-consistent field (CASSCF) method and from 4.3 to 1.6 Hz for the restricted active-space self-consistent field (RASSCF) method. For SOPPA, CCSD, and CC3, the mean

TABLE IX. Statistics of calculated indirect nuclear spin–spin coupling constants relative to the experimental total coupling constants $J_{\text{tot}}^{\text{exp}}$ and the empirical equilibrium coupling constants $J_{\text{eq}}^{\text{emp}}$ of Table VIII.

	CAS		RAS		SOPPA		CCSD		B3LYP		CC3	
	$J_{\text{tot}}^{\text{exp}}$	$J_{\text{eq}}^{\text{emp}}$										
Mean abs. err. (Hz)	5.8	3.3	4.3	1.6	3.8	3.1	3.8	3.7	9.1	11.7	6.4	6.1
Std. dev. (Hz)	11.3	4.0	10.3	2.7	8.1	4.4	8.0	6.5	20.7	28.5	12.6	10.3
Mean err. (Hz)	1.2	−0.2	1.6	0.8	2.7	1.4	−0.5	−1.4	1.3	0.5	−0.3	−3.2
Mean abs. rel. err. (%)	30	43	11	10	11	19	11	20	12	13	4	7

absolute error is reduced from 4.1 to 3.4 Hz, from 3.8 to 3.7 Hz, and from 6.4 to 6.1 Hz, respectively.

Among the different theoretical methods in Table IX, the RASSCF results are closest to the empirical equilibrium constants with a mean absolute error of 1.6 Hz, the corresponding errors for the CASSCF, SOPPA, CCSD, CC3, and B3LYP methods being 3.3, 3.4, 3.7, 6.1, and 11.7 Hz, respectively.

The relatively poor performance of the coupled-cluster methods is somewhat surprising but arises from the relatively small basis sets used in the calculations—in particular, no tight *s*-functions have been used in the CC3 calculations. Clearly, the statistical errors in Table IX cannot directly be used as measures of the intrinsic errors associated with the different methods. Indeed, the good performance of the RASSCF method is to some extent a reflection of the fact that, for most of the molecules in our sample, this method has been applied with great care so as to arrive at the most accurate possible coupling constants, although, for a few molecules such as N₂, there is still room for improvement. As a very recent investigation of the indirect nuclear spin–spin coupling constant in BH has shown, the CCSD and CC3 methods are capable of very high accuracy—provided sufficiently large basis sets are used and provided that all electrons (not just the valence electrons) are correlated in the calculations.⁵⁶

The large mean absolute error of DFT in Table IX compared to the wave-function methods is striking. As is well documented, the performance of the B3LYP method depends critically on the nature of the coupled nuclei. In particular, poor indirect nuclear spin–spin couplings are obtained for electronegative atoms such as fluorine, whereas other atoms such as hydrogen and carbon are quite well described.³³ Thus, for HF, the B3LYP method in Table VIII underestimates the indirect nuclear spin–spin coupling by more than 100 Hz. If this molecule is omitted from the statistics, the mean absolute error of B3LYP is reduced to 4 Hz—that is, similar to the error of the wave-function methods.

Focusing on the mean absolute *relative* errors in Table IX, we find that for all methods except RAS, the errors *increase* when we compare with the empirical equilibrium constants instead of the observed total constants. This behavior is different from that of the mean absolute error, which, for all methods except B3LYP, becomes *smaller* when we compare with the empirical equilibrium constants, suggesting that the vibrational corrections improve the agreement with experiment, mostly for the large spin–spin coupling constants. One possible explanation for this behavior are solvent effects, since many of the experiments have been performed in solution. In general, however, solvent effects on spin–spin coupling constants are rather small, rarely exceeding a few Hz,^{57–60} suggesting that the error mostly arises from a poor description of the electronic system.

F. Experimental equilibrium values for benzene

To illustrate the usefulness of the presented method, we have calculated the vibrational corrections to the indirect nuclear spin–spin coupling constants of the benzene molecule. In Table X, we have listed the vibrational corrections

TABLE X. Indirect nuclear spin–spin coupling constants of benzene (Hz).

	$J_{\text{eq}}^{\text{B3LYPa}}$	$J_{\text{eq}}^{\text{MCSCFb}}$	$J_{\text{eq}}^{\text{empe}}$	$J_{\text{vib}}^{\text{B3LYPd}}$	$J_{\text{tot}}^{\text{expe}}$
¹ J_{CC}	60.0	70.9	56.1	−0.1	56.0
² J_{CC}	−1.8	−5.0	−1.7	−0.8	−2.5
³ J_{CC}	11.2	19.1	9.4	0.7	10.1
¹ J_{CH}	166.3	176.7	153.8	4.8	158.6
² J_{CH}	2.0	−7.4	1.4	−0.4	1.0
³ J_{CH}	8.0	11.7	7.0	0.5	7.5
⁴ J_{CH}	−1.2	−1.3	−1.0	−0.3	−1.3
³ J_{HH}	8.7		7.0	0.5	7.5
⁴ J_{HH}	1.3		1.2	0.2	1.4
⁵ J_{HH}	0.8		0.6	0.1	0.7

^asHIII basis.

^bSee Reference 61.

^cObtained by combining the entries in columns 5 and 6 according to Eq. (23).

^dHII basis except sHIII for FC.

^eSee Reference 61 except for the HH couplings. For HH couplings, see Ref. 62.

calculated with the B3LYP functional, using the sHIII basis set for the FC contribution and the HII basis for the remaining contributions. In addition, we have included the equilibrium spin–spin coupling constants calculated at the B3LYP/sHIII by us and at the MCSCF level by Kaski, Vaara, and Jokisaari.⁶¹ From the experimental indirect nuclear spin–spin coupling constants of Ref. 61, we have obtained a set of empirical equilibrium constants by applying Eq. (23).

The vibrational corrections to the indirect nuclear spin–spin coupling constants in benzene are small. In fact, the only vibrational correction greater than 1 Hz is the one-bond CH correction of 4.8 Hz. Next, we note that inclusion of vibrational corrections does not improve the agreement between theory and experiment. Indeed, only for three of the ten coupling constants in benzene does the agreement with experiment improve with the inclusion of vibrational corrections.

Considering the quality of the vibrational corrections to spin–spin coupling constants, the reason for this unexpected behavior is either that the calculations are not sufficiently accurate or effects of the liquid crystal used in experiment. Since the results of Ref. 61 are in good agreement with a detailed liquid-phase investigation by Laatikainen *et al.*,⁶² this indicates that the single-point calculations of equilibrium spin–spin coupling constants are not sufficiently accurate. This is also supported by the recently calculated gas-phase equilibrium value of ¹ $J_{\text{HC}} = 152.7$ Hz.⁵⁷

Nevertheless, the agreement between theory and experiment is much better for B3LYP than for MCSCF, which for this molecule produces rather poor couplings. The mean absolute error is 2 Hz for B3LYP and about four times larger for MCSCF.

G. Conclusions

An automated method for the calculation of vibrational corrections to indirect nuclear spin–spin couplings has been presented and applied at the DFT/B3LYP level of theory to a number of small molecular systems. Our results compare

favorably with previous computed and experimentally determined vibrational corrections to the indirect spin–spin coupling constants, the computational cost at the DFT level being significantly smaller. To illustrate potential and usefulness of the method, we have calculated the vibrational corrections to the indirect spin–spin coupling constants of benzene.

Having calculated a set of vibrational corrections to the indirect spin–spin coupling constants, a list of empirical equilibrium spin–spin coupling constants was generated by subtracting the vibrational correction from the experimental coupling constant. Comparing these empirical equilibrium coupling constants with calculations carried out at different levels of theory in the literature, we found that, for small molecular systems, the best indirect spin–spin coupling constants available in literature are those obtained with the RASSCF method. It should be noted, however, that the good RASSCF performance is to some extent due to the fact that this method has been applied with great care, so as to arrive at the most accurate possible coupling constants. The SOPPA and DFT/B3LYP methods perform similarly, although DFT fails badly for molecules containing fluorine. The performance of coupled-cluster theory is difficult to establish due to basis-set deficiencies. In short, to establish the relative performance of the different theoretical methods unequivocally, a more consistent set of calculations needs to be carried out for all methods.

ACKNOWLEDGMENTS

The work has received support from the Norwegian Research Council (Program for Supercomputing) through a grant of computer time.

- ¹T. Helgaker, M. Jaszuński, and K. Ruud, *Chem. Rev.* **99**, 293 (1999).
- ²T. Helgaker, M. Jaszuński, K. Ruud, and A. Górska, *Theor. Chem. Acc.* **99**, 175 (1998).
- ³O. Vahtras, H. Ågren, P. Jørgensen, T. Helgaker, and H. J. Aa. Jensen, *Chem. Phys. Lett.* **209**, 201 (1993).
- ⁴M. Pečul and J. Sadlej, *Chem. Phys.* **234**, 111 (1998).
- ⁵P.-O. Åstrand, K. Ruud, K. V. Mikkelsen, and T. Helgaker, *J. Chem. Phys.* **110**, 9463 (1999).
- ⁶P. Lantto and J. Vaara, *J. Chem. Phys.* **114**, 5482 (2001).
- ⁷J. Guilleme and J. San Fabián, *J. Chem. Phys.* **109**, 8168 (1998).
- ⁸M. Jaszuński and K. Ruud, *Chem. Phys. Lett.* **336**, 473 (2001).
- ⁹O. Vahtras, H. Ågren, P. Jørgensen, H. J. A. Jensen, S. B. Padkjaer, and T. Helgaker, *J. Chem. Phys.* **96**, 6120 (1992).
- ¹⁰J. Casanueva, J. San Fabián, E. Diéz, and A. L. Esteban, *J. Mol. Struct.* **565–566**, 449 (2001).
- ¹¹J. San Fabián, J. Casanueva, E. San Fabián, and J. Guillerne, *J. Chem. Phys.* **112**, 4143 (2000).
- ¹²J. Casanueva, J. San Fabián, E. Diéz, and A. L. Esteban, *Chem. Phys. Lett.* **361**, 159 (2002).
- ¹³J. Geertsen, J. Oddershede, and G. E. Scuseria, *J. Chem. Phys.* **87**, 2138 (1987).
- ¹⁴R. D. Wigglesworth, W. T. Raynes, S. P. A. Sauer, and J. Oddershede, *Mol. Phys.* **94**, 851 (1998).
- ¹⁵R. D. Wigglesworth, W. T. Raynes, S. P. A. Sauer, and J. Oddershede, *Mol. Phys.* **92**, 77 (1997).
- ¹⁶S. P. A. Sauer, W. T. Raynes, and R. A. Nicholls, *J. Chem. Phys.* **115**, 5994 (2001).
- ¹⁷R. D. Wigglesworth, W. T. Raynes, S. Kirpekar, J. Oddershede, and S. P. A. Sauer, *J. Chem. Phys.* **112**, 3735 (2000); *ibid.* **114**, 9192 (2001) E.
- ¹⁸B. Bennett, W. T. Raynes, and C. W. Anderson, *Spectrochim. Acta A* **45**, 821 (1989).
- ¹⁹S. P. A. Sauer, C. K. Møller, H. Koch, I. Paidarová, and V. Špirko, *Chem. Phys.* **238**, 385 (1998).
- ²⁰T. Enevoldsen, J. Oddershede, and S. P. A. Sauer, *Theor. Chem. Acc.* **100**, 275 (1998).
- ²¹S. P. A. Sauer, I. Paidarova, and V. Spirko (unpublished).
- ²²P. F. Provasi, G. A. Aucar, and S. P. A. Sauer, *J. Chem. Phys.* **115**, 1324 (2001).
- ²³J. Oddershede, J. Geertsen, and G. E. Scuseria, *J. Phys. Chem.* **92**, 3056 (1988).
- ²⁴L. B. Krivdin, S. P. A. Sauer, J. E. Peralta, and R. H. Contreras, *Magn. Reson. Chem.* **40**, 187 (2002).
- ²⁵A. A. Auer and J. Gauss, *J. Chem. Phys.* **115**, 1619 (2001).
- ²⁶S. A. Perera, H. Sekino, and R. J. Bartlett, *J. Chem. Phys.* **101**, 2186 (1994).
- ²⁷S. A. Perera, M. Nooijen, and R. J. Bartlett, *J. Chem. Phys.* **104**, 3290 (1996).
- ²⁸H. Sekino and R. J. Bartlett, *Chem. Phys. Lett.* **225**, 486 (1994).
- ²⁹A. Wu, D. Cremer, A. A. Auer, and J. Gauss, *J. Phys. Chem. A* **106**, 657 (2002).
- ³⁰V. G. Malkin, O. L. Malkina, and D. R. Salahub, *Chem. Phys. Lett.* **221**, 91 (1994).
- ³¹R. M. Dickson and T. Ziegler, *J. Phys. Chem.* **100**, 5286 (1996).
- ³²V. Sychrovsky, J. Gräfenstein, and D. Cremer, *J. Chem. Phys.* **113**, 3530 (2000).
- ³³T. Helgaker, M. Watson, and N. C. Handy, *J. Chem. Phys.* **113**, 9402 (2000).
- ³⁴S. M. Bass, R. L. DeLeon, and J. S. Muentzer, *J. Chem. Phys.* **86**, 4305 (1987); J. S. Muentzer and W. Klemperer, *ibid.* **52**, 6033 (1970).
- ³⁵C. W. Kern and R. L. Matcha, *J. Chem. Phys.* **49**, 2081 (1968).
- ³⁶W. C. Ermler and C. W. Kern, *J. Chem. Phys.* **55**, 4851 (1971).
- ³⁷B. J. Křohn, W. C. Ermler, and C. W. Kern, *J. Chem. Phys.* **60**, 22 (1974).
- ³⁸P.-O. Åstrand, K. Ruud, and P. Taylor, *J. Chem. Phys.* **112**, 2655 (2000).
- ³⁹M. Toyama, T. Oka, and Y. Morino, *J. Mol. Spectrosc.* **13**, 193 (1964).
- ⁴⁰W. T. Raynes, J. Geertsen, and J. Oddershede, *Int. J. Quantum Chem.* **52**, 153 (1994).
- ⁴¹“DALTON, a molecular electronic structure program,” Release 1.2, 2001, written by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, *et al.*
- ⁴²N. F. Ramsey, *Phys. Rev.* **91**, 303 (1953).
- ⁴³J. Olsen and P. Jørgensen, *J. Chem. Phys.* **82**, 3235 (1985).
- ⁴⁴T. A. Ruden, W. Klopper, and M. Quack (unpublished).
- ⁴⁵B. Bennett, W. T. Raynes, and W. Anderson, *Spectrochim. Acta, Part A* **45**, 821 (1989).
- ⁴⁶A. J. Russel and M. A. Spackman, *Mol. Phys.* **84**, 1239 (1995).
- ⁴⁷A. J. Russel and M. A. Spackman, *Mol. Phys.* **88**, 1109 (1996).
- ⁴⁸A. J. Russel and M. A. Spackman, *Mol. Phys.* **90**, 251 (1997).
- ⁴⁹T. A. Ruden, P. R. Taylor, and T. Helgaker, *J. Chem. Phys.* (to be published).
- ⁵⁰S. Huzinaga, *Approximate Atomic Functions* (University of Alberta, Edmonton, 1971).
- ⁵¹S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ⁵²W. Kutzelnigg, U. Fleischer, and M. Schindler, *NMR—Basic Principles and Progress* (Springer Verlag, Berlin, 1990), Vol. 23, p. 165; C. van Wüllen, Ph.D. thesis, Ruhr-Universität, Bochum, 1992.
- ⁵³A. Miani, E. Cané, P. Palmieri, A. Trombetti, and N. C. Handy, *J. Chem. Phys.* **112**, 248 (2000).
- ⁵⁴J. Martin, J. El-Yazal, and J. P. François, *Mol. Phys.* **86**, 1437 (1995).
- ⁵⁵M. Rosenstock, P. Rosmus, E. A. Reinsch, O. Treutler, S. Carter, and N. C. Handy, *Mol. Phys.* **93**, 853 (1998).
- ⁵⁶A. A. Auer, J. Gauss, and M. Pecul, *Chem. Phys. Lett.* **368**, 172 (2003).
- ⁵⁷K. Ruud, L. Frediani, R. Cammi, and B. Mennucci, *Int. J. Mol. Sci.* (to be published).
- ⁵⁸I. Ando and G. A. Webb, *Org. Magn. Reson.* **15**, 111 (1981).
- ⁵⁹K. V. Mikkelsen, K. Ruud, and T. Helgaker, *J. Comput. Chem.* **20**, 1281 (1999).
- ⁶⁰P.-O. Åstrand, K. V. Mikkelsen, P. Jørgensen, K. Ruud, and T. Helgaker, *J. Chem. Phys.* **108**, 2528 (1998).
- ⁶¹J. Kaski, J. Vaara, and J. Jokisari, *J. Am. Chem. Soc.* **118**, 8879 (1996).
- ⁶²R. Laatikainen, J. Ratilainen, R. Sebastian, and H. Santa, *J. Am. Chem. Soc.* **117**, 11006 (1995).
- ⁶³K. Ruud, unpublished material.
- ⁶⁴R. E. Wasylishen, J. O. Friedrich, S. Mooibroek, and J. M. MacDonald, *J. Chem. Phys.* **83**, 548 (1985).
- ⁶⁵J. O. Friedrich and R. E. Wasylishen, *J. Chem. Phys.* **83**, 3707 (1985).

- ⁶⁶N. M. Sergeyev, N. D. Sergeyeva, Y. A. Strelenko, and W. T. Raynes, *Chem. Phys. Lett.* **277**, 144 (1997).
- ⁶⁷K. J. Friesen and R. E. Wasylshen, *J. Magn. Reson.* **41**, 189 (1980).
- ⁶⁸G. Dombi, P. Diehl, J. Lounila, and R. Wasser, *Org. Magn. Reson.* **22**, 573 (1984).

- ⁶⁹J. O. Friedrich and R. E. Wasylshen, *Can. J. Chem.* **65**, 2238 (1987).
- ⁷⁰K. Jackowski, M. Wilczek, M. Pecul, and J. Sadlej, *J. Phys. Chem. A* **104**, 9806 (2000).
- ⁷¹J. Kaski, P. Lantto, J. Vaara, and J. Jokisaari, *J. Am. Chem. Soc.* **120**, 3993 (1998).