

Indirect nuclear spin–spin coupling constants from multiconfiguration linear response theory

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We have used multiconfiguration self-consistent-field theory to determine indirect nuclear spin–spin coupling constants. The Fermi contact, spin dipole, and paramagnetic spin–orbit contributions are evaluated as multiconfiguration linear response functions at zero frequency and the diamagnetic spin–orbit contribution as an average value of the multiconfiguration wave function. Sample calculations on HD and CH₄ demonstrate that most of the correlation contributions can be recovered in relatively small complete active space (CAS) reference state calculations.

I. INTRODUCTION

The energy shift that has its origin in the electron-coupled interactions between two nuclear spins I_N and $I_{N'}$ may be expressed as

$$E = \sum_{N > N'} J_{NN'} I_N \cdot I_{N'}, \quad (1)$$

where $J_{NN'}$ is the indirect nuclear spin–spin coupling constant and the summation is over all pairs of magnetic nuclei. Ramsey showed that $J_{NN'}$ has four contributions, one being an average value of the diamagnetic spin–orbit (DSO) operator and the three others second-order contributions involving the Fermi contact (FC), the spin dipole (SD), and the paramagnetic spin–orbit (PSO) operator.¹ In early *ab initio* calculations of the indirect nuclear spin–spin coupling constants, the second-order contribution originating from the Fermi-contact operator was thought to be dominant. Recent applications have shown that the size of the contributions depends strongly on the molecule considered and that none of the terms can be *a priori* neglected (consider, e.g., the nitrogen molecule where both the SD and PSO contributions are larger in magnitude than the FC contribution²). The Fermi-contact term is the most difficult to evaluate. It requires tight basis functions to appropriately describe the spin density at the nuclei and it cannot be described properly at the Hartree–Fock level. The early *ab initio* calculations of $J_{NN'}$ were therefore discouraging. Later applications where all terms have been considered and where a higher level of correlation has been used, have shown that spin–spin coupling constants can be calculated accurately using *ab initio* methods. In particular, the second-order polarization propagator approximation (SOPPA) and its coupled-cluster extension (CCSDPPA) have given accurate *ab initio* nuclear spin–spin coupling constants. These methods have their origin in perturbation theory with the fluctuation po-

tential as perturbation operator and their major application range are therefore molecules with small static correlation effects. In this communication we use multiconfiguration linear response (MCLR) theory to determine the nuclear spin–spin coupling constants. The multiconfiguration self-consistent-field (MCSCF) method is capable of describing electronic systems with large static correlation effects, thus making it possible to calculate spin–spin couplings for a large variety of molecules.

The DSO contribution is evaluated as an average value with respect to the MCSCF reference state while the second-order contributions from the PSO, FC, and SD operators are obtained as multiconfiguration linear response functions at zero frequency. The PSO contributions are obtained from singlet linear response functions (the PSO operator is a tensor operator of rank zero in spin space) and the FC and SD contributions from triplet linear response functions (the FC and SD operators are tensor operators of rank one in spin space).

The evaluation of the nuclear spin–spin coupling constants are implemented as part of our multiconfiguration response program. It is designed to treat large configuration spaces and large orbital basis sets. Direct, iterative techniques are used to solve the response matrix equations. The evaluation of the singlet multiconfiguration linear response function is described in Ref. 3 and the evaluation of the triplet multiconfiguration linear response function is given in Ref. 4.

In the next section we briefly summarize the theory which is necessary to evaluate the nuclear spin–spin coupling constants. In Sec. III we report sample calculations on the hydrogen and methane molecules. The last section contains some concluding remarks.

II. THEORY

The spin–spin coupling constant $J_{NN'}$ is defined in terms of a spin–spin coupling tensor

$$J_{NN'} = \frac{1}{3} \text{Tr } \mathbf{J}_{NN'} \quad (2)$$

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The contributions to the spin–spin coupling tensor fall naturally into two classes, the orbit coupled the interactions and the electron spin coupled interactions. The first class, the orbit coupled interaction contain the DSO and PSO Hamiltonians

$$H_{\text{DSO}} = \frac{e^2}{2m_e^2} \left(\frac{\mu_0}{4\pi} \right)^2 \sum_{nNN'} \gamma_N \gamma_{N'} \times \frac{(\mathbf{I}_N \cdot \mathbf{I}_{N'}) (\mathbf{r}_{nN} \cdot \mathbf{r}_{nN'}) - (\mathbf{I}_N \cdot \mathbf{r}_{nN'}) (\mathbf{I}_{N'} \cdot \mathbf{r}_{nN})}{r_{nN}^3 r_{nN'}^3}, \quad (3)$$

$$H_{\text{PSO}} = \frac{e}{m_e} \frac{\mu_0}{4\pi} \sum_{nN} \gamma_N \mathbf{I}_N \frac{\mathbf{l}_{nN}}{r_{nN}^3}, \quad (4)$$

where $\mathbf{r}_{nN} = \mathbf{r}_n - \mathbf{r}_N$ is the displacement of electron n relative to nucleus N and $\mathbf{l}_{nN} = \mathbf{r}_{nN} \times \mathbf{p}_n$ is the orbital angular momentum of electron n relative to nucleus N . The DSO contribution is evaluated as an expectation value and the PSO contribution as a second-order energy expression.

The second class of terms involves the SD and FC Hamiltonians

$$H_{\text{SD}} = \frac{\mu_B g_e}{\hbar} \frac{\mu_0}{4\pi} \sum_{nN} \gamma_N \frac{3(\mathbf{s}_n \cdot \mathbf{r}_{nN}) (\mathbf{r}_{nN} \cdot \mathbf{I}_N) - r_{nN}^2 \mathbf{s}_n \cdot \mathbf{I}_N}{r_{nN}^5}, \quad (5)$$

$$H_{\text{FC}} = \frac{\mu_B g_e}{\hbar} \frac{2\mu_0}{3} \sum_{nN} \gamma_N \delta(\mathbf{r}_{nN}) \mathbf{s}_n \cdot \mathbf{I}_N, \quad (6)$$

which both contribute to second order in perturbation theory.

The second-order energy correction due to a time-independent perturbation V can be expressed in terms of a linear response function at zero frequency

$$\epsilon^{(2)} = \frac{1}{2} \langle \langle V; V \rangle \rangle_{\omega=0}. \quad (7)$$

Its evaluation for an MCSCF reference wave function has been described previously for singlet³ and triplet perturbations⁴ of a singlet reference state. In our case the PSO operator is a singlet perturbation operator and the FC and SC operators triplet perturbation operators.

We give below the working equations for the evaluation of the second-order contributions to the nuclear spin–spin coupling parameters. In what follows greek superscripts denote the spherical components of a vector operator and roman superscripts Cartesian components. The description of electronic spin is simplified by using the Wigner–Eckart theorem. Consider first the FC term in second quantization

$$H_{\text{FC}} = \frac{\mu_B g_e}{\hbar} \frac{2\mu_0}{3} \sum_{N\mu pq} \gamma_N (-1)^\mu I_N^\mu \delta_{N;pq} s_{pq}^{-\mu}. \quad (8)$$

I_N^μ are the spherical components of the nuclear spin operators,

$$I_N^1 = -\frac{I_N^x + iI_N^y}{\sqrt{2}}, \quad (9)$$

$$I_N^0 = I_N^z, \quad (10)$$

$$I_N^{-1} = \frac{I_N^x - iI_N^y}{\sqrt{2}}, \quad (11)$$

and

$$s_{pq}^1 = -\frac{a_{p\alpha}^\dagger a_{q\beta}}{\sqrt{2}} \tilde{\eta}, \quad (12)$$

$$s_{pq}^0 = \frac{a_{p\alpha}^\dagger a_{q\alpha} - a_{p\beta}^\dagger a_{q\beta}}{2} \tilde{\eta}, \quad (13)$$

$$s_{pq}^{-1} = \frac{a_{p\beta}^\dagger a_{q\alpha}}{\sqrt{2}} \tilde{\eta}, \quad (14)$$

are the components of the triplet orbital excitation tensor operator. The $\delta_{N;pq}$ are the integrals of the Dirac delta function at nucleus N ,

$$\delta_{N;pq} = \langle p | \delta(\mathbf{r}_N) | q \rangle. \quad (15)$$

The second-order energy involves the sum over all allowed triplet states ψ_K^σ ,

$$\epsilon_{\text{FC}}^{(2)} = \left(\frac{\mu_B g_e}{\hbar} \frac{2\mu_0}{3} \right)^2 \sum_{NN'} \gamma_N \gamma_{N'} \sum_{\mu\nu} (-1)^{\mu+\nu} I_N^\mu I_{N'}^{-\nu} \times \sum_{K,\sigma} \frac{\langle 0 | \sum_{pq} \delta_{N;pq} s_{pq}^{-\mu} | \psi_K^\sigma \rangle \langle \psi_K^\sigma | \sum_{rs} \delta_{N';rs} s_{rs}^\nu | 0 \rangle}{E_0 - E_K}. \quad (16)$$

It follows from the Wigner–Eckart theorem that the non-vanishing terms in Eq. (16) satisfy $\mu = \nu = \sigma$. Furthermore, we have the simplifications

$$\langle 0 | s_{pq}^{-\mu} | \psi_K^\mu \rangle = (-1)^\mu \langle 0 | s_{pq}^0 | \psi_K^0 \rangle, \quad (17)$$

$$\langle \psi_K^0 | s_{pq}^\mu | 0 \rangle = \langle \psi_K^0 | s_{pq}^0 | 0 \rangle. \quad (18)$$

Substituting this into Eq. (16) we obtain

$$\epsilon_{\text{FC}}^{(2)} = \left(\frac{\mu_B g_e}{\hbar} \frac{2\mu_0}{3} \right)^2 \sum_{NN'} \gamma_N \gamma_{N'} \sum_{\mu} (-1)^\mu I_N^- I_{N'}^\mu \times \sum_K \frac{\langle 0 | \sum_{pq} \delta_{N;pq} s_{pq}^0 | \psi_K^0 \rangle \langle \psi_K^0 | \sum_{rs} \delta_{N';rs} s_{rs}^0 | 0 \rangle}{E_0 - E_K}. \quad (19)$$

We may now identify the Fermi-contact contribution to the spin–spin coupling constant as

$$J_{NN'}^{\text{FC}} = N_{\text{FC}} g_N g_{N'} \langle \langle \delta_N; \delta_{N'} \rangle \rangle_{\omega=0}, \quad (20)$$

where

$$\delta_N = \sum_{pq} \langle p | \delta(\mathbf{r}_N) | q \rangle s_{pq}^0. \quad (21)$$

We have here rewritten the magnetogyric ratios in terms of the dimensionless g factors, $\gamma_N = g_N \mu_N / \hbar$, with μ_N being the nuclear magneton, which gives the constant N_{FC}

$$N_{\text{FC}} = \left(\frac{\mu_B g_e}{\hbar} \frac{2\mu_0}{3} \frac{\mu_N}{\hbar} \right)^2. \quad (22)$$

Similarly, the Cartesian kl component of the spin-dipole tensor is

$$J_{NN'}^{\text{SD};kl} = N_{\text{SD}} g_N g_{N'} \sum_{i=1}^3 \langle \langle \zeta_N^{ki}; \zeta_{N'}^{li} \rangle \rangle_{\omega=0}, \quad (23)$$

where

$$\zeta_N^{ki} = \sum_{pq} \langle p | \frac{3x_N^k x_N^i - r_N^2 \delta^{ki}}{r_N^5} | q \rangle s_{pq}^0, \quad (24)$$

where δ^{ki} is the Kronecker delta and

$$N_{\text{SD}} = \left(\frac{\mu_B g_e}{\hbar} \frac{\mu_0}{4\pi} \frac{\mu_N}{\hbar} \right)^2. \quad (25)$$

The paramagnetic contribution is given as

$$J_{NN'}^{\text{PSO},kl} = -N_{\text{PSO}} g_N g_{N'} \langle \langle \lambda_N^k; \lambda_{N'}^l \rangle \rangle_{\omega=0}, \quad (26)$$

where the constant is

$$N_{\text{PSO}} = \left(\frac{e}{m_e} \frac{\mu_0}{4\pi} \frac{\mu_N}{\hbar} \right)^2 \quad (27)$$

and the operator

$$\lambda_N^k = \sum_{pq} \langle p | \frac{(\mathbf{r}_N \times \nabla)^k}{r_N^3} | q \rangle E_{pq} \quad (28)$$

is expressed in terms the singlet excitation operators

$$E_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}. \quad (29)$$

Finally the DSO contribution is given by the expectation value

$$J_{NN'}^{\text{DSO},kl} = N_{\text{DSO}} g_N g_{N'} \langle p | \frac{(\mathbf{r}_N \cdot \mathbf{r}_{N'}) \delta^{kl} - x_{N'}^k x_N^l}{r_N^3 r_{N'}^3} | q \rangle D_{pq}, \quad (30)$$

where now

$$N_{\text{DSO}} = \left(\frac{e}{m_e} \frac{\mu_0}{4\pi} \frac{\mu_N}{\hbar} \right)^2 \quad (31)$$

and D_{pq} is the first-order reduced density matrix.

From the perturbation analysis, one also has the possibility of indirect nuclear self-interactions, but tradition has been to avoid these terms since the empirical spin Hamiltonian used to interpret the spectra does not include them. Furthermore, for the DSO interaction one would need a more sophisticated description of the magnetic vector potential near the nucleus since the dipole approximation breaks down so that Eq. (3) leads to divergent integrals for $N = N'$.

We finish this section with a comment on the evaluation of the spin–spin coupling integrals. The calculation of FC integrals is trivial, involving only the evaluation of the Gaussian functions at the nuclear positions. The SD integrals are evaluated in terms of field-gradient integrals using the McMurchie–Davidson scheme.⁵ Since the field-gradient operator contains both SD and FC contributions

$$\nabla \times \frac{\mathbf{m} \times \mathbf{r}}{r^3} = \left(\frac{3\mathbf{r}\mathbf{r} - r^2 \mathbf{1}}{r^5} + \frac{8\pi}{3} \delta(\mathbf{r}) \right) \cdot \mathbf{m} \quad (32)$$

we must subtract the FC contributions from the calculated field-gradient integrals to obtain the SD integrals. Traditionally, the SD and FC contributions to the calculated spin–spin coupling parameters are quoted separately. For anisotropies, there is also a contribution from the cross-term FC/SD. But if we are only interested in total couplings and isotropies, there is no need for this since all information is contained in Eq. (32). The PSO integrals are evaluated in the McMurchie–Davidson scheme by a small modification of our implementation of spin–orbit integrals described in Ref. 6. The DSO integrals are evaluated using the method described by Matsuoka *et al.*⁷ The method includes a numerical integration using a one-dimensional 40-point Legendre quadrature and scaling factor of $m = 0.75$. All integrals are evaluated over symmetrized orbitals and operators in the largest Abelian subgroup of the molecular point group.

III. SAMPLE CALCULATIONS

We have carried out sample calculations of the nuclear spin–spin coupling constants for HD and CH₄. Correlated results have previously been reported for these systems using the SOPPA and CCSDPPA approaches.

All physical constants and conversion factors were taken from Cohen and Taylor⁸ to obtain spin–spin coupling constants in Hz. The bare integral expressions in Eqs. (20), (23), (26), and (30) are then multiplied by the following factors:

$$N_{\text{FC}} = 97.343\,06,$$

$$N_{\text{SD}} = 1.386\,97,$$

$$N_{\text{PSO}} = N_{\text{DSO}} = 1.383\,76.$$

The difference between the SD and the two PSO and DSO factors arises from the anomalous magnetic moment of the electron. Sometimes this is neglected, as for instance in the original equations by Ramsey.¹ This introduces an error of the order α (the fine-structure constant), consistent within this level of perturbation theory. We have, however, chosen to use the experimental (or equivalently the QED) value.

A. The spin–spin coupling constant of HD

Oddershede *et al.* have carried out extensive calculations of the nuclear spin–spin coupling constants of HD, examining the effect of correlation and basis set saturation.⁹ We have carried out calculations using two of the basis sets of Oddershede *et al.*; basis set *A* and basis set *H*. Set *A* is a $10s5p$ basis composed of Duijneveldt's $10s$ basis¹⁰ and a $5p$ set from Schulman and Kaufman.¹¹ This basis is used to calibrate our approximate correlated calculations since full configuration interaction (FCI) results can straightforwardly be obtained within this basis. Basis set *H* is an extension of basis *A* with two *d* functions (with exponents 2.0 and 5.0) and four tight *s* functions (exponents 5000, 15 000, 50 000, and 150 000) added. Basis *H* was believed by Oddershede *et al.* to introduce errors smaller than ± 0.1 Hz. Analyzing their results we find that this basis is saturated with respect to *s* and *p* functions. Adding a tight *d* function (exponent 12.6), Oddershede *et al.* found that the SD value changed by 0.06 Hz (see results of basis *H* and *M* in Table I of Ref. 9). To saturate the *d* space we have successively added more *d* functions to basis *H* (see Table I). We also investigated the importance of the *f* functions by adding to basis *Q* single *f* functions with various exponents (basis set *R–V* in Table I). In all cases we carried out calculations using SCF and two CAS wave functions, except for the calculations involving *f* functions where we restricted ourselves to the largest CAS. The two active spaces are $(2\sigma_g 1\pi_u 1\sigma_u)$ for CAS I and $(4\sigma_g 2\pi_u 2\sigma_u 1\pi_g)$ for CAS II. The active spaces were designed based on an MP2 natural orbital occupation number analysis.

The calculated contributions to the spin–spin coupling constant are given in Table I. The SD contribution decreases by about 0.1 Hz adding the *d*(0.8) function (basis *N*) and increases by 0.1 Hz adding the *d*(12.8). Adding the diffuse *d*(0.27) has little effect, while the *d*(37.8) lowers the SD value by 0.05 Hz. Only smaller effects are observed adding

TABLE I. The Fermi contact (FC), spin dipole (SD), paramagnetic (PSO), and diamagnetic spin–orbit (DSO) contributions to the spin–spin coupling constants for various basis sets and correlation levels for HD.

Correlation level	Basis set	FC	SD	PSO	DSO	Total
HF	<i>A</i> (10s5p)	52.013	0.468	0.778	−0.320	52.939
	<i>H</i> (14s5p2d)	53.234	0.574	0.830	−0.330	54.308
	<i>N</i> [<i>H</i> + <i>d</i> (0.8)]	53.233	0.486	0.833	−0.330	54.222
	<i>O</i> [<i>N</i> + <i>d</i> (12.6)]	53.233	0.589	0.833	−0.330	54.325
	<i>P</i> [<i>O</i> + <i>d</i> (0.27)]	53.232	0.578	0.834	−0.330	54.314
	<i>Q</i> [<i>P</i> + <i>d</i> (37.8)]	53.231	0.525	0.834	−0.330	54.260
	<i>Q</i> 1 [<i>Q</i> + <i>d</i> (0.09)]	53.229	0.524	0.834	−0.330	54.257
	<i>Q</i> 2 [<i>Q</i> + <i>d</i> (112)]	53.231	0.541	0.834	−0.330	54.276
CAS I	<i>A</i>	39.533	0.283	0.750	−0.291	40.275
	<i>H</i>	40.516	0.486	0.811	−0.305	41.508
	<i>N</i>	40.509	0.401	0.817	−0.305	41.422
	<i>O</i>	40.509	0.504	0.817	−0.305	41.525
	<i>P</i>	40.506	0.494	0.818	−0.305	41.513
	<i>Q</i>	40.506	0.440	0.818	−0.305	41.459
	<i>Q</i> 2	40.505	0.440	0.818	−0.305	41.458
CAS II	<i>A</i>	39.245	0.379	0.749	−0.292	40.081
	<i>H</i>	40.243	0.484	0.811	−0.307	41.231
	<i>N</i>	40.194	0.398	0.817	−0.307	41.102
	<i>O</i>	40.194	0.501	0.817	−0.307	41.205
	<i>P</i>	40.186	0.492	0.818	−0.307	41.189
	<i>Q</i>	40.186	0.438	0.818	−0.307	41.135
	<i>Q</i> 1	40.185	0.438	0.818	−0.307	41.134
	<i>Q</i> 2	40.185	0.455	0.818	−0.307	41.151
	<i>R</i> [<i>Q</i> + <i>f</i> (0.5)]	40.185	0.438	0.818	−0.307	41.134
	<i>S</i> [<i>Q</i> + <i>f</i> (1.0)]	40.190	0.445	0.820	−0.308	41.147
	<i>T</i> [<i>Q</i> + <i>f</i> (1.5)]	40.193	0.451	0.822	−0.308	41.158
	<i>U</i> [<i>Q</i> + <i>f</i> (4.5)]	40.190	0.450	0.826	−0.310	41.156
	<i>V</i> [<i>Q</i> + <i>f</i> (14.5)]	40.186	0.437	0.818	−0.307	41.134
FCI	<i>A</i>	39.189	0.379	0.749	−0.292	40.025

further *d* functions. It is seen that adding *f* functions (Basis *R–V*) have little effect on any of the contributions. Comparing the FCI and CAS II results for basis *A*, we find that the CAS II results are 0.06 above the FCI results.

To introduce vibrational corrections we evaluated the spin–spin coupling constants at the 11 internuclear distances used by Oddershede *et al.* (see Table II). Along the direction of increasing internuclear distance, static correlation becomes more important so we would expect deviations from

TABLE II. Internuclear distance dependence of the nuclear spin–spin coupling constants of HD (Hz). Calculated at the CAS II level for basis set *O*.

<i>R</i> , au	<i>J</i> ^{FC}	<i>J</i> ^{SD}	<i>J</i> ^{PSO}	<i>J</i> ^{DSO}	<i>J</i> ^{total}
1.20	27.615	0.648	1.153	−0.230	29.186
1.25	31.088	0.630	1.056	−0.266	32.508
1.30	34.302	0.596	0.969	−0.289	35.578
1.35	37.320	0.551	0.889	−0.302	38.459
1.40	40.194	0.501	0.817	−0.307	41.206
1.45	42.970	0.452	0.752	−0.308	43.867
1.50	45.686	0.408	0.693	−0.304	46.483
1.55	48.375	0.369	0.639	−0.298	49.086
1.60	51.068	0.338	0.590	−0.289	51.707
1.70	56.569	0.292	0.505	−0.269	57.097
1.80	62.383	0.261	0.433	−0.246	62.831

perturbation-based methods at large distances. However, in the range considered by us (1.20–1.80 bohr), we did not observe significant differences between our results and the results of Oddershede *et al.*

The vibrational–rotational wave functions were calculated using the finite element method.¹² For the potential energy function we used a spline fit of the data of Kolos and Wolniewicz.¹³ The integration of the nuclear spin–spin coupling constant over the wave function was obtained by a least-square fit of coupling constant data at the 11 internuclear distances listed in Table II with linear, quadratic, and cubic polynomials, and integrating the numerical wave function with these polynomials over all internuclear distances.

TABLE III. Rotationally and vibrationally averaged spin–spin coupling constants (Hz) at 40 K.

<i>J</i> (<i>R</i> _{<i>v</i>} = 1.40 bohr)	41.21
<i>J</i> (<i>v</i> = <i>N</i> = 0)	43.17
<i>J</i> (<i>T</i> = 40 K)	43.18
<i>J</i> (expt) ^a	42.94 ± 0.04
<i>J</i> (expt) ^b	43.11 ± 0.02

^aReference 14.

^bReference 15.

TABLE IV. Electron correlation dependence on spin–spin coupling constants (Hz) of CH₄ at the experimental geometry $r_{\text{CH}} = 1.0858 \text{ \AA}$ (Ref. 18).

Coupling	Method	FC	SD	PSO	DSO	Total
C–H	SCF	155.90	−0.23	1.39	0.25	157.31
	CAS I	130.78	−0.08	1.31	0.26	132.27
	CAS II	123.53	0.02	1.48	0.27	125.30
	CCSDPPA ^a	122.12	−0.01	1.50	0.25	123.87
	Experiment ^b	120.78 ± 0.05				
H–H	SCF	−27.69	0.44	3.63	−3.54	−27.16
	CAS I	−21.26	0.36	3.56	−3.50	−20.84
	CAS II	−15.73	0.35	3.59	−3.51	−15.30
	CCSDPPA ^a	−14.70	0.33	3.60	−3.54	−14.31
	Experiment ^c	−12.564 ± 0.004				

^a Reference 17.^b Reference 18.^c Reference 19.

The linear, quadratic, and cubic polynomial fits gave results differing by less than 0.04 Hz. The reported results (Table III) are obtained using the cubic extrapolation scheme.

The calculated vibrational contribution to the nuclear spin–spin coupling constant is very similar to the one found by Oddershede *et al.* From our calculated value of $J(T = 40 \text{ K})$ of 43.18 Hz we should subtract 0.06 Hz as suggested by the calibration of the FC contribution in basis set *A*. Oddershede *et al.* found a value of $J(T = 40 \text{ K})$ of 42.79 Hz. Based on the FCI calibration of basis set *A* the FC contribution in CCSDPPA was underestimated by 0.50 Hz, giving $J(T = 40 \text{ K})$ of 43.30 Hz. The difference between the result we obtain and the one that would be obtained by Oddershede *et al.* is mainly due to the fact that Oddershede used the value 2.0 for the electronic *g* factor. Both the results of Oddershede *et al.* using CCSDPPA and ours using MCLR suggest a nuclear spin–spin coupling constant of about 43.15 Hz. Of two experimental results in the gas phase, 42.94(04) Hz by Beckett¹⁴ and 43.111(20) Hz by Neronov *et al.*¹⁵ our value agrees well with the latter. We don't claim to have that accuracy, so this agreement is most likely coincidental. Beckett's experiment was performed at the temperature 40 K. We don't have the corresponding value from Neronov's experiment, but since our calculated values hardly change in the range 0–40 K, the temperature is not crucial for the sake of comparison.

B. The spin–spin coupling constant of CH₄

The first *ab initio* calculations of the spin–spin coupling constants of methane were performed at the SCF level by Lazzaretti *et al.*¹⁶ The importance of correlation was established by Geertsen *et al.*¹⁷ Their CCSDPPA method reduced the coupling constants considerably compared to the SCF value, the C–H coupling by 20% and the H–H coupling by about a half!

We use basis B24 in Ref. 17, a $[10s5p4d/6s2p]$ set optimized to give an expected basis set error of $\pm 0.2 \text{ Hz}$. It includes tight *s* functions to appropriately describe the FC term, and polarization functions for the noncontact terms. We have performed an SCF calculation, reproducing the

results of Geertsen *et al.*, and two CAS calculations. The HF configuration of methane is $1a_1^2 2a_1^2 1t_2^6$ in the tetrahedral group T_d .

The choice of active spaces was based on a natural orbital analysis of an MP2 calculation. For CAS I (Table IV) the active space is $(2a_1, 2t_2)$ and for CAS II $(4a_1, 3t_2)$. We see the same trends as Geertsen *et al.*; a decrease in the absolute values by 20% for the C–H coupling and by 44% for the H–H coupling, as compared to the SCF values. We also note that correlation hardly changes the value of the DSO contribution. We recover about 80% of the correlation contribution for the FC term in the CAS II calculations. Our results are very similar to the CCSDPPA results with our FC contribution being about 1 Hz above the CCSDPPA value.

IV. CONCLUSIONS

We have shown that the indirect NMR spin–spin coupling constants can be efficiently evaluated in a multiconfiguration linear response framework. The sample calculations indicate that most of the correlation contributions can be recovered in rather small CAS reference state calculations. We have essentially reproduced previously reported values calculated from SOPPA and CCSDPPA methods. These methods rely on molecular states that are reasonably described at the SCF level. The strength of the MCLR approach is its capability to describe systems where near-degeneracy correlation is important.

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