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# On the truncation of the number of excited states in density functional theory sum-over-states calculations of indirect spin spin coupling constants

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It is investigated, whether the number of excited (pseudo)states can be truncated in the sum-over-states expression for indirect spin-spin coupling constants (SSCCs), which is used in the Contributions from Localized Orbitals within the Polarization Propagator Approach and Inner Projections of the Polarization Propagator (IPPP-CLOPPA) approach to analyzing SSCCs in terms of localized orbitals. As a test set we have studied the nine simple compounds, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, SiH<sub>4</sub>, PH<sub>3</sub>, SH<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. The excited (pseudo)states were obtained from time-dependent density functional theory (TD-DFT) calculations with the B3LYP exchange-correlation functional and the specialized core-property basis set, aug-cc-pVTZ-J. We investigated both how the calculated coupling constants depend on the number of (pseudo)states included in the summation and whether the summation can be truncated in a systematic way at a smaller number of states and extrapolated to the total number of (pseudo)states for the given one-electron basis set. We find that this is possible and that for some of the couplings it is sufficient to include only about 30% of the excited (pseudo)states. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4937572>]

## I. INTRODUCTION

In recent years, there has been an increasing interest in the analysis of the parameters of a NMR spectrum, the indirect nuclear spin-spin coupling constant (SSCC)  $J$  and the nuclear magnetic shielding constant  $\sigma$ , in terms of localized molecular orbitals (LMOs).<sup>1</sup> Several methods have been developed for this, which can essentially be grouped into three different approaches. In the probably oldest approach the Hessian or principal propagator of an approximate response function is diagonalized leading to an approximation to the standard Raleigh-Schrödinger perturbation theory sum-over-states (SOS) expression for response properties.<sup>2</sup> Transforming the eigenvectors to localized orbitals allows expressing the response properties as summation over contributions from two pairs of localized occupied and two pairs of localized unoccupied orbitals. This approach, often called Contributions from Localized Orbitals within the Polarization Propagator Approach and Inner Projections of the Polarization Propagator (IPPP-CLOPPA), had originally been used in connection with semi empirical methods<sup>3-6</sup> but has later on been extended to the level of *ab initio* coupled perturbed Hartree-Fock theory,<sup>7-11</sup> also called random phase approximation (RPA), and Kohn-Sham density functional theory (DFT) linear response functions.<sup>12-14</sup> Equivalent DFT-SOS expressions for magnetic linear response properties in terms of transition densities had previously been presented by Autschbach *et al.*<sup>15</sup> In the second approach the first-

order perturbed orbitals of coupled perturbed DFT or the solution vectors of approximate linear response functions are transformed to localized orbitals leading to an analysis in terms of only one occupied and one virtual orbital. This approach was frequently employed, e.g., by Contreras and co-workers,<sup>16-20</sup> in combination with the natural bond orbitals of Weinberg.<sup>21-26</sup> Recently such an approach has also been devised for response functions at the level of the second order polarization propagator approximation (SOPPA)<sup>27-29</sup> and for relativistic DFT calculations at the level of the zeroth-order regular approximation (ZORA).<sup>30</sup> The third class of approaches proposed by Cremer and co-workers<sup>31-37</sup> essentially obtains the contribution of a given orbital indirectly by removing the contribution of this orbital in the coupled perturbed DFT calculations.

Compared to the latter two approaches the SOS or CLOPPA approach offers the advantage that the coupling constants can be analyzed in terms of a simultaneous interaction of both nuclei with the orbitals leading to coupling pathways and that one can understand the couplings also in terms of contributions from different excited states. However, this is also an apparent disadvantage of this approach. The inclusion of all excited states in the SOS expression, as done in the previous studies on smaller systems,<sup>12-14</sup> becomes prohibitive for larger molecules, while in a previous study of SSCCs at the coupled perturbed Hartree-Fock and SOPPA level<sup>38</sup> the truncation of the number of excited states in the SOS expression lead to erratic results. However, the one-electron basis sets employed in this study were much smaller than modern specialized core-property basis sets. Furthermore, for other response properties such as the optical rotatory dispersion<sup>39-43</sup> or the hyperpolarizability<sup>44</sup> it was observed,

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that the necessary number of excited states for convergence is large but smaller than the total number.

In the present study we discuss therefore based on the couplings in the nine small molecules, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, SiH<sub>4</sub>, PH<sub>3</sub>, H<sub>2</sub>S, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, whether the number of states necessary in the SOS expression of IPPP-CLOPPA could anyway be truncated also for coupling constants. Furthermore we investigate whether it is possible to find a functional form, which allows extrapolation to the full value of the coupling constants based on the results for a smaller number of excited states. However one should note that the purpose of such a truncated SOS approach is by no means to replace the more efficient linear response approach for the calculation of total coupling constants, but simply to reduce the computational cost in the localized orbital analysis of coupling constants via the IPPP-CLOPPA method in order to make IPPP-CLOPPA studies feasible for larger molecules.

## II. METHOD OF CALCULATION

The theory of indirect nuclear spin–spin coupling constants,  $J$ ,<sup>45</sup> and different computational methods for calculating them has been described extensively in the literature.<sup>1,2,46–50</sup> One should mention, though, that there are four contributions to the SSCC: the Fermi contact (FC) and the spin-dipolar (SD), which come from the interaction of the nuclear magnetic moments with the spin of the electrons, as well as the diamagnetic spin orbital (DSO) and the paramagnetic spin orbital (PSO), which are due to the interaction of the nuclear spins with the orbital angular momentum of the electrons.

At the coupled perturbed DFT (or coupled perturbed Hartree-Fock) level the isotropic indirect nuclear spin-spin coupling constant between two nuclei  $K$  and  $L$  can thus be expressed as<sup>51</sup>

$$J(KL) = \frac{1}{3} \frac{\gamma_K \gamma_L}{h} \sum_{\alpha=x,y,z} \{ \langle \langle \hat{O}_{K\alpha}^{FC} + \hat{O}_{K\alpha}^{SD}; \hat{O}_{L\alpha}^{FC} + \hat{O}_{L\alpha}^{SD} \rangle \rangle_{\omega=0} + \langle \langle \hat{O}_{K\alpha}^{PSO}; \hat{O}_{L\alpha}^{PSO} \rangle \rangle_{\omega=0} + \langle \Psi_0 | \hat{O}_{KL,\alpha\alpha}^{DSO} | \Psi_0 \rangle \}, \quad (1)$$

where the perturbing operators are given as

$$\hat{O}_{K\alpha}^{FC} = \left( \frac{\mu_0 g_e e \hbar}{3m_e} \right) \sum_i \hat{s}_{i\alpha} \delta(r_{iK}), \quad (2)$$

$$\hat{O}_{K\alpha}^{SD} = \left( \frac{\mu_0 g_e e \hbar}{8\pi m_e} \right) \sum_i \frac{3 (\hat{s}_i \cdot \hat{r}_{iK}) \hat{r}_{iK,\alpha} - \hat{r}_{iK}^2 \hat{s}_{i\alpha}}{\hat{r}_{iK}^5}, \quad (3)$$

$$\hat{O}_{K\alpha}^{PSO} = \left( \frac{\mu_0 e \hbar}{4\pi m_e} \right) \sum_i \frac{\hat{l}_{i\alpha} (\vec{R}_K)}{\hat{r}_{iK}^3}, \quad (4)$$

and

$$\hat{O}_{KL,\alpha\alpha}^{DSO} = \left( \frac{\mu_0}{4\pi} \right)^2 \left( \frac{e^2 \hbar^2}{m_e} \right) \sum_i \frac{\hat{r}_{iL} \cdot \hat{r}_{iK} - \hat{r}_{iL,\alpha} \hat{r}_{iK,\alpha}}{\hat{r}_{iL}^3 \hat{r}_{iK}^3}. \quad (5)$$

The linear response function  $\langle \langle \hat{O}^A; \hat{O}^B \rangle \rangle_{\omega=0}$  of two operators  $\hat{O}^A = \sum_i \hat{O}^A(i)$  and  $\hat{O}^B = \sum_i \hat{O}^B(i)$  at the DFT or Hartree-Fock level has the form

$$\begin{aligned} \langle \langle \hat{O}^A; \hat{O}^B \rangle \rangle_{\omega=0} &= -(\tilde{\mathbf{T}}(\hat{O}^A) \quad -\tilde{\mathbf{T}}^*(\hat{O}^A)) \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{T}^*(\hat{O}^B) \\ -\mathbf{T}(\hat{O}^B) \end{pmatrix}, \quad (6) \end{aligned}$$

where the elements of a property gradient column vector  $\mathbf{T}(\hat{O}^A)$  evaluate to

$$\mathbf{T}_{ai}(\hat{O}^A) = \langle \varphi_i | \hat{O}^A | \varphi_a \rangle \quad (7)$$

in terms of occupied and virtual spatial orbitals  $\varphi_i(1)$  and  $\varphi_a(1)$ , respectively.

Diagonalising the molecular Hessian matrix,  $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}$ , which is equivalent to solving the RPA or time-dependent DFT (TD-DFT) eigenvalue problem,<sup>52</sup>

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} \begin{pmatrix} \boldsymbol{\omega} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{\omega} \end{pmatrix}, \quad (8)$$

the response function can also be written as

$$\begin{aligned} \langle \langle \hat{O}^A; \hat{O}^B \rangle \rangle_{\omega=0} &= -(\tilde{\mathbf{T}}(\hat{O}^A) \quad -\tilde{\mathbf{T}}^*(\hat{O}^A)) \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} \\ &\quad \times \begin{pmatrix} \boldsymbol{\omega} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{\omega} \end{pmatrix}^{-1} \begin{pmatrix} \tilde{\mathbf{X}} & \tilde{\mathbf{Y}} \\ -\tilde{\mathbf{Y}} & -\tilde{\mathbf{X}} \end{pmatrix} \begin{pmatrix} \mathbf{T}^*(\hat{O}^B) \\ -\mathbf{T}(\hat{O}^B) \end{pmatrix}, \quad (9) \end{aligned}$$

where  $\boldsymbol{\omega}$  is a diagonal matrix, whose diagonal elements,  $\Delta E_{0 \rightarrow n}$ , are the RPA or TD-DFT approximations to the electronic excitation energies of the system, and where the  $n$ th column of the matrix  $\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$  is the corresponding eigenvector.

The coupling constant can then alternatively also be calculated as the following summation over all eigenvalues of the molecular Hessian, i.e.,

$$\begin{aligned} J(KL) &= \frac{2}{3} \frac{\gamma_K \gamma_L}{h} \sum_{\alpha=x,y,z} \left\{ - \sum_n \frac{\tilde{\mathbf{T}}(\hat{O}_{K\alpha}^{FC} + \hat{O}_{K\alpha}^{SD})(\mathbf{X}^n - \mathbf{Y}^n)(\tilde{\mathbf{X}}^n - \tilde{\mathbf{Y}}^n) \mathbf{T}(\hat{O}_{L\alpha}^{FC} + \hat{O}_{L\alpha}^{SD})}{\Delta E_{0 \rightarrow n}} \right. \\ &\quad \left. + \sum_n \frac{\tilde{\mathbf{T}}(\hat{O}_{K\alpha}^{PSO})(\mathbf{X}^n + \mathbf{Y}^n)(\tilde{\mathbf{X}}^n + \tilde{\mathbf{Y}}^n) \mathbf{T}(\hat{O}_{L\alpha}^{PSO})}{\Delta E_{0 \rightarrow n}} + \sum_i \langle \phi_i | \hat{O}_{KL,\alpha\alpha}^{DSO} | \phi_i \rangle \right\}. \quad (10) \end{aligned}$$

The three response function contributions to the coupling constants can therefore be written as summation over these eigenvalues, i.e.,

$$J^{FC/SD/PSO}(KL) = \sum_n J_n^{FC/SD/PSO}(KL). \quad (11)$$

The lowest eigenvalues of the RPA or TD-DFT molecular Hessian are approximations to the bound excited states of the molecules, while all other eigenvalues correspond to pseudo states with energies above the ionization potential of the molecule. Although these pseudo states do not correspond to physical states of the molecule, they can be employed as a discretized representation of the continuum as frequently

employed in the calculation of mean excitation energies and stopping powers.<sup>53–58</sup>

The original basis for the RPA or TD-DFT molecular Hessian matrix is the set of single excitations with respect to the Hartree-Fock or Kohn-Sham ground state Slater determinant  $|\Psi_0\rangle$  and the corresponding de-excitations. The three response function contributions to the coupling constants can thus be split even further into contributions from 2 pairs of occupied and virtual orbitals  $ai$  and  $bj$  according to

$$J^{FC/SD/PSO}(KL) = \sum_{ai \geq bj} J_{ai,bj}^{FC/SD/PSO}(KL), \quad (12)$$

which for  $ai \neq bj$  becomes

$$J_{ai,bj}^{FC/SD/PSO}(KL) = \mp \frac{2}{3} \frac{\gamma_K \gamma_L}{h} \sum_{\alpha=x,y,z} \left\{ \sum_n \frac{\tilde{\mathbf{T}}_{ai}(\hat{O}_{K\alpha}^{FC/SD/PSO})(\mathbf{X}_{ai}^n \mp \mathbf{Y}_{ai}^n)(\tilde{\mathbf{X}}_{bj}^n \mp \tilde{\mathbf{Y}}_{bj}^n) \mathbf{T}_{bj}(\hat{O}_{L\alpha}^{FC/SD/PSO})}{\Delta E_{0 \rightarrow n}} + \sum_n \frac{\tilde{\mathbf{T}}_{bj}(\hat{O}_{K\alpha}^{FC/SD/PSO})(\mathbf{X}_{bj}^n \mp \mathbf{Y}_{bj}^n)(\tilde{\mathbf{X}}_{ai}^n \mp \tilde{\mathbf{Y}}_{ai}^n) \mathbf{T}_{ai}(\hat{O}_{L\alpha}^{FC/SD/PSO})}{\Delta E_{0 \rightarrow n}} \right\}, \quad (13)$$

and for  $ai = bj$

$$J_{ai,ai}^{FC/SD/PSO}(KL) = \mp \frac{2}{3} \frac{\gamma_K \gamma_L}{h} \sum_{\alpha=x,y,z} \sum_n \frac{\tilde{\mathbf{T}}_{ai}(\hat{O}_{K\alpha}^{FC/SD/PSO})(\mathbf{X}_{ai}^n \mp \mathbf{Y}_{ai}^n)(\tilde{\mathbf{X}}_{ai}^n \mp \tilde{\mathbf{Y}}_{ai}^n) \mathbf{T}_{ai}(\hat{O}_{L\alpha}^{FC/SD/PSO})}{\Delta E_{0 \rightarrow n}}, \quad (14)$$

where the upper signs apply to the FC and SD terms and the lower to the PSO term. The occupied,  $i,j$ , and virtual,  $a,b$ , orbitals can be the canonical orbitals normally obtained in the solution of the Hartree-Fock or Kohn-Sham equations, but have been in most applications some sort of localized orbitals, obtained by separate unitary transformations among the occupied and virtual orbitals. These can be carried out before or after the solution of the RPA/TD-DFT eigenvalue problem. The former requires, however, that the RPA/TD-DFT formulas for non-diagonal Fock matrices have been implemented. In the case of the latter, as implemented in the DALTON program package,<sup>59–62</sup> one carries out the unitary transformations on the property gradient vectors,  $\mathbf{T}$ , and eigenvectors,  $\mathbf{X}^n$  and  $\mathbf{Y}^n$ .

One should mention that Autschbach *et al.*<sup>15</sup> had derived alternative SOS-DFT expressions for real and imaginary response properties, which involve summations over the square root of the eigenvalues of  $-(\mathbf{A} - \mathbf{B})^{-1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{-1/2}$  instead of over the eigenvalues of  $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}$ .

### III. RESULTS AND DISCUSSION

The spin-spin coupling constants and their contributions from individual excited (pseudo)states in this study were calculated at the DFT level with the B3LYP exchange-correlation functional and the core-property basis set aug-cc-pVTZ-J.<sup>63–69</sup> The calculations were carried with the Dalton

program package at the equilibrium geometries, which are reported at the bottom of Table I. All couplings in this study are dominated by the Fermi contact term, a situation for which the aug-cc-pVTZ-J basis set has been shown to give results close to the basis set limit. We have therefore refrained from carrying out a basis set study in this work. We have chosen the B3LYP functional for this study, as it is still one of the most widely employed functionals also for the calculation of SSCCs and gives in general acceptable results for molecules without  $\pi$ -bonds or too many lone pairs,<sup>62,66,70–73</sup> e.g., our previous study of localized orbital contributions to the couplings in  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ .<sup>12–14</sup> In future applications of the IP-PP-CLOPPA approach, however, it would be worthwhile to study the dependence of the localized orbital contributions to SSCCs on the choice of exchange-correlation functional.

All the SSCCs, which were obtained in this study directly from Equation (1) or equivalently from Equation (10) by summing over all excited (pseudo)states, are collected in Table I and compared to selected theoretical values from the literature and experimental values. However, the comparison with the experimental values can only be qualitative as neither our values nor the previous theoretical values include vibrational/temperature<sup>88,89</sup> or solvent effects. For the theoretical values from the literature we have only selected the most recent high-level wave function calculations at the level of unrelaxed coupled cluster singles and doubles response (CCSD) theory,<sup>90,91</sup> of the second-order polarization propagator approximation

TABLE I. Comparison of the spin-spin coupling constants in (Hz) calculated in the present work at B3LYP/aug-cc-pVTZ-J level at equilibrium geometries<sup>a</sup> with selected values from the literature.

Coupling	Molecule	Present work	Other calculations	Expt.	
<sup>1</sup> J(X, H)	CH <sub>4</sub>	133.61	123.85 <sup>74,b</sup>	125.30 ± 0.04 <sup>75</sup>	
	NH <sub>3</sub>	45.92	44.26 <sup>76,b</sup>	43.81 ± 0.02 <sup>77</sup>	
	H <sub>2</sub> O	-76.81	-81.56 <sup>78,b</sup>	-80.62 ± 0.06 <sup>79</sup>	
	SiH <sub>4</sub>	-209.85	-192.06 <sup>80,b</sup>	-201.3 ± 0.4 <sup>80</sup>	
	PH <sub>3</sub>	176.81	183.29 <sup>66,b</sup>	188.7 <sup>81</sup>	
	H <sub>2</sub> S	27.24	31.08 <sup>66,b</sup>		
	C <sub>2</sub> H <sub>2</sub>	276.27	254.95 <sup>82,b</sup>	248.24 <sup>82</sup>	
	C <sub>2</sub> H <sub>4</sub>	169.86	152.33 <sup>83,c</sup>	156.30 <sup>84</sup>	
	C <sub>2</sub> H <sub>6</sub>	131.34	116.13 <sup>85,c</sup>	125.21 <sup>84</sup>	
	<sup>2</sup> J(H, H)	CH <sub>4</sub>	-13.59	-14.45 <sup>74,b</sup>	-12.80 ± 0.13 <sup>75</sup>
NH <sub>3</sub>		-10.58	-11.27 <sup>76,b</sup>	-9.61 ± 0.03 <sup>77</sup>	
H <sub>2</sub> O		-7.98	-8.58 <sup>78,b</sup>	-7.30 ± 0.03 <sup>79</sup>	
SiH <sub>4</sub>		3.72	2.59 <sup>80,b</sup>	2.61 ± 0.08 <sup>80</sup>	
PH <sub>3</sub>		-12.76			
H <sub>2</sub> S		-12.58	-15.45 <sup>86,d</sup>		
C <sub>2</sub> H <sub>4</sub>		4.07	1.05 <sup>83,c</sup>	2.39 <sup>84</sup>	
C <sub>2</sub> H <sub>6</sub>		-13.66	-10.86 <sup>85,c</sup>	-13.12 <sup>87</sup>	
<sup>1</sup> J(C, C)		C <sub>2</sub> H <sub>2</sub>	205.81	190.00 <sup>82,b</sup>	166.01 <sup>82</sup>
		C <sub>2</sub> H <sub>4</sub>	73.21	68.77 <sup>83,c</sup>	67.46 <sup>84</sup>
	C <sub>2</sub> H <sub>6</sub>	32.83	33.42 <sup>85,c</sup>	34.52 <sup>84</sup>	
<sup>2</sup> J(C, H)	C <sub>2</sub> H <sub>2</sub>	56.52	51.73 <sup>82,b</sup>	49.75 <sup>82</sup>	
	C <sub>2</sub> H <sub>4</sub>	-1.44	-2.42 <sup>83,c</sup>	-2.40 <sup>84</sup>	
	C <sub>2</sub> H <sub>6</sub>	-3.54	-4.45 <sup>85,c</sup>	-4.66 <sup>84</sup>	
<sup>3</sup> J(H, H)	C <sub>2</sub> H <sub>2</sub>	11.21	11.31 <sup>82,b</sup>	9.54 <sup>82</sup>	
	Trans C <sub>2</sub> H <sub>4</sub>	20.47	17.46 <sup>83,c</sup>	19.02 <sup>84</sup>	
	Cis C <sub>2</sub> H <sub>4</sub>	13.07	11.37 <sup>83,c</sup>	11.66 <sup>84</sup>	
Average	C <sub>2</sub> H <sub>6</sub>	8.68	7.25 <sup>85,c</sup>	8.0 <sup>84</sup>	

<sup>a</sup>Geometry: R<sub>CH</sub> = 1.0858 Å for CH<sub>4</sub>; R<sub>NH</sub> = 1.0124 Å, ∠<sub>HNH</sub> = 106.67° for NH<sub>3</sub>; R<sub>OH</sub> = 0.9584 Å, ∠<sub>HOH</sub> = 104.44° for H<sub>2</sub>O; R<sub>SiH</sub> = 1.4684 Å for SiH<sub>4</sub>; R<sub>PH</sub> = 1.4124 Å, ∠<sub>HPH</sub> = 93.63° for PH<sub>3</sub>; R<sub>SH</sub> = 1.3359 Å, ∠<sub>HSH</sub> = 92.30° for H<sub>2</sub>S; R<sub>CH</sub> = 1.0625 Å, R<sub>CC</sub> = 1.2024 Å for C<sub>2</sub>H<sub>2</sub>; R<sub>CH</sub> = 1.0870 Å, R<sub>CC</sub> = 1.3384 Å, ∠<sub>HCH</sub> = 117.37°, ∠<sub>HCC</sub> = 121.32° for C<sub>2</sub>H<sub>4</sub> and R<sub>CH</sub> = 1.0910 Å, R<sub>CC</sub> = 1.5360 Å, ∠<sub>HCH</sub> = 108.00°, ∠<sub>HCC</sub> = 110.91°, ∠<sub>HCC</sub> = 60.00° for C<sub>2</sub>H<sub>6</sub>.

<sup>b</sup>SOPPA(CCSD).

<sup>c</sup>CCSD.

<sup>d</sup>MCSCF.

with coupled cluster singles and doubles amplitudes—SOPPA(CCSD)<sup>92</sup> and of multiconfigurational self-consistent field (MCSCF) response theory.<sup>61</sup> The comparison with these reference values is reasonably good and reflects the usual performance of DFT with the B3LYP exchange-correlation functional and proper core-property basis sets tuned for the calculation of SSCCs.<sup>62,66,70–73</sup> We conclude therefore, that the DFT/B3LYP/aug-cc-pVTZ-J model is sufficient for answering the question, whether the number of excitations can be truncated in sum-over-states expressions (10) or (13) and (14) for the SSCCs.

For the exemplary analysis of the one-bond couplings in terms of localized molecular orbitals we have localized the B3LYP Kohn-Sham orbitals using the Foster-Boys procedure<sup>93</sup> as in our previous studies.<sup>12–14,29</sup> Again in future applications of the IPPP-CLOPPA approach it will be useful to test the dependence of the localized orbital contributions on the localization scheme.

In the following we will discuss separately the one-bond <sup>1</sup>J(XH) coupling constants and the geminal <sup>2</sup>J(HH)

couplings for all 9 molecules and then collectively all the other couplings.

### A. One-bond couplings <sup>1</sup>J(XH) with X = C, N, O, Si, P, and S

The one-bond couplings, <sup>1</sup>J(XH) with X = C, N, O, Si, P, and S in CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, SiH<sub>4</sub>, PH<sub>3</sub>, H<sub>2</sub>S, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> as a function of the number of excited (pseudo)states *n* included in the summation in Equation (10), are shown in Figure 1, plotted as dots. We have chosen to plot them as function of the number of (pseudo)states and not as that of the excitation energies themselves for the reason that the total number of excited (pseudo)states, *n*<sub>max</sub>, can be determined beforehand for a given molecule and basis set contrary to the values of the excitation energies. It is simply the product of the number of occupied molecular orbitals times the number of virtual molecular orbitals. Using point group symmetry in the calculations would reduce this, but the current implementation of the IPPP-CLOPPA method in DALTON does not permit the use of point group symmetry. The value in the limit of all (pseudo)states or equivalently the value obtained directly from the response function, Equation (1), is shown as a horizontal line.

Comparing the curves of the different compounds in Figure 1, we observe that there is a fundamental difference between the results of the hydrocarbons and silane on one side and ammonia, water, phosphine and hydrogen sulfide on the other. In the latter molecules, which all have lone-pairs at the central atom, the results of the partial summations in Equation (10) change sign after very roughly 10%–15% of the excited (pseudo)states have been included. This leads to the question, whether the contributions to the coupling constants from the lone-pair orbitals play a special role in these molecules, which an analysis in terms of localized molecular orbitals could answer.

The form of the curves in Figure 1 suggests fitting them to an analytical function. The election of the particular form of the function is of course somewhat arbitrary and we have tried several. Here we report and discuss the results obtained with the function,

$${}^1J(XH) = A + B \tanh(Cn), \quad (15)$$

where *A*, *B*, and *C* are the fitting parameters and *n* is the independent variable, i.e., the number of excited (pseudo)states included in Equation (10). The values of the fitting parameters are given in Table II and the resulting functions are shown as solid curves in Figure 1. The agreement is satisfying as the errors are in the same order of magnitude as the differences between the B3LYP results and the results of the more accurate calculations shown in Table I.

The important question is that, whether one could obtain an acceptable approximation to this function and the parameters *A*, *B*, and *C* by fitting to only a subset of the data in Figure 1, i.e., the results of partial summations including a significantly smaller number of excited (pseudo)states *n* than the total number for the given basis set and molecule. Assuming that the same holds for the contributions to the couplings from localized molecular orbitals, one

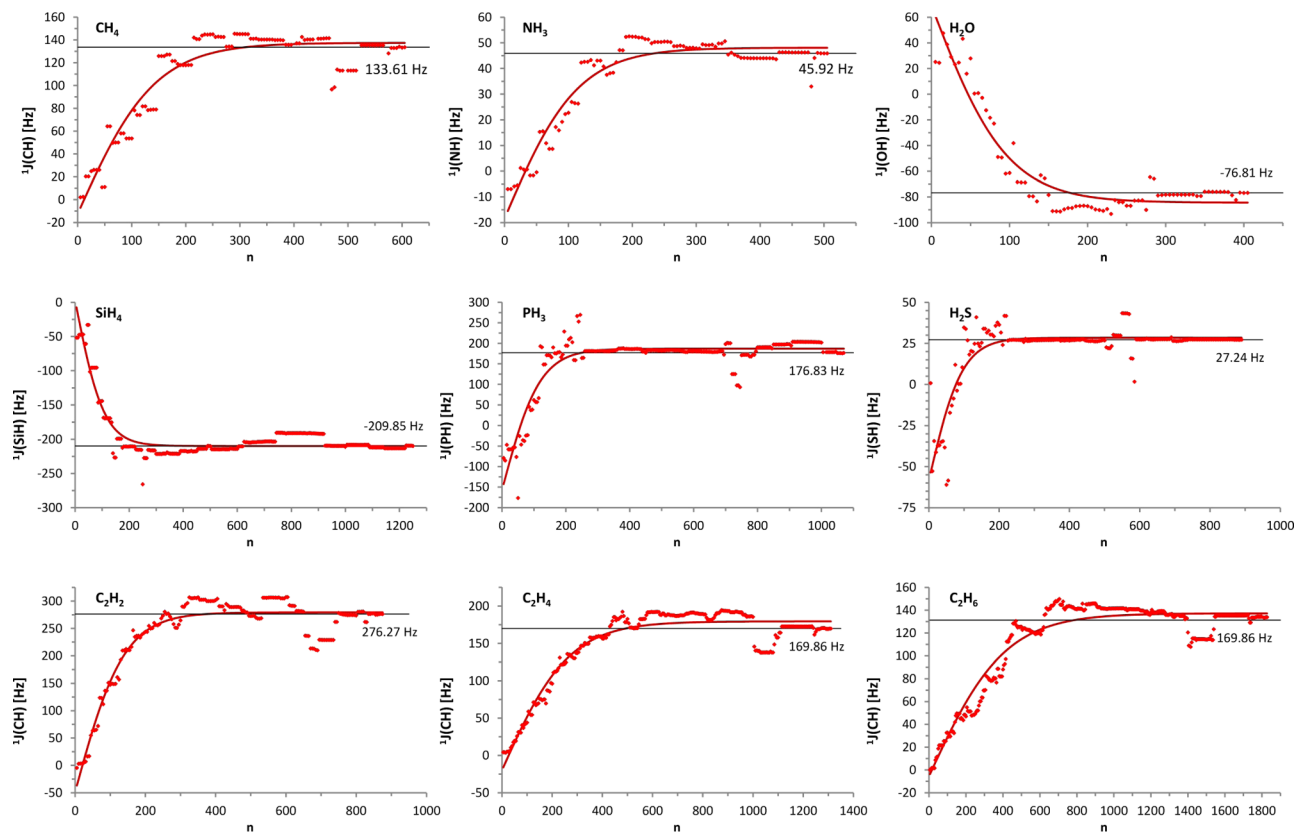


FIG. 1. The one-bond couplings,  ${}^1J(XH)$  (in Hz), in  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  as a function of the number of excited (pseudo)states,  $n$ , included in the summation in Equation (10). The partial summation has been carried out in steps of 5 eigenvalues. The solid lines are the results of fitting to Equation (15) and the horizontal line indicates the value obtained by summing over all states or equivalently obtained from Equation (1).

could imagine an iterative procedure for obtaining these contributions, where in each step one

- (1) extends the set of calculated excited (pseudo)states by  $\Delta n$  states
- (2) obtains new approximate values of the parameters  $A$ ,  $B$ , and  $C$  by fitting to the current set of data
- (3) extrapolates to the total number of excited states  $n_{\text{max}}$
- (4) checks, whether the difference between the total coupling constant obtained from this partial summation, Equation (10), and directly from the response function, Equation (6), is below the desired threshold.

TABLE II. Parameters in the fit of the one-bond coupling constants  ${}^1J(XH)$  with  $X = \text{C}, \text{N}, \text{O}, \text{Si}, \text{P},$  and  $\text{S}$  in  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  to the analytical function  ${}^1J(XH) = A + B \tanh(Cn)$ . In the last column the relative error  $\Delta^1J(XH)$  of the extrapolated value is given.

Compound	$A$	$B$	$C$	$\Delta^1J(XH)$ (%)
$\text{CH}_4$	-12.3876	149.8729	0.0070	2.9
$\text{NH}_3$	-18.4227	66.5234	0.0087	4.7
$\text{H}_2\text{O}$	69.0636	-153.5295	0.0103	-9.9
$\text{SiH}_4$	2.6530	-212.5401	0.0094	<0.01
$\text{PH}_3$	-157.2586	344.2211	0.0085	5.7
$\text{H}_2\text{S}$	-58.1416	86.6058	0.0106	4.5
$\text{C}_2\text{H}_2$	-48.6091	327.9585	0.0072	1.1
$\text{C}_2\text{H}_4$	-19.8508	199.2563	0.0038	5.6
$\text{C}_2\text{H}_6$	-5.4648	142.7367	0.0025	4.5

Hopefully, one could then stop the iterations after calculating a significantly smaller number of excited (pseudo)states than the total number and thus treat much larger molecules with the IPPP-CLOPPA approach.

Strictly the values of the parameters  $A$ ,  $B$ , and  $C$  vary with the number of data points considered during the curve fitting. However, this change becomes small, when the number of data points considered goes beyond a certain threshold, which is characteristic of each compound and coupling constant. This is reasonably true for the parameter  $C$  as can be seen from Tables S1-S9 in the supplementary material.<sup>94</sup> In order to get an idea of what such a threshold would be, we set the maximum relative error of the coupling constants to be, e.g., 10%, i.e.,

$$0.1 = \frac{\Delta J}{J} = \frac{J - J_{\text{approx}}}{J} = \frac{A + B \tanh(Cn_{\text{max}}) - A + B \tanh(Cn_{\text{thresh}})}{A + B \tanh(Cn_{\text{max}})}, \quad (16)$$

where  $n_{\text{max}}$  is the total number of excited states for the given molecule. The threshold  $n_{\text{thresh}}$  then becomes

$$n_{\text{thresh}} = \frac{1}{C} \tanh^{-1} \left[ -0.1 \frac{A}{B} + 0.9 \cdot \tanh(Cn_{\text{max}}) \right]. \quad (17)$$

Using now the converged values of the parameters  $A$ ,  $B$ , and  $C$ , we can see that for all the cases studied here it holds that  $|\frac{A}{B}| < 1$ , which is furthermore multiplied by 0.1 and is therefore neglected. Moreover  $\tanh(Cn_{\text{max}}) \sim 1.0$  for all the

molecules studied here, as can easily be seen by multiplying the values of  $C$  in Table II with  $n_{\max}$  in Table III. Equation (17) thus gives  $n_{\text{thresh}} \approx \frac{1.47}{C}$ . To be on the safe side, we choose a value twice as large, so that our first guess for the minimum number of excitations is  $n_{\text{thresh}} \approx \frac{3}{C}$ . Table III shows the values of  $n_{\max}$ , and  $n_{\text{thresh}} \approx \frac{3}{C}$ , their ratio and the relative error of the value of  ${}^1J(XH)$ , which is predicted with the approximate fit function, i.e., with Equation (15) using the parameters  $A$ ,  $B$ , and  $C$  obtained by fitting to only  $n_{\text{thresh}}$  excited states. The results in Table III show, that this approach is already partly successful. For the second row hydrides  $n_{\text{thresh}}$  corresponds to  $\sim 70\%$  of the excited states and about half of it for that of the third row hydrides. However, not in all cases are we below the desired 10% error, which reflects the approximations made in the derivation of  $n_{\text{thresh}}$ , but we are close to it with the exception of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ .

A more accurate way to determine the necessary minimum number of excited states is the procedure outlined above. In Tables S1-S9 of the supplementary material<sup>94</sup> we have collected the values of the parameters  $A$ ,  $B$ , and  $C$ , the corresponding extrapolated values of  $J$  and their relative errors obtained by fitting to the coupling constants calculated from 10%, 20%, 25%, 30%, ..., 100% of the excited (pseudo)states. In the last two columns of Table III we give the approximate minimum number of excited (pseudo)states  $n_{<10\%}$ , which give an error of  $J$  less than 10%, and the corresponding percentage of the total number of states  $n_{\max}$ . In order to determine the exact minimum number of excited (pseudo)states, one would have to extend the set of states in our procedure by one state

TABLE III. One-bond coupling constants  ${}^1J(XH)$ : the total number of excited states ( $n_{\max}$ ), the required minimum number of excited states ( $n_{\text{thresh}} \approx \frac{3}{C}$ ), the ratio of both in percentage, the relative error in the coupling constants obtained from fitting to  $n_{\text{thresh}} \approx \frac{3}{C}$  excited states and the approximate minimum number of excited states  $n_{<10\%}$ , which would give an error below 10%.

Compound	$n_{\max}$	$n_{\text{thresh}} \approx \frac{3}{C}$	$\frac{n_{\text{thresh}}}{n_{\max}}$ (%)	$\Delta^1J(XH)$ (%)	$n_{<10\%}$	$\frac{n_{<10\%}}{n_{\max}}$ (%)
$\text{CH}_4$	605	429	71	9.6	182	30
$\text{NH}_3$	505	344	68	13.4	151	30
$\text{H}_2\text{O}$	405	290	72	18.2	122	30
$\text{SiH}_4$	1251	318	25	9.0	250	20
$\text{PH}_3$	1070	353	33	15.5	535	50
$\text{H}_2\text{S}$	891	284	32	25.7	490	55
$\text{C}_2\text{H}_2$	875	417	47	8.6	219	25
$\text{C}_2\text{H}_4$	1327	797	61	13.6	394	30
$\text{C}_2\text{H}_6$	1827	1224	67	11.2	548	30

at a time, which would be unnecessarily time consuming. This procedure turned out to be very successful. By including only 30% or less excited (pseudo)states in Equation (10), we could determine an approximate fitting function, which extrapolate to the full number of states and gave an estimate of the coupling constant with an error of less than 10%. The only exceptions are  $\text{PH}_3$  and  $\text{H}_2\text{S}$ , where 50% or 55% were necessary. Interestingly, for methane, ethane, ammonia, and water there seems to be an island of fitting functions with the desired 10% accuracy between 30% and 35% of the excited

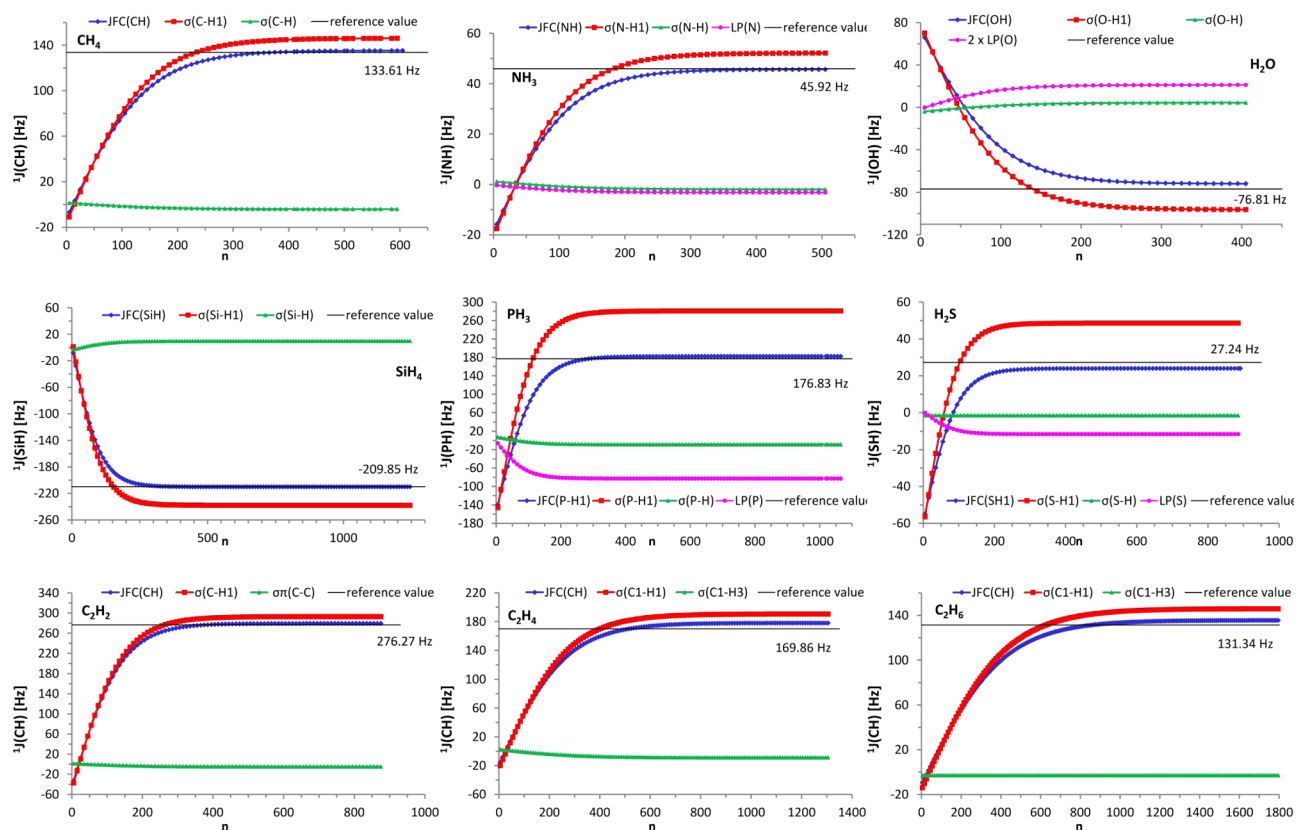


FIG. 2. Fitted localized occupied orbital contributions to the one-bond couplings,  ${}^1J(XH)$  (in Hz), in  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  as a function of the number of excited (pseudo)states  $n$  in Equation (15).

states, while the agreement deteriorates again for more excited states until one has included about 70%–80% of the states.

### 1. Contributions from localized molecular orbitals to the one-bond couplings ${}^1J(XH)$

In Sec. III A, we have discussed the dependence of the total isotropic one-bond coupling constants on the number of excited (pseudo)states. In this section we want to illustrate the usefulness of the sum-over-states calculations by discussing the contributions from individual localized occupied orbitals to the one-bond couplings. For this purpose we sum  ${}^1J_{ai,bj}^{FC}(XH)$  in Equation (12) over all virtual orbitals  $a$  and  $b$ . We limit, however, our analysis to the Fermi contact term, as it completely dominates the one-bond  ${}^1J(XH)$  couplings in the studied nine molecules similar to many other molecules.<sup>62–68,70–74,76,78,80,82–85,95</sup>

In Figure 2 the fitted functions  ${}^1J(XH) = A + B \tanh(Cn)$  are plotted for the contributions from localized molecular orbitals to the Fermi contact term of the one-bond coupling constants,  ${}^1J(XH)$ . The value of the total coupling constants are again indicated as horizontal lines. The original calculated values were omitted in order not to clutter the figures. In all cases we can confirm from previous findings<sup>12–14,31</sup> that the contribution from the binding  $\sigma$ -orbital between the coupled atoms X and H is the dominant contribution to the Fermi contact term. Furthermore, it is responsible for the shape of the Fermi contact curve and thus total SSCC curve, i.e., their dependence on the number of excited (pseudo)states

TABLE IV. Binding  $\sigma$ -orbital contributions to the Fermi contact term of the one-bond coupling constants  ${}^1J(XH)$ : fitting parameters in the analytical function  $A + B \tanh(Cn)$  obtained by fitting to the results for up to  $n_{<10\%}$  excited (pseudo)states and relative error in the binding  $\sigma$ -orbital contributions to the Fermi contact term by extrapolating to the total number of states  $n_{\max}$ .

Compound	$n_{<10\%}$	$A$	$B$	$C$	$\Delta {}^1J(XH)$ (%)
CH <sub>4</sub>	180	-3.2070	753.8653	0.0010	8.0
NH <sub>3</sub>	150	-15.0836	4220.6361	0.0001	3.2
H <sub>2</sub> O	120	64.9958	-3578.6342	0.0003	11.8
SiH <sub>4</sub>	250	-1.9603	-283.1433	0.0063	10.9
PH <sub>3</sub>	535	-161.7761	459.1080	0.0083	10.7
H <sub>2</sub> S	490	-62.0855	113.1739	0.0104	10.2
C <sub>2</sub> H <sub>2</sub>	220	-32.9470	370.3392	0.0054	4.9
C <sub>2</sub> H <sub>4</sub>	395	-10.4841	254.9658	0.0024	1.5
C <sub>2</sub> H <sub>6</sub>	550	-2.8609	454.1559	0.0006	3.1

included in the summation. The remaining other-bond and/or lone-pair contributions have the opposed sign than the  $\sigma$ -bond contribution and their curves have the opposite curvature—the value and curvature of the lone-pair contributions being larger.

Analyzing coupling constants in this way, i.e., in the IPPP-CLOPPA approach, in terms of contributions from localized orbitals requires also calculation of all excited states like for the total coupling constants. For larger molecules it is therefore again essential to be able to reduce the required number of excited states via the procedure outlined in Sec. III A. In Table IV we have thus shown how large an error one makes on transferring approximately the number of states,

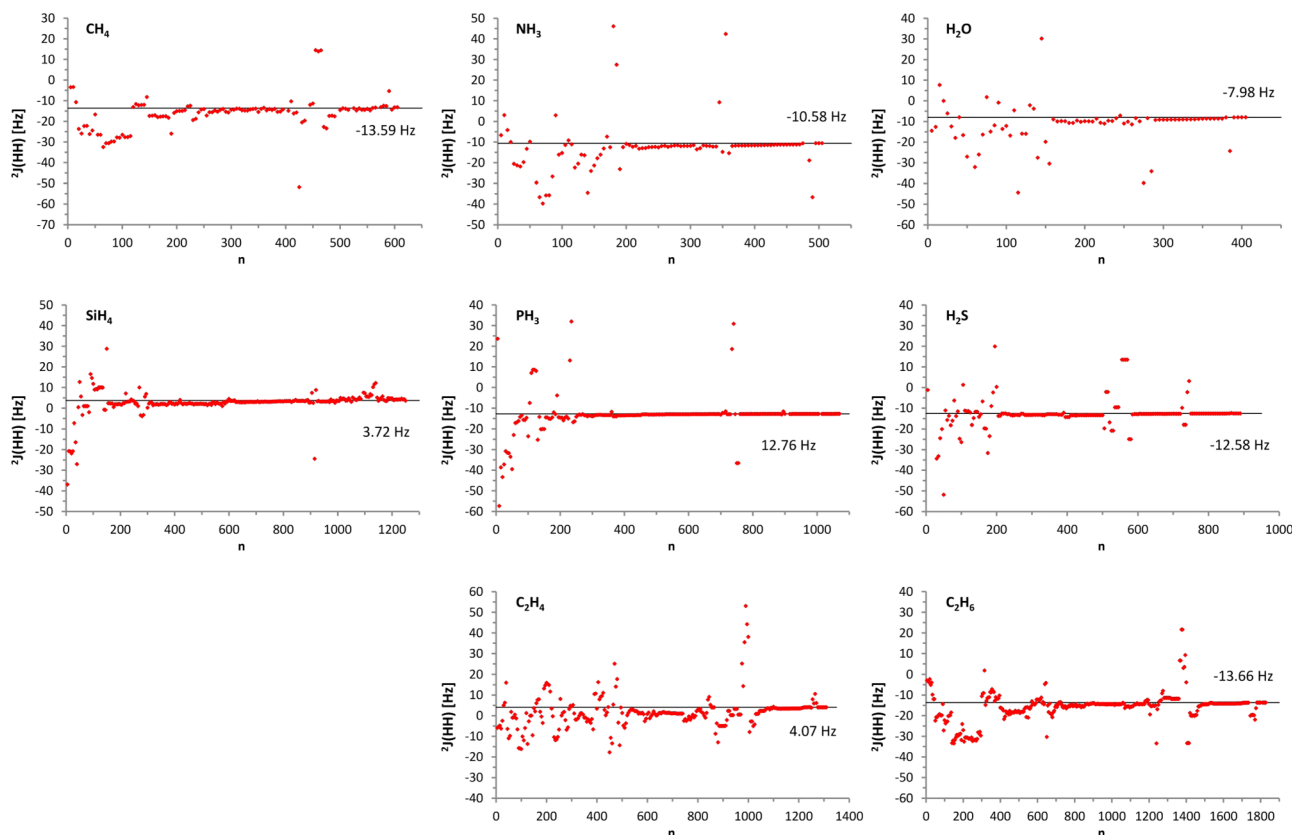


FIG. 3. The two-bond couplings,  ${}^2J(HH)$  in (Hz), in CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, SiH<sub>4</sub>, PH<sub>3</sub>, H<sub>2</sub>S, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> as a function of the number of excited (pseudo)states,  $n$ , included in the summation in Equation (10). The partial summation has been carried out in steps of 5 eigenvalues.



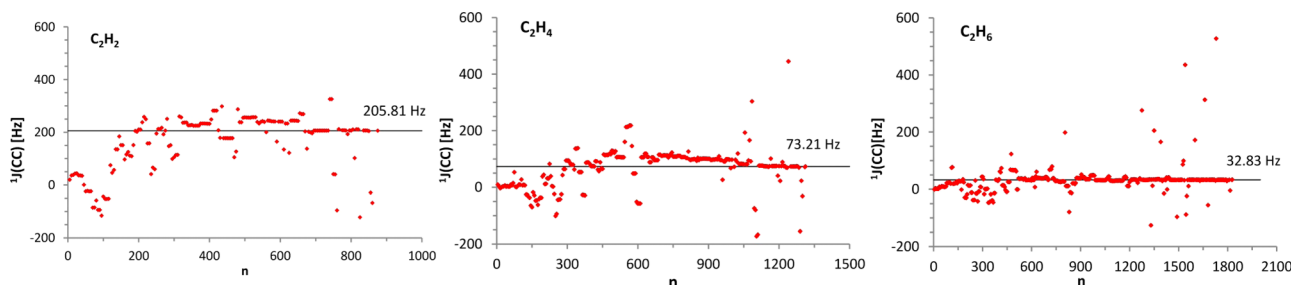


FIG. 4. The one-bond couplings,  ${}^1J(\text{CC})$  in (Hz), in  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  as a function of the number of excited (pseudo)states,  $n$ , included in the summation in Equation (10). The partial summation has been carried out in steps of 5 eigenvalues.

$n_{<10\%}$ , used for determining the fitting function from the total coupling constants in Table III to the binding  $\sigma$ -orbital contributions to the Fermi contact term. The error in this contribution is still around 10% and in half of the cases even better, which shows that this is a promising approach for obtaining at least qualitatively correct results for the localized orbital contributions without having to calculate all eigenvalues of the TD-DFT eigenvalue problem.

## B. Geminal ${}^2J(\text{H}, \text{H})$ couplings

The dependence of the geminal H-H couplings on the number of excited (pseudo)states  $n$  included in the summation in Equation (10) is shown in Figure 3. The dots are again the results of the partial summations and the horizontal lines represent the values in the limit of all states or equivalently the coupling constants calculated directly from Equation (1).

The curves of the geminal couplings differ significantly from the corresponding curves of the one-bond couplings. After a rather erratic behavior for summations over the first one third of the excited (pseudo)states the curves become more or less straight lines. This holds in particular for the third row hydrides, ammonia and water and less for the hydrocarbons—ethene showing the largest variations. In addition, there are some spikes in the curves, i.e., sudden large changes in the values, even for much larger numbers of excited (pseudo)states. Taking  $\text{NH}_3$  as an example, we have analyzed some of the large changes of the geminal coupling constants and find that these occurred in connection with triply degenerate excited states, where a very large contribution from one of the three components is almost canceled again by the two other components. The appearance of these spikes is then a consequence of having a fixed step length, which

then sometimes includes only parts of a degenerate set of states.

The initial erratic behavior and the spikes are somewhat similar to the behavior Oddershede and co-workers had observed for the one-bond couplings in HD, HF, CO, and  $\text{CH}^+$ .<sup>38</sup> However, one has to keep in mind, that the number of excited (pseudo)state was an order of magnitude smaller than in the present work due to significantly smaller one-electron basis sets in the previous study.

The special form of the curves, first somewhat chaotic and then essential flat, makes it unnecessary to fit and extrapolate them. One only has to add excited (pseudo)states to the summation until the result is sufficiently close the value obtained from Equation (1), which happens already after  $\sim 1/3$  of the states with the exception of ethene.

## C. The remaining couplings: ${}^1J(\text{CC})$ , ${}^2J(\text{CH})$ , and ${}^3J(\text{HH})$

Finally we analyze the dependence of the remaining intramolecular J-couplings,  ${}^1J(\text{CC})$ ,  ${}^2J(\text{CH})$ , and  ${}^3J(\text{HH})$ , on the number of excited (pseudo)states,  $n$ , included in the partial summations for the three hydrocarbons ethane, ethene and ethyne. The results of the partial summations are collected in Figures 4-6 represented as dots. The straight horizontal lines represent again the values in the limit of all states or equivalently the coupling constants calculated directly from Equation (1). Results from only three molecules are of course not representative of these types of couplings in general, but can at least give a first indication of their behavior.

The first observation for the one-bond couplings  ${}^1J(\text{CC})$  in Figure 4 is that even after more than  $2/3$  of the excited

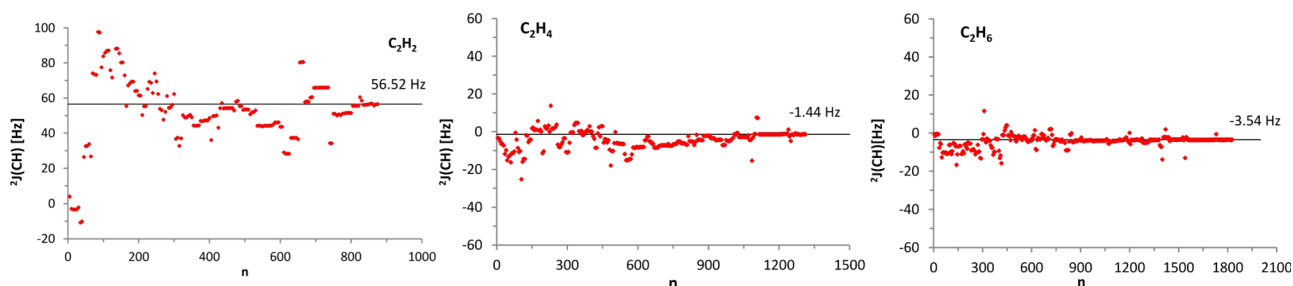


FIG. 5. The two-bond couplings,  ${}^2J(\text{CH})$  in (Hz), in  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  as a function of the number of excited (pseudo)states,  $n$ , included in the summation in Equation (10). The partial summation has been carried out in steps of 5 eigenvalues.

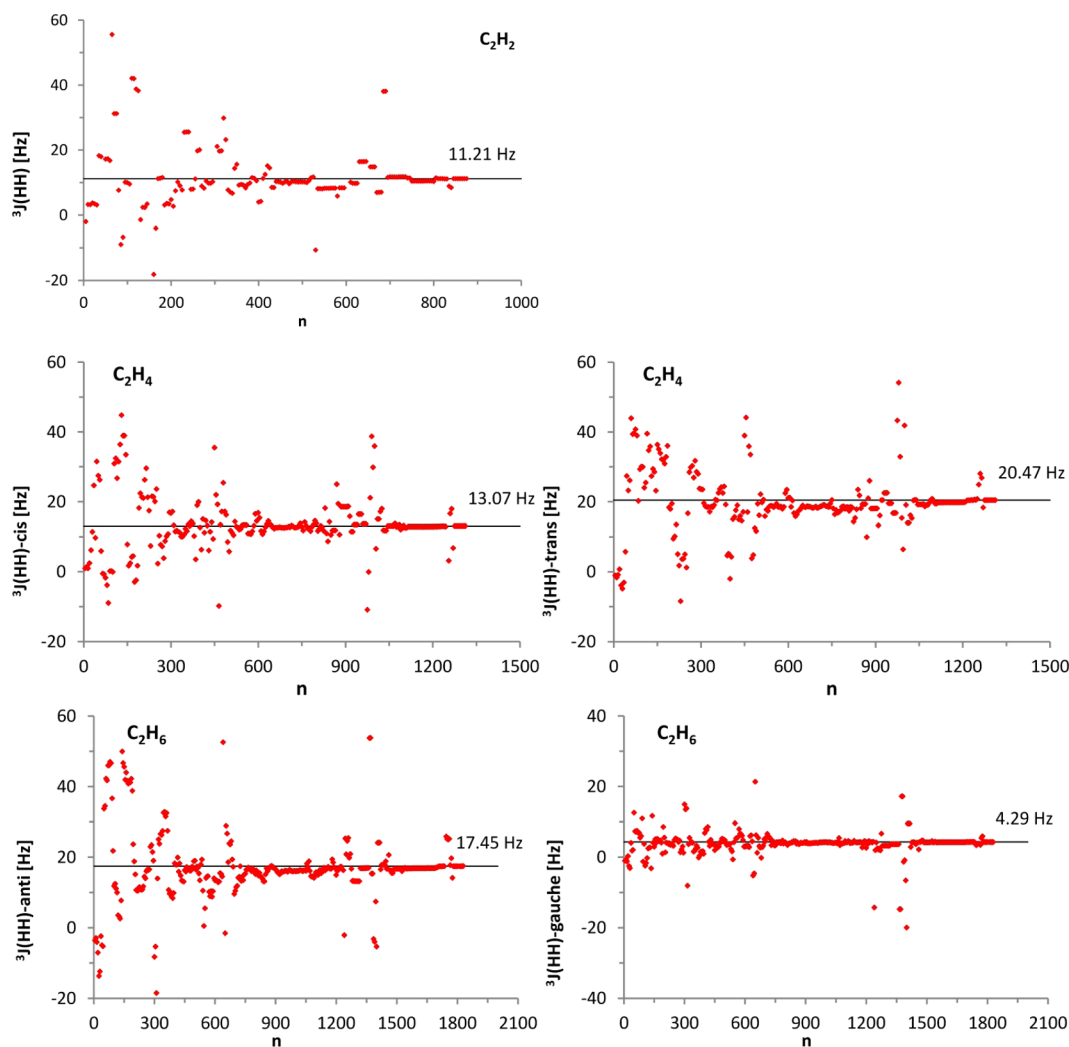


FIG. 6. The three-bond couplings,  ${}^3J(\text{HH})$  in (Hz), in  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  as a function of the number of excited (pseudo)states included in the summation in Equation (10). The partial summation has been carried out in steps of 5 eigenvalues.

(pseudo)states are included in the partial summation, there appear again large changes in the values of the coupling constants. This is similar to the geminal couplings in Figure 3, but the changes are larger and somewhat more frequent. For ethane this does not prevent one from obtaining values close to the final value already after 30% of the states are included, while for ethene and ethyne more than 75% are necessary. Ethyne shows in general the largest fluctuations and requires the largest number of excited (pseudo)states to be included.

The geminal carbon-hydrogen couplings  ${}^2J(\text{CH})$  in Figure 5 show another dependence again. While ethyne and ethene exhibit an oscillatory behavior similar to the optical rotation in norbornenone,<sup>42</sup> the curve for ethane settles down to a more or less straight line already after  $\sim 50\%$  of the states have been included. For ethyne one obtains temporary values close to the converged values for around 50% being included, while it requires  $\sim 85\%$  for ethene to converge.

Finally, the vicinal  ${}^3J(\text{HH})$  couplings, Figure 6, in the three hydrocarbons exhibit a behavior similar to the geminal  ${}^2J(\text{HH})$  couplings in Figure 2. For smaller number excited (pseudo)states included in the summations the results are rather erratic, but when  $\sim 50\%$  of the states are included for

ethyne and ethene (40% for ethane) the partial summations yield for the first time results, which differ by 10% or less from the final value. From there on the curves are more or less flat lines, however, with several spikes or oscillations.

#### IV. CONCLUSIONS

We have calculated the NMR indirect nuclear spin-spin coupling constants of nine small molecules at the coupled perturbed DFT level both directly from the linear response function and by explicit summation over all the electronically excited (pseudo)states obtained from the corresponding TD-DFT eigenvalue problem. The B3LYP exchange-correlation functional and the aug-cc-pVTZ-J core-property basis set were employed in the calculations.

We have analyzed in detail the dependence of all the different SSCs in these molecules on the number of (pseudo)states included in the sum-over-states expression. We find that it is in general possible to obtain with the sum-over-states approach values for the coupling constants, which are sufficiently close to the results of corresponding linear response calculations, although only a reduced number

of excited (pseudo)states are included in the summation. This implies that the IPPP-CLOPPA approach for analyzing coupling constants in terms of localized molecular orbitals can be applied to significantly larger molecules than previously.

However, a truncated sum-over-states approach is not useful as a method for predicting coupling constants, as the value of the coupling constant can still oscillate until the last few excited (pseudo)states are included in the summation. On the other hand, in combination with the calculation of the total coupling constant directly from the linear response function, the summation can be truncated and an IPPP-CLOPPA analysis performed, when the linear response function result is obtained.

In more detail, we find that the different types of coupling constants, one-bond, geminal, vicinal, etc., exhibit quite different behavior. While the one-bond X–H coupling constants as a function of the number of (pseudo)states in the summation follow roughly a monotonically increasing or decreasing function, the geminal and vicinal H–H couplings become after an initial erratic behavior flat lines with different amounts of spikes or intermediate oscillations.

In the case of the X–H one-bond couplings we could obtain approximate SSCCs, which differ by less than 10% from the linear response function result, by fitting the results from summations including up to ~30% of the states (50% or 55% for PH<sub>3</sub> and H<sub>2</sub>S) to a  ${}^1J(XH) = A + B \tanh(Cn)$  function and extrapolating to the total number of (pseudo)states. For the geminal and vicinal coupling constants, one only has to add (pseudo)states to the summation until the value is sufficiently close to the linear response function result. The same procedure, i.e., minimum number of necessary (pseudo)states, can then be applied in the IPPP-CLOPPA calculation of contributions from localized orbitals.

With this study we have shown, that the truncation of the sum-over-states expression is possible. In future studies on larger molecules one should investigate whether the percentage of states necessary for the IPPP-CLOPPA analysis varies with the size of the molecule, and how much the results depend on the choice of localization scheme and exchange-correlation functional.

## ACKNOWLEDGMENTS

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