

# The effect of lone pairs and electronegativity on the indirect nuclear spin–spin coupling constants in $\text{CH}_2\text{X}$ ( $\text{X}=\text{CH}_2, \text{NH}, \text{O}, \text{S}$ ): *Ab initio* calculations using optimized contracted basis sets

Patricio F. Provasi and Gustavo A. Aucar<sup>a)</sup>

Department of Physics, Northeastern University, Av. Libertad 5500, W 3404 AAS Corrientes, Argentina

Stephan P. A. Sauer<sup>b)</sup>

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

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The indirect nuclear spin–spin coupling constants of  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{NH}$ ,  $\text{CH}_2\text{O}$ , and  $\text{CH}_2\text{S}$  were investigated by means of correlated *ab initio* calculations at the level of the second order polarization propagator approximation (SOPPA) and the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes—SOPPA(CCSD) using large basis sets, which are optimized for the calculation of coupling constants. It is found that at the self-consistent-field (SCF) level  $\text{CH}_2\text{NH}$  and  $\text{CH}_2\text{S}$  exhibit triplet instabilities whereas  $\text{CH}_2\text{CH}_2$  and  $\text{CH}_2\text{O}$  show triplet quasi-instabilities, which renders the SCF results meaningless. Our best results deviate between 0.3 and 2.7 Hz from the experimental values. We find that although the one-bond C–H and Y–H couplings as well as the two- and three-bond H–H couplings are dominated by the Fermi contact term, significant contributions of the orbital paramagnetic and sometimes even spin–dipolar terms are observed for the one-bond C–Y and two-bond C–H and Y–H coupling constants. Similarly the changes in the couplings caused by the electronegativity and the lone-pair of Y are mostly due to changes in the Fermi contact (all couplings) and the orbital paramagnetic contribution (C–Y and two-bond Y–H couplings). However, the trend in the changes are neither the same for both terms not for all couplings. In particular, the position of  $\text{CH}_2\text{S}$  in the series varies indicating that either the electronegativity or the lone pairs are the dominating perturbation. Furthermore, small but optimized Gaussian basis sets for the calculation of indirect nuclear spin–spin coupling constants are presented. They were obtained by contraction of the *s*- and *p*-type basis functions for C, N, O, and S and of the *s*-type basis functions for H of the large uncontracted basis sets. Molecular orbital coefficients of self-consistent-field calculations on  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and  $\text{H}_2$  with the uncontracted basis sets were used as contraction coefficients. Applied in the calculation of all coupling constants in  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{NH}$ ,  $\text{CH}_2\text{O}$ , and  $\text{CH}_2\text{S}$  the contraction leads to a maximum basis set error of  $\sim 0.5$  Hz. © 2001 American Institute of Physics. [DOI: 10.1063/1.1379331]

## I. INTRODUCTION

Accurate *ab initio* calculations of the indirect nuclear spin–spin coupling constants  $J$  of nuclear magnetic resonance (NMR) spectroscopy are still a difficult and demanding task.<sup>1</sup> Nevertheless, good agreement with measured coupling constants is possible if the following four issues are properly taken care of.

First the molecular orbitals have to be expanded in a set of one-electron Gaussian basis functions which are specifically optimized for calculations of coupling constants.<sup>2–5</sup> In particular the inclusion of *s*-type Gaussian functions with very large exponents is essential for a correct description of the Fermi contact contribution<sup>2,4–6</sup> and polarization and diffuse functions are important for the orbital paramagnetic contribution. The resulting basis sets are therefore rather

large and several attempts<sup>3,5,7</sup> have been made to reduce the size of the basis sets without significantly reducing the accuracy of the calculated coupling constants. Provasi *et al.*<sup>5</sup> used locally dense basis sets in the calculation of vicinal proton–proton coupling constants in halogen monosubstituted ethane. In their studies of the coupling constants in methane, Geertsen *et al.*<sup>7</sup> as well as Guilleme and San Fabián<sup>3</sup> tried to reduce the size of the basis sets by partially contracting them with the molecular orbital coefficients of methane. However, from these studies it is not obvious whether this basis set could also be used for other molecules and how to generate basis sets for other atoms. One of the purposes of the present work was therefore to investigate whether the approach of Geertsen, Guilleme, and San Fabián can be generalized in such a way that contracted atomic basis sets for the calculation of spin–spin coupling constants of arbitrary molecules are generated using the molecular orbital coefficients of a small set of selected molecules. We studied therefore the dependence of the coupling constants in  $\text{CH}_2\text{O}$  on different contraction schemes at the level of the second order polar-

<sup>a)</sup>Member of Carrera del Investigador, CONICET, Argentina. Electronic mail: gaa@unne.edu.ar

<sup>b)</sup>Author to whom correspondence should be addressed; electronic mail: sauer@kiku.dk; see: <http://fyskem.ki.ku.dk/sauer>

ization propagator approximation (SOPPA)<sup>4,8</sup> using either the molecular orbital coefficients of CH<sub>2</sub>O or the molecular orbital coefficients of CH<sub>4</sub>, H<sub>2</sub>O, and H<sub>2</sub> for the contraction of the carbon, oxygen, and hydrogen atomic basis sets. Corresponding basis sets for nitrogen and sulfur were generated using the molecular orbital coefficients of NH<sub>3</sub> and H<sub>2</sub>S. The performance of these basis sets were then investigated with calculations of the spin–spin coupling constants in CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>NH, and CH<sub>2</sub>S.

The second issue is the basis set for the many-electron wave function or the so-called electron correlation problem. The results for the Fermi contact term and the spin–dipolar term, the two contributions to the coupling constants which involve the electron spin, change dramatically on application of methods which go beyond the mean field approximation of the coupled Hartree–Fock method (CHF)<sup>9</sup> or the equivalent random phase approximation (RPA).<sup>10,11</sup> Furthermore CHF/RPA calculations exhibit sometimes Hartree–Fock triplet instabilities or quasi-instabilities.<sup>12–14</sup> Consequently, CHF/RPA calculations of coupling constants are often not even qualitatively correct.<sup>1,4</sup> Hartree–Fock triplet instabilities or quasi-instabilities,<sup>12–14</sup> i.e., the existence of a triplet state with energy lower than or close to the lowest singlet state (ground state), occur mainly in calculations using semi-empirical methods,<sup>15–22</sup> although some cases have also been reported for *ab initio* calculations.<sup>4,23</sup> These phenomena are related to  $\pi$ -like electronic systems for both saturated and unsaturated compounds. One important factor influencing the  $\pi$  system in CH<sub>2</sub>X systems is the presence of lone pairs in the substituent X.<sup>24</sup> We have therefore performed uncorrelated CHF/RPA calculations as well as correlated calculations of all the coupling constants in CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>NH, CH<sub>2</sub>O, and CH<sub>2</sub>S in order to search for triplet instabilities and to study the effects of the substituent X and of electron correlation on the four contributions to the coupling constants in these CH<sub>2</sub>X model compounds. In addition to the second order polarization propagator approximation (SOPPA)<sup>4,8</sup> we have employed also the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes—SOPPA(CCSD),<sup>4,25</sup> which had been applied with great success recently.<sup>4,26–32</sup>

The third and fourth important issue in the calculation of spin–spin coupling constants are relativistic effects and the contributions from nuclear motion. Relativistic contributions can be obtained either by the calculation of relativistic corrections in a perturbation theory approach<sup>33,34</sup> or directly by four-component relativistic RPA calculations.<sup>35–37</sup> For the molecules studied here, relativistic effects are not significant. The contributions from the motion of the nuclei, on the other hand, can be expected to be of importance. Recent calculations of the coupling constants in CH<sub>4</sub>,<sup>26</sup> H<sub>2</sub>O,<sup>27</sup> C<sub>2</sub>H<sub>2</sub>,<sup>29</sup> and SiH<sub>4</sub>,<sup>32</sup> showed that the zero point vibrational corrections are typically about 5%, but can amount to 10%. The calculation of vibrational corrections requires at least the calculation of all first and second derivatives of the coupling constants with respect to normal coordinates or internal coordinates, which is beyond the scope of this study.

## II. COMPUTATIONAL ASPECTS

The indirect nuclear spin–spin coupling constant between nuclei  $M$  and  $N$  was originally explained by Ramsey<sup>38</sup> by two basic mechanisms, which are as follows.

- (i) The interaction of the nuclear spin with the spins of the electrons surrounding it; this is accounted for by the Fermi-contact (FC) and spin–dipolar (SD) contributions.
- (ii) The interaction of the nuclear spin with the orbital angular momentum of the electrons which gives rise to the orbital paramagnetic (OP) and orbital diamagnetic (OD) contributions.

The first three contributions depend on the first order wave function and are thus given by the following sum-over-states expressions:

$$J_{MN}^A = \frac{2}{3} \frac{\gamma_M \gamma_N}{h} \sum_{\alpha=x,y,z} \sum_{n \neq 0} \frac{\langle 0 | (\tilde{O}_M^A)_\alpha | n \rangle \langle n | (\tilde{O}_N^A)_\alpha | 0 \rangle}{E_0 - E_n}, \quad (1)$$

where A stands for OP, FC, SD and their corresponding operators are defined as

$$(\tilde{O}_M^{\text{OP}})_\alpha = \left( \frac{\mu_0}{4\pi} \right) \left( \frac{e\hbar}{m_e} \right) \sum_i \frac{(\vec{l}_{iM})_\alpha}{r_{iM}^3}, \quad (2)$$

$$(\tilde{O}_M^{\text{FC}})_\alpha = \left( \frac{\mu_0}{4\pi} \right) \left( \frac{4\pi g_e e\hbar}{3m_e} \right) \sum_i (\vec{s}_i)_\alpha \delta(\vec{r}_{iM}), \quad (3)$$

$$(\tilde{O}_M^{\text{SD}})_\alpha = \left( \frac{\mu_0}{4\pi} \right) \left( \frac{g_e e\hbar}{2m_e} \right) \sum_i \frac{3(\vec{s}_i \cdot \vec{r}_{iK})(\vec{r}_{iK})_\alpha - r_{iK}^2 (\vec{s}_i)_\alpha}{r_{iK}^5}. \quad (4)$$

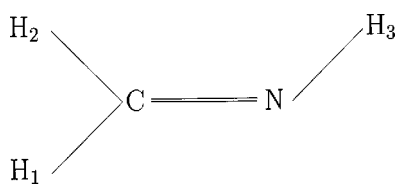
The OD term is obtained as a ground state average value with the operator

$$(\tilde{O}_{MN}^{\text{OD}})_{\alpha\beta} = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{e^2 \hbar^2}{m_e} \sum_i \left( \frac{\vec{r}_{iN} \cdot \vec{r}_{iM} - (\vec{r}_{iN})_\alpha (\vec{r}_{iM})_\alpha}{r_{iN}^3 r_{iM}^3} \right), \quad (5)$$

although it can be expressed also as a sum-over-states.<sup>39</sup>

In Eqs. (1)–(5) the magnetogyric ratio of nucleus  $M$  is  $\gamma_M$ ,  $\vec{r}_{iM} = \vec{r}_i - \vec{r}_M$  is the difference of the position vectors of electron  $i$  and nucleus  $M$ ,  $\vec{s}_i$  is the spin angular momentum operator, and  $\vec{l}_i$  is the orbital angular momentum operator for electron  $i$ ,  $\delta(x)$  is the Dirac delta function and all other symbols have their usual meaning.<sup>40</sup>

All excited triplet states  $|n\rangle$  with energy  $E_n$  in Eq. (1) are included in the sum for the FC and SD terms, whereas excited singlet states contribute to the OP term. By using propagator methods the first three contributions can be evaluated without explicit calculation of the excited states involved. The scheme for calculations of indirect nuclear spin–spin coupling constants using polarization propagator methods has been described and explained previously.<sup>41,4</sup> In the present study three levels of approximation to the polarization propagator have been used: SOPPA,<sup>8</sup>

FIG. 1. Geometry of the CH<sub>2</sub>NH molecule.

SOPPA(CCSD),<sup>25</sup> and RPA, which can also be derived as a first order polarization propagator approximation.<sup>41</sup>

For a proper comparison of the same kind of couplings among different nuclei, e.g.,  $^1J_{C-Y}$  with (Y=C, N, O, S) in the series CH<sub>2</sub>X (X=CH<sub>2</sub>, NH, O, S), it is necessary to separate the pure electronic effects from the changes in the nuclear magnetic moments. This is commonly done by defining a reduced coupling constant  $K$ ,

$$K_{AB} = \frac{J_{AB}}{h} \frac{2\pi}{\gamma_A} \frac{2\pi}{\gamma_B}, \quad (6)$$

which is essentially the coupling constant divided by the magnetogyric ratios of the nuclei.

We have used a version of the DALTON program package,<sup>42</sup> in which the calculation of indirect nuclear spin–spin coupling constants at the SOPPA and SOPPA(CCSD) level had been implemented in the property module<sup>4,25</sup> and which is interfaced to the integral direct coupled cluster program of Koch and co-workers.<sup>43,44</sup>

Spherical Gaussian basis sets were used in all calculations. The basis sets, which we call aug-cc-pVTZ-Juc, are the aug-cc-pVTZ basis sets<sup>45–47</sup> completely uncontracted, augmented with four tight  $s$ -type functions and without the most diffuse second polarization function. Basis sets aug-cc-pVTZ-Juc of hydrogen, carbon, nitrogen, and oxygen were called basis set  $J$  in Ref. 4 or basis set  $A$  in Ref. 5 and consists of (10 $s$ 3 $p$ 1 $d$ ) functions for hydrogen and (15 $s$ 6 $p$ 3 $d$ 1 $f$ ) functions for C, N, and O. The basis set for sulfur (20 $s$ 10 $p$ 6 $d$ 1 $f$ ), is new and includes in addition to the above-described modifications<sup>48</sup> also three additional tight  $d$ -type functions<sup>48</sup> which are necessary for a proper description of the Fermi contact term as was observed previously for silicon.<sup>30</sup> The exponents of basis set aug-cc-pVTZ-Juc for all the atoms studied here can be downloaded from the internet.<sup>49</sup>

Experimental geometries<sup>50–52</sup> were used for all molecules. (The details are given in the footnotes to Tables IV–VII and the labeling of the hydrogens in CH<sub>2</sub>NH is shown in Fig. 1.)

### III. THE COUPLING CONSTANTS OF CH<sub>2</sub>X

#### A. Triplet instabilities and quasi-instabilities

The condition<sup>12–14</sup> for the stability of a restricted Hartree–Fock wave function is that the matrix of the second derivatives of the restricted Hartree–Fock energy with respect to the orbital rotation parameters is positive definite, i.e., has only positive eigenvalues. This Hessian matrix is the same as the principal propagator matrix<sup>41</sup> at the RPA level. An instability of the restricted Hartree–Fock wave function

employed in a RPA calculation will therefore lead to a negative eigenvalue in the principal propagator matrix, i.e., a negative excitation energy. In the case of positive but very small eigenvalues (very small excitation energies) one talks about quasi-instabilities.<sup>15–22</sup> These lead normally to unrealistic large values of second order properties like the indirect nuclear spin–spin coupling constants. Corresponding to the spin adaptation of the orbital rotation parameters one can distinguish between singlet and triplet instabilities.<sup>13,14</sup> In previous *ab initio* studies of coupling constants<sup>4,23</sup> triplet instabilities were observed for BH and AIH and triplet quasi-instabilities are found in CO and N<sub>2</sub>.<sup>4</sup> Previously these problems were circumvented in two ways.<sup>4,17–20,22,23</sup> One is to remove some electronic correlation or the molecular orbitals which cause the problem. Such a procedure is inconvenient in the calculation of properties like the coupling constants which should reproduce quantitatively experimental values. The other way is to add more correlation in order to get a better description of the excited states as well as the ground state. In SOPPA calculations of the coupling constants of AIH, CO, and N<sub>2</sub> there is thus no sign of triplet instabilities.<sup>4,23</sup> However, in the case of BH the triplet instability only disappears in a SOPPA(CCSD) calculation.<sup>4,23</sup>

Among the four molecules CH<sub>2</sub>X analyzed here, we found at the RPA level triplet instabilities, for X=NH and S, and triplet quasi-instability problems for X=O and X=CH<sub>2</sub>. This makes it meaningless to report results for the total coupling constants at the RPA.<sup>21</sup> However, the two singlet contributions, the orbital diamagnetic and paramagnetic terms, are not affected by this. The differences between the RPA and SOPPA results for the OD contributions to all coupling constants are very small (<0.03 Hz). The correlation effect is in general somewhat larger for the OP term. Nevertheless significant changes in the OP term are only observed for  $^1J(C-Y)$ ,  $\sim 0.5$  Hz for Y=C, N, O and 1.5 Hz for Y=S, or the one-bond couplings  $^1J(C-H)$  in all molecules where the correlation contribution can amount up to 0.3 Hz.

#### B. Comparison of the coupling mechanisms in the CH<sub>2</sub>X molecules

In this section we analyze the four contributions to the coupling constants of the molecules CH<sub>2</sub>X with particular emphasis on the effect of the number of lone pairs in the substituent X and the electronegativity of the central atom Y in the substituent. For that purpose we present in Tables I–III the four contributions to the reduced coupling constants calculated at the SOPPA(CCSD) level using basis set aug-cc-pVTZ-Juc, i.e., the highest level of theory employed in this study. However, the results of this analysis is the same at the SOPPA level. The molecules are listed with increasing number of lone pairs on Y and electronegativity of Y. For the atoms from the second row, Y=C, N, and O, this is unambiguous, but CH<sub>2</sub>S could be listed according to the electronegativity of S between C and N or due to its two lone pairs after CH<sub>2</sub>O. One should expect to observe a difference between the lone-pair effects in CH<sub>2</sub>O and CH<sub>2</sub>S, as the  $s$  orbital character of lone pairs is known<sup>19,20</sup> to increase in a group of the periodic table. The effect of lone pairs on spin–spin couplings has been studied extensively (see, e.g., Ref.

TABLE I. One-bond spin-spin coupling in  $C_2H_4$ ,  $CH_2NH$ ,  $CH_2O$ , and  $CH_2S$ . Coupling constants,  $^1J_{C-Y}$  and  $^1J_{Y-H}$  (in Hz), and reduced coupling constants,  $^1K_{C-Y}$  and  $^1K_{Y-H}$  (in  $10^{19} T^2 J^{-1}$ ), calculated at SOPPA(CCSD) level with basis set aug-cc-pVTZ-Juc.

| Molecule   | Coupling         | $K^{OD}$ | $K^{OP}$ | $K^{SD}$ | $K^{FC}$ | $K$       | $J$                   | $J^{expt.}$          |
|------------|------------------|----------|----------|----------|----------|-----------|-----------------------|----------------------|
| $C_2H_4$   | C-C              | 0.0807   | -11.7968 | 3.9143   | 100.3594 | 92.5576   | 70.3262 <sup>a</sup>  | 67.4620 <sup>b</sup> |
| $CH_2NH^c$ | C-N              | 0.0405   | -27.5161 | 4.4543   | 33.1019  | 10.0803   | -3.0879               |                      |
| $CH_2O$    | C-O              | -0.0066  | -52.4384 | 2.9308   | -27.2707 | -76.7849  | 31.4596               |                      |
| $CH_2S$    | C-S              | 0.0302   | -97.8371 | 8.1316   | -65.3004 | -154.9758 | -35.9767              |                      |
| $C_2H_4$   | C-H              | 0.1318   | 0.1197   | 0.0372   | 51.7326  | 52.0212   | 157.1597 <sup>d</sup> | 156.309 <sup>b</sup> |
| $CH_2NH^c$ | N-H <sub>3</sub> | 0.1154   | 0.4506   | -0.1336  | 40.3919  | 40.8244   | -49.7238              |                      |
| $C_2H_4$   | C-H              | 0.1318   | 0.1197   | 0.0372   | 51.7326  | 52.0212   | 157.1597 <sup>d</sup> | 156.309 <sup>b</sup> |
| $CH_2NH$   | C-H <sub>1</sub> | 0.1655   | -0.1020  | 0.0392   | 56.4226  | 56.5254   | 170.7672              | 172.9 <sup>e</sup>   |
|            | C-H <sub>2</sub> | 0.1668   | -0.0929  | 0.0619   | 53.1998  | 53.3355   | 161.1304              | 163.7 <sup>e</sup>   |
| $CH_2O$    | C-H              | 0.1987   | -0.2925  | 0.0942   | 58.0458  | 58.0463   | 175.3619              | 172 <sup>f</sup>     |
| $CH_2S$    | C-H              | 0.1704   | -0.3800  | 0.1754   | 56.6904  | 56.6563   | 171.1626              |                      |

<sup>a</sup>Compare 75.0 Hz [EOM (Ref. 61)], 70.1 Hz [EOM-CCSD (Ref. 62)], 70.2 Hz [RASSCF (Ref. 59)], 70.1 Hz [RASSCF (Ref. 1)].

<sup>b</sup>Reference 59 in liquid crystal VI.

<sup>c</sup>Coupling constants  $J$  for  $^{15}N$ .

<sup>d</sup>Compare 142.87 Hz [EOM (Ref. 61)], 153.23 Hz [EOM-CCSD (Ref. 63)], 147.7 Hz [RASSCF (Ref. 59)], 154.0 Hz [RASSCF (Ref. 1)].

<sup>e</sup>Reference 58.

<sup>f</sup>Reference 56 in 38% aq. soln.

TABLE II. Two-bond (geminal) spin-spin coupling in  $C_2H_4$ ,  $CH_2NH$ ,  $CH_2O$ , and  $CH_2S$ . Coupling constants,  $^2J_{Y-H}$  and  $^2J_{H-H}$  (in Hz), and reduced coupling constants,  $^2K_{Y-H}$  and  $^2K_{H-H}$  (in  $10^{19} T^2 J^{-1}$ ), calculated at SOPPA(CCSD) level with basis set aug-cc-pVTZ-Juc.

| Molecule   | Coupling         | $K^{OD}$ | $K^{OP}$ | $K^{SD}$ | $K^{FC}$ | $K$     | $J$                  | $J^{expt.}$         |
|------------|------------------|----------|----------|----------|----------|---------|----------------------|---------------------|
| $C_2H_4$   | C-H              | -0.2235  | -0.3294  | 0.0357   | -0.4925  | -1.0096 | -3.0500 <sup>a</sup> | -2.415 <sup>b</sup> |
| $CH_2NH$   | C-H <sub>3</sub> | -0.2744  | -0.8197  | -0.0181  | -3.4278  | -4.5399 | -13.7155             | -13.1 <sup>c</sup>  |
| $C_2H_4$   | C-H              | -0.2235  | -0.3294  | 0.0357   | -0.4925  | -1.0096 | -3.0500 <sup>a</sup> | -2.415 <sup>b</sup> |
| $CH_2NH^d$ | N-H <sub>1</sub> | -0.2291  | -1.0967  | 0.1287   | 8.7263   | 7.5292  | -9.1705              |                     |
|            | N-H <sub>2</sub> | -0.2949  | -0.8027  | 0.1840   | -2.8535  | -3.7671 | 4.5883               |                     |
| $CH_2O$    | O-H              | -0.2988  | -1.9349  | 0.5848   | 3.4403   | 1.7915  | -2.9184              |                     |
| $CH_2S$    | S-H              | -0.1775  | -3.7968  | 1.2618   | 0.4219   | -2.2905 | -2.1142              |                     |
| $C_2H_4$   | H-H              | -0.3174  | 0.3393   | 0.0294   | 0.0332   | 0.0845  | 1.0150 <sup>e</sup>  | 2.32 <sup>b</sup>   |
| $CH_2NH$   | H-H              | -0.3072  | 0.3175   | 0.0313   | 1.4053   | 1.4469  | 17.3798              | 17.6 <sup>c</sup>   |
| $CH_2O$    | H-H              | -0.2785  | 0.2787   | 0.0306   | 3.4247   | 3.4554  | 41.5065              | 42.20 <sup>f</sup>  |
| $CH_2S$    | H-H              | -0.2872  | 0.2931   | 0.0400   | 0.5227   | 0.5685  | 6.8287               |                     |

<sup>a</sup>Compare -5.07 Hz [EOM (Ref. 61)], -2.95 Hz [EOM-CCSD (Ref. 63)], -3.3 Hz [RASSCF (Ref. 59)], -3.0 Hz [RASSCF (Ref. 1)].

<sup>b</sup>Reference 59 in liquid crystal VI.

<sup>c</sup>Reference 58.

<sup>d</sup>Coupling constants  $J$  for  $^{15}N$ .

<sup>e</sup>Compare -4.04 Hz [EOM (Ref. 61)], 0.44 Hz [EOM-CCSD (Ref. 63)], 0.9 Hz [RASSCF (Ref. 59)], 1.3 Hz [RASSCF (Ref. 1)].

<sup>f</sup>Reference 57.

TABLE III. Three-bond (vicinal) spin-spin coupling in  $C_2H_4$  and  $CH_2NH$ . Coupling constants,  $^3J_{H-H}$  (in Hz), and reduced coupling constants,  $^3K_{H-H}$  (in  $10^{19} T^2 J^{-1}$ ), calculated at SOPPA(CCSD) level with basis set aug-cc-pVTZ-Juc.

| Molecule | Coupling  | $K^{OD}$ | $K^{OP}$ | $K^{SD}$ | $K^{FC}$ | $K$    | $J$                  | $J^{expt.}$         |
|----------|-----------|----------|----------|----------|----------|--------|----------------------|---------------------|
| $C_2H_4$ | cis-H-H   | -0.0863  | 0.0600   | -0.0046  | 1.0130   | 0.9820 | 11.7964 <sup>a</sup> | 11.53 <sup>b</sup>  |
|          | trans-H-H | -0.2900  | 0.2605   | 0.0215   | 1.5408   | 1.5328 | 18.4122 <sup>c</sup> | 18.997 <sup>b</sup> |
| $CH_2NH$ | cis-H-H   | -0.0800  | 0.0291   | 0.0054   | 1.5283   | 1.4827 | 17.8105              | 17.0 <sup>d</sup>   |
|          | trans-H-H | -0.3737  | 0.3236   | 0.0278   | 2.0818   | 2.0596 | 24.7395              | 25.2 <sup>d</sup>   |

<sup>a</sup>Compare 9.10 Hz [EOM (Ref. 61)], 11.57 Hz [EOM-CCSD (Ref. 63)], 10.4 Hz [RASSCF (Ref. 59)], 11.6 Hz [RASSCF (Ref. 1)].

<sup>b</sup>Reference 59 in liquid crystal VI.

<sup>c</sup>Compare 14.27 Hz [EOM (Ref. 61)], 17.8 Hz [EOM-CCSD (Ref. 63)], 17.0 Hz [RASSCF (Ref. 59)], 18.5 Hz [RASSCF (Ref. 1)].

<sup>d</sup>Reference 58.

24) mainly based on measured coupling constants and some semiempirical calculations (see, e.g., Refs. 19 and 20). But only by means of high accuracy calculations, like the ones presented here, it is possible to get a more precise understanding of the role of the four different coupling mechanisms to this effect.

### 1. One-bond couplings

The one-bond couplings are presented in Table I. One can observe a systematic change in the reduced coupling constants  ${}^1K_{C-C-N-O-S}$ . The reduced coupling constants are dramatically reduced going from a positive value in  $C_2H_4$  to a negative value in  $CH_2O$  and  $CH_2S$ . This is the well-known<sup>24</sup> negative effect of lone pairs on one-bond couplings. And the comparison of  $CH_2O$  and  $CH_2S$  shows again<sup>19,20</sup> that this negative contribution increases with the *s* character of the lone pair, i.e., within a group of the periodic table.

Analyzing the four contributions, one can see that this lone-pair effect is due to both the Fermi contact and the orbital paramagnetic term. The FC contribution to the  ${}^1K_{C-C-N-O-S}$  reduced coupling constants becomes more negative with increasing number of lone pairs, being positive for  $C_2H_4$  and  $CH_2NH$  and negative for  $CH_2O$  and  $CH_2S$ . The OP decreases also from  $C_2H_4$  to  $CH_2S$ , but is negative for all four molecules. The combination of both trends has the effect that  ${}^1K_{C-S}$  is larger than  ${}^1K_{C-C}$  in absolute values and has the opposite sign. The overall sign of  ${}^1K_{C-C-N-O-S}$  is still determined by the FC contribution, but the absolute value is modified by the increasingly negative OP term.

The OD contribution to  ${}^1K_{C-C-N-O-S}$  is completely negligible in all four molecules, whereas the SD term becomes significant for  $CH_2NH$ , where it amounts to  $\sim 45\%$  of  ${}^1K_{C-N}$  due to a near cancellation of the OP and FC contributions. In the other three molecules the SD term contributes between 4% and 5% of the total reduced coupling constant. The OP contribution is about twice as large as the FC term for  $X=O$  and about 1.5 times the FC term for  $X=S$ . Finally, in  $C_2H_4$  the OP contribution is, in absolute values, only approximately 10% of the FC term which is the dominant contribution.  $C_2H_4$  shows a complete different pattern of contributions compared with the other three molecules. This could be explained by the complete absence of lone pairs in ethene.

In other words, for one-bond C–Y couplings the lone pairs belonging to Y affect both the FC and OP contributions in such a way that when the number of lone pairs increase both FC and OP decrease, but to a much larger extent in the case of the FC term.

The second and third part of Table I show N–H and C–H couplings. The N–H<sub>3</sub> coupling in  $CH_2NH$  is again a one-bond coupling with a lone pair on one of the two atoms, whereas the C–H couplings belong to the type A.3 of Gil and von Philipsborn,<sup>24</sup> one-bond couplings with one or more lone pairs on the adjacent atom. One can see that the total reduced coupling constants ( ${}^1K_{N-H}$  and  ${}^1K_{C-H}$ ) are entirely dominated by the FC contributions for all the substituents as it is observed for most one-bond couplings involving hydrogen. In particular for  $X=O$  the FC term is up to the first decimal equal to the total reduced coupling constants.

Analyzing the lone-pair effects we can see that the FC contribution to  ${}^1K_{N-H_3}$  in  $CH_2NH$  is considerably smaller than the FC contribution to the C–H couplings in  $C_2H_4$  or any of the other molecules, a direct consequence of the negative lone-pair contribution discussed above. The OP contribution on the other hand, is increased by the lone-pair contrary to the one-bond C–Y couplings above. Again for the compound  $CH_2NH$  the FC contribution to C–H<sub>1</sub> coupling, which is *cis* to the lone pair on nitrogen, is larger than the corresponding FC term to the C–H<sub>2</sub> coupling *trans* to the lone pair. This is called the Perlin effect<sup>53</sup> and results from a positive effect of the lone-pair on one-bond CH couplings *cis* to a  $sp^2$  lone pair and a negative effect on the couplings *trans* to it.<sup>24,54</sup> It is worth mentioning that the discrepancy between the theoretical predictions and the experimental results for the difference between this *trans*- and *cis*- ${}^1J_{C-H}$  coupling is less than 0.5 Hz. Considering the OP contribution, although it is negligible compared with the FC term, we observe that this contribution becomes more negative when the substituent changes in the series  $X=CH_2$ , NH, O, and S.

### 2. Two-bond couplings

In the first two parts of Table II the reduced  ${}^2K_{Y-H}$  couplings are presented. With respect to the lone pairs we distinguish between the case where a lone pair is introduced in the central atom (Gil and von Philipsborn<sup>24</sup> type B.1) in the first part of the table and the case where a lone pair is introduced in one of the coupled atoms (type B.3) in the second part of the table.

The reduced  ${}^2K_{Y-H}$  couplings show a diverse pattern of contributions for each substituent. Comparing the geminal C–H reduced couplings in  $C_2H_4$  and  $CH_2NH$  we can see that the lone pair on the central atom or the change in electronegativity of the central atom contributes with a negative term to all four contributions, but the effect is most pronounced for the FC term. The SD term becomes therefore negative, whereas the absolute value of the other three terms, which are always negative, increases. Consequently in  $C_2H_4$  the FC, OP, and OD terms make all significant contributions to the total reduced coupling constants, whereas the C–H coupling in  $CH_2NH$  is dominated by the FC term with some contribution by the OP term. Therefore the lone pair or electronegativity effect in the total reduced coupling is mainly due to the FC term for this type of coupling.

Comparison of the B.3 type geminal Y–H reduced couplings shows that the OD term is always negative and varies only little with the atom Y. The OP term is also always negative, whereas the SD term remains positive. The absolute value of both terms increases in the series  $Y=C, N, O, S$ , which indicates that the changes are mainly due to the lone pairs and not the electronegativity of the atom Y. The largest change in both terms is observed on going from O to S. The FC contribution varies most. It increases along the series  $Y=C, S, N, O$ , if one takes the average of the two geminal N–H<sub>1/2</sub> couplings in  $CH_2NH$ . This means that the electronegativity of Y is responsible for the overall trend. However, there is a large difference between the two geminal N–H couplings in  $CH_2NH$  which is due to the single lone pair on N. It gives rise to a positive *cis* effect and a negative *trans* or

*gauche* effect.<sup>24</sup> These different trends for the four contributions imply that there is no trend for the total reduced coupling constants. In C<sub>2</sub>H<sub>4</sub> the FC, OP, and OD terms are of the same order of magnitude and the SD term is unimportant. For the two N–H couplings in CH<sub>2</sub>NH and for the O–H coupling in CH<sub>2</sub>O the FC and OP terms are the two dominating contributions with the OP term being 13%, 28%, and 56% of the FC term. The importance of the SD term increase for the same couplings from 1% to 17%. In CH<sub>2</sub>S on the other hand, there is a complete different situation. Here we find in absolute terms the largest OP and SD terms for this type of coupling in the four molecules and the smallest FC term. Consequently the total coupling is dominated by the OP and SD term. It is worth to stress that the difference between <sup>2</sup>K<sub>N–H<sub>1</sub></sub> and <sup>2</sup>K<sub>N–H<sub>2</sub></sub> is nevertheless mainly due to the FC contribution. Interestingly the reduced <sup>2</sup>K<sub>C–H<sub>3</sub></sub> and <sup>2</sup>K<sub>N–H<sub>2</sub></sub> couplings have almost identical OD and OP contributions and the difference between the two FC terms is also rather small.

In the third part of Table II the geminal H–H couplings are shown. One can see that the couplings are dominated by the FC terms due to an almost perfect cancellation of the OD and OP terms, as it is found for many other molecules. Besides the OD and OP are rather small and their absolute values are even more reduced in the series X=CH<sub>2</sub>, NH, S, O, i.e., with increasing electronegativity. The SD contribution is even smaller and is almost unchanged by the substituents. On the other hand, the FC term and therefore also the total coupling constant increases with increasing electronegativity of X as predicted by the theory of Pople and Bothner-By.<sup>55</sup> The lone pairs on N, O, and S, a lone pair in  $\alpha$ -position, should also lead to an increase in the FC term, however, the fact that the increase in CH<sub>2</sub>S compared to C<sub>2</sub>H<sub>4</sub> is smaller than in CH<sub>2</sub>NH shows that the dominating contribution is due to the electronegativity of the substituents.

### 3. Three-bonds coupling

In Table III the calculated and experimental values for the vicinal couplings in C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>NH are shown. With respect to the lone pair this is an example for type C.1.<sup>24</sup> These couplings are clearly dominated by the FC term similarly to what we found for the vicinal H–H couplings in the CH<sub>3</sub>CH<sub>2</sub>X systems.<sup>5</sup> The lone pair and/or electronegativity of N leads to an almost equal increase in the FC contribution to the *cis* and *trans* coupling. Much smaller changes are also observed for the OD and OP contribution to the *trans* coupling, whereas the changes in the other terms are insignificant.

### C. Comparison with previous calculations and experiment

In the following we compare the results of our calculations at the SOPPA(CCSD) level using basis set aug-cc-pVTZ-Juc with the few experimental values<sup>56–59</sup> and results of previous calculations.<sup>1,59–63</sup> Calculations of the spin–spin coupling constants in ethene have been reported by some authors. Among these are the equation-of-motion (EOM) or higher RPA calculation of Galasso,<sup>61</sup> the equation-of-motion

coupled cluster singles and doubles (EOM–CCSD) calculations by Bartlett and co-workers<sup>62,63</sup> and restricted active space self-consistent-field (RASSCF) calculations by Kaski *et al.*<sup>59</sup> and Helgaker *et al.*<sup>1</sup> (see the footnotes of Tables I–III). Helgaker *et al.*<sup>1</sup> have pointed out that it is not sufficient to include only valence orbitals in the active space in an MCSCF calculation. Consequently their RAS-II wave function has an enlarged active space and gives better results, specifically when hydrogen atoms are involved in the couplings, than the best RASSCF calculation of Kaski *et al.*<sup>59</sup> Comparing our results with the RAS-II results of Helgaker *et al.*<sup>1</sup> and the EOM–CCSD results of Bartlett and co-workers<sup>62,63</sup> we can see that the differences are 0.8 Hz or less with the exception of the <sup>1</sup>J<sub>C–H</sub> coupling where our SOPPA(CCSD) result is ~3–4 Hz larger and actually closer to the experimental value. To our knowledge there have not been reported results of high-level correlated *ab initio* calculations for the other model compounds.

We observe a very good agreement of our results with few experimental values found in the literature<sup>56–59</sup> for C<sub>2</sub>H<sub>4</sub>, CH<sub>2</sub>O, and CH<sub>2</sub>NH. In the worst case, <sup>1</sup>J<sub>C–H</sub> in CH<sub>2</sub>O, the difference is 3.4 Hz or 2%. However, this rather old experimental value was measured in a 38% aqueous solution for which very large solvent effects should be expected and is therefore not really comparable with our calculated result. For some of the one-bond couplings, <sup>1</sup>J<sub>C–C</sub> in C<sub>2</sub>H<sub>4</sub> and <sup>1</sup>J<sub>C–H</sub> in CH<sub>2</sub>NH we observe deviations of ~2.5 Hz, whereas for all the other couplings the errors are less than 1.5 Hz. It is particularly satisfying that the difference between the <sup>1</sup>J<sub>C–H</sub> couplings *cis* and *trans* to the lone pair in CH<sub>2</sub>NH is reproduced with an accuracy of 0.5 Hz. Similarly, for the differences between the *trans* and *cis* vicinal H–H couplings in C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>NH we find an error of 0.9 Hz and 1.3 Hz, respectively. Taking into account that vibrational corrections to coupling constants can be in the order of 5 Hz<sup>26–29</sup> we cannot expect a better agreement between experiment and calculations at an equilibrium geometry.

## IV. CONTRACTED GAUSSIAN BASIS SETS

It is well known that *s*-type Gaussian basis functions with very large exponents are necessary for accurate calculations of the Fermi contact contribution to coupling constants and that these functions are not included in standard basis sets, i.e., energy optimized basis sets. Consequently many authors augmented standard basis sets with one or more tight *s*-type Gaussian functions. However, care has to be taken in the case of small contracted basis sets as the Fermi contact term can be overestimated dramatically due to an unbalance in the basis set if the *s*-type Gaussian functions are kept contracted.<sup>4</sup> On the other hand, completely uncontracted basis sets, as used in the first part of this work, are rather large which severely restricts their applicability.

A possible solution is to recontract the basis sets. In calculations of the coupling constants of methane by Geertsen *et al.*<sup>7</sup> and by Guilleme and San Fabián<sup>3</sup> the molecular orbital coefficients of methane have been used as contraction coefficients. In this work we generalize now their approach and generate contracted atomic basis sets which can be used

TABLE IV. Basis set dependence of the contributions to the coupling constants  $J$  (in Hz) in  $^{13}\text{C}_2^1\text{H}_4$  at the SOPPA level.<sup>a</sup>

| Coupling                  | Basis           | #   | $J^{\text{OD}}$ | $J^{\text{OP}}$ | $J^{\text{SD}}$ | $J^{\text{FC}}$ | $J$      |
|---------------------------|-----------------|-----|-----------------|-----------------|-----------------|-----------------|----------|
| $^1J_{\text{C-C}}$        | aug-cc-pVTZ-Juc | 206 | 0.0631          | -9.4610         | 3.2986          | 77.1566         | 71.0573  |
|                           | aug-cc-pVTZ-J   | 172 | 0.0662          | -9.4997         | 3.2994          | 77.6800         | 71.5459  |
|                           | sad-Juc         | 192 | 0.0659          | -9.4403         | 3.3527          | 79.1901         | 73.1684  |
|                           | sad-J           | 160 | 0.0689          | -9.4959         | 3.3733          | 79.1263         | 73.0726  |
| $^1J_{\text{C-H}}$        | aug-cc-pVTZ-Juc | 206 | 0.3956          | 0.3543          | 0.0975          | 162.5578        | 163.4050 |
|                           | aug-cc-pVTZ-J   | 172 | 0.4057          | 0.3502          | 0.0784          | 163.0898        | 163.9241 |
|                           | sad-Juc         | 192 | 0.4119          | 0.2820          | -0.0192         | 163.7418        | 164.4166 |
|                           | sad-J           | 160 | 0.4222          | 0.2575          | 0.0325          | 163.7169        | 164.4290 |
| $^2J_{\text{C-H}}$        | aug-cc-pVTZ-Juc | 206 | -0.6783         | -1.0578         | 0.1149          | -2.4841         | -4.1053  |
|                           | aug-cc-pVTZ-J   | 172 | -0.6781         | -1.0816         | 0.1169          | -2.5096         | -4.1525  |
|                           | sad-Juc         | 192 | -0.6733         | -1.0683         | 0.0493          | -3.0613         | -4.7536  |
|                           | sad-J           | 160 | -0.6750         | -1.0954         | 0.0476          | -3.1208         | -4.8418  |
| $^2J_{\text{H-H}}$        | aug-cc-pVTZ-Juc | 206 | -3.8384         | 4.1011          | 0.3637          | -0.4652         | 0.1612   |
|                           | aug-cc-pVTZ-J   | 172 | -3.8458         | 4.0218          | 0.3632          | -0.5018         | 0.0373   |
|                           | sad-Juc         | 192 | -3.8044         | 3.9952          | 0.3109          | -0.8534         | -0.3517  |
|                           | sad-J           | 160 | -3.8110         | 3.9169          | 0.3119          | -0.9374         | -0.5195  |
| cis- $^3J_{\text{H-H}}$   | aug-cc-pVTZ-Juc | 206 | -1.0439         | 0.7338          | -0.0630         | 13.1835         | 12.8104  |
|                           | aug-cc-pVTZ-J   | 172 | -1.0450         | 0.7251          | -0.0630         | 13.2074         | 12.8245  |
|                           | sad-Juc         | 192 | -1.0346         | 0.6586          | -0.0671         | 13.4610         | 13.0179  |
|                           | sad-J           | 160 | -1.0353         | 0.6500          | -0.0672         | 13.5565         | 13.1039  |
| trans- $^3J_{\text{H-H}}$ | aug-cc-pVTZ-Juc | 206 | -3.5012         | 3.1243          | 0.2874          | 19.7577         | 19.6682  |
|                           | aug-cc-pVTZ-J   | 172 | -3.5114         | 3.0398          | 0.2875          | 19.7900         | 19.6059  |
|                           | sad-Juc         | 192 | -3.4872         | 3.1111          | 0.3065          | 19.9533         | 19.8837  |
|                           | sad-J           | 160 | -3.4969         | 3.0280          | 0.3067          | 20.0098         | 19.8476  |

<sup>a</sup>Geometry:  $R_{\text{C-C}}=1.3384$  Å,  $R_{\text{C-H}}=1.0870$ ,  $\angle(\text{HCH})=117.367^\circ$ ,  $\angle(\text{HCC})=121.316^\circ$  (Ref. 50).

in an arbitrary molecule. The first issue to be investigated is therefore whether one should use always the MO coefficients of the molecule in question<sup>3,7</sup> or whether it is possible to develop universal contracted basis sets by using MO coefficients from arbitrary but well chosen molecules.

We used two different uncontracted basis sets. The first basis set is the aug-cc-pVTZ-Juc employed in the first part of this work. As second basis set, named sad-Juc, we use Sadlej's medium size polarized basis sets,<sup>64,65</sup> which have been totally uncontracted and augmented with four  $s$ -type functions with very large exponents. For carbon, nitrogen, and oxygen it consists of (15 $s6p4d$ ) functions. Again the basis set for sulfur (17 $s10p6d$ ), includes two additional tight  $d$ -type functions. Basis set sad-Juc for hydrogen (10 $s4p$ ), has been used as basis set  $E$  in our previous study of locally dense basis sets.<sup>5</sup> The exponents of both basis sets can be downloaded from the internet.<sup>49</sup>

As a test molecule we choose  $\text{CH}_2\text{O}$ , as it is the smallest molecule of the series studied in this work and consists of three different atoms. In a first series of calculations we investigated different contraction schemes using MO coefficients of  $\text{CH}_2\text{O}$  as contraction coefficients. To reduce the number of options, we adopted a contraction scheme in which all except for the two most diffuse  $s$ - and  $p$ -type functions on C, O, and  $s$ -type functions on H were contracted and some of the contracted functions were added to the basis set also as uncontracted functions. In a second series we studied in the same way the performance of contracted basis sets where we used MO coefficients of  $\text{CH}_4$  for the carbon basis set, MO coefficients of  $\text{H}_2\text{O}$  for the oxygen basis set, and MO coefficients of  $\text{H}_2$  for hydrogen. No significant differences in the four contributions to all the coupling constants

in  $\text{CH}_2\text{O}$  were found between the two series of calculations, i.e., between using MO coefficients of  $\text{CH}_2\text{O}$  or  $\text{fC H}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2$ . One might expect this due to the fact that the  $1s$  orbitals of carbon and oxygen are almost unaffected by different bonding situations. A comparison of the coefficients for the molecular orbitals in  $\text{CH}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  which are essentially carbon and oxygen  $1s$  orbitals shows that they are indeed almost identical. Larger differences between the MO coefficients exist only for the two most diffuse basis functions, which we therefore excluded from the contraction. However, the same is also true for the coefficients of the  $p$ -type basis functions in the molecular orbitals corresponding to the C-H and O-H single bonds. In the following we used therefore only the MO coefficients of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{S}$  as contraction coefficients for the hydrogen, carbon, nitrogen, oxygen, and sulfur basis sets.

In a third series of calculations on all four molecules we tested different contraction schemes. Again we contracted all but the two most diffuse  $s$ - and  $p$ -type functions on C, N, and O and  $s$ -type functions on H in one contracted function and included also some of the contracted functions as uncontracted functions. In the case of sulfur we contracted all but the three most diffuse  $s$ - and  $p$ -type functions into two contracted functions and added again some of the contracted functions also as uncontracted functions. As selection criteria we required that the error in all coupling constants due to the contraction is smaller than  $\sim 0.5$  Hz. This led us to the following contractions of basis set aug-cc-pVTZ-Juc: hydrogen [6 $s3p1d$ ]; carbon, nitrogen, oxygen [9 $s5p3d1f$ ]; sulfur [10 $s7p6d1f$ ], and of basis set sad-Juc: hydrogen [6 $s4p$ ]; carbon, nitrogen, oxygen [9 $s5p4d$ ]; sulfur [9 $s7p6d$ ]. In the fol-

TABLE V. Basis set dependence of the contributions to the coupling constants  $J$  (in Hz) in  $^{13}\text{C}^1\text{H}_2^{15}\text{N}^1\text{H}$  at the SOPPA level.<sup>a</sup>

| Coupling                  | Basis           | #   | $J^{\text{OD}}$ | $J^{\text{OP}}$ | $J^{\text{SD}}$ | $J^{\text{FC}}$ | $J$      |
|---------------------------|-----------------|-----|-----------------|-----------------|-----------------|-----------------|----------|
| $^1J_{\text{C-N}}$        | aug-cc-pVTZ-Juc | 182 | -0.0128         | 8.7337          | -1.4291         | -9.7237         | -2.4318  |
|                           | aug-cc-pVTZ-J   | 152 | -0.0126         | 8.7673          | -1.4301         | -9.8930         | -2.5683  |
|                           | sad-Juc         | 170 | -0.0144         | 8.6846          | -1.4641         | -10.3822        | -3.1761  |
|                           | sad-J           | 142 | -0.0139         | 8.7207          | -1.4749         | -10.3410        | -3.1091  |
| $^1J_{\text{C-H}_1}$      | aug-cc-pVTZ-Juc | 182 | 0.4931          | -0.2911         | 0.1136          | 177.3098        | 177.6253 |
|                           | aug-cc-pVTZ-J   | 152 | 0.4937          | -0.2941         | 0.0922          | 177.8942        | 178.1861 |
|                           | sad-Juc         | 170 | 0.5091          | -0.3428         | -0.0662         | 178.3707        | 178.4708 |
|                           | sad-J           | 142 | 0.5101          | -0.3614         | -0.0139         | 178.3630        | 178.4977 |
| $^1J_{\text{C-H}_2}$      | aug-cc-pVTZ-Juc | 182 | 0.4962          | -0.2671         | 0.1843          | 166.5515        | 166.9649 |
|                           | aug-cc-pVTZ-J   | 152 | 0.4970          | -0.2704         | 0.1637          | 167.0943        | 167.4846 |
|                           | sad-Juc         | 170 | 0.5135          | -0.3256         | 0.0242          | 167.6594        | 167.8715 |
|                           | sad-J           | 142 | 0.5148          | -0.3472         | 0.0745          | 167.7249        | 167.9670 |
| $^1J_{\text{N-H}_3}$      | aug-cc-pVTZ-Juc | 182 | -0.1381         | -0.5415         | 0.1893          | -50.9145        | -51.4048 |
|                           | aug-cc-pVTZ-J   | 152 | -0.1373         | -0.5048         | 0.2006          | -51.1153        | -51.5567 |
|                           | sad-Juc         | 170 | -0.1481         | -0.5100         | 0.2164          | -51.4907        | -51.9323 |
|                           | sad-J           | 142 | -0.1472         | -0.4802         | 0.1946          | -51.6741        | -52.1068 |
| $^2J_{\text{N-H}_1}$      | aug-cc-pVTZ-Juc | 182 | 0.2805          | 1.3701          | -0.1628         | -10.8310        | -9.3433  |
|                           | aug-cc-pVTZ-J   | 152 | 0.2804          | 1.3838          | -0.1637         | -10.8450        | -9.3445  |
|                           | sad-Juc         | 170 | 0.2778          | 1.3687          | -0.1020         | -10.6473        | -9.1028  |
|                           | sad-J           | 142 | 0.2781          | 1.3846          | -0.1027         | -10.6520        | -9.0920  |
| $^2J_{\text{N-H}_2}$      | aug-cc-pVTZ-Juc | 182 | 0.3611          | 1.0066          | -0.2291         | 3.7085          | 4.8471   |
|                           | aug-cc-pVTZ-J   | 152 | 0.3612          | 1.0244          | -0.2295         | 3.7206          | 4.8767   |
|                           | sad-Juc         | 170 | 0.3587          | 1.0110          | -0.1391         | 3.8972          | 5.1276   |
|                           | sad-J           | 142 | 0.3593          | 1.0288          | -0.1406         | 3.9147          | 5.1622   |
| $^2J_{\text{C-H}_3}$      | aug-cc-pVTZ-Juc | 182 | -0.8297         | -2.5619         | -0.0561         | -11.2221        | -14.6698 |
|                           | aug-cc-pVTZ-J   | 152 | -0.8299         | -2.5772         | -0.0557         | -11.3290        | -14.7918 |
|                           | sad-Juc         | 170 | -0.8228         | -2.5881         | -0.1176         | -11.8220        | -15.3505 |
|                           | sad-J           | 142 | -0.8233         | -2.6035         | -0.1203         | -11.9580        | -15.5051 |
| $^2J_{\text{H-H}}$        | aug-cc-pVTZ-Juc | 182 | -3.7163         | 3.8405          | 0.3848          | 17.2916         | 17.8006  |
|                           | aug-cc-pVTZ-J   | 152 | -3.7157         | 3.7650          | 0.3844          | 17.2899         | 17.7235  |
|                           | sad-Juc         | 170 | -3.6820         | 3.7471          | 0.3247          | 17.1368         | 17.5266  |
|                           | sad-J           | 142 | -3.6814         | 3.6721          | 0.3256          | 17.1261         | 17.4424  |
| cis- $^3J_{\text{H-H}}$   | aug-cc-pVTZ-Juc | 182 | -0.9655         | 0.3595          | 0.0649          | 19.3656         | 18.8245  |
|                           | aug-cc-pVTZ-J   | 152 | -0.9654         | 0.3578          | 0.0647          | 19.4281         | 18.8852  |
|                           | sad-Juc         | 170 | -0.9541         | 0.2500          | 0.0714          | 19.6901         | 19.0574  |
|                           | sad-J           | 142 | -0.9540         | 0.2484          | 0.0713          | 19.8282         | 19.1938  |
| trans- $^3J_{\text{H-H}}$ | aug-cc-pVTZ-Juc | 182 | -4.5016         | 3.8801          | 0.3478          | 26.2389         | 25.9652  |
|                           | aug-cc-pVTZ-J   | 152 | -4.5011         | 3.7828          | 0.3479          | 26.2770         | 25.9066  |
|                           | sad-Juc         | 170 | -4.4823         | 3.8801          | 0.3770          | 26.4634         | 26.1975  |
|                           | sad-J           | 142 | -4.4818         | 3.7432          | 0.3772          | 26.5574         | 26.1959  |

<sup>a</sup>Geometry:  $R_{\text{C-N}}=1.2730$  Å,  $R_{\text{C-H}}=1.0930$ ,  $R_{\text{N-H}}=1.0210$ ,  $\angle(\text{HCH})=117.000^\circ$ ,  $\angle(\text{H}_1\text{CN})=116.999^\circ$  (see Fig. 1 for details),  $\angle(\text{CNH})=110.400^\circ$  (Ref. 51).

lowing these basis sets are called aug-cc-pVTZ-J and sad-J, respectively. The contractions coefficients can also be downloaded from the internet.<sup>49</sup>

The results for all the coupling constants in  $\text{C}_2\text{H}_4$ ,  $\text{CH}_2\text{NH}$ ,  $\text{CH}_2\text{O}$ , and  $\text{CH}_2\text{S}$  obtained with basis sets aug-cc-pVTZ-Juc, aug-cc-pVTZ-J, sad-Juc, and sad-J at the SOPPA level are shown in Tables IV–VII. In general the contracted basis sets exceed our initial requirements, the differences between the results for the total coupling constants in the contracted and uncontracted basis sets are 0.2 Hz or smaller for all couplings except for the  $^1J_{\text{C-H}}$  and  $^1J_{\text{C-C}}$  couplings in basis set aug-cc-pVTZ-J, where the differences are between 0.5 Hz and 0.6 Hz. The differences are always due to the Fermi contact term as the changes in the other three contributions, the orbital diamagnetic, orbital paramagnetic, and the spin–dipolar contributions are smaller than 0.1 Hz. In percentage the changes in the total coupling constants are 2% or smaller with six exceptions, where the coupling con-

stants are so small that a change of 0.2 Hz amounts to more than 2%. For the same reasons the percent changes in the OD, OP, and SD contributions can be quite large without any visible effect on the total coupling constants.

Analyzing the differences between all four basis sets we observe a nice pattern for all but three couplings:  $^2J_{\text{H-H}}$  in  $\text{CH}_2\text{O}$ ,  $^1J_{\text{C-S}}$  and  $^2J_{\text{S-H}}$  in  $\text{CH}_2\text{S}$ . The one- and three-bond couplings between atoms without lone pairs are always numerically smaller in basis set aug-cc-pVTZ-Juc (aug-cc-pVTZ-J) than basis set sad-Juc (sad-J), whereas the two-bond couplings are larger. For the one- and two-bond couplings between atoms where one has one or more lone pairs the opposite trend is found.

Discussing in more detail now the differences between the basis sets for each molecule we notice first of all that in  $\text{CH}_2\text{CH}_2$  the total coupling constants for all but geminal couplings are roughly given by their FC contributions, see Table IV. The same holds also for the basis set dependence of the



TABLE VI. Basis set dependence of the contributions to the coupling constants  $J$  (in Hz) in  $^{13}\text{C}^1\text{H}_2^{17}\text{O}$  at the SOPPA level.<sup>a</sup>

| Coupling           | Basis           | #   | $J^{\text{OD}}$ | $J^{\text{OP}}$ | $J^{\text{SD}}$ | $J^{\text{FC}}$ | $J$      |
|--------------------|-----------------|-----|-----------------|-----------------|-----------------|-----------------|----------|
| $^1J_{\text{C-O}}$ | aug-cc-pVTZ-Juc | 158 | 0.0021          | 21.7718         | -1.2204         | 12.3539         | 32.9074  |
|                    | aug-cc-pVTZ-J   | 132 | 0.0019          | 21.8539         | -1.2178         | 12.2033         | 32.8412  |
|                    | sad-Juc         | 148 | -0.0017         | 21.6932         | -1.2957         | 11.7658         | 32.1617  |
|                    | sad-J           | 124 | -0.0010         | 21.7708         | -1.3104         | 11.8748         | 32.3342  |
| $^1J_{\text{C-H}}$ | aug-cc-pVTZ-Juc | 158 | 0.5935          | -0.8274         | 0.2793          | 181.8991        | 181.9446 |
|                    | aug-cc-pVTZ-J   | 132 | 0.5952          | -0.8301         | 0.2580          | 182.4785        | 182.5017 |
|                    | sad-Juc         | 148 | 0.6096          | -0.8735         | 0.0679          | 182.9524        | 182.7563 |
|                    | sad-J           | 124 | 0.6123          | -0.8877         | 0.1110          | 183.0100        | 182.8456 |
| $^2J_{\text{O-H}}$ | aug-cc-pVTZ-Juc | 158 | 0.4900          | 3.1969          | -0.9622         | -5.6578         | -2.9332  |
|                    | aug-cc-pVTZ-J   | 132 | 0.4900          | 3.2292          | -0.9645         | -5.6747         | -2.9200  |
|                    | sad-Juc         | 148 | 0.4855          | 3.2139          | -0.7053         | -5.5721         | -2.5779  |
|                    | sad-J           | 124 | 0.4862          | 3.2464          | -0.7103         | -5.5727         | -2.5504  |
| $^2J_{\text{H-H}}$ | aug-cc-pVTZ-Juc | 158 | -3.3774         | 3.3753          | 0.3755          | 43.6840         | 44.0573  |
|                    | aug-cc-pVTZ-J   | 132 | -3.3771         | 3.3107          | 0.3750          | 43.7116         | 44.0202  |
|                    | sad-Juc         | 148 | -3.3462         | 3.2914          | 0.3308          | 44.0816         | 44.3576  |
|                    | sad-J           | 124 | -3.3453         | 3.2263          | 0.3314          | 44.1069         | 44.3193  |

<sup>a</sup>Geometry:  $R_{\text{C-O}} = 1.2070 \text{ \AA}$ ,  $R_{\text{C-H}} = 1.1166$ ,  $\angle(\text{HCH}) = 116.207^\circ$ ,  $\angle(\text{HCO}) = 121.897^\circ$  (Ref. 50).

coupling constants. The OD, OP, and SD contributions are almost basis set independent, with few exceptions like  $^1J_{\text{C-H}}$  where the variations in OP and SD are large in percent but insignificant for the total coupling constant. The FC basis set dependence is most pronounced for  $^1J_{\text{C-C}}$  and  $^1J_{\text{C-H}}$  where the spread of the results from the four basis sets is 2.0 Hz and 1.2 Hz, respectively. It is remarkable that about 0.4 Hz difference in the FC contribution to  $^2J_{\text{H-H}}$  between basis sets aug-cc-pVTZ-Juc and sad-Juc leads to a change of sign in the total coupling constant.

Similarly to  $\text{CH}_2\text{CH}_2$  all coupling constants in  $\text{CH}_2\text{NH}$ , see Table V, apart from  $^1J_{\text{C-H}}$  are dominated by the Fermi contact contribution and the variation in the total coupling constants with the basis set is also due to the changes in the FC terms. The only exception is  $^2J_{\text{H-H}}$  where the spread in the results for the OP and FC term are both 0.17 Hz, the smallest value for an FC term and the largest value for an OP

term in  $\text{CH}_2\text{NH}$ . The largest spread of results is found for  $^1J_{\text{C-H}_2}$  with 1.2 Hz for the FC term and 1.0 Hz for the total coupling constant.

In  $\text{CH}_2\text{O}$ , see Table VI, only  $^1J_{\text{C-H}}$  and  $^2J_{\text{H-H}}$  are dominated by the FC term, whereas for all but  $^2J_{\text{O-H}}$ , the variation of the basis set mainly affects the Fermi contact contribution. The largest spread of results for the FC term, 1.1 Hz, is observed for  $^1J_{\text{C-H}}$ . Interestingly with 0.26 Hz, the spin-dipolar term in most basis set dependent contribution to  $^2J_{\text{O-H}}$ .

As for  $\text{CH}_2\text{O}$ , the Fermi contact term dominates only  $^1J_{\text{C-H}}$  and  $^2J_{\text{H-H}}$  in  $\text{CH}_2\text{S}$ , Table VII. The changes in the FC term with the variation of the basis set are dominating for  $^1J_{\text{C-S}}$  and  $^1J_{\text{C-H}}$ , whereas for  $^2J_{\text{S-H}}$  the changes in the SD and FC terms and for  $^2J_{\text{H-H}}$  the changes in the OP and FC terms are almost equally large. The basis set dependence of

TABLE VII. Basis set dependence of the contributions to the coupling constants  $J$  (in Hz) in  $^{13}\text{C}^1\text{H}_2^{33}\text{S}$  at the SOPPA level.<sup>a</sup>

| Coupling           | Basis           | #   | $J^{\text{OD}}$ | $J^{\text{OP}}$ | $J^{\text{SD}}$ | $J^{\text{FC}}$ | $J$      |
|--------------------|-----------------|-----|-----------------|-----------------|-----------------|-----------------|----------|
| $^1J_{\text{C-S}}$ | aug-cc-pVTZ-Juc | 190 | 0.0070          | -23.9284        | 1.9675          | -16.1839        | -38.1378 |
|                    | aug-cc-pVTZ-J   | 154 | 0.0070          | -24.0130        | 1.9791          | -16.1144        | -38.1413 |
|                    | sad-Juc         | 173 | 0.0080          | -23.5279        | 2.0656          | -14.9204        | -36.3747 |
|                    | sad-J           | 140 | 0.0081          | -23.6334        | 2.0748          | -14.6125        | -36.1630 |
| $^1J_{\text{C-H}}$ | aug-cc-pVTZ-Juc | 190 | 0.5086          | -1.1542         | 0.5641          | 177.8497        | 177.7682 |
|                    | aug-cc-pVTZ-J   | 154 | 0.5091          | -1.1596         | 0.5420          | 178.4499        | 178.3413 |
|                    | sad-Juc         | 173 | 0.5242          | -1.1661         | 0.3332          | 178.9327        | 178.6241 |
|                    | sad-J           | 140 | 0.5237          | -1.1865         | 0.3877          | 179.0785        | 178.8034 |
| $^2J_{\text{S-H}}$ | aug-cc-pVTZ-Juc | 190 | -0.1649         | -3.6100         | 1.3477          | 0.1693          | -2.2578  |
|                    | aug-cc-pVTZ-J   | 154 | -0.1649         | -3.6135         | 1.3512          | 0.1641          | -2.2630  |
|                    | sad-Juc         | 173 | -0.1634         | -3.5906         | 1.0168          | -0.1932         | -2.9304  |
|                    | sad-J           | 140 | -0.1633         | -3.5961         | 1.0219          | -0.3004         | -3.0378  |
| $^2J_{\text{H-H}}$ | aug-cc-pVTZ-Juc | 190 | -3.4801         | 3.5563          | 0.4853          | 5.9553          | 6.5167   |
|                    | aug-cc-pVTZ-J   | 154 | -3.4795         | 3.4814          | 0.4849          | 5.9060          | 6.3927   |
|                    | sad-Juc         | 173 | -3.4466         | 3.4802          | 0.4857          | 5.8763          | 6.3957   |
|                    | sad-J           | 140 | -3.4460         | 3.4119          | 0.4866          | 5.7911          | 6.2436   |

<sup>a</sup>Geometry:  $R_{\text{C-S}} = 1.6101 \text{ \AA}$ ,  $R_{\text{C-H}} = 1.0932$ ,  $\angle(\text{HCH}) = 116.778^\circ$ ,  $\angle(\text{HCS}) = 121.611^\circ$  (Ref. 52).

the  ${}^2J_{S-H}$  coupling in  $CH_2S$  is remarkable as basis set aug-cc-pVTZ-Juc and sad-Juc predict a different sign. However, the largest spread of results, 1.6 Hz, is still found for FC term in  ${}^1J_{C-S}$ .

Summarizing we can state that the results obtained with basis sets aug-cc-pVTZ-Juc and sad-Juc, or their contracted versions aug-cc-pVTZ-J and sad-J, differ by about 2 Hz for  ${}^1J_{C-C}$  in  $C_2H_4$  and  ${}^1J_{C-S}$  in  $CH_2S$  and 1 Hz or less for all the other coupling constants in this study. Based on previous experience<sup>5</sup> and the comparison with the experimental results, given in Tables I–III, we believe that basis set aug-cc-pVTZ-Juc (or aug-cc-pVTZ-J) gives the more accurate results.

Finally, the effect of performing SOPPA(CCSD) calculations with the four basis sets is a significant reduction of the absolute value of all coupling constants but  ${}^2J_{H-H}$  in  $CH_2S$  and *trans*- ${}^3J_{H-H}$  in  $CH_2NH$ : see Tables I–III for the SOPPA(CCSD) results obtained with basis aug-cc-pVTZ-Juc. The largest correlation effects ( $\sim 6$  Hz) are observed for the  ${}^1J_{13C-1H}$  couplings in all molecules. The  ${}^2J_{17O-1H}$  coupling in  $CH_2O$ , on the other hand, is almost unchanged. Despite these correlation corrections are the changes due to the contraction of the basis sets aug-cc-pVTZ-Juc and sad-Juc almost identical at the SOPPA and SOPPA(CCSD) level, i.e., the basis set effect is independent of the additional correlation introduced at the SOPPA(CCSD) level.

## V. CONCLUDING REMARKS

The SOPPA and SOPPA(CCSD) methods have been used to calculate all four contributions to the indirect nuclear spin–spin coupling constants in the model compounds  $CH_2X$  ( $X=CH_2, N, O, S$ ) where the substituents  $X$  vary in electronegativity and the number of lone pairs. The SOPPA(CCSD) results with the largest basis set are in close agreement with the comparable experimental results. The differences are in the range of 0.3 and 2.7 Hz. It is also observed that the calculated difference between  ${}^1J_{C-H_1}$  and  ${}^1J_{C-H_2}$  in  $CH_2NH$  is 9.64 Hz which is very close to the experimental value of 9.20 Hz. An almost equally good agreement is found for the splitting of the vicinal couplings in  $C_2H_4$  and  $CH_2NH$  where the calculated values are 6.62 Hz and 6.93 Hz, respectively, to be compared with the experimental values of 7.47 Hz and 8.2 Hz. Our results for  $C_2H_4$  are also in good agreement with the results of previous EOM–CCSD and RASSCF calculations apart from the  ${}^1J_{C-C}$  coupling where our result is closer to experiment.

With respect to the lone pair or electronegativity effects on the reduced coupling constants we observe for one-bond couplings C–Y that the well-known negative contribution of a lone pair on Y gives a drastic reduction of the Fermi contact and the orbital paramagnetic term, whereas in the case of C–H and Y–H one-bond couplings mainly the dominating Fermi contact term is affected by the lone pair. In the Y–H couplings the Fermi contact term is also strongly reduced by the lone pair, but the OP contribution to the one-bond N–H coupling in  $CH_2NH$  is actually increased with respect to the one-bond C–H coupling in  $C_2H_4$ . The changes in the one-bond couplings with a lone pair in  $\alpha$  position are much

smaller and the FC term increases with the number of lone pairs. The so-called Perlin effect which is observed in these type of couplings is caused by changes in the FC term.

In the geminal Y–H couplings the FC, OP, and SD term vary significantly with Y and most pronounced the FC term. The SD and FC terms increase with the number of lone pairs or electronegativity whereas the OP term which is negative becomes even more negative. This leads to a more complicated picture for the total reduced coupling constant. Nevertheless the large difference between the two geminal N–H couplings in  $CH_2NH$  is mainly due to changes in the FC term. It is worth mentioning that  ${}^2K_{Y-H}^{OP}$  is larger than  ${}^2K_{Y-H}^{FC}$  when  $Y=S$ , but smaller when  $Y=O$ . For the two-bond C–H couplings with a lone pair on the central Y atom, the negative lone-pair effect shows up in all four contributions to the couplings but most important in the FC term. The geminal H–H couplings are strongly dominated by the FC term. The variation of these couplings with electronegative substituents in the  $\alpha$  position is therefore due to the FC term. Finally the vicinal H–H couplings are dominated by the FC contribution and the changes in couplings between  $C_2H_4$  and  $CH_2NH$  are also due to changes in the FC term.

Summarizing we can conclude a lot about lone-pair effects and the effect of electronegativity on coupling constants can be learned by state-of-the art calculations of all four contributions to the coupling constants. Nevertheless, we consider it worthwhile to investigate the dominating contributions even further with methods which can identify contributions from individual bonding or lone-pair orbitals.

Furthermore we have generated smaller optimized basis sets by contracting the *s*- and *p*-type basis functions of C, N, O, and S and the *s*-type basis functions of H with appropriate molecular orbital coefficients from self-consistent-field calculations on  $H_2$ ,  $CH_4$ ,  $NH_3$ ,  $H_2O$ , and  $H_2S$ . The reduction in the number of basis functions is approximately 17%. The changes in the coupling constants due to the contraction are 0.2 Hz or smaller apart from some one-bond coupling constants where the errors are between 0.5 Hz and 0.6 Hz.

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