

Systematic Comparison of Second-Order Polarization Propagator Approximation (SOPPA) and Equation-of-Motion Coupled Cluster Singles and Doubles (EOM-CCSD) Spin–Spin Coupling Constants for Molecules with C, N, and O Double and Triple Bonds and Selected F-Substituted Derivatives

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Abstract: Ab initio EOM-CCSD and SOPPA calculations with the Ahlrichs (qzp,qz2p) basis set have been carried out to evaluate one-, two-, and three-bond spin–spin coupling constants for molecules $H_mX=YH_n$ and $H_mX\equiv YH_n$ for $X, Y = {}^{13}\text{C}, {}^{15}\text{N},$ and ${}^{17}\text{O}$, and selected ${}^{19}\text{F}$ -substituted derivatives. In the great majority of cases, EOM-CCSD one-bond C–C, C–N, C–O, C–F, N–N, N–O, and N–F coupling constants and three-bond F–F coupling constants are smaller in absolute value than the corresponding SOPPA coupling constants, with the EOM-CCSD values in better agreement with experimental data. SOPPA tends to significantly overestimate the absolute values of large one- and three-bond couplings involving fluorine. The majority of two-bond SOPPA coupling constants are in better agreement with experiment than EOM-CCSD, although differences between EOM-CCSD and experimental values are not dramatic. A statistical analysis of thirty EOM-CCSD and SOPPA coupling constants versus experimental coupling constants demonstrates that better agreement with experiment is found when EOM-CCSD is the computational method.

Introduction

In a previous paper,¹ we reported a comparison between computed spin–spin coupling constants obtained by two different theoretical methods: the second-order polarization propagator approximation (SOPPA) and the equation-of-motion coupled cluster singles and doubles method (EOM-CCSD). That study was carried out with the Ahlrichs (qzp,qz2p) basis set on a series of molecules H_mX-YH_n , for $X-Y$ a single bond involving C, N, O, and F, as well as a set of fluorine derivatives of these molecules for which experimental spin–spin coupling constants were available. Also included were the neutral hydrides NH_3 , H_2O , and HF and their protonated and deprotonated ions, as well as the

hydrogen-bonded complexes which could be formed from these species. The methods chosen for investigation, EOM-CCSD and SOPPA, explicitly treat electron correlation effects, with EOM-CCSD providing a higher level of treatment. However, the higher level treatment of correlation effects makes EOM-CCSD significantly more expensive computationally and limits its application to relatively small systems and/or those with high computational symmetry. On the other hand, SOPPA is much more tractable computationally. The question then is how well does SOPPA perform.

It was not surprising to find in ref 1 that for the neutral molecules H_mX-YH_n and their F-substituted derivatives, EOM-CCSD coupling constants were in better agreement with experimental coupling constants than SOPPA, particular for couplings involving fluorine, in which cases the SOPPA data were significantly in error. However, SOPPA coupling constants were consistent with EOM-CCSD coupling con-

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stants for some of the one-bond couplings and for the hydrogen-bonded complexes. In the present paper, we report an extension of our previous study to molecules H_mXYH_n in which X and Y are doubly- ($X=Y$) and triply bonded ($X\equiv Y$) and selected F-substituted derivatives. These derivatives have been included because of the availability of experimental coupling constants and the discrepancies observed in ref 1 between experimental and computed SOPPA coupling constants involving F. In this paper we compare computed EOM-CCSD and SOPPA coupling constants with each other and with experimental data.

Methods

Molecular structures have been optimized at second-order Møller–Plesset perturbation theory (MP2)^{2–5} with the 6–31+G(d,p) basis set.^{6–9} Vibrational frequencies have been computed to establish that each structure is a local minimum on its potential surface. These optimized geometries were used for the calculation of coupling constants for the majority of molecules. However, for molecules with experimentally determined ground-state geometries^{10–15} and experimentally measured coupling constants,^{16–21} the experimental ground-state geometry was used in an effort to minimize the effect of neglecting zero-point vibrational corrections.²² Although the importance of zero-point vibrational corrections has been demonstrated previously by others, imposing such corrections does not always lead to better agreement with experiment. For example, in a previous study of FCCF,¹⁸ we demonstrated that the three-bond F–F coupling constant was extremely sensitive to geometry. Optimized geometries even at CCSD(T)/aug-cc-pVTZ had C–C and C–F distances that were too long and absolute values of $^3J(F-F)$ which were significantly greater than the experimental value of this coupling constant. Imposing zero-point corrections increased these distances and led to even larger discrepancies. It was only when the experimental geometry of FCCF was used that computed values of $^3J(F-F)$ at both levels of theory approached the experimental value, with the absolute value of the EOM-CCSD coupling constant in very good agreement with experiment.

Spin–spin coupling constants involving ^{13}C , ^{15}N , ^{17}O , and ^{19}F were computed using the second-order polarization propagator approximation (SOPPA)^{23–27} and the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI(configuration interaction)-like approximation,^{28,29} with all electrons correlated. Both of these methods explicitly include electron correlation effects. For these calculations, only one basis set has been employed, namely, the Ahlrichs³⁰ qzp basis set for ^{13}C , ^{15}N , ^{17}O , and ^{19}F atoms and the qz2p basis set for 1H atoms. Thus, the levels of theory may be represented as EOM-CCSD/(qzp,qz2p) and SOPPA/(qzp,qz2p). Coupling constants have not been evaluated at SOPPA(CCSD),^{23,31} a method in which the MP2 amplitudes are replaced by CCSD amplitudes. In ref 1 it was observed that SOPPA significantly overestimates the absolute values of $^1J(O-F)$ for FOF and FOF. These coupling constants increase in absolute value at SOPPA(CCSD) and are further removed from the EOM-CCSD and experimental values.

In the Ramsey approximation, the total coupling constant (J) is a sum of four contributions: the paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO), Fermi-contact (FC), and spin-dipole (SD). All terms have been computed for all molecules. Geometry optimizations were carried out with the Gaussian 03 suite of programs.³² SOPPA calculations were performed using Dalton-2³³ on the IQM computers, and the EOM-CCSD calculations were done with ACES II³⁴ on the Itanium Cluster at the Ohio Supercomputer Center.

Results and Discussion

Table 1 presents computed SOPPA and EOM-CCSD spin–spin coupling constants, along with the available experimental data. The components of J can be found in Tables S1 and S2 of the Supporting Information. Listed first in Table 1 are molecules with triple bonds, beginning with $HC\equiv CH$ and its F-substituted derivatives, followed by molecules with $C\equiv N$ bonds, and then $C\equiv O$ and $N\equiv N$. Molecules with double bonds are arranged starting with $H_2C=CH_2$ and its derivatives, followed by molecules with $C=N$, $C=O$, $N=N$, and $N=O$ double bonds. Three molecules originally included in this list ($HN=O$ and *cis* and *trans* $HN=NH$) have been removed because of large t_2 amplitudes of 0.15, which are indicative of the inadequacy of a single-reference treatment. The last three entries in Table 1 are the cumulenes, $H_2C=C=CH_2$, $H_2C=C=NH$, and $H_2C=C=O$.

One-Bond Coupling Constants. Table 1 shows that the computed SOPPA and EOM-CCSD 1-bond C–C coupling constants are always positive and usually similar, with the SOPPA coupling constants greater than EOM-CCSD. $^1J(C-C)$ has been determined experimentally for only 3 molecules included in this study, $HCCH$, H_2CCH_2 , and H_2CCCH_2 . For each of these, the computed values overestimate the experimental, although the EOM-CCSD coupling constants are closer to experiment. Both EOM-CCSD and SOPPA overestimate $^1J(C-C)$ for coupling across the C–C triple bond, with computed values of 198.6 and 194.9 Hz, respectively, compared to the experimental gas-phase value of 174.8 Hz.²¹ Unfortunately, experimental $^1J(C-C)$ values for $FCCH$ and $FCCF$ are not available. However, both methods predict that F-substitution would significantly increase $^1J(C-C)$ for $FCCH$ (288.5 and 281.0 at SOPPA and EOM-CCSD, respectively) and for $FCCF$ (430.2 and 417.5 Hz, respectively).

SOPPA and EOM-CCSD values of $^1J(C-N)$ are similar, relatively small, and may be positive or negative. $^1J(C-O)$ is always positive, while $^1J(N-N)$ and $^1J(N-O)$ are negative. The absolute values of the SOPPA coupling constants are greater than the corresponding EOM-CCSD coupling constants, with the EOM-CCSD values in better agreement with available experimental data. Since the magnetogyric ratios of ^{13}C and ^{19}F are positive while those of ^{15}N and ^{17}O are negative, the reduced one-bond coupling constants $^1K(C-O)$, $^1K(N-N)$, and $^1K(N-O)$ are negative and thus in violation of the Dirac Vector Model.³⁵

What makes $^1K(C-O)$, $^1K(N-N)$, and $^1K(N-O)$ negative? From Tables S1 and S2 it can be seen that all $^1J(C-O)$ are positive because both the PSO and FC terms are positive.

Table 1. SOPPA, EOM-CCSD, and Experimental Spin-Spin Coupling Constants J (Hz)^a

molecule	ⁿ J(X–Y)	SOPPA	EOM-CCSD	exptl
Molecules with Triple Bonds				
1 HC≡CH ^b	¹ J(C–C)	198.6	194.9	174.8 ^c
2 FC≡CH	¹ J(C–C)	288.5	281.0	
	¹ J(C–F)	–363.2	–323.2	
3 FC≡CF ^d	¹ J(C–C)	430.2	417.5	
	¹ J(C–F)	–318.3	–277.7	–287.3 ^e
	² J(C–F)	37.9	40.2	28.7 ^f
	³ J(F–F)	–9.5	1.4	2.1 ^e
4 HC≡N	¹ J(C–N)	–9.7	–12.6	
5 H ₃ CC≡N ^g	¹ J(C–N)	–13.5	–16.6	–17.5 ^h
6 FC≡N	¹ J(C–N)	13.3	5.9	
	¹ J(C–F)	–515.8	–465.9	
7 C≡O ^b	¹ J(C–O)	23.1	18.6	16.4 ⁱ
8 N≡N ^b	¹ J(N–N)	–4.8	–3.1	–1.8 ^j
Molecules with Double Bonds				
9 H ₂ C=CH ₂ ^g	¹ J(C–C)	75.0	71.1	67.2 ^k
10 F ₂ C=CH ₂ ^l	¹ J(C–C)	123.7	119.7	
	¹ J(C–F)	–319.0	–290.2	–287 ^m
	² J(F–F)	24.1	45.3	32.7 ⁿ
11 FHC=CHF <i>cis</i> ^o	¹ J(C–C)	109.7	105.0	
	¹ J(C–F)	–283.1	–259.4	
	² J(C–F)	14.1	8.4	5.9 ^p
	³ J(F–F)	–8.4	–15.1	–18.7 ^q
12 FHC=CHF <i>trans</i>	¹ J(C–C)	123.1	117.2	
	¹ J(C–F)	–271.6	–246.5	
	² J(C–F)	54.8	48.0	
	³ J(F–F)	–150.2	–137.6	–132.7 ^q
13 F ₂ C=CF ₂ ^o	¹ J(C–C)	210.5	204.3	
	¹ J(C–F)	–302.1	–270.1	
	² J(C–F)	52.1	46.8	
	² J(F–F)	122.0	134.1	124 ^q
	³ J(F–F) <i>cis</i>	86.7	67.6	73.3 ^q
	³ J(F–F) <i>trans</i>	–124.1	–115.2	–114 ^q
14 H ₂ C=NH	¹ J(C–N)	–1.5	–1.9	
15 F ₂ C=NH	¹ J(C–N)	–9.7	–11.6	
	¹ J(C–F) <i>cis to H</i>	–398.1	–360.7	
	¹ J(C–F) <i>trans to H</i>	–308.8	–278.3	
	² J(F–F)	–88.7	–61.8	–54.6 ^q
16 FHC=NF <i>cis</i>	¹ J(C–N)	2.3	3.9	
	¹ J(C–F)	–382.7	–347.5	
	¹ J(N–F)	131.2	116.1	
	³ J(F–F)	–60.3	–49.3	
17 FHC=NF <i>trans</i>	¹ J(C–N)	2.6	1.3	
	¹ J(C–F)	–308.4	–277.7	
	¹ J(N–F)	114.0	99.6	
	³ J(F–F)	–247.6	–213.4	
18 H ₂ C=O	¹ J(C–O)	38.0	32.8	
19 F ₂ C=O	¹ J(C–O)	30.5	22.9	
	¹ J(C–F)	–375.4	–337.1	
	² J(F–F)	–165.2	–141.7	
20 FN=NF <i>cis</i> ^o	¹ J(N–N)	0.93	–0.59	
	¹ J(N–F)	240.9	211.8	211.0 ^r
	² J(N–F)	–19.3	–17.9	–25.4 ^r
	³ J(F–F)	–190.1	–128.8	
21 FN=NF <i>trans</i> ^s	¹ J(N–N)	–20.7	–19.1	
	¹ J(N–F)	194.6	171.8	172.8 ^r
	² J(N–F)	–58.7	–53.8	–62.8 ^r
	³ J(F–F)	–381.9	–307.1	
22 FN=O	¹ J(N–O)	–47.9	–38.5	
	¹ J(N–F)	131.7	84.2	
Cumulenes				
23 H ₂ C=C=CH ₂ ^g	¹ J(C–C)	111.6	105.4	98.7 ^t
24 H ₂ C=C=NH	¹ J(C–C)	112.5	109.0	
	¹ J(C–N)	–12.4	–14.5	
25 H ₂ C=C=O	¹ J(C–C)	110.7	110.3	
	¹ J(C–O)	30.3	23.2	

^a J for molecules with experimentally determined coupling constants were computed at experimental geometries, except for molecules **12** (FHC=CHF *trans*) and **15** (F₂C=NH). ^b Reference 10. ^c Reference 21. ^d Reference 11. ^e Reference 17. ^f Reference 18. ^g Reference 12. ^h Reference 16, p 375. ⁱ Reference 19, p 386. ^j Reference 19, p 274. ^k Reference 16, p 370. ^l Reference 13. ^m Reference 20, p 579. ⁿ Reference 19, p 636. ^o Reference 14. ^p Reference 20, p 581. ^q Reference 19, p 646. ^r Reference 19, p 277. ^s Reference 15. ^t Reference 20, p 550.

Similarly, ¹J(N–N) for N₂ and *trans* FNNF and ¹J(N–O) for FNO are negative because both PSO and FC terms are negative. The only molecule that does not fit this pattern is *cis* FNNF, in which case the PSO term is relatively small and negative, and the FC and SD terms are small but positive.

¹J(N–N) for *cis* FNNF has opposite signs at SOPPA and EOM-CCSD, but its absolute value is less than 1 Hz.

In the set of molecules included in this study, there are 12 one-bond C–F coupling constants and 5 one-bond N–F coupling constants. All one-bond C–F coupling constants

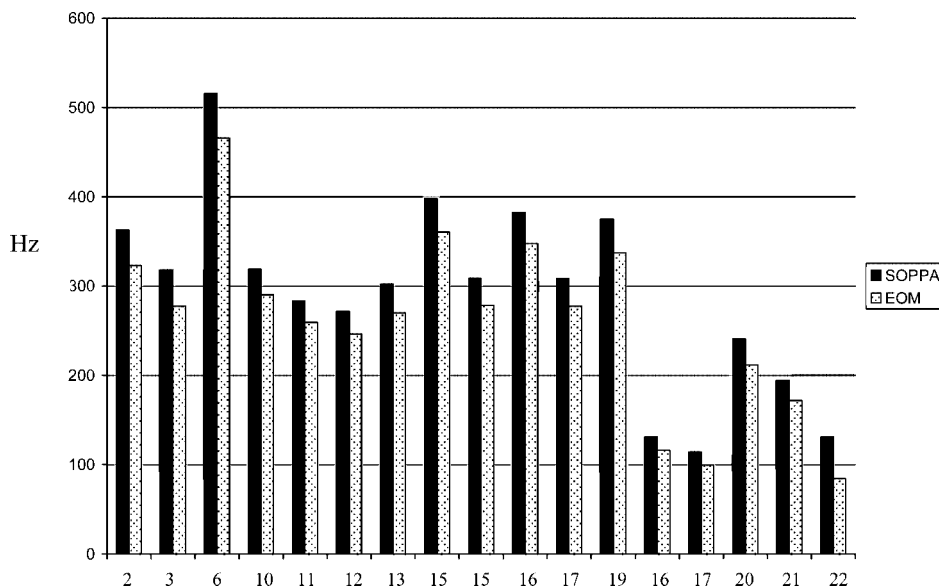


Figure 1. SOPPA and EOM-CCSD one-bond coupling constants. The numbers on the x-axis correspond to the molecule numbers in Table 1. The first 12 pairs of bars are the absolute values of $^1J(\text{C}-\text{F})$; the remaining 5 pairs are $^1J(\text{N}-\text{F})$.

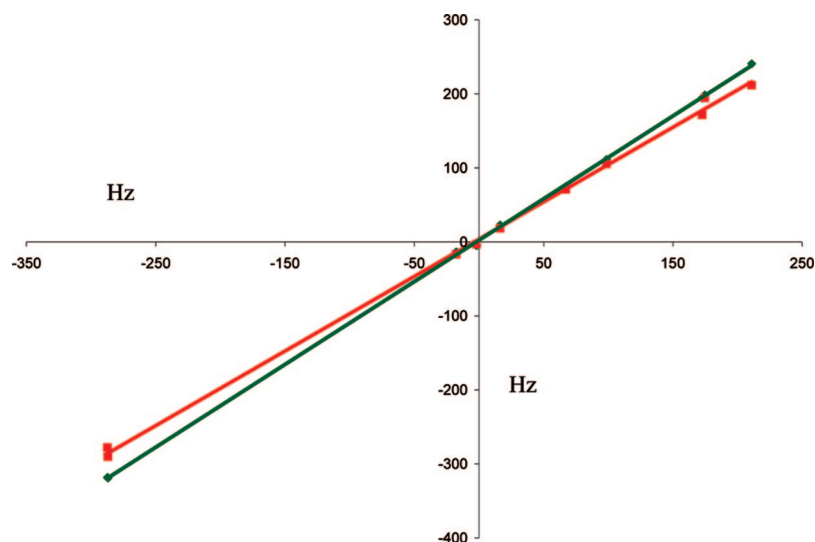


Figure 2. EOM-CCSD (■) and SOPPA (◆) one-bond coupling constants $^1J(\text{X}-\text{Y})$ plotted against the experimental values.

are negative, and all one-bond N–F coupling constants are positive, which means that the reduced one-bond coupling constants $^1K(\text{C}-\text{F})$ and $^1K(\text{N}-\text{F})$ are also negative and in violation of the Dirac Vector Model. This is most likely a consequence of the presence of lone pairs of electrons on the coupled atoms.³⁶ The bar graph of Figure 1 shows the absolute values of SOPPA and EOM-CCSD $^1J(\text{C}-\text{F})$ (pairs 1–12) and the values of $^1J(\text{N}-\text{F})$ (pairs 13–17). The numbers on the horizontal axis correspond to the molecule numbers in Table 1. It is evident that there can be a significant difference between coupling constants computed at these two levels of theory, with the absolute values of the SOPPA couplings always greater than EOM-CCSD. This difference arises from the difference in the absolute values of the FC terms, which are 20 to 50 Hz greater at SOPPA compared to EOM-CCSD. One-bond C–F coupling constants for molecules 3 (FCCF) and 10 (F₂CCH₂) and one-bond N–F couplings for molecules 20 and 21 (“*cis*” and “*trans*” FNNF) have been measured experimentally. The

EOM-CCSD values are in much better agreement with experiment than the SOPPA values, which overestimate $^1J(\text{C}-\text{F})$ and $^1J(\text{N}-\text{F})$ in these molecules by 31, 22, 30, and 22 Hz, respectively. Figure 2 shows a plot of the SOPPA and EOM-CCSD one-bond coupling constants versus the experimental values. If the correlation between theory and experiment were perfect, the trendline would have a slope of 1.00, an intercept of 0.00 Hz, and a correlation coefficient of 1.00. The equations of the trendlines in Figure 2 are

$$^1J(\text{SOPPA}) = 1.12 \cdot ^1J(\text{exptl}) + 2.34 \quad n = 10; R^2 = 1.000$$

$$^1J(\text{EOM-CCSD}) = 1.01 \cdot ^1J(\text{exptl}) + 3.76 \quad n = 10;$$

$$R^2 = 0.999$$

Both SOPPA and EOM-CCSD coupling constants correlate linearly with experimental data. Although the intercept of the SOPPA trendline is closer to 0.00 Hz, its greater slope can be traced to the tendency of SOPPA to overestimate the absolute values of the large one-bond C–F and N–F

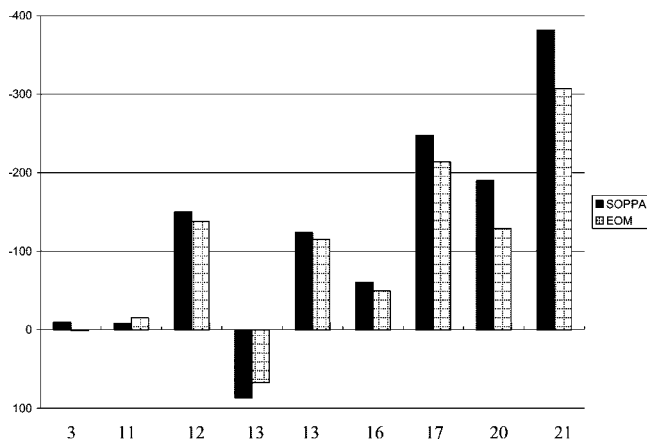


Figure 3. SOPPA and EOM-CCSD three-bond F–F coupling constants $^3J(\text{F-F})$.

coupling constants. The slope of the EOM-CCSD trendline is very close to 1.00, which means that EOM-CCSD gives better agreement with experiment over the entire range of coupling constant values.

Three-Bond F–F Coupling Constants. The only three-bond couplings included in this study are F–F couplings. Figure 3 presents a bar graph showing the nine three-bond SOPPA and EOM-CCSD F–F coupling constants. $^3J(\text{F-F})$ for **3** (FCCF) and **11** (*cis* HFC=CFH) are relatively small, with the absolute value of the SOPPA F–F coupling for **11** less than the EOM-CCSD value, but the EOM-CCSD coupling constants for both **3** and **11** are in better agreement with experiment. These small couplings result from competing contributions from negative PSO terms and positive FC and SD terms, as can be seen in Table S1. In a previous study,¹⁸ it was shown that $^3J(\text{F-F})$ for FCCF (**3**) is extremely sensitive to both C–C and C–F distances, and only at the experimental geometry do the computed EOM-CCSD and SOPPA coupling constants approach the experimental value.

Only $^3J(\text{F-F})$ for *cis* F–F coupling in molecule **13** (F_2CCF_2) is positive, in which case the PSO and SD terms are both positive and the major contributors to J . The remaining six couplings are negative and dominated by large negative PSO terms. The absolute values of the SOPPA coupling constants are greater than the corresponding EOM-CCSD coupling constants, a reflection of the larger PSO terms. This difference is dramatic for F–F coupling in *cis* and *trans* FNNF (**20** and **21**). Experimental coupling constants are available for three of these seven molecules, and, in each case, the EOM-CCSD value is in better agreement with experiment, with SOPPA overestimating the experimental values by 18, 13, and 10 Hz, respectively, for **12** (*trans* FHC=CHF) and for *cis* and *trans* F–F couplings in **13** (F_2CCF_2).

Figure 4 presents plots of SOPPA and EOM-CCSD three-bond coupling constants $^3J(\text{F-F})$ versus the experimental coupling constants. The equations of the trendlines are

$$^3J(\text{SOPPA}) = 1.13 \cdot ^3J(\text{exptl}) + 1.66 \quad n = 5; R^2 = 0.991$$

$$^3J(\text{EOM-CCSD}) = 1.00 \cdot ^3J(\text{exptl}) - 1.83 \quad n = 5; R^2 = 0.998$$

Once again, the slope of the EOM-CCSD trendline is significantly better than that of the SOPPA trendline.

Two-Bond X–F Coupling Constants. From the above analysis and ref 1, it is apparent that one- and three-bond SOPPA coupling constants in molecules with single, double, and triple bonds tend to have greater absolute values than EOM-CCSD coupling constants, with the latter in overall better agreement with experiment data, particularly for couplings involving F. However, the two-bond coupling constants do not fit this pattern. Figure 5 presents bar graphs comparing the EOM-CCSD and SOPPA values. The first 4 pairs are $^2J(\text{C-F})$; pairs 5–8 are $^2J(\text{F-F})$; and the remaining two are $^2J(\text{N-F})$. It is apparent from Figure 5 that SOPPA and EOM-CCSD $^2J(\text{C-F})$ and $^2J(\text{N-F})$ values are quite similar. Nevertheless, the SOPPA values for molecules **3**, **20**, and **21** are closer to experiment than the EOM-CCSD values. Both SOPPA and EOM-CCSD overestimate $^2J(\text{C-F})$ for FCCF by 9 and 12 Hz, respectively. Both underestimate the absolute values of $^2J(\text{N-F})$ for *cis* FNNF by 6 and 8 Hz and for *trans* FNNF by 4 and 9 Hz, respectively. In contrast, EOM-CCSD overestimates $^2J(\text{C-F})$ for *cis* FHC=CHF by only 3 Hz, while SOPPA overestimates it by 8 Hz.

The data for $^2J(\text{F-F})$ do not fit a simple pattern. It is interesting to note that both levels of theory predict that $^2J(\text{F-F})$ is positive for $\text{F}_2\text{C}=\text{CH}_2$ and $\text{F}_2\text{C}=\text{CF}_2$ but negative for $\text{F}_2\text{C}=\text{NH}$ and $\text{F}_2\text{C}=\text{O}$. This suggests that the sign of this two-bond coupling constant is influenced by whether or not the double bond is homonuclear or heteronuclear. That is, the presence of lone pairs of electrons on the remote atom of the double bond strongly influences the two-bond F–F coupling of the fluorines bonded to C. When $^2J(\text{F-F})$ is positive, either PSO, FC, and SD terms are all positive ($\text{F}_2\text{C}=\text{CF}_2$), or positive FC and SD terms dominate the negative PSO term ($\text{F}_2\text{C}=\text{CH}_2$). For these two couplings, the EOM-CCSD values are greater than the SOPPA values, with the SOPPA values closer to experiment. SOPPA underestimates $^2J(\text{F-F})$ for $\text{F}_2\text{C}=\text{CH}_2$ and $\text{F}_2\text{C}=\text{CF}_2$ by 9 and 2 Hz, respectively, while EOM-CCSD overestimates the experimental values by 13 and 10 Hz, respectively. In contrast, $^2J(\text{F-F})$ values are negative for $\text{F}_2\text{C}=\text{NH}$ and $\text{F}_2\text{C}=\text{O}$ and are dominated by very large and negative PSO terms. The absolute values of the SOPPA coupling constants are greater than the EOM-CCSD. Only $^2J(\text{F-F})$ for $\text{F}_2\text{C}=\text{NH}$ has been measured experimentally, and while EOM-CCSD overestimates its absolute value by 7 Hz, SOPPA overestimates it significantly by 34 Hz. Thus, while 5 of 7 SOPPA two-bond X–F coupling constants are in better agreement with experiment than EOM-CCSD, the differences between these two methods are relatively small except for $\text{F}_2\text{C}=\text{NH}$. This exception has a dramatic effect on the relationship between computed and experimental two-bond coupling constants, as illustrated in Figure 6. The equations of the trendlines are

$$^2J(\text{SOPPA}) = 1.055 \cdot ^2J(\text{exptl}) - 2.82 \quad n = 7; R^2 = 0.954$$

$$^2J(\text{EOM-CCSD}) = 1.054 \cdot ^2J(\text{exptl}) + 6.20 \quad n = 7; R^2 = 0.992$$

Thus, the two trendlines are parallel, and the intercept for the SOPPA data is closer to 0.0 Hz. However, as evident from Figure 6, the SOPPA point for $\text{F}_2\text{C}=\text{NH}$ lies far from

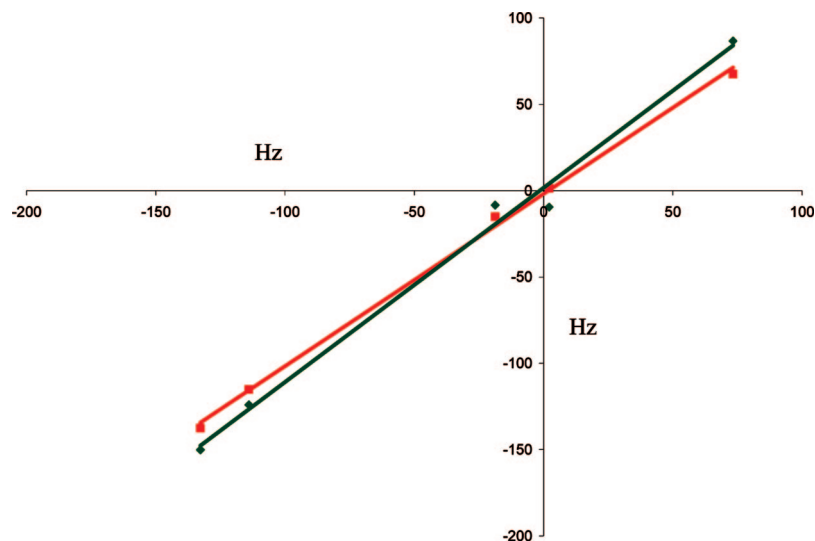


Figure 4. EOM-CCSD (■) and SOPPA (◆) three-bond coupling constants $^3J(\text{F}-\text{F})$ plotted against the experimental values.

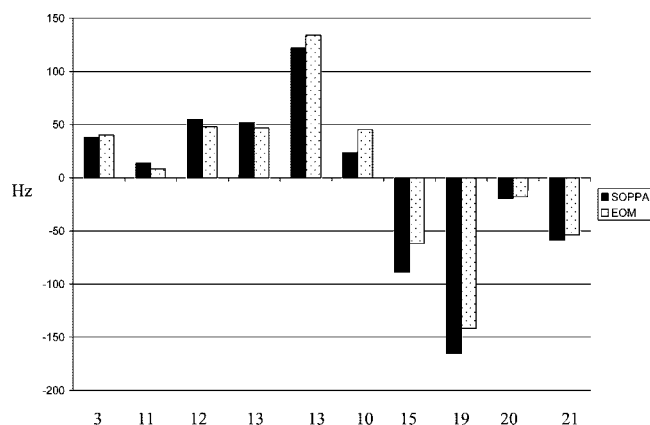


Figure 5. SOPPA and EOM-CCSD two-bond coupling constants. The first 4 pairs are $^2J(\text{C}-\text{F})$; the next 4 are $^2J(\text{F}-\text{F})$; and the final 2 pairs are $^2J(\text{N}-\text{F})$.

the trendline and is responsible for the decrease in the correlation coefficient. Can this difference be attributed at least in part to the use of an optimized rather than an experimental geometry for this molecule? Why these two-

bond coupling constants behave so differently is a subject for future study.

Statistical Analysis of One-, Two-, and Three-Bond Couplings. Figure 7 shows a plot of SOPPA and EOM-CCSD coupling constants versus all of the experimental coupling constants reported in Table 1 and also includes the one-bond $\text{X}-\text{Y}$ and $\text{X}-\text{F}$ coupling constants from ref 1. It is obvious from the trendlines shown in Figure 7 that both SOPPA and EOM-CCSD coupling constants correlate linearly with the experimental coupling constants. The equations of the trendlines are

$$J(\text{SOPPA}) = (1.25 \pm 0.04) * J(\text{exptl}) - (6.72 \pm 6.59) \\ n = 30; R^2 = 0.970; \text{RMS} = 35.8 \text{ Hz}$$

$$J(\text{EOM-CCSD}) = (1.02 \pm 0.01) * J(\text{exptl}) + (2.41 \pm 1.84) \\ n = 30; R^2 = 0.996; \text{RMS} = 10.0 \text{ Hz}$$

As judged by the slope, intercept, and correlation coefficient, the agreement between theory and experiment is better at EOM-CCSD/(qzp,qz2p) than at SOPPA/(qzp,qz2p). The SOPPA coupling constant which lies farthest from the trendline is $^1J(\text{F}-\text{O})$ for FOOF, which has a value of -690 Hz

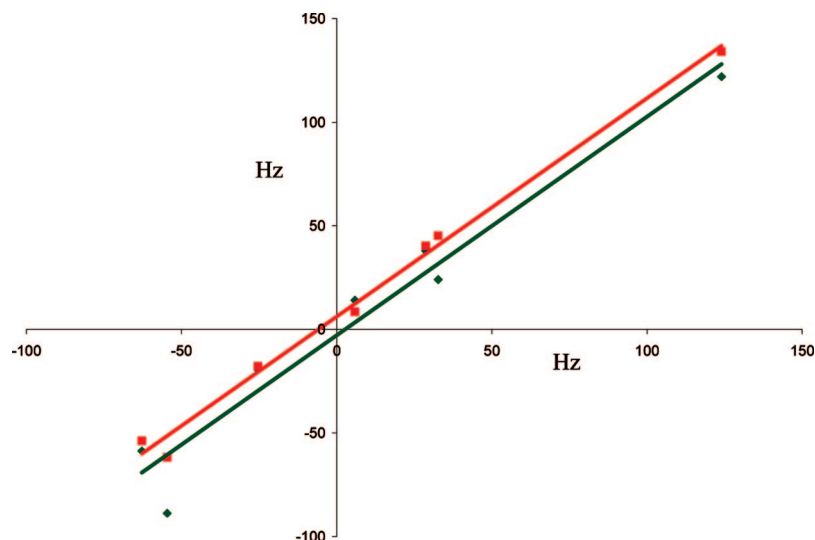


Figure 6. EOM-CCSD (■) and SOPPA (◆) two-bond coupling constants $^2J(\text{X}-\text{F})$ plotted against the experimental values.

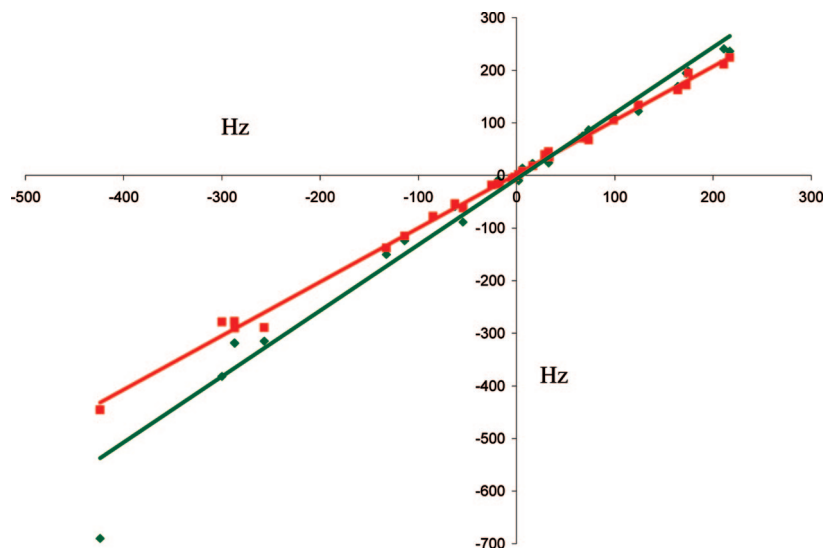


Figure 7. EOM-CCSD (■) and SOPPA (◆) one-, two-, and three-bond X–Y coupling constants plotted against the experimental values.

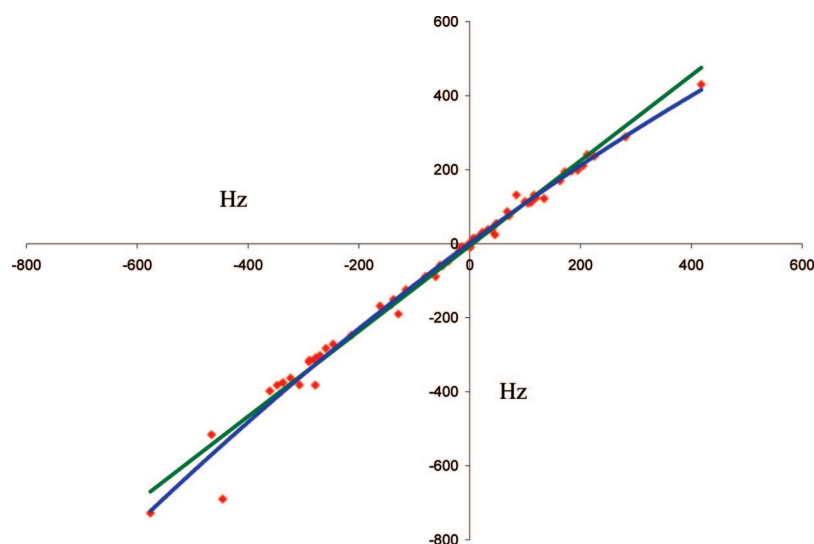


Figure 8. SOPPA vs EOM-CCSD one-, two-, and three-bond coupling constants showing first-order (green) and second-order (blue) trendlines.

and significantly overestimates the absolute value of the experimental coupling constant, -424 Hz. The EOM-CCSD value is -446 Hz. Removing this point significantly improves the SOPPA statistics, but the slope of the trendline still remains too high at 1.14. Once again, the greater slope for the SOPPA trendline results from the tendency of SOPPA to overestimate the absolute values of large one- and three-bond coupling constants which involve fluorine. Although it would be possible to present further statistics including percent errors and deviations, these are not very useful given the large range of values of coupling constants. For example, the percent error for $^3J(\text{F}-\text{F})$ for FCCF is 33 and 352% at EOM-CCSD and SOPPA, respectively, but the differences between computed and experimental coupling constants are 0.7 and 7.4 Hz. On the other hand, SOPPA overestimates $^1J(\text{C}-\text{F})$ for $\text{F}_2\text{C}=\text{CH}_2$ by 32 Hz, but the percent error is only 11%.

In our comparison between theory with experiment, there are some limitations in our treatment of the experimental data which should be noted. For some molecules more than one experimental value of a particular coupling constant has been reported, and we have used that one judged to be the

most reliable. We have made no adjustments for uncertainties in the experimental assignments or for reported error bars. Finally, we have not taken into account the fact that the experimental coupling constants have been measured under different conditions, some in the gas phase and others in solution, and no adjustments have been made to account for possible interactions between the solute and the solvent.

Figure 8 presents a plot of SOPPA vs EOM-CCSD coupling constants for all one-, two-, and three-bond X–Y, X–F, and F–F couplings reported in this work and in ref 1. The equations of the first- and second-order trendlines are

$$\text{SOPPA} = 1.15 * \text{EOM} - 5.73 \quad n = 80; R^2 = 0.985$$

$$\text{SOPPA} = -0.0003 * \text{EOM}^2 + 1.10 * \text{EOM} + 1.60$$

$$n = 80; R^2 = 0.989$$

Although the quadratic term has only a very small coefficient, this term becomes significant for large coupling constants and introduces curvature into the relationship between computed SOPPA and EOM-CCSD coupling constants. It

reflects primarily the tendency of SOPPA to overestimate large coupling constants involving F.

Conclusions

Ab initio EOM-CCSD/(qzp,qz2p) and SOPPA/(qzp,qz2p) calculations have been carried out to evaluate one-, two-, and three-bond coupling constants for molecules $H_mX=YH_n$ and $H_mX\equiv YH_n$ for $X, Y = {}^{13}\text{C}, {}^{15}\text{N}$, and ${}^{17}\text{O}$ and selected ${}^{19}\text{F}$ -substituted derivatives. The results of these calculations support the following statements.

1. ${}^1J(\text{C}-\text{C})$ are always positive at the two levels of theory, whereas ${}^1J(\text{C}-\text{N})$ are relatively small and either positive or negative. SOPPA and EOM-CCSD coupling constants are similar. One-bond coupling constants ${}^1J(\text{C}-\text{O})$ are always positive, whereas ${}^1J(\text{N}-\text{N})$ and ${}^1J(\text{N}-\text{O})$ are negative, in violation of the Dirac Vector Model which states that reduced one-bond coupling constants are positive. The EOM-CCSD coupling constants are usually in better agreement with experiment.

2. All one-bond C-F coupling constants are negative, and all one-bond N-F coupling constants are positive, once again violating the Dirac Vector Model. The absolute values of the SOPPA coupling constants are greater than the EOM-CCSD values, with the latter in better agreement with experimental data. As observed previously, SOPPA tends to overestimate the absolute values of large one-bond couplings involving ${}^{19}\text{F}$.

3. Three-bond coupling constants ${}^3J(\text{F}-\text{F})$ are usually larger in absolute value when evaluated at SOPPA compared to EOM-CCSD, a result of larger contributions from the PSO terms. In all cases, the three-bond EOM-CCSD coupling constants are in better agreement with experimental data.

4. There is no simple identifiable pattern for the relationship between SOPPA and EOM-CCSD two-bond coupling constants. For the majority of these, SOPPA is in better agreement with experiment, although the differences between the computed EOM-CCSD values and experimental values are not dramatic. However, SOPPA significantly overestimates the absolute value of ${}^2J(\text{F}-\text{F})$ for $\text{F}_2\text{C}=\text{NH}$.

5. A statistical analysis of 30 EOM-CCSD/(qzp,qz2p) and SOPPA/(qzp,qz2p) coupling constants versus experimental one-, two-, and three-bond coupling constants demonstrates that better agreement with experiment is found when EOM-CCSD is used as the computational method.

It is well-known that the performance of any given method for the calculation of coupling constants depends on the quality of the method, the geometry, and the basis set used for the calculations. Since SOPPA does give reasonable values for many coupling constants, a question for future study is whether the performance of SOPPA can be systematically improved, particularly for couplings involving fluorine, if a different basis set were used for the calculations. Some studies of the basis sets used for SOPPA calculations have been reported.^{23,36a,37} A systematic basis-set dependence investigation of the SOPPA coupling constants presented in this paper which identified an optimal basis set would be of immense value, allowing this method to be applied with confidence to much larger molecules of interest to both theorists and experimentalists.

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Supporting Information Available: SOPPA and EOM-CCSD PSO, DSO, FC, and SD components of J for all molecules investigated in this study and full references for refs 32, 33, and 34. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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