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A 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 Selected Singly Bonded Molecules, and the Hydrides NH_3 , H_2O , and HF and Their Protonated and Deprotonated Ions and Hydrogen-Bonded Complexes

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Abstract: Second-order polarization propagator approximation (SOPPA) and equation-of-motion coupled cluster singles and doubles (EOM–CCSD) methods have been employed for the calculation of one-bond spin–spin coupling constants in series of small molecules and ions, and of one- and two-bond coupling constants across $\text{X–H}\cdots\text{Y}$ hydrogen bonds. For isolated molecules, one-bond SOPPA coupling constants $^1J(\text{X–Y})$ involving ^{13}C , ^{15}N , ^{17}O , and ^{19}F have larger absolute values than corresponding EOM–CCSD coupling constants, with the EOM–CCSD values being in significantly better agreement with available experimental data. The difference between SOPPA and EOM–CCSD tends to increase as the number of nonbonding electrons on the coupled atoms increases, and the SOPPA values for O–F coupling are significantly in error. Similarly, the absolute values of SOPPA one-bond coupling constants $^1J(\text{X–H})$ for the hydrides NH_3 , H_2O , and FH and their protonated and deprotonated ions are greater than EOM–CCSD values, with the largest differences occurring for F–H coupling. One- and two-bond coupling constants $^1J(\text{X–H})$, $^{1h}J(\text{H–Y})$, and $^{2h}J(\text{X–Y})$ across $\text{X–H}\cdots\text{Y}$ hydrogen bonds in neutral, protonated, and deprotonated complexes formed from the hydrides are similar at SOPPA and EOM–CCSD, with the largest differences again found for $^1J(\text{F–H})$ in complexes with F–H as the proton donor, and $^{2h}J(\text{F–F})$ for $(\text{FHF})^-$. The signs of $^1J(\text{X–H})$, $^{1h}J(\text{H–Y})$, and $^{2h}J(\text{X–Y})$ are the same at both levels of theory, as is their variation across the proton-transfer coordinate in $\text{F–H}\cdots\text{NH}_3$. SOPPA would appear to provide a reliable and more cost-effective alternative approach for computing coupling constants across hydrogen bonds, although couplings involving F may be problematic.

Introduction

In an early paper on coupling constants, Enevoldsen et al. noted the critical dependence of computed coupling constants (J) on the quality of the wave function used to evaluate this

NMR property¹ and employed the second-order polarization propagator approximation (SOPPA)^{1–5} to obtain indirect spin–spin coupling constants. More recently, Barone and co-workers compared SOPPA and density functional theory (DFT) methods for two- and three-bond F–F coupling constants⁶ and found the former to be in better agreement with experimental data, due in part to the treatment of electron-correlation effects in SOPPA. Indeed, it has been

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recognized that the quality of DFT coupling constants often decreases as the number of nonbonding pairs of electrons on the coupled atoms increases and electron correlation effects assume increased importance.⁷

Coupling constants may also be evaluated at an even higher level of electron correlation treatment using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method.^{8–11} This method is generally viewed as the benchmark method, but unfortunately, the computational cost of EOM-CCSD limits its applicability to relatively small systems or systems with high computational symmetry. Since SOPPA is a computationally much less expensive method than EOM-CCSD, we decided to undertake a systematic comparison of one-bond spin-spin coupling constants (J) obtained using these two methods on a set of small molecules H_mX-YH_n with $X-Y$ single bonds, where X and $Y = C, N, O$, and F ; selected fluorine derivatives of these molecules; and the hydrides NH_3 , H_2O , and HF and their protonated and deprotonated ions, along with CH_4 . In addition, one-bond $^1J(X-H)$ and $^{1h}J(H-Y)$ and two-bond $^{2h}J(X-Y)$ coupling constants across the $X-H-Y$ hydrogen bonds in the neutral and charged hydrogen-bonded complexes formed from these hydrides and their ions, and the changes in these coupling constants along the proton-transfer coordinate for $F-H\cdots NH_3$, have been evaluated at both levels of theory. For this study, we have used the same geometries and the same basis set for both SOPPA and EOM-CCSD calculations, so that the only difference in coupling constants is a consequence of differences in the wave function model. In this paper, we compare the SOPPA and EOM-CCSD coupling constants and evaluate the performance of these methods by comparison with experimental data whenever possible. Previous comparisons of computed coupling constants obtained using SOPPA and CCSD-based methods have been reported,¹² but these are on a much more limited scope.

Methods

Computed optimized geometries for all monomers and complexes were obtained at second-order Møller-Plesset perturbation theory (MP2)^{13–16} with the 6-31+G(d,p) basis set.^{17–20} Vibrational frequencies were computed to verify that the computed geometries are equilibrium structures on the potential energy surfaces. These geometries were used for calculations of coupling constants, except for a few cases specifically identified below.

Spin-spin coupling constants involving ^{13}C , ^{15}N , ^{17}O , ^{19}F , and 1H in all monomers and complexes were computed using the SOPPA^{1–5} and EOM-CCSD methods in the configuration-interaction-like approximation,^{8–11} with all electrons correlated. For these calculations, the Ahlrichs²¹ qzp basis set was placed on nonhydrogen atoms and the qz2p basis set on all H atoms. 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 systems. Geometry optimizations were carried out with the Gaussian 03 suite of programs;²² SOPPA calculations were performed using Dalton-2²³ at the

Table 1. SOPPA and EOM-CCSD One-Bond Heavy-Atom Coupling Constants $^1J(X-Y)$ (Hz) for Selected Small Molecules with $X-Y$ Single Bonds^a

molecule	SOPPA	EOM-CCSD	exptl.
$H_3C-CH_3^b$	37.7	34.6	33.4 ^c
H_3C-NH_2	-6.3	-5.7	-4.5 ^d
H_3C-OH $^1J(C-O)$	13.7	13.4	
H_3C-OH $^1J(O-H)$	-80.0	-77.5	-85 ^e
H_3C-F	-168.2	-161.9	
CF_4	-315.1	-289.4	-257 ^f
H_2N-NH_2	-5.9	-5.7	
F_2N-NF_2 $^1J(N-N)$	-18.4	-17.3	
F_2N-NF_2 $^1J(N-F)$	196.0	183.7	164 ^g
F_2N-NF_2 $^1J(N-F)$	169.4	162.8	
H_2N-OH	-1.5	-2.5	
H_2N-F	-8.0	-4.1	
NF_3^h	236.4	224.7	217 ⁱ
$HO-OH$	26.2	22.2	
$FO-OF$ $^1J(O-F)$	-690.0	-445.7	-424 ^k
$FO-OF$ $^1J(O-O)$	-88.1	-79.4	
$HO-F$	-727.8	-576.1	
$FO-F^j$	-382.0	-278.6	-300 ± -30^k

^a Calculations were carried out on molecules at optimized MP2/6-31+G(d,p) geometries, except as noted. If the sign of the experimental coupling constant was not reported, the computed sign was given. ^b Geometry from ref 34a. ^c See ref 25a. ^d See ref 25b. ^e See ref 26a. ^f See ref 25c. ^g See ref 26b. ^h Geometry from ref 31. ⁱ See ref 29. ^j Geometry from ref 33. ^k See ref 26a. ^l Geometry from ref 32.

CSIC Computing Center, and the EOM-CCSD calculations were done with ACES II²⁴ on the Itanium Cluster at the Ohio Supercomputer Center.

Results and Discussion

Small Molecules with $X-Y$ Single Bonds. Table 1 lists SOPPA, EOM-CCSD, and experimental^{25–30} one-bond spin-spin coupling constants for the set of small molecules H_mX-YH_n , with $X-Y$ being a single-bond. To this set, CF_4 , F_2N-NF_2 , NF_3 , FOF , and $FOOF$ have been added since experimental one-bond couplings are available for these molecules. When experimental coupling constants are available, the experimental geometry has been used if it is available,^{31–34} since this circumvents to some extent the effect of zero-point motion on computed coupling constants.³⁵ The molecule F_2 has been omitted from this study since it has a very large CCSD t_2 amplitude.

From Table 1, it can be seen that the signs of the computed coupling constants at both levels of theory are the same, and with one exception, namely, H_2N-OH , the absolute value of the SOPPA coupling constant is greater than the EOM-CCSD value. Table S1 of the Supporting Information reports the PSO, DSO, FC, and SD components of J . From Table S1, it can be seen that the DSO terms computed by both methods are relatively small and do not influence the comparisons. What is most interesting is that the absolute values of SOPPA PSO, FC, and SD terms are also greater than the corresponding EOM-CCSD values, with the only exceptions being the FC term for H_2N-OH and the PSO term for NF_3 .

Table 1 lists the computed SOPPA and EOM-CCSD one-bond couplings and the available experimental data. The listing in Table 1 for the molecules H_mX-YH_n is in the order

of increasing electronegativity and increasing number of electron pairs on the coupled atoms. Thus, the first set of molecules consists of $\text{H}_3\text{C}-\text{CH}_3$, $\text{H}_3\text{C}-\text{NH}_2$, $\text{H}_3\text{C}-\text{OH}$, and $\text{H}_3\text{C}-\text{F}$ and its derivative CF_4 . The next set has $\text{H}_2\text{N}-\text{NH}_2$ and its derivative $\text{F}_2\text{N}-\text{NF}_2$, $\text{H}_2\text{N}-\text{OH}$, and $\text{H}_2\text{N}-\text{F}$ and its derivative NF_3 . For all of these molecules except $\text{H}_2\text{N}-\text{OH}$, SOPPA coupling constants have larger absolute values than EOM-CCSD. In the case of $\text{H}_2\text{N}-\text{OH}$, the computed coupling constants are very small at -1.5 and -2.5 Hz, respectively. For the series of C-containing molecules $\text{H}_3\text{C}-\text{CH}_3$, $\text{H}_3\text{C}-\text{NH}_2$, $\text{H}_3\text{C}-\text{OH}$, and $\text{H}_3\text{C}-\text{F}$, the SOPPA and EOM-CCSD coupling constants are similar. It is interesting to note that the EOM-CCSD value of $^1J(\text{C}-\text{C})$ for $\text{H}_3\text{C}-\text{CH}_3$ at its experimental geometry differs from the experimental coupling constant by only 1 Hz, while the SOPPA value is 4 Hz too high. For $\text{H}_3\text{C}-\text{NH}_2$, the EOM-CCSD coupling constant $^1J(\text{C}-\text{N})$ of -5.7 Hz is closer to the experimental coupling constant of -4.5 Hz,^{25b} for which the SOPPA value is -6.3 Hz. The only significant difference found for coupling constants in the subset of C-containing molecules is $^1J(\text{C}-\text{F})$ for CF_4 , for which SOPPA and EOM-CCSD give -315.1 and -289.4 Hz, respectively, at the equilibrium geometry of this molecule. These overestimate the experimental value of -257 Hz,^{25c} but part of this difference may be attributed to the use of an equilibrium geometry. Nevertheless, the EOM-CCSD value is closer to the experimental value.

SOPPA and EOM-CCSD coupling constants $^1J(\text{N}-\text{N})$ are similar for both $\text{H}_2\text{N}-\text{NH}_2$ and $\text{F}_2\text{N}-\text{NF}_2$. There are two unique one-bond N-F coupling constants for $\text{F}_2\text{N}-\text{NF}_2$ in this molecule of C_2 symmetry. The average SOPPA and EOM-CCSD values are 182 and 173 Hz, respectively, with the EOM-CCSD average being closer to the experimental coupling constant of 164 Hz.^{26b} The two remaining N-containing molecules $\text{H}_2\text{N}-\text{OH}$ and $\text{H}_2\text{N}-\text{F}$ have small coupling constants. For these, the SOPPA and EOM-CCSD values are -1.5 and -2.5 Hz and -8.0 and -4.1 Hz, respectively. Finally, SOPPA and EOM-CCSD values of $^1J(\text{N}-\text{F})$ for NF_3 at its experimental geometry are 236.4 and 224.7 Hz, respectively. Once again, the EOM-CCSD value is closer to the experimental coupling constant of 217 Hz.²⁹ Thus, for the subset of N-containing molecules, the difference between the SOPPA and EOM-CCSD values is greatest when N is coupled to O and F.

SOPPA and EOM-CCSD coupling constants $^1J(\text{O}-\text{O})$ for $\text{HO}-\text{OH}$ and $\text{FO}-\text{OF}$ are 26.2 and 22.2 Hz and -88.1 and -79.4 Hz, respectively. However, significantly larger differences between SOPPA and EOM-CCSD coupling constants are found for $^1J(\text{O}-\text{F})$ for $\text{FO}-\text{OF}$, $\text{HO}-\text{F}$, and $\text{FO}-\text{F}$. At the experimental geometry of $\text{FO}-\text{OF}$, the SOPPA $^1J(\text{O}-\text{F})$ is -690.0 Hz, compared to the EOM-CCSD value of -445.7 Hz. The EOM-CCSD value agrees with the experimental value of -424 Hz.^{26a} However, it should be noted that, in the original paper,²⁸ this value was measured using ^{17}O NMR for a sample of ^{17}O -enriched FOOF and incorrectly assigned to a triplet. Hence, this value should be viewed with caution. $^1J(\text{O}-\text{F})$ for $\text{HO}-\text{F}$ is significantly overestimated by SOPPA at -727.8 Hz, compared to the EOM-CCSD value of -576.1 Hz, but no experimental value

Table 2. SOPPA and EOM-CCSD One-Bond Coupling Constants $^1J(\text{X}-\text{H})$ for NH_3 , H_2O , and HF and Their Protonated and Deprotonated Ions^a

species	SOPPA	EOM-CCSD	exptl.
CH_4	123.7	116.4	125.3 ^b
NH_2^-	-44.2	-43.1	
NH_3	-63.9	-61.5	-61.2 ^c
NH_4^+	-78.4	-75.0	-73.3 ^c
OH^-	-65.7	-62.8	
H_2O^d	-81.8	-79.7	-79 ^e
OH_3^+	-124.3	-120.7	
FH^d	531.4	520.9	529 ^f
FH_2^+	648.5	631.5	

^a Calculations were carried out on molecules at optimized MP2/6-31+G(d,p) geometries, except as noted. If the sign of the experimental coupling constant was not reported, the computed sign was given. ^b See ref 25d. ^c See ref 26c. ^d Geometry from ref 34b. ^e See ref 26a. ^f See ref 26d.

is available for comparison. Finally, $^1J(\text{O}-\text{F})$ for $\text{FO}-\text{F}$ at its experimental geometry is -382.0 Hz for SOPPA and -278.6 Hz for EOM-CCSD, the latter being within the uncertainty of the experimental value of -300 ± 30 Hz.^{26a}

Since the above data suggest that the SOPPA method fails to describe O-F coupling properly, it is reasonable to ask whether this description could be improved by employing the SOPPA(CCSD) method, in which CCSD amplitudes are used instead of MP2.¹ The SOPPA(CCSD) values of $^1J(\text{O}-\text{F})$ for FOF and FOOF are -391 and -777 Hz, respectively, both greater in absolute value than the corresponding SOPPA values and, therefore, further removed from the EOM-CCSD and experimental values. Therefore, no additional SOPPA(CCSD) calculations were done.

NH_3 , H_2O , FH , and Their Protonated and Deprotonated Ions. Table 2 lists values of $^1J(\text{X}-\text{H})$ for CH_4 , and for the hydrides NH_3 , H_2O , and FH , and their protonated and deprotonated ions. Table S2 (Supporting Information) lists the individual components of these coupling constants. A familiar pattern emerges, insofar as the absolute values of the SOPPA total coupling constants and their major components are greater than the corresponding EOM-CCSD values. Moreover, there is an overall increase in the difference between SOPPA and EOM-CCSD as the number of nonbonding electrons increases. The largest differences are found for $^1J(\text{F}-\text{H})$ for FH and FH_2^+ , but in these two cases, the differences are relatively small given the magnitude of $^1J(\text{F}-\text{H})$.

Experimental values of $^1J(\text{X}-\text{H})$ are available for CH_4 ,^{25d} NH_4^+ ,^{26c} NH_3 ,^{26c} H_2O ,^{26a} CH_3OH ,^{26a} and FH .^{26d} The SOPPA $^1J(\text{C}-\text{H})$ value of 123.7 Hz is closer to the experimental value of 125.3 Hz than is the EOM-CCSD value of 116.4 Hz. The SOPPA $^1J(\text{N}-\text{H})$ value for NH_4^+ is -78.4 Hz compared to -75.0 Hz for EOM-CCSD and -73.3 Hz for the experimental value. Similarly, the EOM-CCSD value of $^1J(\text{O}-\text{H})$ for H_2O of -79.7 Hz is closer to the experimental value of -79 Hz than is the SOPPA value of -81.8 Hz, both evaluated at the experimental geometry of H_2O . At the equilibrium geometry of CH_3OH , both the computed SOPPA and EOM-CCSD values of $^1J(\text{O}-\text{H})$ underestimate the experimental value. What is most interesting is the SOPPA $^1J(\text{F}-\text{H})$ value for FH , which is 531.4 Hz at the

experimental geometry, and in closer agreement with the experimental value of 529 Hz than the EOM–CCSD value of 520.9 Hz.

Statistical Analysis of SOPPA and EOM–CCSD versus Experimental Results. A quantitative comparison of the performance of the SOPPA and EOM–CCSD methods versus experimental results can be achieved through a correlation analysis. Included in this analysis are two-bond H–H coupling constants for H₂O, NH₃, NH₄⁺, and CH₄, which are known experimentally³⁰ and which are reported in the Supporting Information. Ideally, a perfect correlation between theory and experiment in a regression analysis yields a slope of 1.00, an intercept of 0.00 Hz, and a correlation coefficient of 1.00. The regression analysis for the SOPPA coupling constants versus the experimental ones yields a slope of 0.80 ± 0.04, an intercept of 13.1 ± 10.0 Hz, and a correlation coefficient of 0.962. For the computed EOM–CCSD coupling constants versus experimental results, the slope is 0.99 ± 0.01, the intercept is 2.0 ± 2.6 Hz, and the correlation coefficient is 0.997. Thus, the superiority of EOM–CCSD is manifest. Using reduced coupling constants (*K*) for the analysis yields similar results. It was noted above that SOPPA values of ¹*J*(F–O) coupling constants for F–O–F and F–O–O–F are in poor agreement with experimental values. If these two molecules are removed from the regression analysis, the performance of SOPPA significantly improves, as indicated by a slope of 0.95 ± 0.02, an intercept of 4.0 ± 3.1 Hz, and a correlation coefficient of 0.995. Eliminating these two molecules from the comparison of EOM–CCSD versus experimental results does not significantly change the statistics, yielding a slope of 0.99 ± 0.01, an intercept of 2.7 ± 2.1, and a correlation coefficient of 0.995. However, the agreement between computed and experimental coupling constants is still better for EOM–CCSD compared to SOPPA.

Some of the limitations of the treatment of the experimental data in the above analysis should be noted. If more than one experimental value of the coupling constant has been reported, the one judged to be the most reliable has been used. There has been no adjustment made for uncertainties in the experimental assignments and error bars given for the experimental data. Finally, there has been no attempt to take into account the fact that the experimental coupling constants have been measured under different conditions, some in the gas phase and others in solution. In the latter circumstance, no adjustments have been made to account for possible interactions between the solute and the solvent.

Hydrogen-Bonded Complexes. One-bond ¹*J*(X–H) and ¹*hJ*(H–Y) and two-bond ²*J*(X–Y) spin–spin coupling constants across X–H···Y hydrogen bonds for N₂H₅[–], (NH₃)₂, N₂H₇⁺, H₂NH:OH[–], HOH:NH₃, H₃NH⁺:OH₂, H₂NH:F[–], FH:NH₃, H₃NH⁺:FH, O₂H₃[–], (H₂O)₂, O₂H₅⁺, HOH:F[–], FH:OH₂, H₂OH⁺:FH, (FHF)[–], (FH)₂, and F₂H₃⁺ are reported in Table 3, and the components of *J* are listed in Table S3 (Supporting Information). For heterodimers, the species listed first is the proton donor. The first important observation is that the signs of the coupling constants computed at these two levels of theory are identical. As a result, the generalizations made previously about the signs

Table 3. SOPPA and EOM–CCSD Coupling Constants ¹*J*(X–H), ¹*hJ*(H–Y), and ²*J*(X–Y) Across X–H···Y Hydrogen Bonds in Neutral, Anionic, and Protonated Complexes Formed from NH₃, H₂O, and FH^a

complex	¹ <i>J</i> (X–H)		¹ <i>hJ</i> (H–X)		² <i>J</i> (X–Y)	
	SOPPA	EOM	SOPPA	EOM	SOPPA	EOM
N ₂ H ₅ [–]	–67.0	–64.4	6.4	6.3	10.5	10.2
(NH ₃) ₂	–67.3	–64.7	1.6	1.6	1.9	1.9
N ₂ H ₇ ⁺	–64.4	–61.3	–0.4	–0.1	13.1	12.9
H ₂ NH:OH [–]	–66.0	–63.5	9.2	9.0	6.9	6.8
HOH:NH ₃	–83.1	–80.8	3.3	3.4	3.4	3.4
H ₃ NH ⁺ :OH ₂	–76.1	–73.0	9.7	9.7	12.0	11.7
H ₂ NH:F [–]	–66.3	–63.8	–55.6	–54.6	–24.1	–24.4
FH:NH ₃	440.3	430.8	2.4	2.6	–42.5	–43.1
H ₃ NH ⁺ :FH	–79.1	–75.8	–42.7	–41.5	–29.0	–28.1
O ₂ H ₃ [–]	–53.2	–51.4	0.8	1.4	13.6	13.8
(H ₂ O) ₂	–83.3	–81.0	4.8	4.8	1.3	1.3
O ₂ H ₅ ⁺	–49.3	–47.4	–49.5	–47.4	39.9	39.5
HOH:F [–]	–68.6	–66.8	–65.2	–66.0	–36.5	–38.5
FH:OH ₂	492.4	482.5	7.0	7.1	–18.0	–18.2
H ₂ OH ⁺ :FH	–113.6	–110.3	–54.0	–55.0	–72.0	–71.1
(FHF) [–] ^b	109.2	106.0	109.2	106.0	228.6	254.4
(FH) ₂	507.9	498.0	–26.6	–26.6	–40.7	–39.5
F ₂ H ₃ ⁺	203.4	195.4	203.4	195.4	612.0	609.8

^a Calculations carried out at optimized MP2/6-31+G(d,p) geometries, except where noted. ^b Calculation carried out at the optimized CCSD(T)/aug'-cc-pVTZ geometry.

of coupling constants and their significance which were based on EOM–CCSD coupling constants can be applied to SOPPA coupling constants. In particular, since the magnetogyric ratios of ¹⁵N and ¹⁷O are negative and that of ¹⁹F is positive, all two-bond reduced coupling constants ²*K*(X–Y) are positive³⁶ except for (HF)₂. Since the magnetogyric ratio of ¹H is also positive, all reduced one-bond coupling constants ¹*K*(X–H) are positive.³⁷ Finally, a negative value of ¹*hK*(H–Y) indicates that the hydrogen bond is traditional, while a positive value is indicative of the proton-shared character of the hydrogen bond.³⁸

As observed above, the SOPPA coupling constants ¹*J*(X–H) for the isolated monomers have larger absolute values than the corresponding EOM–CCSD coupling constants. This same pattern is seen when X–H acts as the proton donor in hydrogen-bonded complexes. Moreover, the largest differences in the complexes are about 10 Hz for ¹*J*(F–H) in FH:NH₃, FH:OH₂, (FH)₂, and even F₂H₃⁺. This difference reflects the monomer difference of 10.5 Hz.

Only small differences are found between SOPPA and EOM–CCSD ¹*hJ*(H–Y) values, except for ¹*hJ*(H–F) for the symmetric hydrogen bond in F₂H₃⁺, in which case the SOPPA value of 203.4 Hz is 8.0 Hz greater than the EOM–CCSD value. Moreover, the two-bond coupling constants ²*J*(X–Y) are similar at the two levels of theory, except for (FHF)[–], in which case the SOPPA value is 228.6 Hz and less than the EOM–CCSD value of 254.4 Hz. The geometry used for this ion is the CCSD(T)/aug'-cc-pVTZ geometry, since these coupling constants are extremely sensitive to distance, and vibrationally averaged coupling constants for this system have been reported.³⁹ Zero-point vibrational averaging decreases ²*J*(F–F) from its EOM–CCSD equilibrium value of 254 Hz to 210 Hz and brings it into good agreement with the estimated experimental value of about 220 Hz.^{40,41} Since the effect of vibrational averaging

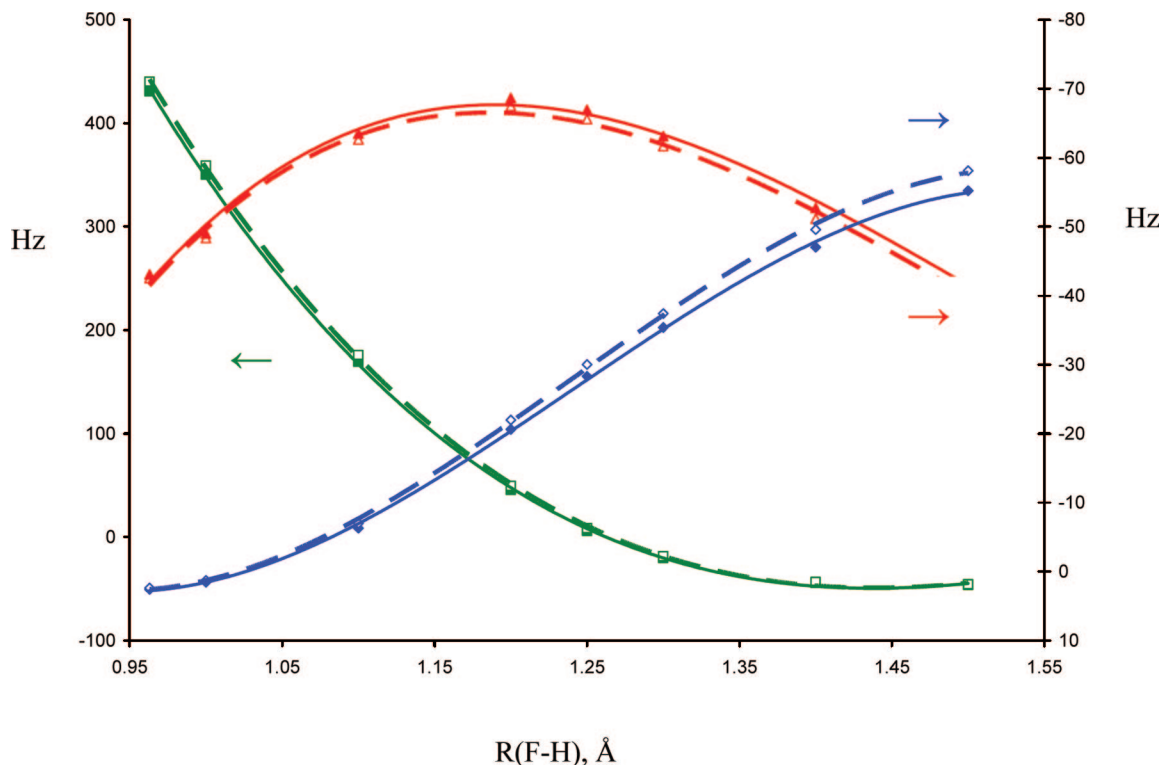


Figure 1. $^1J(\text{F-H})$ (■), $^1J(\text{H-N})$ (◆), and $^2J(\text{F-N})$ (▲) across the proton-transfer coordinate for $\text{FH}\cdots\text{NH}_3$. SOPPA (open symbols and dashed lines); EOM-CCSD (solid symbols and lines).

is to reduce this coupling constant by about 40 Hz, the reduced SOPPA value would be about 190 Hz, significantly less than the experimental value.

Changes in Coupling Constants along the Proton-Transfer Coordinate. Changes in one- and two-bond coupling constants for the $\text{FH}:\text{collidine}$ complex as a function of temperature have been measured experimentally and attributed to proton transfer from F to N due to solvent ordering.^{42,43} Such changes have been reproduced by EOM-CCSD calculations for proton transfer across $\text{F-H}\cdots\text{N}$ hydrogen bonds.⁴⁴ As part of the present investigation, SOPPA coupling constants along the proton transfer coordinate of $\text{F-H}\cdots\text{NH}_3$ have also been evaluated, and these are compared with the EOM-CCSD coupling constants in Figure 1. The similarities between the two sets of data are striking. Both show that $^2J(\text{F-N})$ has its maximum absolute value in the proton-shared region of this coordinate; $^1J(\text{F-H})$ decreases rapidly and changes sign, as observed experimentally, and $^1J(\text{H-N})$ asymptotically approaches the value for NH_4^+ . Thus, the SOPPA and EOM-CCSD characteristics of coupling constants for proton transfer across the $\text{F-H}\cdots\text{N}$ hydrogen bond for $\text{F-H}\cdots\text{NH}_3$ are very similar.

Conclusions

This study reports an evaluation of the performance of SOPPA and EOM-CCSD methods for determining spin-spin coupling constants. In particular, one-bond coupling constants in a series of small molecules and ions, and one- and two-bond coupling constants across hydrogen bonds in a set of neutral, cationic, and anionic complexes, have been compared. The following statements are supported by the computed results.

1. For isolated molecules, the one-bond SOPPA coupling constants $^1J(\text{X-Y})$ involving C, N, O, and F have larger absolute values than the EOM-CCSD coupling constants, with the latter being in better agreement with available experimental data. The difference between SOPPA and EOM-CCSD tends to increase as the number of nonbonding electrons on the coupled atoms increases. SOPPA values for O-F coupling are significantly in error.

2. The absolute values of one-bond coupling constants $^1J(\text{X-H})$ for the hydrides NH_3 , H_2O , and FH and their protonated and deprotonated ions are also greater at SOPPA compared to EOM-CCSD. The difference between them is largest for F-H coupling.

3. One- and two-bond coupling constants $^1J(\text{X-H})$, $^1J(\text{H-Y})$, and $^2J(\text{X-Y})$ across $\text{X-H}\cdots\text{Y}$ hydrogen bonds in neutral, protonated, and deprotonated complexes formed from the hydrides are similar at SOPPA and EOM-CCSD, with the largest differences occurring for $^1J(\text{F-H})$ in complexes with F-H as the proton donor, and $^2J(\text{F-F})$ for $(\text{FHF})^-$. Moreover, the signs of $^1J(\text{X-H})$, $^1J(\text{H-Y})$, and $^2J(\text{X-Y})$ are the same at both levels of theory, as are their variations across the proton-transfer coordinate in $\text{F-H}\cdots\text{NH}_3$.

On the basis of this study, it appears that SOPPA one-bond X-Y coupling constants, particularly those involving electronegative atoms, may not be reliable. However, SOPPA would appear to provide a reliable and more cost-effective approach for computing coupling constants across hydrogen bonds, although couplings involving F may be problematic. Further comparisons in other larger, more complicated systems should be made.

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Supporting Information Available: SOPPA and EOM-CCSD PSO, DSO, FC, and SD components of *J* for all molecules, ions, and complexes investigated in this study. Also included are the full citations for refs 22 and 24. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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