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Communication: Localized molecular orbital analysis of the effect of electron correlation on the anomalous isotope effect in the NMR spin-spin coupling constant in methane

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We discuss the effect of electron correlation on the unexpected differential sensitivity (UDS) in the ^{1}J(C–H) coupling constant of CH_4 using a decomposition into contributions from localized molecular orbitals and compare with the ^{1}J(N–H) coupling constant in NH_3. In particular, we discuss the well known fact that uncorrelated coupled Hartree-Fock (CHF) calculations are not able to reproduce the UDS in methane. For this purpose we have implemented for the first time a localized molecular orbital analysis for the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes—SOPPA(CCSD) in the DALTON program. Comparing the changes in the localized orbital contributions at the correlated SOPPA and SOPPA(CCSD) levels and at the uncorrelated CHF level, we find that the latter overestimates the effect of stretching the bond between the coupled atoms on the contribution to the coupling from the localized bonding orbital between these atoms. This disturbs the subtle balance between the molecular orbital contributions, which lead to the UDS in methane. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4897625]

I. INTRODUCTION

Isotope effects play an important role in different fields of chemistry, for example, reaction kinetics of atmospheric reactions. In the case of isotope effects on NMR spin-spin coupling constants (SSCC) one distinguishes[1] between a *primary isotope effect*, $\Delta_P^n J(A - B)$, on a coupling ^{n}J(A-B) between nuclei A and B, where atom B has two isotopes and a *secondary isotope effect*, $\Delta_S^n J(A - B)$, where a neighbor nucleus C has two isotopes. They have been measured in several molecules (see, e.g., Refs. 1–13) and can be reproduced by including vibrational corrections to the calculated coupling constants (see, e.g., Refs. 1 and 14–21).

A particularly interesting case of an anomalous isotope effect is the one-bond carbon-hydrogen SSCC in methane, where experimentally the secondary isotope effect, $\Delta_S^a J(C-H) = -0.356 \pm 0.01$ Hz was found to be ~5 times larger than the primary isotope effect, $\Delta_P^1 J$(C-H) $= -0.067 \pm 0.06$ Hz[6] which could quantitatively be reproduced with vibrational averaging calculations at the SOPPA(CCSD) level leading to $\Delta_S^a J(C-H) = -0.397$ Hz and $\Delta_P^1 J(C-H) = -0.154$ Hz.[16] Furthermore, the variation of this carbon-hydrogen coupling on changing the length of the bond of carbon to one of the other hydrogens, $\frac{\partial^1 J_{(C-H)}}{\partial R_{other}}$, was predicted to be ~5 times as large as the variation with respect to the bond to the coupled hydrogen, $\frac{\partial^1 J_{(C-H)}}{\partial R_{own}}$.[14] The phenomenon was named *unexpected differential sensitivity* (UDS)[22] and was later found also in other molecules.[18,19,23,24] In all cases the affected coupling is a one-bond coupling over a single bond, which implies that it is dominated by the Fermi contact (FC) term. It is therefore not surprising that the UDS can be studied by only considering the FC term.[22]

Based on the comparison of molecules with and without UDS it was proposed that the absence of lone pairs would be a prerequisite for the UDS.[23,24] Later, through an analysis of the one-bond couplings in CH_4, NH_3, and H_2O in terms of contributions from localized occupied molecular orbitals (LMO), carried out at the coupled perturbed density functional theory (DFT) level with the B3LYP functional, Provasi and Sauer[25–27] could show that the lone pairs are at least not directly responsible for the lack of UDS in neither NH_3 nor H_2O, as removing the lone-pair contributions to the couplings in these two molecules did not provoke an UDS. On the other hand, it turned out to be a subtle balance in the sensitivity of the bond-core, bond-other bond, and other bond-other bond contributions to changes in the bond length between the coupled atoms, R_{own}, which is responsible for the appearance of the UDS in methane and its absence in ammonia or water.

A still unsettled problem, however, is the connection between the UDS and electron correlation. Already in the first computational study on the UDS in methane it was observed that inclusion of electron correlation at the level of the second order polarization propagation approximation (SOPPA) or higher is necessary for reproducing the phenomena[22] and the following SOPPA(CCSD) calculations lead to quantitative agreement with the experimental values.[16] Uncorrelated calculations at the CHF level, however, fail to show an UDS for methane, while DFT/B3LYP calculations reproduce the

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phenomena again.[25–27] Hence the present work is devoted to an analysis of the effect of electron correlation on each individual localized occupied molecular contribution to the one-bond coupling constants in CH_4 and NH_3 at the CHF and SOPPA(CCSD) levels, which will shed light on the failure of the CHF calculations.

II. COMPUTATIONAL DETAILS

The different quantum chemical methods for calculating SSCCs at the non-relativistic level[28, 29] are often described in the literature[30, 31] and we will therefore only discuss here their analysis in LMOs. Common to all localized molecular orbital analysis is that the isotropic SSCC, $J(X-Y)$, between two nuclei X and Y is expressed as a sum over contributions from orbitals. In the oldest approach CLOPPA,[25–27, 32, 33] which is implemented at the semi-empirical as well as CHF and DFT levels, the coupling constant can be decomposed into contributions from two occupied (i and j) and two unoccupied (a and b) localized molecular orbitals, i.e., $J_{ij}^{ab}(X-Y)$. This, however, requires that one calculates all eigenvalues of the molecular Hessian, which becomes basically impossible for any correlated wavefunction method. Alternatively,[34–37] one decomposes the SSCC in contributions from only one occupied and one unoccupied localized orbital, $J_i^a(X-Y)$, or even only one occupied localized orbital, $J_i(X-Y)$. This requires only a small modification of the typical implementation of SSCCs,[30, 31, 38, 39] which involves the contraction of a first order density matrix or solution vector N^X perturbed by the nuclear magnetic moment of nucleus X with the property gradient P^Y of the perturbation due to the nuclear magnetic moment of nucleus Y, i.e., $J(X-Y) = \sum_{ai} N_{ai}^X P_{ai}^Y$. The transformation to localized molecular orbitals can hereby be carried out either directly on the elements of the solution vector, N_{ai}^X, and property gradient, P_{ai}^Y, before they are contracted to $J_i^a(X-Y)$ or alternatively already directly after the solution of the Hartree-Fock or Kohn-Sham equations, i.e., before the eventual calculation of any correlated wavefunction and the calculation of the solution vector and property gradient.

For the current project we have implemented in the DALTON program[40, 41] such a decomposition into contributions from one occupied and one virtual localized molecular orbital, $J_i^a(X-Y)$, of SSCC calculated at the level of the second order polarization propagator approximation with coupled cluster singles and doubles amplitudes—SOPPA(CCSD).[39, 42] Here and in the previous implementation[36, 37] for the second order polarization propagator approximation[38, 43, 44] the transformation to localized molecular orbitals according to the Foster and Boys localization scheme[45] is carried out before the calculation of MP2 correlation coefficients or CCSD amplitudes and the solution of the SOPPA equations.[29] This deserves two comments, because the SOPPA equations are in general not invariant to a unitary transformation of the orbitals, i.e., SOPPA results in canonical and localized molecular orbitals will not be exactly identical. Second, the implementation of the correlation coefficients and the SOPPA equations in the DALTON program assumes a diagonal Fock matrix as in the case of canonical orbitals. The numerical con-

sequences of these approximations are illustrated for CH_4 and NH_3 in Sec. III.

In order to determine how electron correlation provokes the UDS in methane we have calculated LMO contributions to the FC term for the one-bond coupling constants in CH_4 and NH_3 at the CHF, SOPPA, SOPPA(CCSD), and DFT/B3LYP[46, 47] levels of theory with the aug-cc-pVTZ-J basis set.[39, 48] Calculations were carried out at the equilibrium geometries, $R_{CH} = 1.08580$ Å for CH_4 and $R_{NH} = 1.01240$ Å, $\angle_{HNH} = 106.67°$ for NH_3, and at geometries where one of the bonds was changed by ± 0.05 and ± 0.1 Å. In the following we will in addition to the normal coupling constant, $J(X-Y)$, also discuss the so-called reduced coupling constant $K(X-Y) = \frac{4\pi^2 J(X-Y)}{h\gamma_X\gamma_Y}$.

III. RESULTS

In Table I we present the results for the four non-relativistic contributions to the SSCCs of CH_4 and NH_3 calculated with canonical and localized orbitals in order to investigate the effect of using localized orbitals in the SOPPA and SOPPA(CCSD) calculations. First of all, we note the excellent agreement between the experimental values and our SOPPA(CCSD) results. Second, it can be seen that the largest difference between canonical and localized results is for the FC term of NH_3 calculated at SOPPA level. But this deviation amounts only to 2%, which implies that the approximations involved in employing localized orbitals in SOPPA calculations are insignificant. Interestingly, the localized and canonical orbital results are closer to each other in the SOPPA(CCSD) calculations. It can also be seen that the FC term dominates indeed the ^1J(X-H) coupling constants. We will therefore only analyze this term in terms of localized molecular orbitals in the following.

The LMO decomposition of the FC term to the reduced coupling constants K(X-H) in CH_4 and NH_3 calculated at the CHF, SOPPA, SOPPA(CCSD), and DFT/B3LYP levels with the aug-cc-pVTZ-J basis set are presented in Tables II and III, respectively. In addition to the decomposition at the equilibrium geometry also the changes in each LMO contribution on extending or contracting the bond between the central atom X and the first of the hydrogen atoms, H1, are shown.

TABLE I. Comparison of contributions to $^1J(X-H)$ for CH_4 and NH_3 in [Hz] calculated at the SOPPA and SOPPA(CCSD) levels with canonical or localized orbitals. The calculations were carried out at the equilibrium geometries using the aug-cc-pVTZ-J basis set.[a]

	SOPPA				SOPPA(CCSD)			
	CH_4		NH_3		CH_4		NH_3	
	Can.	Loc.	Can.	Loc.	Can.	Loc.	Can.	Loc.
DSO	0.25	0.25	-0.07	-0.07	0.25	0.25	-0.07	-0.07
PSO	1.53	1.51	-2.87	-2.89	1.49	1.49	-2.83	-2.84
SD	-0.01	-0.02	-0.13	-0.12	0.01	0.00	-0.14	-0.13
FC	125.43	125.50	-60.31	-59.16	120.88	121.02	-58.69	-58.19
Total	127.20	127.25	-63.38	-62.23	122.63	122.76	-61.74	-61.22

[a]Experimental values for CH_4 120.9 Hz[22] and NH_3 -61.45 ± 0.03 Hz.[4]

TABLE II. Localized CHF, SOPPA, SOPPA(CCSD), and B3LYP orbital contributions to the FC term of $K(C–H)$ of methane at equilibrium geometry, in $[10^{19}\ T^2\ J^{-1}]$, and their differences ($\Delta K = K_{final} - K_{equilibrium}$) due to a change in the bond lengths by ± 0.1 Å.

ΔR_{CH1}		CHF		SOPPA		SOPPA(CCSD)		DFT/B3LYP	
in Å	Contrib.	$K(C–H1)$	$K(C–H2)$	$K(C–H1)$	$K(C–H2)$	$K(C–H1)$	$K(C–H2)$	$K(C–H1)$	$K(C–H2)$
−0.1	$\Delta core_{(C)}$	0.47	−0.53	0.86	−0.42	0.87	−0.42	0.94	−0.40
	$\Delta\sigma_{(C–H1−)}$	−6.48	−0.34	−3.68	−0.15	−3.27	−0.14	−4.00	−0.13
	$\Delta\sigma_{(C–H2)}$	0.65	−2.33	0.62	−1.86	0.57	−1.79	0.75	−1.95
	$\Delta\sigma_{(C–H3)}$	0.65	0.21	0.62	0.19	0.57	0.17	0.75	0.22
	$\Delta\sigma_{(C–H4)}$	0.65	0.21	0.62	0.19	0.57	0.17	0.75	0.22
	Δ Total FC	−4.07	−2.78	−0.97	−2.07	−0.67	−2.00	−0.84	−2.07
0.0	$core_{(C)}$	7.59	7.59	6.17	6.17	6.08	6.08	6.32	6.32
	$\sigma_{(C–H1eq.)}$	48.30	−1.42	40.52	−1.72	38.94	−1.65	43.36	−2.05
	$\sigma_{(C–H2)}$	−1.42	48.30	−1.72	40.52	−1.65	38.94	−2.05	43.36
	$\sigma_{(C–H3)}$	−1.42	−1.42	−1.72	−1.72	−1.65	−1.65	−2.05	−2.05
	$\sigma_{(C–H4)}$	−1.42	−1.42	−1.72	−1.72	−1.65	−1.65	−2.05	−2.05
	Total FC	51.63	51.63	41.54	41.54	40.06	40.06	43.55	43.55
+0.1	$\Delta core_{(C)}$	−0.45	0.49	−0.93	0.38	−0.94	0.38	−1.01	0.36
	$\Delta\sigma_{(C–H1+)}$	7.71	0.39	3.48	0.16	2.88	0.13	3.83	0.13
	$\Delta\sigma_{(C–H2)}$	−0.68	2.39	−0.59	1.85	−0.55	1.77	−0.73	1.95
	$\Delta\sigma_{(C–H3)}$	−0.68	−0.24	−0.59	−0.20	−0.55	−0.20	−0.73	−0.23
	$\Delta\sigma_{(C–H4)}$	−0.68	−0.24	−0.59	−0.20	−0.55	−0.20	−0.73	−0.23
	Δ Total FC	5.23	2.79	0.76	1.98	0.29	1.90	0.61	1.96

The UDS effect in CH_4 is clearly seen in Table II. The three methods including electron correlation predict that the coupling to the other, non-coupled hydrogen, $K(C–H2)$, varies more than the coupling to the coupled hydrogen, $K(C–H1)$, by about $1.1 \times 10^{19}\ T^2\ J^{-1}$ for SOPPA, $1.3 \times 10^{19}\ T^2\ J^{-1}$ for SOPPA(CCSD) and $1.2 \times 10^{19}\ T^2\ J^{-1}$ for B3LYP on contracting the bond and by $1.2 \times 10^{19}\ T^2\ J^{-1}$ for SOPPA, $1.6 \times 10^{19}\ T^2\ J^{-1}$ for SOPPA(CCSD) and $1.4 \times 10^{19}\ T^2\ J^{-1}$ for B3LYP on extending the bond length in good agreement with the earlier results.[16,25–27] In the CHF calculations the change in $K(C–H2)$ is about 40% larger than at the correlated levels, but only about 53% (on contracting) or 68% (on extending) of the change in $K(C–H1)$. In the case of NH_3 in Table III, on the other hand, all methods agree on the fact that $K(N–H1)$ changes more than $K(N–H2)$ but here CHF predicts a smaller change in $K(N–H1)$ than all the correlated

TABLE III. Localized CHF, SOPPA, SOPPA(CCSD), and B3LYP orbital contributions to the FC term of $K(N–H)$ of ammonia at equilibrium geometry, in $[10^{19}\ T^2\ J^{-1}]$, and their differences ($\Delta K = K_{final} - K_{equilibrium}$) due to a change in the bond lengths by ± 0.1 Å.

| ΔR_{NH1}		CHF		SOPPA		SOPPA(CCSD)		DFT/B3LYP	
in Å	Contrib.	$K(N–H1)$	$K(N–H2)$	$K(N–H1)$	$K(N–H2)$	$K(N–H1)$	$K(N–H2)$	$K(N–H1)$	$K(N–H2)$
−0.1	$\Delta core_{(N)}$	2.94	−0.18	3.09	−0.18	3.02	−0.20	3.27	−0.16
	$\Delta\sigma_{(N–H1−)}$	−5.11	−0.64	−0.89	−0.34	−0.56	−0.31	−1.04	−0.32
	$\Delta\sigma_{(N–H2)}$	0.87	−2.15	0.84	−1.71	0.81	−1.70	1.07	−1.82
	$\Delta\sigma_{(N–H3)}$	0.87	0.25	0.84	0.25	0.81	0.25	1.07	0.31
	$\Delta LP_{(N)}$	2.87	1.02	2.36	0.80	2.21	0.76	2.89	0.96
	Δ Total FC	2.45	−1.69	6.25	−1.17	6.29	−1.19	7.26	−1.01
0.0	$core_{(N)}$	5.85	5.85	4.66	4.66	4.74	4.74	4.75	4.75
	$\sigma_{(N–H1eq)}$	69.26	−3.00	57.07	−3.45	55.65	−3.37	61.06	−4.20
	$\sigma_{(N–H2)}$	−3.00	69.26	−3.45	57.07	−3.37	55.65	−4.20	61.06
	$\sigma_{(N–H3)}$	−3.00	−3.00	−3.45	−3.45	−3.37	−3.37	−4.20	−4.20
	$LP_{(N)}$	−7.24	−7.24	−6.25	−6.25	−5.88	−5.88	−7.31	−7.31
	Total FC	61.87	61.87	48.57	48.57	47.77	47.77	50.09	50.09
+0.1	$\Delta core_{(N)}$	−3.50	0.00	−3.29	0.05	−3.18	0.06	−3.49	0.02
	$\Delta\sigma_{(N–H1+)}$	7.17	0.80	0.51	−0.26	−0.01	0.34	0.64	−0.31
	$\Delta\sigma_{(N–H2)}$	−0.66	1.90	−0.60	1.47	−0.55	1.44	−0.78	1.53
	$\Delta\sigma_{(N–H3)}$	−0.66	−0.24	−0.60	0.36	−0.55	−0.24	−0.78	0.35
	$\Delta LP_{(N)}$	−4.30	−1.26	−3.01	−0.96	−2.73	−0.90	−3.77	−1.16
	Δ Total FC	−1.95	1.20	−6.99	0.68	−7.03	0.71	−8.17	0.43
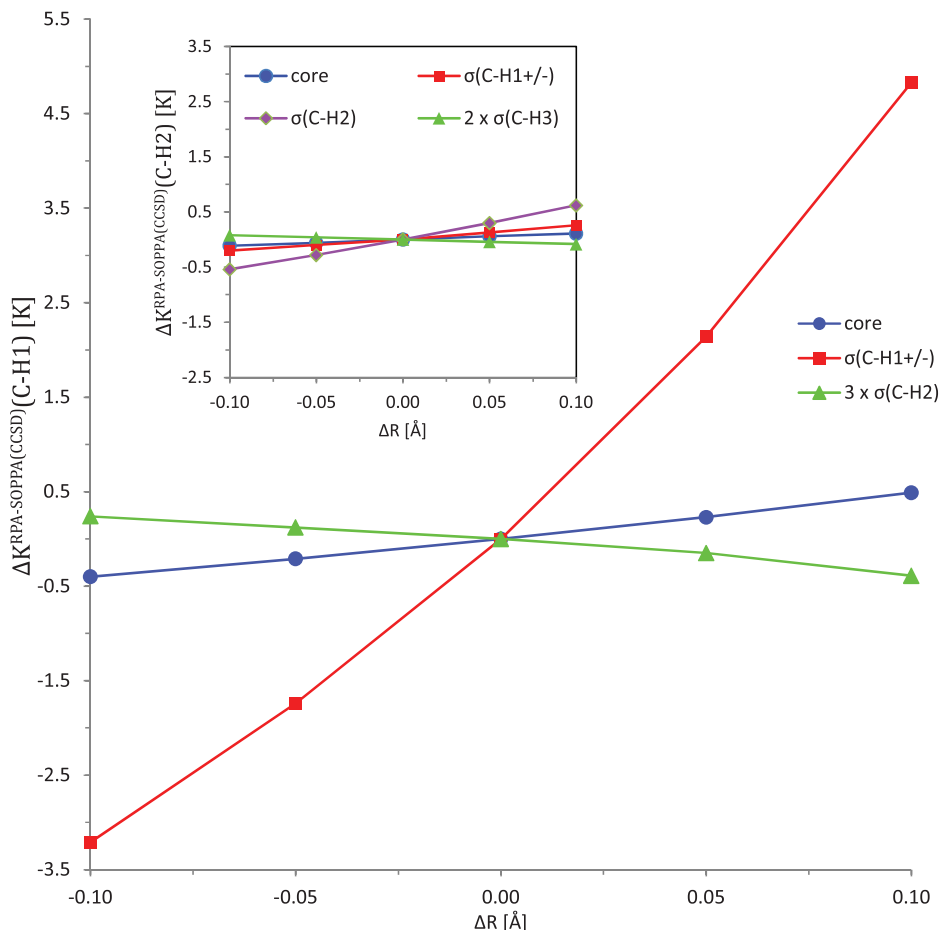
FIG. 1. CH$_4$: Variation of the difference in the CHF and SOPPA(CCSD) orbital contributions to $^1K^{FC}_{X-H}$ with the length of the coupled bond R_{own} and in the inset (up): the other bond R_{other}.

methods. Furthermore, from Table II one can see that the largest change on extending or contracting the C–H1 bond happens for the contribution from the bonding orbital between these atoms, $\sigma_{(C-H1)}$, and not for any of the other bond contributions, $\sigma_{(C-H2/3/4)}$, implying that at the level of the individual localized orbital contributions there is no unexpected sensitivity of the individual orbital contributions, i.e., *orbital* UDS, as previously pointed out.[25–27]

Comparing the LMO contributions in the three correlated calculations for both CH$_4$ and NH$_3$, one can see that with a few exceptions DFT/B3LYP gives the largest (in absolute values) LMO contributions and changes in these contributions followed by SOPPA while SOPPA(CCSD) typically gives the smallest LMO contributions.

We now turn to the question how electron correlation affects the orbital contributions and in particular the changes in these contributions on changing R_{CH1}, i.e., the differences between the changes in the LMO contributions obtained at the CHF level and at the DFT/B3LYP, SOPPA or SOPPA(CCSD) level. In Figures 1 and 2 the differences between the CHF changes and SOPPA(CCSD) changes in the LMO contributions to $^1K^{FC}_{X-H}$ are shown.

Among the contributions to K(C–H1), $\sigma_{(C-H1\pm)}$ is not only the largest but also the one which is most affected by electron correlation followed by $core_{(C)}$, for which the cor-

relation effects are similar though an order of magnitude smaller. The uncorrelated CHF calculations overestimate the negative/positive change in $\sigma_{(C-H1\pm)}$ on contraction/extension of the R_{CH1} bond by 76%/121% compared to SOPPA(CCSD), while the much smaller changes in the core contribution $core_{(C)}$ have the opposite sign and are underestimate at the CHF level.

Thus, when passing from SOPPA(CCSD) to CHF the absolute value of $\sigma_{(C-H1\pm)}$ increases by 3.21×10^{19} T^2 J^{-1} on contraction and by 4.83×10^{19} T^2 J^{-1} on extension of the bond to H1. The opposite sign $core_{(C)}$ contribution decreases in absolute value by 0.4×10^{19} T^2 J^{-1} on contraction and by 0.49×10^{19} T^2 J^{-1} on extension which further enhances the overestimation of the changes in K(C–H1) on changing its own bond. Also the changes in the bonding orbital contribution on changing the other bond, as seen from the $\sigma_{(C-H2)}$ contribution to K(C–H2), are overestimated but only by about 30% or 0.54 or 0.62×10^{19} T^2 J^{-1}. The disappearance of the UDS in CH$_4$ at the CHF level is thus solely due to the overestimation of the effect of changing the bond length on the contribution from the associated bonding orbital.

For NH$_3$, Table III and Figure 2, the changes in the $\sigma_{(N-H\pm)}$ contributions are also most strongly affected by electron correlation as seen for CH$_4$, and CHF overestimates the changes due to changing the corresponding bond length even
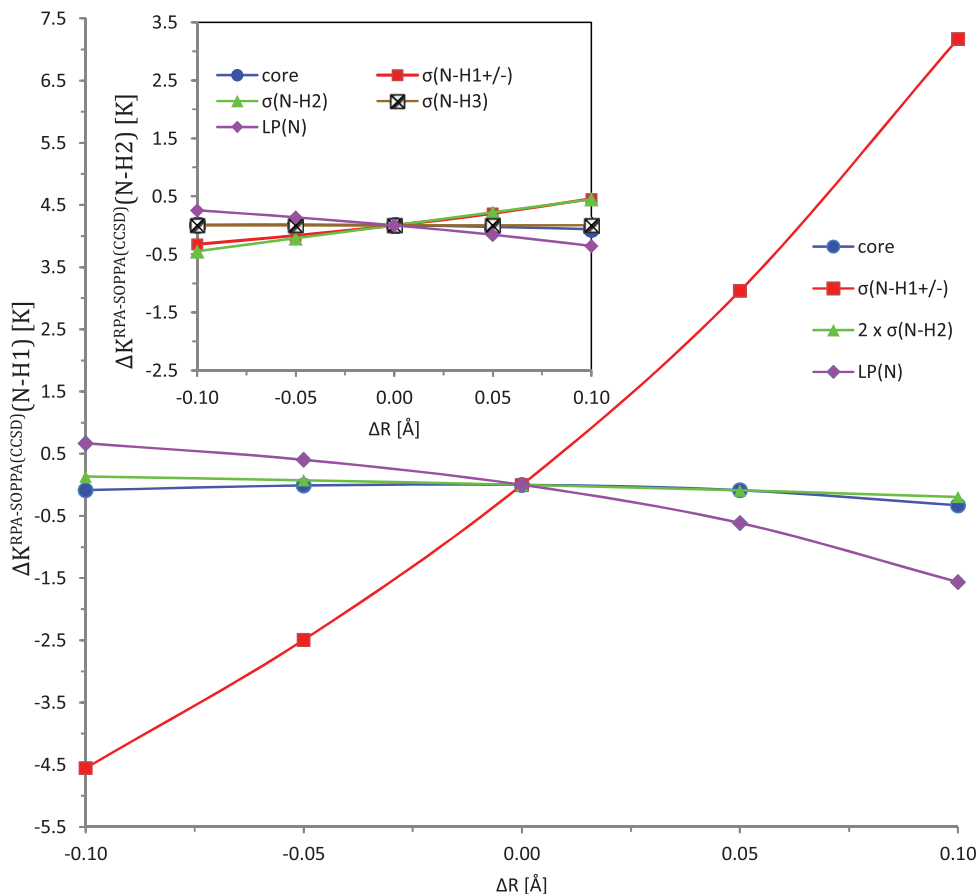
FIG. 2. NH_3: Variation of the difference in the CHF and SOPPA(CCSD) orbital contributions to $^1K^{FC}_{X-H}$ with the length of the coupled bond R_{own} and in the inset (up): the other bond R_{other}.

more than in CH_4. In addition, the changes in the $LP_{(N)}$ contribution are overestimated at the CHF level, but only by 30% or 57%. Overall due to the opposite signs of the changes in $\sigma_{(N-H\pm)}$ on one side and in $LP_{(N)}$ and $core_{(N)}$ on the other, the changes in the total FC term of K(N–H1) are smaller than in the correlated calculations quite contrary to CH_4. Looking finally at the changes in K(N–H) on changing the other bond, as seen from the $\sigma_{(N-H2)}$ contribution to K(N–H2), we observe again that the CHF calculations overestimate this LMO contribution and therefore the change in the total FC term. Consequently due the subtle balance between the different LMO contributions, the dependence on changes in the own bond is reduced in the uncorrelated calculations in NH_3 but still larger than the slightly increase dependence on the other bond.

IV. DISCUSSION AND CONCLUDING REMARKS

In conclusion, we summarize that in both molecules the dominating effect is that the uncorrelated CHF calculations overestimate the effect of changing the bond length between two coupled atoms on the contribution of their localized bonding orbital $\sigma_{(X-H\pm)}$ to the coupling constant between these atoms. However, this is not the only LMO contribution and summing all leads to the disappearance of the UDS in CH_4 in CHF calculations, while in NH_3 one gets a bit closer to an UDS in the CHF calculations.

Previous studies of $^1J(X-H)$ in terms of LMO contributions in saturated compounds at their equilibrium geometries have also shown that the main contribution to the coupling is given by the bond orbital, which links the coupled nuclei, and that such a contribution is the most affected by electron correlation.[36,37] Recalling the well-known fact that the restricted Hartree-Fock method poorly describes dissociation of bonds and gives generally too large vibrational frequencies, i.e., too large curvature of the potential energy surface, it is probably reasonable to conclude that CHF calculations also overestimate the changes in the contributions from the bonding orbital to any molecular property on extending or contracting the associated bond. What makes the situation more complicated for indirect nuclear SSCCs is the fact that the contributions from the different LMOs have often different signs and that the total value of the coupling constants are the result of a subtle balance between these LMO contributions—a situation whose details only a LMO analysis as presented in this study can unravel.

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