

Analysis of isotope effects in NMR one-bond indirect nuclear spin–spin coupling constants in terms of localized molecular orbitals

Patricio F. Provasi*^a and Stephan P. A. Sauer^b

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We recently showed, by analyzing contributions from localized molecular orbitals, that the anomalous deuterium isotope effect in the one-bond indirect nuclear spin–spin coupling constant of methane, also called the unexpected differential sensitivity, can be explained by the transfer of s-orbital character from the stretched bond to the other unchanged bonds [*ChemPhysChem*, 2008, **9**, 1259]. We now extend this analysis of isotope effects to the molecules BH₄[−], NH₄⁺, SiH₄, H₂O and NH₃ in order to test our conclusions on a wider range of XH₄ compounds and to investigate whether the lone-pair orbitals are really responsible for the absence of a similar effect in water and ammonia as proposed earlier [*J. Chem. Phys.*, 2000, **113**, 3121].

1. Introduction

The isotope effect on nuclear magnetic shielding constants has been investigated widely and many aspects of it are very well known. However, the same phenomenon for the indirect spin–spin coupling constants (SSCC) has not been studied in such detail and many aspects remain still unknown. Isotope effects on the SSCC were pioneered by Jameson *et al.*,^{1,2} Lukevics and co-workers,^{3,4} Sergeyev *et al.*^{5–12} and Raynes *et al.*^{10–22} More recently Limbach *et al.*,²³ and Schilf *et al.*²⁴ have also contributed to the unravelling of the physics behind them.

For the SSCC one distinguishes between two isotope effects:

- The primary isotope effect (PIE) on SSCC between nuclei A and B, ${}^nJ_{A-B}$, where B has two isotopes (ⁱB/^jB), is the difference between the coupling constants for the two isotopes:

$$\Delta_P^n J_{A-B} = |{}^nJ_{A-iB}| \left(\frac{\gamma_i^B}{\gamma_j^B} \right) - |{}^nJ_{A-jB}| \quad (1)$$

- The secondary isotope effect (SIE) on SSCC between nuclei A and B, ${}^nJ_{A-B}$, where a neighbor nucleus C has two isotopes (ⁱC/^jC), is the difference between the coupling constants for the two isotopes:

$$\Delta_S^n J_{A-B} = |{}^nJ_{A-B}({}^iC)| - |{}^nJ_{A-B}({}^jC)| \quad (2)$$

A particularly well-studied example for isotope effects is methane, where Bennett *et al.*¹⁴ found that the secondary isotope effect, $\Delta_S^1 J_{C-H} = -0.35$ Hz, is about five times as large as the primary isotope effect $\Delta_P^1 J_{C-H} = -0.07$ Hz. Fitting the measured SSCCs of all isotopomers to a coupling constant surface and taking derivatives of this coupling surface, Raynes¹³ found that the derivative with respect to the length of the bond to one of the other hydrogen atoms,

i.e. $\partial^1 J_{C-H} / \partial R_{\text{other}}$, is approximately 4.5 times larger than the derivative with respect to the length of the bond between the coupled atoms, *i.e.* $\partial^1 J_{C-H} / \partial R_{\text{own}}$. This implies that the carbon–hydrogen coupling constant in methane is more dependent on the length of the bond of carbon to one of the other hydrogen atoms than to the hydrogen atom involved in the coupling which thus causes the anomalous deuterium isotope effect. Raynes *et al.*¹⁶ called this phenomena the unexpected differential sensitivity (UDS) and stated that it is not easy to explain in physical terms why this happens. From a computational chemistry point of view this effect was reproduced appropriately only by including electron correlation in the *ab initio* calculations.^{16,17} Furthermore, it was attributed to the Fermi contact term of the Ramsey decomposition²⁵ of the SSCC and it was suggested that a necessary condition for the UDS to arise is that the central atom has no lone pairs, but no deeper explanation of this claim was given.²¹

More recently, we have presented an explanation of the UDS and anomalous deuterium isotope effects in CH₄ in terms of localized molecular orbitals.²⁶ The main conclusion was that the individual localized molecular orbital contributions to the C–H coupling constant are more dependent on changes in the bond length of the coupled bond than of the other bonds, which means that at the level of individual molecular orbital contributions there is no UDS. The UDS, on the other hand, arises because of two reasons. One is, that the major contributions, the ‘bond–bond’ and the ‘bond–other bond’ pathways, exhibit the opposite dependence on the bond length. The ‘bond–bond’ contribution increases with increasing bond length whereas the ‘bond–other bond’ contribution decreases. However, the extent to which the positive and negative changes in the localized molecular orbital contributions cancel each other is different for the bond between the coupled nuclei and the other bonds. The second reason is, that the s-orbital character of a bond-orbital is reduced when the bond is extended and consequently the coupling pathway through the carbon 1s core orbital and this bond orbital, the core–bond contribution, is weakened, when the corresponding bond is extended. At the same time the s-orbital character of the other

^a Department of Physics, Northeastern National University, Av. Libertad 5500, Corrientes, W 3404 AAS, Argentina. E-mail: patricio@unne.edu.ar

^b Department of Chemistry, University of Copenhagen, Universitetsparken 5, Copenhagen Ø, DK-2100, Denmark. E-mail: sauer@kiku.dk

three bonds is increased and therefore the core–bond coupling pathways for these C–H couplings are strengthened. We concluded therefore that this transfer of s-orbital character from the stretched bond to the other unchanged bonds is the main reason for the UDS and anomalous deuterium isotope effects in CH₄.

Although methane is the most widely studied example for anomalous deuterium isotope effects, it is not the only one. Similar effects were deduced from the NMR spectra of phenylsilanes,⁴ acetylene,⁵ nitromethane,⁶ toluene⁸ and halomethanes.¹¹ Computational studies showed that the one-bond coupling constants in acetylene,²⁰ in BH₄[−],²¹ NH₄⁺²¹ and SiH₄^{21,22} as well as the carbon shielding in acetylene¹⁹ exhibit a UDS, but not water,¹⁸ ammonia²⁷ or the oxonium ion.²⁸

In this work we want to study now: (a) whether the explanation found for methane also applies to the other XH₄ (with X = B, N and Si) compounds, for which UDS was found previously; and (b) whether the suggestion of Raynes and Sauer,²¹ that the lone pairs are responsible for the absence of an UDS in H₂O and NH₃, can be supported by our localized molecular orbitals analysis.

2. Methods of calculation

The theory of indirect nuclear spin–spin coupling constants (SSCC)²⁵ and of different computational methods for calculating them has been described extensively in the literature.^{29–33} However, one should mention that there are four contributions to the SSCC: the Fermi contact (FC) and the spin-dipolar (SD), which come from the interaction of the nuclear magnetic moments with the spin of the electrons; the diamagnetic spin orbital (DSO) and the paramagnetic spin orbital (PSO), which are due to the interaction of the nuclear spins with the orbital angular momentum of the electrons.

Calculations of the SSCC for both equilibrium geometries (see footnotes of Table 1) and distorted geometries, where one of the X–H bonds was changed by ±0.05 Å or ±0.1 Å, were performed with a development version of the Dalton program package,^{34–37} at the DFT/B3LYP^{38–40} and SOPPA(CCSD)^{41–43} level of approximation, using the completely uncontracted aug-cc-pVTZ-J (aug-cc-pVTZ-Juc) basis set,^{41–45} which was especially optimized for the calculation

Table 1 Calculated ^aof one-bond ¹J_(X–H) couplings in Hz, at the DFT/B3LYP and SOPPA(CCSD) levels of approximation using the aug-cc-pVTZ-Juc basis set

Molecule	B3LYP	SOPPA(CCSD)	Other values	
H ₂ O	−77.15	−81.02	−78.7	Ref. 52
NH ₃	−64.00	−61.59	−61.2	Ref. 53
BH ₄ [−]	87.99	75.46	82.0	Ref. 54
CH ₄	132.49	122.32	120.9	Ref. 16
NH ₄ ⁺	−81.36	−77.67	−73.3	Ref. 53
SiH ₄	−207.35	−190.90	−203.0	Ref. 55

^a The equilibrium geometries are: R_(O–H) = 0.958390 Å, ∠_(H–O–H) = 104.45 for H₂O; R_(N–H) = 1.01240 Å, ∠_(H–N–H) = 106.67 for NH₃; R_(B–H) = 1.23368 Å for BH₄[−]; R_(C–H) = 1.08580 Å for CH₄; R_(N–H) = 1.01959 Å for NH₄⁺, R_(Si–H) = 1.46839 Å for SiH₄.

of SSCCs and ensures therefore a very good description of the FC term.⁴⁶

The analysis in localized molecular orbitals was performed in terms of B3LYP Kohn–Sham orbitals using the Foster–Boys procedure⁴⁷ for localization. Our approach is a generalization of the CLOPPA method by Contreras and co-workers⁴⁸ to *ab initio* wavefunctions and involves the calculation of the coupling constants as a sum over all excited states. It differs therefore from two other schemes for the analysis of SSCCs in terms of localized Kohn–Sham orbitals, which have recently been presented.^{49–51}

We have generated localized molecular orbital contributions for all four Ramsey’s contributions and therefore also to the total coupling, but we will discuss only the Fermi contact term in the following, because only this term contributes significantly to the X-hydrogen coupling and its geometry dependence for the set of molecules studied here. In the case of H₂O the PSO contribution is significant compared to the FC one, but the effect of geometry variation in the PSO term is one order of magnitude smaller than for the FC term.

In this work only the valence orbitals were localized. For all but silicon the 1s core orbital was kept as it is. For silicon the 1s, 2s, 2p_{x,y,z} orbitals were kept delocalized.

All previous studies of UDS effects in BH₄[−], NH₄⁺, SiH₄, NH₃ and H₂O were carried out at the level of the SOPPA(CCSD) method. Since we know at least in the case of CH₄ that uncorrelated calculations are not able to reproduce this effect, we have investigated first whether the DFT/B3LYP calculations will give coupling constants in close enough agreement with the more correlated SOPPA(CCSD) calculations or experiment. The results of our equilibrium geometry B3LYP calculations using the aug-cc-pVTZ-Juc basis set are compared with corresponding SOPPA(CCSD) calculations and experimental coupling constants in Table 1. The agreement between the theoretical and experimental values is quite satisfactory and clearly sufficient for our purposes.

3. Results and discussion

In Tables 2 to 7 we have collected the most important contributions to the FC terms from localized molecular orbitals as well as the changes in these contributions due to elongation and contraction of either the bond between the coupled atoms (R_{own}) or to one of the other hydrogen atoms (R_{other}) by 0.10 Å. In order to allow for a direct comparison between the different molecules we report only reduced coupling constants

$$K_{X-H} = \frac{4\pi^2}{h\gamma_X\gamma_H} J_{X-H} \quad (3)$$

where γ_X and γ_H are the gyromagnetic ratios of nucleus X and H and h is Planck’s constant.

In the following we will first discuss our results for the XH₄ molecules before we will analyze the results for the water and ammonia molecules.

3.1 XH₄ compounds

For all XH₄ compounds including methane, the largest contribution to the FC term turns out to be the ‘bond–bond’

Table 2 CH₄: Localized occupied orbital contributions to the reduced Fermi contact term of ${}^1K_{\text{B-H}}$ ($10^{18} \text{ J}^{-1} \text{ T}^2$) as well as total Fermi contact term and total reduced coupling constant and their changes due to a change in the bond lengths by $\pm 0.1 \text{ \AA}$ calculated using the aug-cc-pVTZ-Juc basis set

	Contribution ^a	Equilibrium	Shortening		Elongation	
			R_{own}	R_{other}	R_{own}	R_{other}
B3LYP	c-c	2.92	1.27	-0.08	-0.87	0.07
	b-c	37.91	1.74	-2.35	-2.92	2.16
	b-b	127.16	-17.73	-5.43	17.64	5.61
	b-ob	-18.87	8.94	0.82	-9.17	-1.02
	ob-ob	-10.33	3.14	0.61	-3.23	-0.69
	Σ	138.79	-2.63	-6.43	1.44	6.13
	Σ -(b-c)		-4.38	-4.08	4.36	3.97
	FC	137.39	-2.75	-6.52	1.97	6.22
Total	139.59	-2.48	-6.39	1.61	6.08	
SOPPA(CCSD)	FC	126.99	-1.31	-6.02	2.53	6.30
	Total	128.88	-0.98	-5.89	2.27	6.17

^a The localized contributions correspond to: (c) for the core orbital of C, (b) for the C-H^{own} bond orbital and (ob) for the other C-H^{other} bond orbitals.

Table 3 SiH₄: Localized occupied orbital contributions to the reduced Fermi contact term of ${}^1K_{\text{Si-H}}$ ($10^{18} \text{ J}^{-1} \text{ T}^2$) as well as total Fermi contact term and total reduced coupling constant and their changes due to a change in the bond lengths by $\pm 0.1 \text{ \AA}$ calculated using the aug-cc-pVTZ-Juc basis set

	Contribution ^a	Equilibrium	Shortening		Elongation	
			R_{own}	R_{other}	R_{own}	R_{other}
B3LYP	c-c	2.56	1.67	0.56	-0.13	0.70
	b-c	76.96	2.55	-2.88	-2.14	2.18
	b-b	308.45	-21.52	-14.36	24.75	14.72
	b-ob	-69.47	14.42	4.00	-15.61	-4.69
	ob-c	-6.73	0.60	0.18	-0.48	-0.21
	ob-ob	-39.57	4.70	2.43	-4.09	-2.67
	Σ	272.19	2.43	-10.08	2.29	10.04
	Σ -(b-c)		-0.12	-7.20	4.43	7.85
	FC	276.59	0.63	-11.13	2.61	9.99
	Total	276.35	0.25	-11.08	2.76	9.93
SOPPA(CCSD)	FC	254.92	-2.57	-9.46	0.31	10.38
	Total	254.43	-2.72	-9.42	0.66	10.34

^a The localized contributions correspond to: (c) for the 1s, 2s and 2p_{x,y,z} core orbitals of Si, (b) for the Si-H^{own} bond orbital, (ob) for the other Si-H^{other} bond orbitals.

Table 4 BH₄⁻: Localized occupied orbital contributions to the reduced Fermi contact term of ${}^1K_{\text{B-H}}$ ($10^{18} \text{ J}^{-1} \text{ T}^2$) as well as total Fermi contact term and total reduced coupling constant and their changes due to a change in the bond lengths by $\pm 0.1 \text{ \AA}$ calculated using the aug-cc-pVTZ-Juc basis set

	Contribution ^a	Equilibrium	Shortening		Elongation	
			R_{own}	R_{other}	R_{own}	R_{other}
B3LYP	c-c	1.79	0.66	-0.06	-0.50	0.06
	b-c	18.80	0.10	-1.49	-1.23	1.48
	b-b	60.02	-8.72	-3.90	7.00	4.13
	b-ob	-3.48	3.78	0.51	-3.59	-0.67
	ob-ob	-4.06	1.05	0.31	-1.04	-0.34
	Σ	73.07	-3.13	-4.64	0.64	4.66
	Σ -(b-c)		-3.23	-3.15	1.88	3.18
	FC	72.04	-3.09	-4.65	0.69	4.66
SOPPA(CCSD)	Total	72.66	-3.10	-4.57	0.66	4.58
	FC	61.82	0.43	-4.47	2.15	4.43
	Total	62.31	0.45	-4.40	2.16	4.36

^a The localized contributions correspond to: (c) for the core orbital of B, (b) for the B-H^{own} bond orbital and (ob) for the other B-H^{other} bond orbitals.

orbital contribution followed by the ‘bond-core’ and the ‘bond-other bond’ contribution in agreement with earlier findings by Wu *et al.*⁵⁰ Furthermore, in all analyzed

compounds the orbital contributions become negative if at least one of the involved orbitals is an ‘other bond’ or ‘lone pair’ orbital, which differs a bit from the findings of Wu *et al.*⁵⁰

Table 5 NH_4^+ : Localized occupied orbital contributions to the reduced Fermi contact term of ${}^1K_{\text{N-H}}$ ($10^{18} \text{ J}^{-1} \text{ T}^2$) as well as total Fermi contact term and total reduced coupling constant and their changes due to a change in the bond lengths by $\pm 0.1 \text{ \AA}$ calculated using the aug-cc-pVTZ-Juc basis set

	Contribution ^a	Equilibrium	Shortening		Elongation	
			R_{own}	R_{other}	R_{own}	R_{other}
B3LYP	c-c	3.65	1.81	-0.06	-1.15	0.04
	b-c	62.32	5.32	-2.32	-4.97	1.87
	b-b	210.59	-20.60	-6.64	22.27	6.36
	b-ob	-45.73	14.16	1.06	-14.39	-1.92
	ob-ob	-23.34	7.79	2.80	-4.22	0.36
	Σ	207.50	8.48	-5.16	-2.46	6.72
	Σ -(b-c)		3.16	-2.83	2.51	4.85
	FC	208.14	5.88	-6.27	-1.98	5.37
SOPPA(CCSD)	Total	212.63	7.05	-6.21	-3.11	5.32
	FC	198.98	3.07	-5.32	-5.56	6.16
	Total	202.98	4.11	-5.28	-6.66	6.10

^a The localized contributions correspond to: (c) for the core orbital of N, (b) for the N-H^{own} bond orbital and (ob) for the other N-H^{other} bond orbitals.

Table 6 NH_3 : Localized occupied orbital contributions to the reduced Fermi contact term of ${}^1K_{\text{N-H}}$ ($10^{18} \text{ J}^{-1} \text{ T}^2$) as well as total Fermi contact term and total reduced coupling constant and their changes due to a change in the bond lengths by $\pm 0.1 \text{ \AA}$ calculated using the aug-cc-pVTZ-Juc basis set

	Contribution ^a	Equilibrium	Shortening		Elongation	
			R_{own}	R_{other}	R_{own}	R_{other}
B3LYP	c-c	3.15	1.70	-0.08	-1.09	0.06
	b-c	33.09	13.19	-1.13	-15.37	0.47
	b-b	204.46	-18.50	-6.94	18.81	6.60
	b-ob	-28.78	8.27	-0.53	-6.81	0.72
	b-lp	-30.17	11.33	4.17	-14.95	-4.97
	ob-ob	-15.17	4.57	0.79	-3.79	-0.33
	lp-c	-5.68	2.37	0.57	-2.94	-0.65
	lp-lp	-7.95	3.52	1.02	-4.77	-1.24
	Σ	152.95	26.46	-2.12	-30.92	0.65
	Σ -lp		9.24	-7.88	-8.26	7.51
	FC	158.21	22.82	-3.22	-25.87	1.38
	Total	167.27	23.42	-2.59	-26.84	0.61
SOPPA(CCSD)	FC	152.89	20.95	-2.26	-18.89	3.82
	Total	160.96	21.85	-1.54	-19.51	3.22

^a The localized contributions correspond to: (c) for the core orbital of N, (b) for the N-H^{own} bond orbital, (ob) for the other N-H^{other} bond orbitals and (lp) for lone pair of N.

Table 7 H_2O : Localized occupied orbital contributions to the reduced Fermi contact term of ${}^1K_{\text{O-H}}$ ($10^{18} \text{ J}^{-1} \text{ T}^2$) as well as total Fermi contact term and total reduced coupling constant and their changes due to a change in the bond lengths by $\pm 0.1 \text{ \AA}$ calculated using the aug-cc-pVTZ-Juc basis set

	Contribution ^a	Equilibrium	Shortening		Elongation	
			R_{own}	R_{other}	R_{own}	R_{other}
B3LYP	c-c	2.96	2.09	-0.03	-1.24	0.01
	b-c	10.28	26.58	0.93	-27.63	-1.83
	b-b	272.37	-11.98	-5.86	13.10	4.83
	b-ob	-21.02	3.76	-2.90	-1.83	3.28
	b-lp	-94.32	26.88	8.66	-30.55	-9.35
	ob-ob	-11.89	3.19	-0.45	-2.49	0.63
	lp-c	-18.42	6.48	1.44	-6.30	-1.52
	lp-lp	-34.02	13.68	3.55	-15.85	-3.99
	Σ	105.95	70.69	5.33	-72.79	-7.93
	Σ -lp		23.65	-8.32	-20.09	6.93
	FC	125.23	60.72	3.30	-59.14	-5.80
	Total	150.75	63.72	5.06	-84.66	-31.32
SOPPA(CCSD)	FC	134.74	46.69	3.48	-50.22	-1.30
	Total	158.31	49.71	5.82	-53.14	-3.02

^a The localized contributions correspond to: (c) for the core orbital of O, (b) for the O-H^{own} bond orbital, (ob) for the other O-H^{other} bond orbitals and (lp) for lone pair of O.

The most important observation for the XH_4 compounds is, as previously observed for methane,²⁶ that the changes in the individual orbital contributions are almost always larger, if the bond between the coupled atoms (R_{own}) is extended or shortened than if the bond to one of the other hydrogens (R_{other}) is changed. The only three exceptions are the ‘bond–core’ contributions in BH_4^- , CH_4 and SiH_4 , where a change in the other bond has a slightly larger effect and therefore exhibits what we want to call an ‘‘orbital’’ UDS. Therefore, we can conclude also for this larger set of XH_4 compounds that at the level of individual orbital contributions nothing unusual or unexpected occurs for the one-bond couplings apart from the above mentioned exceptions, but that the sum of these contributions is smaller for changes in the bond between the coupled nuclei than for changes in the other bonds due to the particular but systematic variations of the individual orbital contributions.

For all XH_4 compounds we find with two exceptions that, (i) the ‘bond–bond’ contribution increases on extending any bond, and that (ii) the ‘bond–other bond’ and ‘other bond–other bond’ contributions decrease on extending any of the bonds, whereas (iii) the ‘bond–core’ and ‘core–core’ contributions decrease on lengthening the bond between the coupled nuclei and increase on elongation of one of the other bonds. The two exceptions are the ‘other bond–other bond’ contribution in NH_4^+ and the ‘core–core’ contribution in SiH_4 (see Fig. 1 and 2).

The other main observation for CH_4 was²⁶ that the UDS disappears if the ‘bond–core’ contribution is excluded from the FC term, which lead to the conclusion that this is the main culprit for the UDS and thus the anomalous deuterium isotope effect. From Tables 2 to 5 we can see that none of the other XH_4 compounds fits this affirmation completely and that the UDS remains at least partly even after subtracting the ‘bond–core’ contribution. Methane is therefore rather the special case, where a subtle balance between the changes in the other contributions allows the ‘bond–core’ contribution to become decisive, and not the rule.

SiH_4 shows probably the most similar behavior to CH_4 . Nevertheless, all other contributions to the FC term than the ‘core–core’ contribution are at least a factor of two larger in SiH_4 than in CH_4 . Also the variations in the contributions from individual orbitals on changing one of the Si–H bonds are of the same type as in CH_4 but larger in absolute value with two exceptions: the changes in the ‘core–core’ and ‘bond–core’ contributions on elongation of the Si–H_{own} bond, which are less negative in SiH_4 . However, the relative size of the variation in the orbital contributions due to changes in the own and in the other bonds is quite different than in methane, because the changes in the orbital contributions on changing the coupled bond (ΔR_{own}) are less than a factor ~ 2 larger than in CH_4 , whereas the variations on changing one of the other Si–H bonds (ΔR_{other}) are clearly more than twice as large as in CH_4 with one important exception: the changes in the ‘bond–core’ contribution which have almost the same size as in CH_4 . The individual orbital contributions are thus still more dependent on changes in the coupled bond than in the other bonds, but to a lesser extent than in methane with the exception of the ‘bond–core’ contribution which shows an

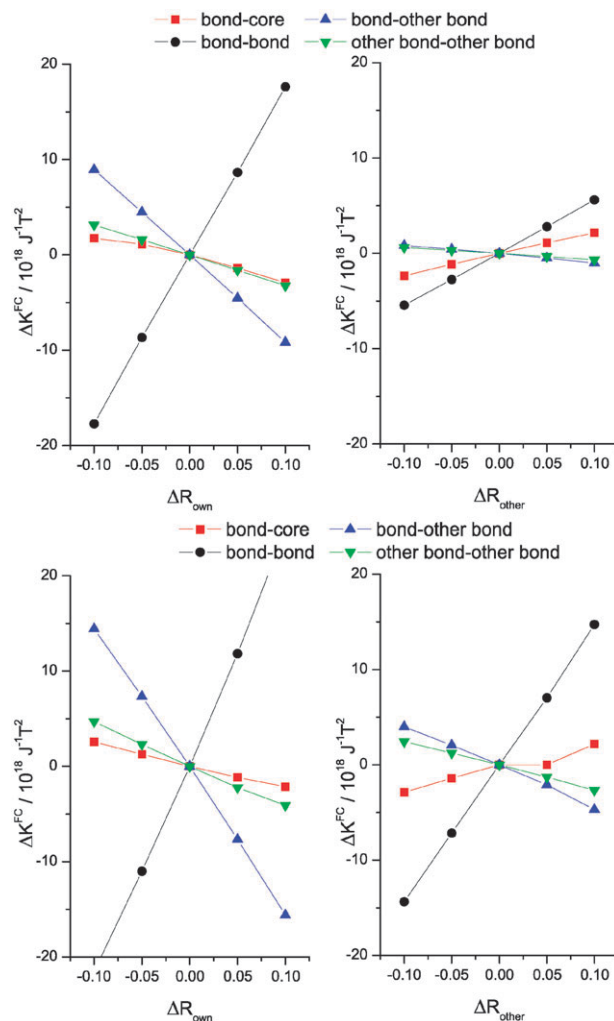


Fig. 1 Variation of the orbital contributions to ${}^1K_{\text{X-H}}^{\text{FC}}$ of CH_4 (up) and SiH_4 (down) with the length of the coupled bond R_{own} and the other bond R_{other} .

even stronger orbital UDS than in methane. Consequently, the difference between the summed changes in the orbital contributions due to ΔR_{other} and ΔR_{own} is with $\sim 8 \times 10^{18} \text{ J}^{-1} \text{ T}^2$ about twice as large in SiH_4 than in CH_4 where it was $\sim 4 \times 10^{18} \text{ J}^{-1} \text{ T}^2$ and thus too large to be solely due to the changes in the ‘bond–core’ contribution, which in SiH_4 like in CH_4 still amounts only to $\sim 5 \times 10^{18} \text{ J}^{-1} \text{ T}^2$. The different behavior of SiH_4 is thus the result of a combination of two factors: that all but the ‘bond–core’ contribution are more susceptible to changes in the bond lengths than in methane and that they are even more sensitive to changes in the other bonds than in methane. One should also note that at least at the B3LYP level the Si–H one-bond coupling increases both when the coupled bond is extended or shortened.

BH_4^- exhibits a similar but somewhat inverse behavior to SiH_4 relative to CH_4 . All the orbital contributions and variations of the orbital contributions due to changes in the bond lengths are now smaller than in CH_4 . But, again like in SiH_4 , the ratio between the variations in the orbital contributions due to changes in the own (ΔR_{own}) and in the other bonds (ΔR_{other}) are smaller than in CH_4 , *i.e.* the orbital

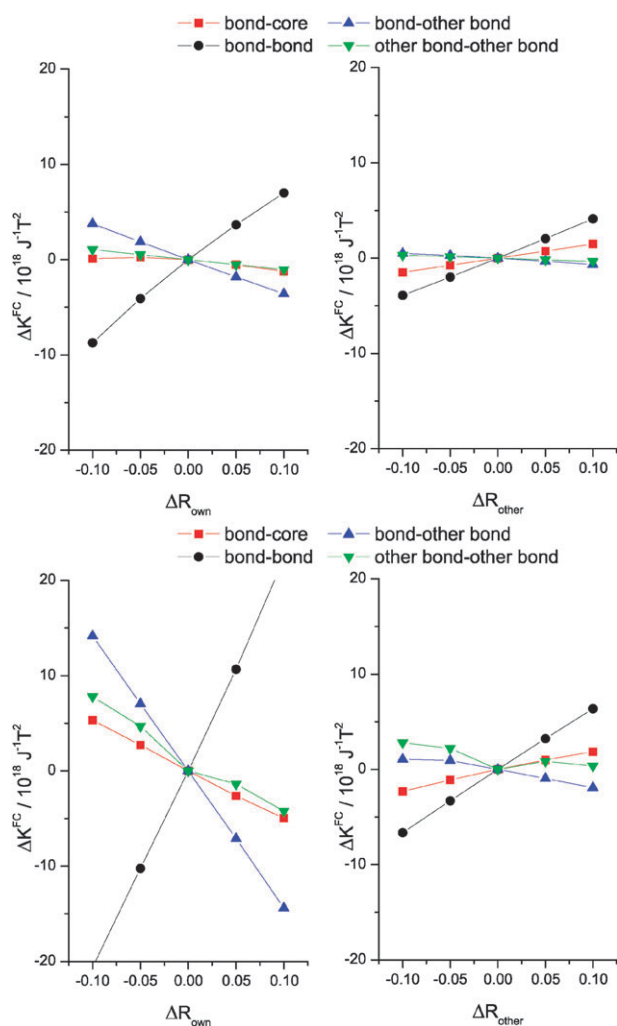


Fig. 2 Variation of the orbital contributions to $^{11}\text{K}_{\text{X-H}}^{\text{FC}}$ of BH_4^- (up) and NH_4^+ (down) with the length of the coupled bond R_{own} and the other bond R_{other} .

contributions become relatively more sensitive to changes in the other bonds than in methane. And in the case of the ‘bond–core’ contribution the orbital UDS also becomes more pronounced than in methane because the ‘bond–core’ contribution hardly changes, when R_{own} is shortened, contrary to CH_4 and for elongation of the bonds the ‘bond–core’ contribution also exhibits now a orbital UDS. However, contrary to SiH_4 there is a difference between extending the bonds and shortening. Subtracting the ‘bond–core’ contribution just removes the UDS for shortening of the bond but clearly does not remove the UDS for extending the bonds. Finally our B3LYP and SOPPA(CCSD) results disagree about whether the one-bond coupling increase or decrease on shortening of the bond between the coupled nuclei, which is similar but inverse to what was seen for SiH_4 .

The UDS in NH_4^+ is a bit more complex than in the other three XH_4 molecules. First of all the total coupling exhibits the same behavior as the ‘core–bond’ contribution, *i.e.* it increases if the bond between the coupled nuclei is shortened or the bond to other hydrogen atoms is extended and *vice versa*. NH_4^+ differs therefore from the other XH_4 compounds.

Furthermore, our B3LYP and SOPPA(CCSD) results do not agree on whether there is an UDS for both changes in the total coupling constants. At the B3LYP level we find only an UDS for extending the bonds, whereas SOPPA(CCSD) predicts the opposite. The reason for this is that B3LYP predicts the change in the FC term to be $\sim 3 \times 10^{18} \text{ J}^{-1} \text{ T}^{-2}$ larger than SOPPA(CCSD), which by chance is large enough to make the difference. Continuing the trend from BH_4^- to CH_4 , the orbital contributions to the total FC and to the change in FC are again larger in NH_4^+ than in CH_4 . There are only a few exceptions, the changes in the ‘core–core’, ‘bond–core’ and partially the ‘bond–other bond’ contributions, which are smaller in NH_4^+ than in methane, but only for changes due to a variation in R_{other} . Furthermore, contrary to BH_4^- , the ratio between the variations in the orbital contributions due to changes in the own (ΔR_{own}) and in the other bonds (ΔR_{other}) is more or less the same as in CH_4 , with one significant exception, the ‘core–bond’ contribution which is more dependent on changes in R_{own} and does therefore not show any sign of an ‘orbital’ UDS contrary to the other three XH_4 compounds. Finally the ‘other bond–other bond’ contribution increases both when the bond to the other hydrogen atoms is lengthened and shortened which none of the other contributions or XH_4 molecules do.

3.2 XH_n ($n = 2$ and 3) compounds

From Tables 6 and 7 one can see that the by far most important orbital contribution to the FC term in ammonia and water is the ‘bond–bond’ term like for the XH_4 compounds. However, while for NH_3 as for the XH_4 molecules the ‘bond–core’ contribution is the second largest term, for water this is only the seventh most important contribution. Apart from this term we can see that the series ‘bond–bond’, ‘bond–other bond’ and ‘other bond–other bond’ as found in the XH_4 compounds is in ammonia and water interlaced with a second series of orbital contributions consisting of ‘bond–lone pair’, ‘lone pair–lone pair’ and ‘lone pair–core’. The fact that water has one lone pair more than ammonia is nicely reflected in the relative order of these two series, because in ammonia the ‘bond–lone pair’ and ‘bond–other bond’ contributions are almost equal whereas in water the three ‘lone pair’ contributions are all larger than any of the three ‘other bond’ contributions. As already mentioned an orbital contribution to the FC term is negative if it comes from at least one ‘other bond’ or ‘lone pair’ orbital. Otherwise the contributions are positive.

For the total one-bond coupling constants in H_2O and NH_3 as well as the total FC contribution it is well known that they do not show a UDS, but rather the normal behavior, *i.e.* the $^1J_{(\text{X-H})}$ is more dependent on its own X–H bond length than on a neighboring X–H bond length. Therefore it is no surprise to see in Fig. 3 and 4 that the changes in the orbital contributions due to ΔR_{own} are always larger than the ones due to ΔR_{other} with one exception the ‘bond–other bond’ contribution on elongation of the bonds in H_2O , which anyway shows an ‘orbital’ UDS. Concerning the sign of the variation we can see that the ‘bond–bond’ contribution still belongs to type (i) from section 1 and increases on extending

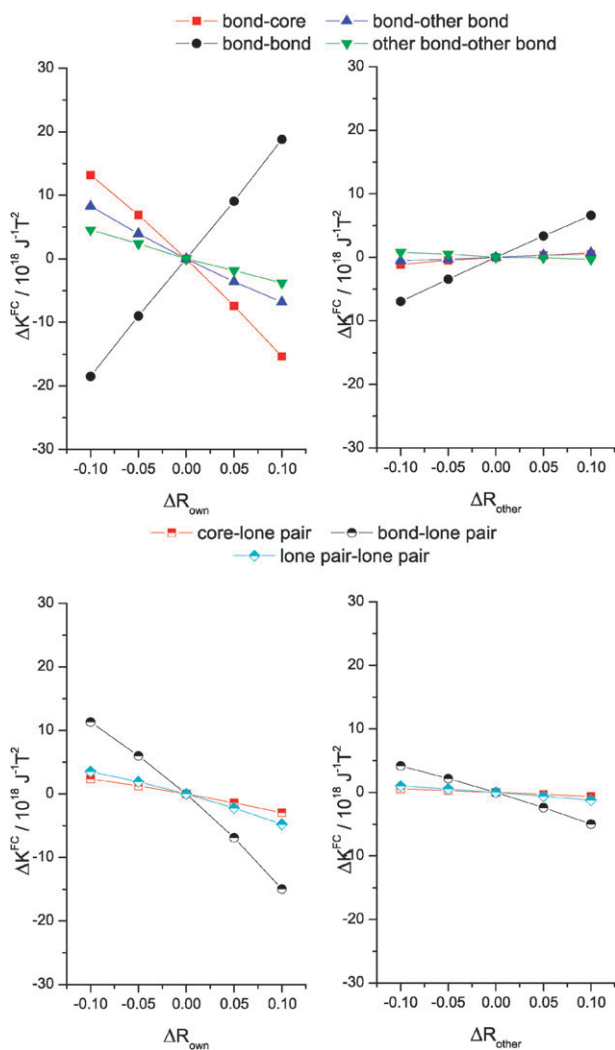


Fig. 3 NH_3 : Variation of the orbital contributions to ${}^1K_{\text{N-H}}^{\text{FC}}$ with the length of the coupled bond R_{own} and the other bond R_{other} .

any bond, whereas the ‘core–core’ contribution still belongs to type (iii) and decreases on lengthening the bond between the coupled nuclei and increases on elongation of one of the other bonds. The new lone pair contributions belong all to type (ii), which means that they increase on extending the bond length and diminish on extending the other bond length. The variation of the remaining contributions differs from the XH_4 molecules. In ammonia the ‘bond–other bond’ and ‘bond–core’ contributions belong to type (iii) while the ‘other bond–other bond’ contribution decreases on extending any bond. In water on the other hand, both ‘other bond’ contributions belong to type (iii) while the ‘bond–core’ contribution decreases on extending both bond lengths. Water is therefore the only molecule in this study, where the derivative of the ‘bond–core’ contribution with respect to the bond length has the same sign for R_{own} and R_{other} (see Fig. 4).

Going from NH_4^+ to NH_3 all the orbital contributions and most of the changes in the orbital contributions become >smaller. But the ratio between changes in the orbital contributions due to ΔR_{own} and ΔR_{other} is very similar to NH_4^+ . The main exception is the ‘core–bond’ contribution

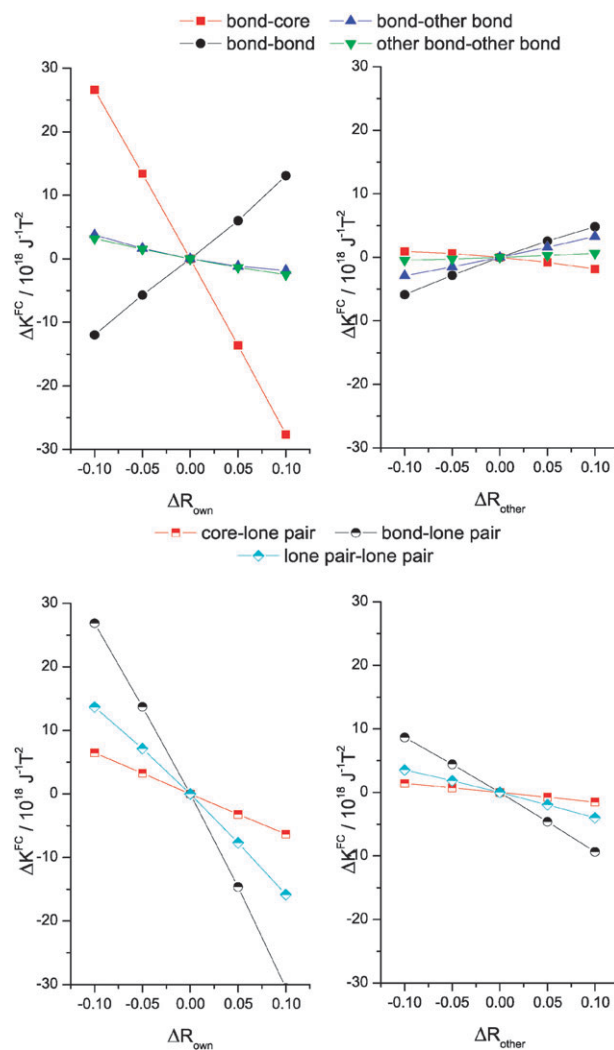


Fig. 4 H_2O : Variation of the orbital contributions to ${}^1K_{\text{O-H}}^{\text{FC}}$ with the length of the coupled bond R_{own} and the other bond R_{other} .

which in NH_3 varies much more with changes in R_{own} than in R_{other} , because the variation with R_{own} is much larger than in NH_4^+ . Continuing to H_2O we can see that the ‘lone pair’ contributions increase in size, whereas the other contributions with the exception of the ‘bond–bond’ contribution further decrease. The same applies also to the variation in the orbital contributions on changing one or the other bond, however, with some exceptions. On varying the coupled bond the ‘bond–core’ and ‘core–core’ contributions change more than in ammonia and ‘bond–other bond’ contributions changes much more on varying the other bond than in ammonia. Consequently the ratio between changes in the orbital contributions due to ΔR_{own} and ΔR_{other} is very similar to NH_3 with the important exception of the ‘bond–other bond’ contribution which in water shows the already mentioned ‘orbital’ UDS. Furthermore the relative importance of the changes in the orbital contributions shows a systematic variation from NH_4^+ to H_2O . In NH_4^+ and NH_3 the changes in the ‘bond–bond’ contributions are largest, followed by changes in the ‘bond–other bond’ and then ‘bond–core’ contributions in NH_4^+ but already by changes in the

'bond-core' and 'bond-lone pair' in NH₃. In water finally the largest changes are found for the 'bond-lone pair' and 'bond-core' contributions followed by 'lone pair-lone pair' and finally 'bond-bond', which again shows the increasing importance of the lone pairs in water.

The most important question to be answered is whether the lone pairs are responsible for the missing UDS in water and ammonia as proposed earlier.²¹ We can test this hypothesis with our orbital contribution analysis by subtracting all the contributions which involve the lone pair orbitals (denoted as Σ -lp in Tables 6 and 7) and we can see that even without the lone-pair orbital contributions neither NH₃ nor H₂O exhibit a UDS. The lone pairs are therefore at least not directly responsible for the lack of UDS in those two molecules. However, if one in addition also subtracts the 'bond-core' contribution which in both molecules is much more sensitive to changes in the own bond, then the remaining contributions exhibit a UDS. This implies that the UDS appears, if one consider only the same four single contributions, 'core-core', 'bond-bond', 'bond-other bond' and 'other bond-other bond' that did not show UDS for XH₄.

4. Concluding remarks

We have investigated the reasons for the unexpected differential sensitivity and associated anomalous isotope effects in the one-bond indirect nuclear spin-spin coupling constants in CH₄, SiH₄, BH₄⁻ and NH₄⁺ and their absence in NH₃ and H₂O by an analysis in terms of contributions from localized occupied molecular orbitals obtained at B3LYP/aug-cc-pVTZ-Juc level of theory.

In particular we have investigated whether the earlier suggested explanation²⁶ that the contribution from the 'bond-core' pathway and thus a transfer of s-orbital character from the extended bond to the other bonds is responsible for the UDS in methane also holds for a wider set of molecules showing a UDS. Secondly we have tested whether the claim²¹ that the lone-pair orbitals are responsible for the lack of an UDS in ammonia and water can be supported by an analysis in localized molecular orbital contributions.

First of all we observe that with increasing nuclear charge of atom X the individual orbital contributions to the FC term and to the changes in the FC increase.

Concerning the UDS in the XH₄ compounds we can conclude that the variation in the 'bond-core' contribution and its interpretation in terms of a transfer of s-orbital character from the extended to the shortened bond surely contributes to the UDS, but that this is not the only reason for the UDS in BH₄⁻, NH₄⁺ and SiH₄, contrary to CH₄. For BH₄⁻ and SiH₄ we observe that most of the other contributions are more sensitive to changes in the other bonds than they have been in CH₄, thereby destroying the subtle balance between them which allowed to 'core-bond' contribution to be decisive. This means that the UDS in all studied molecules has to be attributed to slightly different reasons.

In ammonia and water we observe an increasing importance of contributions from the lone-pair orbitals both to the total FC term and its variation with the bond lengths. However,

excluding these contributions alone does not produce a UDS in neither of the two molecules. Only when also the contribution from the 'bond-core' pathway is excluded, we can observe a UDS for these two molecules. The claim that the presence of lone-pairs alone is responsible for the absence of an unexpected differential sensitivity in water and ammonia is thus not supported by the results of our analysis in orbital contributions.

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