Research Article

Magnetic Resonance in Chemistry

Received: 11 October 2007 Revised: 5 December 2007 Accepted: 6 December 2007 Published online in Wiley Interscience: 13 February 2008

(www.interscience.com) DOI 10.1002/mrc.2181

A computational study of $^2J_{HH}$(*gem*) indirect spin–spin coupling constants in simple hydrides of the second and third periods

Ibon Alkorta,[a*] Patricio F. Provasi,[b] Gustavo A. Aucar[b] and José Elguero[a]

Several theoretical methods have been used to compute $^2J_{HH}$ in neutral, anionic and cationic HXH hydrides, X being the 14 nuclei from Li to Cl (28 molecules). Since the calculations also provide $^1J_{XH}$ spin–spin coupling constants (SSCC), these have also been analyzed. The best results were obtained using Second-order polarization propagator approximation (SOPPA)/sad*J*. The geminal coupling constants appear to be dependent on the electronegativity of the X-atom. **Copyright © 2008 John Wiley & Sons, Ltd.**

Supplementary electronic material for this paper is available in Wiley InterScience at http://www.interscience.wiley.com/jpages/0749-1581/suppmat/

Keywords: hydrides; geminal coupling constants; SOPPA

Introduction

The systematic exploration of structural effects on coupling constants suffers from the difficulty to measure some of them. For instance, geminal $^2J_{HH}$ couplings in XH_2 compounds (X being a divalent atom or a hydrogen substituted atom) must be measured first on the XHD derivative and then $^2J_{HD}$ transformed into $^2J_{HH}$ using the 6.515 magnetogyric ratio.[1] The two aims of the present paper are (i) to compare different methods of calculating indirect spin–spin coupling constants (ISSCC) with experimental data (ii) to analyze the best calculated ISSCC as a function of some properties of X. We have selected all the hydrides of the second and third periods (Scheme 1), anions, neutral and cations, excluding hypervalent atom derivatives like SH_4 and PH_5. The first part of the paper will be devoted to $^2J_{HH}$(*gem*) and the second one to $^1J_{XH}$. There is an extensive literature of *ab initio versus* Density Functional Theory (DFT) and basis set dependencies. It is expected that the *ab initio* would do better than DFT and larger basis sets, which decontract the s function, will substantially improve the (generally dominant) FC contributions.[2]

We have ordered the hydrides first according to the number of hydrogen atoms (2, 3, 4) and then following the atomic number Z value.

Results and Discussion

Practically, since the pioneering work of Ramsey,[3] many have been the attempts to explain some of the main trends of the geminal proton–proton spin–spin coupling constants SSCC. A good summary of the state of the art can be found in the review work by Contreras and Peralta[4] and references cited therein.

We have reported in Table 1 the results concerning $^2J_{HH}$. From the contribution to the SSCC, main finding is that the Fermi Contact (FC) contribution practically determines the total couplings, their sign and magnitude. In some cases, the Diamagnetic Spin Orbit (DSO) term is more important than the FC one, but it is 'almost' cancelled by the Paramagnetic Spin Orbit (PSO) one (See Supporting Information Material).

	IA	IIA	IIIB	IVB	VB	VIB	VIIB
2	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F
3	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl

Scheme 1. The fourteen X atoms studied. The atomic number Z is indicated in the upper-left corner.

The values obtained for the geminal coupling constant are within the known limits of $^2J_{HH}$ (from −25 to +42 Hz)[4] with the exception of the value obtained for MgH_2 (+54.94 Hz). Even though this compound is known and some of their properties have been measured, no available experimental SSCC have been reported.[5]

In the literature, we found experimental values only for six compounds. The values of the third column of Table 1 (Exptl values) yield better correlation coefficients than those of the fourth column (Other exptl values), thus we have used the first ones.

$$J_{exp}(\text{Hz}) = (2.96 \pm 1.14) + (1.13 \pm 0.10)J_{SOPPA/aug\text{-}cc\text{-}pVTZ}(\text{Hz}), n = 6, r^2 = 0.969 \quad (1)$$

$$J_{exp}(\text{Hz}) = (1.37 \pm 0.71) + (0.85 \pm 0.05)J_{SOPPA/sadJ}(\text{Hz}), n = 6, r^2 = 0.984 \quad (2)$$

* Correspondence to: Ibon Alkorta, Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain. E-mail: ibon@iqm.csic.es

a Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain

b Department of Physics, Northeastern University of Argentina, Avenida Libertad 5500, W 3404 AAS Corrientes, Argentina

 Copyright © 2008 John Wiley & Sons, Ltd.

Table 1. $^2J_{HH}$ coupling constants (compounds in bold are those for which experimental data are known)

No.	Hydride[a]	Exptl values	Other exptl values	SOPPA aug-cc-pVTZ	SOPPA sad*J*	B3LYP aug-cc-pVTZ	B3LYP 6–311++G**	Geometry (Å, °) X–H	H–X–H	H···H
1	LiH_2^- (L)	No data		14.22	18.55	22.92	22.79	1.752	180.0	3.504
2	BeH_2 (L)	No data		30.64	39.33	36.94	36.21	1.329	180.0	2.659
3	NaH_2^- (L)	No data		22.24	30.49	40.95	41.41	2.098	180.0	4.196
4	MgH_2 (L)	No data		54.94	72.89	80.50	78.87	1.707	180.0	3.415
5	NH_2^-	No data		−6.30	−8.11	−5.44	−5.85	1.028	102.2	1.600
6	**OH_2**	−7.34[6]		−8.76	−10.81	−7.11	−9.43	0.961	104.1	1.516
7	FH_2^+	No data		−1.66	−4.28	0.16	−4.22	0.966	111.9	1.601
8	PH_2^-	No data		−8.99	−10.75	−6.46	−6.08	1.427	92.1	2.055
9	SH_2	No data		−13.21	−15.90	−10.25	−10.79	1.336	92.2	1.926
10	ClH_2^+	No data		−13.65	−16.59	−11.39	−12.54	1.305	94.2	1.912
11	BeH_3^- (P)	No data		1.63	2.22	2.63	3.14	1.421	120.0	2.462
12	BH_3 (P)	No data		0.29	0.57	2.64	2.79	1.187	120.0	2.057
13	CH_3^+ (P)	No data		−0.29	−1.23	3.91	2.51	1.087	120.0	1.882
14	MgH_3^- (P)	No data		13.77	18.14	18.87	18.45	1.813	120.0	3.140
15	AlH_3 (P)	No data		22.60	29.72	28.29	28.35	1.580	120.0	2.736
16	SiH_3^+ (P)	No data		30.44	39.70	37.10	36.76	1.462	120.0	2.532
17	CH_3^-	No data		−6.44	−7.97	−3.90	−4.59	1.099	109.8	1.798
18	**NH_3**	−10.35[7]		−11.57	−13.20	−9.34	−10.10	1.012	106.8	1.625
19	OH_3^+	No data		−6.58	−8.07	−4.27	−6.51	0.980	111.5	1.619
20	SiH_3^-	No data		−7.22	−8.22	−4.99	−4.24	1.535	95.6	2.274
21	**PH_3**	−13.4[8]	−13.2[6]	−13.62	−16.36	−10.52	−10.52	1.412	93.6	2.060
22	SH_3^+	No data		−16.33	−20.02	−13.22	−14.12	1.351	94.3	1.980
23	BH_4^-	No data		−10.83	−12.74	−8.94	−8.82	1.234	109.5	2.015
24	**CH_4**	−12.4[9]	−12.56[10]	−13.16	−16.08	−10.50	−11.74	1.086	109.5	1.774
25	**NH_4^+**	−11.1[11,12]	−9.58[13]	−14.21	−16.13	−11.97	−12.52	1.022	109.5	1.669
26	AlH_4^-	No data		0.78	2.18	2.64	3.23	1.643	109.5	2.683
27	**SiH_4**	2.8[9]	2.75[10]	−0.41	1.76	1.75	2.33	1.478	109.5	2.413
28	PH_4^+	No data		−3.12	−1.50	−0.25	−0.34	1.392	109.5	2.274

[a] L, linear; P, planar

$$J_{exp}\,(\text{Hz}) = (0.59 \pm 1.21) + (1.16 \pm 0.13)\,J_{B3LYP/aug\text{-}cc\text{-}pVTZ}\,(\text{Hz}),\ n = 6,\ r^2 = 0.951 \quad (3)$$

$$J_{exp}\,(\text{Hz}) = (0.36 \pm 1.59) + (1.04 \pm 0.16)\,J_{B3LYP/6\text{-}311{+}{+}G^{**}}\,(\text{Hz}),\ n = 6,\ r^2 = 0.915 \quad (4)$$

The worse point corresponds to the ammonium cation (no. 25). Removing the mentioned point, the following correlations are obtained:

$$J_{exp}(\text{Hz}) = (3.30 \pm 0.25) + (1.20 \pm 0.02)J_{SOPPA/aug\text{-}cc\text{-}pVTZ}\,(\text{Hz}),\ n = 5,\ r^2 = 0.999 \quad (5)$$

$$J_{exp}(\text{Hz}) = (1.43 \pm 0.46) + (0.88 \pm 0.04)J_{SOPPA/sadJ}\,(\text{Hz}),\ n = 5,\ r^2 = 0.995 \quad (6)$$

$$J_{exp}(\text{Hz}) = (0.86 \pm 0.67) + (1.26 \pm 0.08)J_{B3LYP/aug\text{-}cc\text{-}pVTZ}\,(\text{Hz}),\ n = 5,\ r^2 = 0.988 \quad (7)$$

$$J_{exp}(\text{Hz}) = (0.48 \pm 1.63) + (1.09 \pm 0.17)J_{B3LYP/6\text{-}311{+}{+}G^{**}}\,(\text{Hz}),\ n = 5,\ r^2 = 0.930 \quad (8)$$

Predicted $^2J_{HH}$ for NH_4^+ are −13.80 (from Eqn (5)) and −12.68 (from Eqn (6)), and the experimental are ∼ −11.1[11,12] (used) or −9.58[13] (not used, Table 1). The first observation is the difficulty to ascertain the quality of the computational method using experimental coupling constants, since for NH_4^+ the coupling values differ by 1.5 Hz. The first value[11,12] was obtained from $^{15}NH_4Cl$ between 0.4 and 1 M in H_2O/D_2O mixtures, while the second one[13] came from $^{15}NH_4NO_3$ 1.3 M solution in $H_2O/D_2O/HCl$. Since the predicted value, −13.80 Hz, corresponds to the gas phase, we attribute the lower absolute values in the solutions to the effect of hydrogen bonds with the solvent. A general solvent effect will probably have an opposite effect.

Calculations of J_{gem} in compounds of Table 1 are rather infrequent. Mikkelsen *et al.* reported calculations of the SH_2 molecule (no. 9) taking into account general solvent effects (the basis set used was the aug-cc-pVQZ-s0).[14] The gas phase J_{gem} obtained was −13.30 Hz and in water (dielectric constant 78.54) the absolute value raises to −14.16 Hz. Our calculations afford −13.21 (SOPPA/aug-cc-pVTZ), −15.90 (SOPPA/sad*J*), −10.25 (B3LYP/aug-cc-pVTZ) and −10.79 Hz (B3LYP/6–311++G**).

Enevoldsen *et al.* using SOPPA and SOPPA Coupled-Cluster theory with Single and Double excitations (CCSD) have calculated J_{gem} for OH_2 (no. 6).[15] With SOPPA and SOPPA(CCSD), they obtained −9.14 and −8.81 Hz, respectively. Our values are −8.76 (SOPPA/aug-cc-pVTZ), −10.81 (SOPPA/sad*J*), −7.11 (aug-cc-pVTZ) and −9.43 Hz (6–311++G**), the experimental value being −7.34 Hz (Table 1).

Copyright © 2008 John Wiley & Sons, Ltd.

From the above equations, it is clear that SOPPA methods should be preferred to tB3LYP ones. It is more difficult to choose between SOPPA/aug-cc-pVTZ and SOPPA/sad*J*. Since the calculated and experimental SSCC should be 0 for some cases (nuclei far away), we have imposed intercept = 0:

$$J_{\mathrm{exp}}(\mathrm{Hz}) = (0.89 \pm 0.06) J_{\mathrm{SOPPA/aug\text{-}cc\text{-}pVTZ}} (\mathrm{Hz}), n = 6, r^2 = 0.976 \quad (9)$$

$$J_{\mathrm{exp}}(\mathrm{Hz}) = (0.76 \pm 0.03) J_{\mathrm{SOPPA/sad}J} (\mathrm{Hz}), n = 6, r^2 = 0.992 \quad (10)$$

Statistically, Eqn (10) is better than Eqn (9), but the slope is closer to 1 in the first case. Obviously both the methods are highly correlated:

$$J_{\mathrm{SOPPA/sad}J}(\mathrm{Hz}) = (0.80 \pm 0.19) + (1.29 \pm 0.01)\, J_{\mathrm{SOPPA/aug\text{-}cc\text{-}pVTZ}} (\mathrm{Hz}), n = 28, r^2 = 0.998 \quad (11)$$

A more detailed analysis of the differences between the SOPPA and B3LYP methods shows that the lone pair effect, in both the cases for the H–X–H systems (CH_4/CH_3^-, NH_4^+/NH_3, and PH_3/PH_2^-), is very similar to that when the atom placed in the middle of the coupling pathway has an electronic system with π–symmetry. In this last case, $^2J_{HH}$ has an important positive contribution.

In contrast, important discrepancies are found in the linear XH_2 molecules (LiH_2^-, NaH_2^-, BeH_2 and MgH_2), the B3LYP values being larger than the SOPPA ones. On the other hand, it is interesting to note that $^2J_{HH}$ do not change linearly with the H–H distance.

We have tried to analyze $^2J_{HH}$ (*gem*) as a function of some property of the central atom X. After some tests, we found that its electronegativity[16] χ and the H–X–H angle ϕ (Table 1) are the most important:

$$J_{\mathrm{SOPPA/sad}J}(\mathrm{Hz}) = -(7.7 \pm 1.3)\,\chi - (50 \pm 6)\cos\phi, n = 28, r^2 = 0.713 \quad (12)$$

Some conclusions can be drawn from Eqn (12), for instance, when the electronegativity increases, J_{gem} becomes more negative, and when the H–X–H angle opens ($\cos 90^\circ = 0$, $\cos 180^\circ = -1$), J_{gem} becomes more positive. However, the square correlation coefficient is rather low [an attempt using a^4 as defined by Barfield for geminal couplings in substituted methanes, $a^4 = \cos^2\phi/(1-\cos\phi)^2$, does not improve significantly the correlation, $r^2 = 0.720$].[17] This could signify that the 28 hydrides cannot be treated together and that they must be separated into different classes. A first attempt (Fig. 1) was to separate anions, neutral and cationic hydrides using electronegativity as the property. Although there is a shift from anions to cations, many hydrides are intermingled.

If the results are divided for each row of the periodic table and based on their charge (Fig. 2) and plotted against the atomic number of X, it seems clear that there is a similar behavior for derivatives of the first row on one hand and those of the second row on the other hand. The charge seems to modulate the shift of the value in each series.

Considering only the SOPPA/aug-cc-pVTZ results, it is possible to extract some characteristics of the couplings; i.e. when comparing the nonlinear XH_2, nonplanar XH_3 and XH_4, one can see the following trend: the addition of a hydrogen (proton) to the atom X decreases $^2J_{HH}$, as described in Ref. [4] as effect (c) of the geminal $^2J_{XY}$ SSCC and observed earlier by Pople and Bothner-By[18] in some small hydrocarbons. This pattern is also valid when considering the linear XH_2 (L) and the planar XH_3 (P).

The above-mentioned behavior is not without exceptions. Here, the abnormalities occur for Si and P when going from SiH_3^- (−7.22 Hz) to SiH_4 (−0.41 Hz) and from PH_3 (−13.62 Hz) to PH_4^+ (−3.12 Hz). However, such an abnormality can be justified by the increase of the H–X–H angle which results in a decrease of the corresponding geminal SSCC. This above dependence of the geminal $^2J_{HH}$ was studied earlier by Gutowsky *et al.*[19] and also included in the (d) effect of Ref. [4] as shown explicitly for ammonia.

An important characteristic, worth mentioning, is that the linear compounds XH_2 as well as the planar XH_3 ones have positive couplings whereas all others have negative values. Also, here we find two exceptions, *viz.* CH_3^+ (−0.29 Hz) and AlH_4^- (+0.78 Hz). And, in the same way, they can be explained according to effect (c) of Ref. [4], i.e. CH_3^+ possesses the shortest H–X distance which results in an inductive electron donation to the system and thereby a decrease in the geminal SSCC. However, AlH_4^- also presents the largest H–X distance which produces a net inductive electron withdrawal causing an increase in the geminal SSCC.

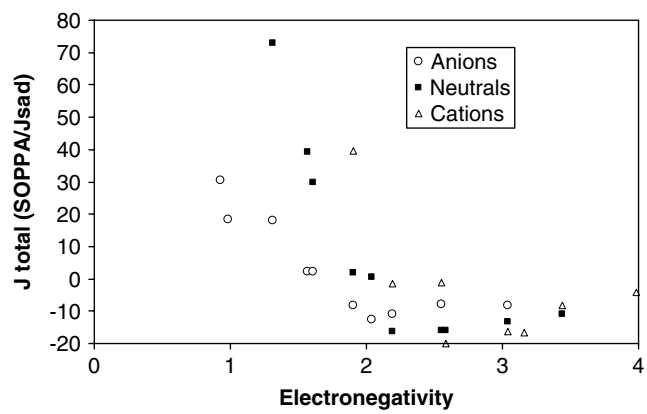

Figure 1. Plot of $^2J_{HH}$ coupling constants (SOPPA/sad*J*) *versus* the electronegativity of X.

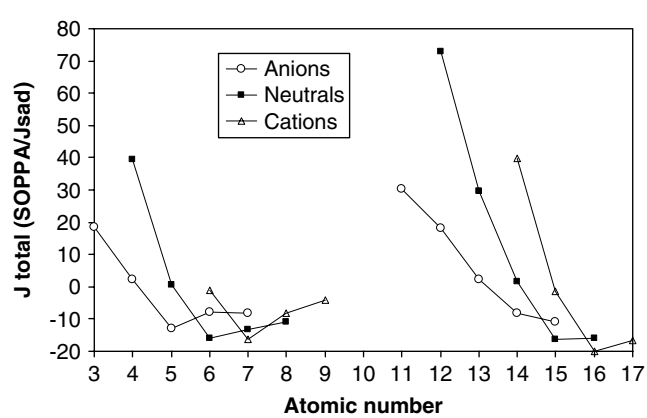

Figure 2. Plots of calculated (SOPPA/sad*J*) $^2J_{HH}$ *versus* the atomic number of X separated into three families and two periods.

Copyright © 2008 John Wiley & Sons, Ltd.

For all but XH_4, when X changes from an element of the second row to one of the third row the geminal SSCC increases in absolute value. The opposite behavior, observed for XH_4 may be directly related to the separation of the hydrogens and the inductive electron donation of the third row elements which is more efficient within the tetrahedral geometry. This is also consistent with what has just been mentioned for AlH_4^-.

Finally, another important finding is that the linear XH_2 and the planar XH_3 compounds do not accomplish the Dirac vector model, in agreement with other reports that have pointed out the limitation of the model.[20,21] They have positive couplings while they should be negative. In Ref. [4] the angular dependence of the geminal J_{HH} in ammonia and phosphine is explicitly shown, and suggested that the sign of this coupling could be used to find out the pyramidality at the N or P atoms of an amino or phosphine group in a larger compound. Thus, the more planar the configuration of the amino or phosphine group, the more positive is the geminal $^2J_{HH}$ coupling. This can be explained by the presence of lone pairs on the N or P atom, which reaccommodate themselves within a π-symmetry for the planar configuration [the (a) effect of Ref. [4]], and therefore offer a positive contribution to the geminal coupling.

The natural extension to the suggestion made in Ref. [4] can be extended naturally to the geminal $^2J_{HH}$ in XH_3 (XH_2); this, in turn, would afford the pyramidality (linearity) at the X-atom in a larger compound. However, this should be with caution for the already planar XH_3 (and linear XH_2) compounds, since they present an increasing geminal $^2J_{HH}$ for decreasing angles HXH. Such a behavior may be due to the back part of the X–H σ-bonds, which also participate in the electronic density of each other, producing a net increase in the electronic density for the planar (linear) configuration and hence, a diminution in the angle HXH of the XH_3 (XH_2). The above results in a diminution in the electronic density of the inner part of the X–H σ-bonds and an increase in the geminal $^2J_{HH}$. Therefore, with certainty we can predict that all the studied XH_3 (XH_2) will have a positive $^2J_{HH}$ for the angle HXH equal to 120° or 180° for a H–H distance of 2 Å or a bit larger.

Discussion of $^1J_{XH}$ coupling constants

The calculated $^1J_{XH}$ and the corresponding reduced coupling constants, *K*, have been reported in Tables 2 and 3, respectively. The one-bond reduced coupling constants, *K*, are positive accordingly to the Dirac vector model prediction. The main trend for these one-bond couplings is that the linear and planar compounds increase their reduced coupling constants when X goes from the second row to the third row of the periodic table, whereas all others experience a decrease. This last fact may be due to linear and planar compounds having a smaller electronic density in their X–H σ-bonds.

Comparison of the experimental and SOPPA calculated $^1J_{XH}$ lead to the following equations:

$$J_{exp}(\text{Hz}) = (1.233 \pm 0.025)J_{SOPPA/aug\text{-}cc\text{-}pVTZ}(\text{Hz}), \quad n = 9, r^2 = 0.997 \tag{13}$$

$$J_{exp}(\text{Hz}) = (0.959 \pm 0.007)J_{SOPPA/sadJ}(\text{Hz}) \quad n = 9, r^2 = 1.000 \tag{14}$$

Clearly, SOPPA/sad*J* provides better values than SOPPA/aug-cc-pVTZ both in terms of r^2 and slopes.

Table 2. $^1J_{XH}$ coupling constants (compounds in bold are those for which experimental data are known)

No.	Hydride[a]	Nucleus	SOPPA aug-cc-pVTZ	SOPPA sad*J*	Exptl
1	LiH_2^- (L)	^{7}Li	44.4	46.3	
2	BeH_2 (L)	^{9}Be	−53.6	−54.4	
3	NaH_2^- (L)	^{23}Na	118.4	151.0	
4	MgH_2 (L)	^{25}Mg	−60.9	−84.6	
5	NH_2^-	^{15}N	−44.9	−48.7	
6	**OH_2**	^{17}O	−77.1	−82.6	−78.7[22]
7	FH_2^+	^{19}F	603.0	655.2	
8	**PH_2^-**	^{31}P	99.3	138.5	139.0[23]
9	SH_2	^{33}S	28.1	35.0	
10	ClH_2^+	^{35}Cl	50.6	56.2	
11	BeH_3^- (P)	^{9}Be	−22.1	−22.0	
12	BH_3 (P)	^{11}B	127.5	130.0	
13	CH_3^+ (P)	^{13}C	171.5	183.6	
14	MgH_3^- (P)	^{25}Mg	−25.3	−36.4	
15	AlH_3 (P)	^{27}Al	204.7	282.7	
16	SiH_3^+ (P)	^{29}Si	−233.9	−312.2	
17	CH_3^-	^{13}C	119.5	128.8	
18	**NH_3**	^{15}N	−57.2	−64.0	−61.2[24]
19	OH_3^+	^{17}O	−116.0	−122.8	
20	SiH_3^-	^{29}Si	−56.0	−80.9	
21	**PH_3**	^{31}P	149.6	201.2	185.6[25]
22	SH_3^+	^{33}S	41.5	49.9	
23	**BH_4^-**	^{11}B	77.0	79.2	82.0[26]
24	**CH_4**	^{13}C	112.3	127.6	125.3[25]
25	**NH_4^+**	^{15}N	−71.3	−80.8	−73.3[24]
26	AlH_4^-	^{27}Al	122.9	170.9	
27	**SiH_4**	^{29}Si	−151.9	−206.7	−203.0[23]
28	**PH_4^+**	^{31}P	441.6	571.8	547.0[23]

[a] L, linear; P, planar

The representation of *K versus* the atomic number for the compounds of each row and a given charge (Fig. 3) shows a similar tendency for the data of the second row of the periodic table, modulated by the charge as previously in the $^2J_{HH}$. The data of the third row presents more complex behavior. Attempts using the electronegativity as classifying criteria, and even separating anions/neutrals/cations and first period/second period, does not produce any useful information.

Computational Details

The geometry of the molecules has been fully optimized at the MP2 computational level[27] with the aug-cc-pVTZ basis set[28] within the Gaussian-03 package.[29] The structures obtained have been confirmed to be energetic minima at the same computational level. The SSCC at the B3LYP[30] computational level with 6–311++G**[31] and aug-cc-pVTZ basis sets have been carried out with the Gaussian-03 program and the corresponding SOPPA[32] level of approximation have been obtained using sad-J[33] and aug-cc-pVTZ basis sets with the DALTON 2.0 program.[34]

Sad-J basis set is based on Sadlej's medium size polarized basis sets (Sadlej-pVTZ),[33c–g] and according to the procedure described in Ref. [32b] (and therein cited references) with the

Copyright © 2008 John Wiley & Sons, Ltd.

Table 3. Reduced coupling constant $^1K_{XH}$ (Hz)

No.	Hydride	Exptl	SOPPA/aug-cc-pVTZ	SOPPA/sadJ
1	LiH_2^-		3.66	3.82
2	BeH_2		12.21	12.41
3	NaH_2^-		14.34	18.28
4	MgH_2		31.85	44.28
5	NH_2^-		14.19	15.40
6	**OH_2**	18.60	18.22	19.53
7	FH_2^+		20.53	22.31
8	PH_2^-	11.00	7.86	10.96
9	SH_2		11.72	14.62
10	ClH_2^+		16.53	18.36
11	BeH_3^-		5.03	5.02
12	BH_3		12.74	12.98
13	CH_3^+		21.86	23.40
14	MgH_3^-		13.26	19.03
15	AlH_3		25.16	34.74
16	SiH_3^+		37.70	50.32
17	CH_3^-		15.23	16.41
18	**NH_3**	19.34	18.09	20.25
19	OH_3^+		27.42	29.01
20	SiH_3^-		9.03	13.05
21	**PH_3**	14.68	11.83	15.92
22	SH_3^+		17.32	20.81
23	BH_4^-	8.19	7.69	7.91
24	**CH_4**	15.97	14.32	16.26
25	NH_4^+	23.23	22.53	25.53
26	AlH_4^-		15.10	21.01
27	**SiH_4**		24.49	33.31
28	PH_4^+	43.27	34.93	45.23

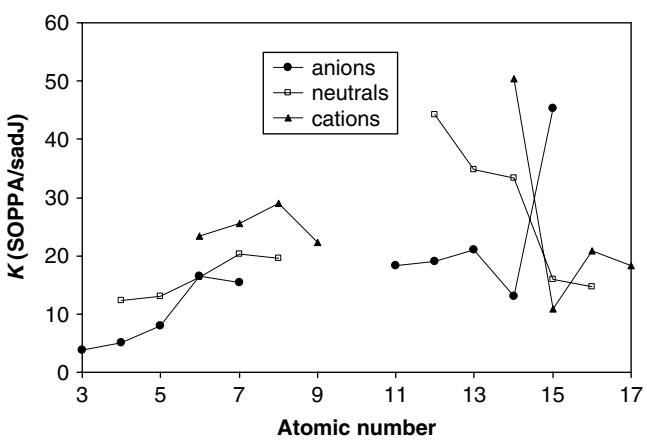

Figure 3. Reduced coupling constant, *K versus* the atomic number of the central atom in the systems studied.

standard basis set totally uncontracted and augmented with four s-type functions with very large exponents in an even-tempered manner. For hydrogen, it consists of (10s4p) functions; (14s5p4d) functions for the elements of the second period and (17s10p6d) functions for the third period. The last period also includes two tight d-type functions. In order to reduce the size of the basis set, it is re contracted using the molecular orbital coefficients at self-consistent-field calculations performed with the uncontracted basis sets for the smallest neutral hydrides. Such procedure ensures a good description of the Fermi contact and dia- and paramagnetic terms as well as provides a small basis set size. Recently, the sad-J basis set was completed for all the elements of the second and third periods.[35] The use of the mentioned procedure has already been shown by other authors to provide good basis sets for the calculation of *J*-coupling constants.[36]

Supplementary material

Supplementary electronic material for this paper is available in Wiley InterScience at http://www.interscience.wiley.com/jpages/0749-1581/suppmat/

Acknowledgements

This work was carried out with financial support from the Ministerio de Ciencia y Tecnología (Projects No. CTQ2006-14487-C02-01/BQU) and Comunidad Autónoma de Madrid (Project MADRISOLAR, ref. S-0505/PPQ/0225). Thanks are due to CTI (CSIC) and CESGA for allocation of computer time. GAA and PFP are members of the Argentinean National Research Council, CONICET, and acknowledge financial support from CONICET (PIP 5119/2004) and FONCYT (PICT 21604/2004).

References

[1] Kalinowski HO, Berger S, Braun S. *Carbon-13 NMR Spectroscopy*. Wiley: Chichester, 1988; 488.
[2] (a) Del Bene JE, Perera SA, Bartlett RJ. *J. Am. Chem. Soc.* 2000; **122**: 3560; (b) Del Bene JE, Bartlett RJ. *J. Am. Chem. Soc.* 2000; **122**: 10480; (c) Krivdin LB, Sauer SPA, Peralta JE, Contreras RH. *Magn. Reson. Chem.* 2002; **40**: 187; (d) Barfield M. *Magn. Reson. Chem.* 2003; **41**: 344; (e) Alkorta I, Elguero J. *Int. J. Mol. Sci.* 2003; **4**: 64; (f) Wu A, Cremer D. *Int. J. Mol. Sci.* 2003 **4**: 158; (g) Kaupp M, Bühl M, Malkin VG (eds). *Calculation of NMR and EPR Parameters, Theory and Applications*. Wiley-VCH: Weinheim, 2004; (h) Jensen F. *J. Chem. Theory Comput.* 2006; **2**: 1360; (i) Zhao H, Pan Q, Zhang W, Carmichael I, Serianni AS. *J. Org. Chem.* 2007; **72**: 7071; (j) Bagno A, Saielli G. *J. Am. Chem. Soc.* 2007; **129**: 11360.
[3] Ramsey NF. *Phys. Rev.* 1953; **91**: 303.
[4] Contreras RH, Peralta JE. *Prog. Nucl. Magn. Reson. Spectrosc.* 2000; **37**: 321.
[5] (a) Shayesteh A, Appadoo DRT, Gordon I, Bernath PF. *J. Chem. Phys.* 2003; **119**: 7785; (b) Wang X, Andrews L. *J. Phys. Chem. A* 2004; **108**: 11511.
[6] Wigglesworth RD, Raynes WT, Sauer SPA, Oddershede J. *Mol. Phys.* 1998; **94**: 851.
[7] Berthier C, Berthier G. *Theor. Chim. Acta* 1969; **14**: 71.
[8] Lazzeretti P, Rossi E, Taddei F, Zanasi R. *J. Phys. Chem.* 1982; **77**: 408.
[9] Dreeskamp H, Schumann C. *Chem. Phys. Lett.* 1968; **1**: 55.
[10] Nair AC, Chandra P. *Theor. Chim. Acta* 1994; **89**: 261.
[11] Sanders JKM, Hunter BK, Jameson CJ, Romeo G. *Chem. Phys. Lett.* 1988; **143**: 471.
[12] Barfield M, Grant DM. *J. Am. Chem. Soc.* 1961; **83**: 4726.
[13] Perrin CL, Engler RE. *J. Phys. Chem.* 1991; **95**: 8431.
[14] Mikkelsen KV, Ruud K, Helgaker T. *J. Comput. Chem.* 1999; **20**: 1281.
[15] Enevoldsen T, Oddershede J, Sauer SPA. *Theor. Chem. Acc.* 1998; **100**: 275.
[16] *CRC Handbook of Chemistry and Physics* (84th edn). Lide DL (ed.), CRC press: Boca Raton, FL, 2004.
[17] Barfield M. *Magn. Reson. Chem.* 2007; **45**: 634.
[18] Pople JA, Bothner-By AA. *J. Chem. Phys.* 1965; **42**: 1339.
[19] Gutowsky HS, Karplus M, Grant DM. *J. Chem. Phys.* 1959; **31**: 1278.
[20] (a) Del Bene JE, Elguero J. *Chem. Phys. Lett.* 2003; **382**: 100; (b) Del Bene JE, Elguero J. *J. Phys. Chem. A* 2005; **109**: 10753; (c) Del Bene JE, Elguero J. *Magn. Reson. Chem.* 2007; **45**: 714.
[21] Aucar GA. Concepts in NMR, accepted.
[22] Wasylishen RE, Friedrich JO. *Can. J. Chem.* 1987; **65**: 2238.

 Copyright © 2008 John Wiley & Sons, Ltd.

[23] Cowley AH, White WD. *J. Am. Chem. Soc.* 1969; **91**: 1917.
[24] Berger S, Braun S, Kalinowski HO. *NMR Spectroscopy of the Nonmetallic Elements*. John Wiley & Sons: Chichester, 1997; 245.
[25] Jameson CJ, Osten HJ. *J. Am. Chem. Soc.* 1986; **108**: 2497.
[26] Giese HH, Nöth H, Schwenk H, Thomas S. *Eur. J. Inorg. Chem.* 1998; 941.
[27] Moller C, Plesset MS. *Phys. Rev.* 1934; **46**: 61.
[28] Dunning TH Jr. *J. Chem. Phys.* 1989; **90**: 1007.
[29] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA. *Gaussian 03, Revision B.05*. Gaussian: Wallingford, 2003.
[30] (a) Becke AD. *J. Chem. Phys.* 1993; **98**: 5648; (b) Lee C, Yang W, Parr RG. *Phys. Rev. B* 1988; **37**: 785; (c) Miehlich B, Savin A, Stoll H, Preuss H. *Chem. Phys. Lett.* 1989; **157**: 200.
[31] Krishnan R, Binkley JS, Seeger R, Pople JA. *J. Chem. Phys.* 1980; **72**: 650.
[32] (a) Nielsen ES, Jorgensen P, Oddershede J. *J. Chem. Phys.* 1980; **73**: 6238; (b) Geertsen J, Oddershede J. *J. Chem. Phys.* 1984; **90**: 301; (c) Packer MJ, Dalskov EK, Enevoldsen T, Jensen HJA, Oddershede J. *J. Chem. Phys.* 1996; **105**: 5886.
[33] (a) Provasi PF, Aucar GA, Sauer SPA. *J. Chem. Phys.* 2000; **112**: 6201; (b) Provasi PF, Aucar GA, Sauer SPA. *J. Chem. Phys.* 2001; **115**: 1324; (c) Sadlej AJ, Urban M. *Theochem-J. Mol. Struct.* 1991; **80**: 147; (d) Sadlej AJ. *Theor. Chim. Acta* 1992; **81**: 339; (e) Sadlej AJ. *Collect. Czech. Chem. Commun.* 1995; **53**: 1988; (f) Urban M, Sadlej AJ. *Mol. Phys.* 1997; **92**: 587; (g) Cernusak I, Kello V, Sadlej AJ. *Collect. Czech. Chem. Commun.* 2003; **68**: 211.
[34] Dalton, a molecular electronic structure program, Release 2.0, 2005.
[35] Provasi PF, Sauer SPA. To be submitted.
[36] (a) Peralta JE, Scuseria GE, Cheeseman JR, Frish MJ. *Chem. Phys. Lett.* 2003; **375**: 452; (b) Deng W, Cheeseman JR, Frish MJ. *J. Chem. Theory Comput.* 2006; **2**: 1028; (c) Jensen F. *J. Chem. Theory Comput.* 2006; **2**: 1360.

 Copyright © 2008 John Wiley & Sons, Ltd.