

Regular article

Karplus-type relationships between scalar coupling constants: ${}^3J_{\text{HH}}$ molecular versus ${}^4\text{h}J_{\text{HH}}$ supramolecular coupling constants

Ibon Alkorta, José Elguero

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

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Abstract. The ${}^3J_{\text{HH}}$ coupling constants in six H–X–Y–H systems (ethane, methylamine, methanol, hydrazine, hydroxylamine and hydrogen peroxide) and ${}^4\text{h}J_{\text{HH}}$ coupling constants in four H–X⋯H⋯Y–H, namely $[\text{H}_3\text{N}\cdots\text{H}\cdots\text{NH}_3]^+$ (two arrangements), $\text{HOH}\cdots\text{NH}_3$ and $\text{HOH}\cdots\text{OH}_2$ have been calculated theoretically as a function of the torsion angle φ . For covalent situations, the corresponding Karplus equations have been fitted to calculated ${}^3J_{\text{HH}} = a\cos 2\varphi + b\cos\varphi + c$. The a , b and c terms have been analyzed as a function of the electronegativities of X and Y . In the case of ammonium/ammonia complexes (proton shared and not), water/ammonia, and water dimer the values are low (maximum 0.5 Hz) but follow closely a Karplus relationship. Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s00214-003-0486-7>.

Keywords: Coupling constants – Karplus relationship – Hydrogen bonds – Density functional theory calculations

Introduction

There are a small number of publications dealing with the calculation of ${}^1\text{H}$ – ${}^1\text{H}$ scalar coupling constants in complexes of two molecules linked by a hydrogen bond and discussing, at the same time, its angular dependence [1]. Amongst the most significant contributions are those by Pecul and Sadlej [2] on the water dimer (${}^4\text{h}J_{\text{HH}} =$

-0.08 Hz for the optimized conformation, dihedral angle $\varphi = 122.8^\circ$), Czernek and Brüschweiler [3] on models of protein–nucleotide complexes, and by Barfield [4] on the formamide dimer, where it is reported that ${}^3\text{h}J_{\text{HH}}$ depends on a torsion angle (see also Ref. [5]). Perera and Bartlett [6] have reported the successful attempt to reproduce the experimental Karplus relation for *N*-methylacetamide, as a model peptide, using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method. With the exception of the water dimer, the other examples show angular dependencies, often in the form of $\cos^2\varphi$, but are not the supramolecular counterparts of the Karplus equation. Therefore, the following question was raised: is there a supravincinal ${}^4\text{h}J_{\text{HH}}$ coupling constant equation similar to the vicinal ${}^3J_{\text{HH}}$ Karplus equation?

To answer this question we proceeded in the following way.

1. Firstly, we calculated the ethane molecule **1** and fitted its ${}^3J_{\text{HH}}$ to a Karplus equation as a test. Ethane has been studied many times at various levels of theory.
2. Secondly, we calculated two molecules related to ethane, where one carbon atom was replaced by nitrogen, methylamine (**2**), and by oxygen, methanol (**3**), as classical examples of perturbation.
3. Thirdly, we calculated three cases where both carbon atoms of ethane were replaced by heteroatoms, hydrazine (**4**), hydroxylamine (**5**) and hydrogen peroxide (**6**), a series of rather neglected compounds (may be owing to the lack of experimental results).
4. Finally, we calculated four supermolecules: $[\text{H}_3\text{N}\cdots\text{H}\cdots\text{NH}_3]^+$ (**7a** and **7b**), $[\text{HOH}\cdots\text{NH}_3]$ (**8**) and $[\text{HOH}\cdots\text{OH}_2]$ (**9**).

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Correspondence to: I. Alkorta
e-mail: ibon@iqm.csic.es

Method of calculation

The geometry of the systems was optimized at the B3LYP/6-311++G** level [7, 8] with the Gaussian98 package [9]. For the supramolecular systems we assumed a linear disposition of the X–

H...Y fragment. All four components of the H–H spin–spin couplings were calculated at the UB3LYP/6-311++G** level of theory using a modified version of Gaussian98 [10, 11, 12, 13]. The B3LYP functional was employed since it has been reported to provide reliable J -coupling prediction [12]. As a practical matter, Fermi-contact (FC) [10] and spin-dipole [12] terms were evaluated by means of finite perturbation theory (FPT), while the paramagnetic spin–orbit (PSO) contribution was obtained via coupled perturbed density functional theory. Since Gaussian98 does not presently calculate one-electron integrals for the PSO and diamagnetic spin–orbit components, these were determined with the DALTON 1.0 package [14] and used within the Gaussian98 program. A convergence criterion for the self-consistent field (SCF) of 10^{-10} au was used. The four terms of the coupling constants were calculated for each conformation resulting from rotating the systems in 10° steps. In the case of the water dimer, the minimum energy corresponds to $\varphi = 117.3^\circ$, close to the value obtained by Pecul and Sadlej [2] ($\varphi = 122.8^\circ$).

For the molecular systems, where there are many high-level calculations available, our results will be compared with both experimental and theoretical results in an attempt to show that our approach is reasonable. Since this is not proof enough that the same will still be true for supermolecules, for one of the hydrogen-bonded systems, $[\text{N}_2\text{H}_7]^+$, we have compared our results (Table 1) with those obtained using the EOM-CCSD theory in the configuration interaction (CI)-like approximation [15, 16, 17, 18].

Since the agreement is acceptable, it is reasonable to assume that, as far as ^1H – ^1H coupling constants are concerned, the FPT/UB3LYP/6-311++G** calculations provide reasonable values. Note also that the CAS2 and RAS4 calculations of Pecul and Sadlej [2] yield a value of $^4hJ_{\text{HH}} = -0.08$ and -0.09 Hz, respectively,

for the optimized structure of the water dimer, while we calculated $^4hJ_{\text{HH}} = -0.05$ Hz for the geometry obtained at the B3LYP/6-311++G** level.

Results and discussion

Ethane (1), methylamine (2), methanol (3), hydrazine (4), hydroxylamine (5) and hydrogen peroxide (6).
Comparison of the six molecules

The results of the calculations are given as supplementary material. In Table 2 are reported the fitted Karplus equations: $^3J_{\text{HH}} = a\cos 2\varphi + b\cos\varphi + c$ [19, 20, 21]. To transform a Karplus equation of the form $^3J_{\text{HH}} = A\cos^2\varphi + B\cos\varphi + C$ into another of the form $^3J_{\text{HH}} = a\cos 2\varphi + b\cos\varphi + c$, it suffices to use $a = A/2$, $b = B$ and $c = C + (A/2)$ [21]. We should note that the FC term is very dominant in the total value of $^3J_{\text{HH}}$ coupling in our case (Table 2) and in all examples described in the literature. In Table 2, the c term corresponds, in the case of ethane assuming free rotation, to the average value of $^3J_{\text{HH}}$. In this case, our value, 6.89 Hz (Eq. 2), is close to the EOM-CCSD calculation (6.67 Hz) [22] but still far from the experimental value (8.02 Hz) [23]. Guilleme et al. have computed an average value of 7.77 Hz (multiconfigurational SCF, MCSCF) [23, 24], while Wigglesworth et al. [25] and Provasi et al. [26] obtained 7.64–7.92 Hz.

Strictly speaking, no empirical Karplus relationship has been devised for ethane itself; those reported in the literature are from CH–CH fragments in molecules without angular strain and electronegative substituents. We have collected in Table 3, our theoretical equation (Table 2) and some equations reported by several authors.

Probably, the empirical equation (Eq. 21) reported by San Fabián et al. [31] is the most representative for ethane itself. The others, in their attempt to be very general, are somewhat less representative of the parent compound (1).

We have reported the cases of methylamine and methanol in Table 4. Here again, our results are comparable to those described by other authors.

Pecul and Sadlej [34] calculated J_{HH} in both compounds at the MCSCF level. They reported the arith-

Table 1. Selected values of $^4hJ_{\text{HH}}$ for $[\text{N}_2\text{H}_7]^+$ hydrogen-bonded complex (all terms in hertz), paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO), Fermi contact (FC), spin dipole (SD)

Complex	Method	PSO	DSO	FC	SD	Total J
C_{3v} (staggered) ^a	EOM-CCSD ^c	1.62	-1.89	0.15	0.04	-0.08
C_{3v} (staggered) ^a	FPT-B3LYP	1.57	-1.89	0.14	0.05	-0.13
C_{3v} (staggered) ^b	EOM-CCSD ^c	0.72	-0.89	0.18	0.00	0.01
C_{3v} (staggered) ^b	FPT-B3LYP	0.69	-0.87	0.18	0.00	0.00
D_{3d} (staggered) ^a	EOM-CCSD ^c	1.74	-2.03	0.23	0.05	-0.01
D_{3d} (staggered) ^a	FPT-B3LYP	1.65	-1.99	0.20	0.05	-0.09
D_{3d} (staggered) ^b	EOM-CCSD ^c	0.76	-0.94	0.26	0.00	0.08
D_{3d} (staggered) ^b	FPT-B3LYP	0.72	-0.91	0.23	0.00	0.04

^aTwo hydrogens in plane (trans)

^bOne hydrogen in plane, one out of plane

^cDel Bene JE (2003) personal communication. MP2/6-31+G** optimized geometries and EOM-CCSD with the Ahlrichs basis sets for the coupling constants

Table 2. Karplus relationships for molecules 1–6

Molecule	Contribution	a	b	c	r^2	Equation
$\text{H}_3\text{C}-\text{CH}_3$ (1)	FC	6.63 ± 0.04	-0.99 ± 0.04	7.15 ± 0.03	0.999	1
	Total	6.73 ± 0.04	-0.64 ± 0.04	6.89 ± 0.03	0.999	2
$\text{H}_3\text{C}-\text{NH}_2$ (2)	FC	6.77 ± 0.06	-1.97 ± 0.06	6.55 ± 0.04	0.997	3
	Total	6.85 ± 0.06	-1.63 ± 0.06	6.27 ± 0.04	0.997	4
$\text{H}_3\text{C}-\text{OH}$ (3)	FC	6.29 ± 0.03	-2.29 ± 0.03	5.76 ± 0.02	0.999	5
	Total	6.53 ± 0.03	-1.79 ± 0.03	5.41 ± 0.02	0.999	6
$\text{H}_2\text{N}-\text{NH}_2$ (4)	FC	6.21 ± 0.17	-1.72 ± 0.18	5.37 ± 0.12	0.990	7
	Total	6.68 ± 0.17	-1.14 ± 0.18	5.15 ± 0.12	0.990	8
$\text{H}_2\text{N}-\text{OH}$ (5)	FC	5.02 ± 0.08	-1.09 ± 0.08	4.40 ± 0.05	0.992	9
	Total	5.81 ± 0.11	-0.38 ± 0.11	4.32 ± 0.08	0.986	10
$\text{HO}-\text{OH}$ (6)	FC	3.32 ± 0.06	-0.22 ± 0.06	3.08 ± 0.04	0.989	11
	Total	5.17 ± 0.06	0.66 ± 0.06	3.55 ± 0.05	0.995	12

Table 3. Comparison of Karplus equations for ethanes

Author	Origin	a	b	c	Equation
This work	Calculated	6.73	-0.64	6.89	13
Guilleme et al. [24]	Calculated	6.99	-0.47	7.76	14
Pecul et al. [27]	Calculated	6.44	-1.16	7.13	15
Fukui et al. [28]	Calculated	5.83	-0.13	5.22	16
Karplus [19]	Empirical	4.5	-0.5	4.22	17
Pachler [29]	Empirical	4.06	-1.3	4.21	18
Imai and Osawa [30]	Empirical	4.96	-1.35		19
Barfield and Smith [21]	Empirical	4.2	-0.5	4.4	20
San Fabián et al. [31]	Empirical	7.1	-1.2	8.02	21

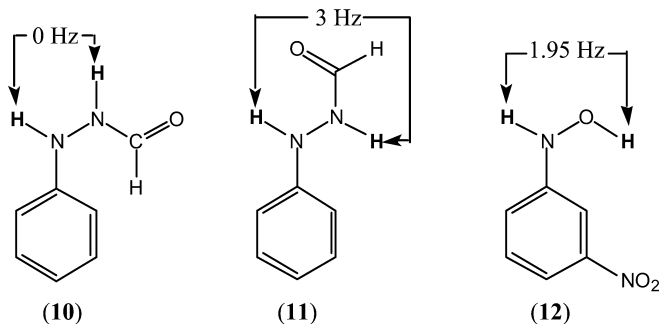
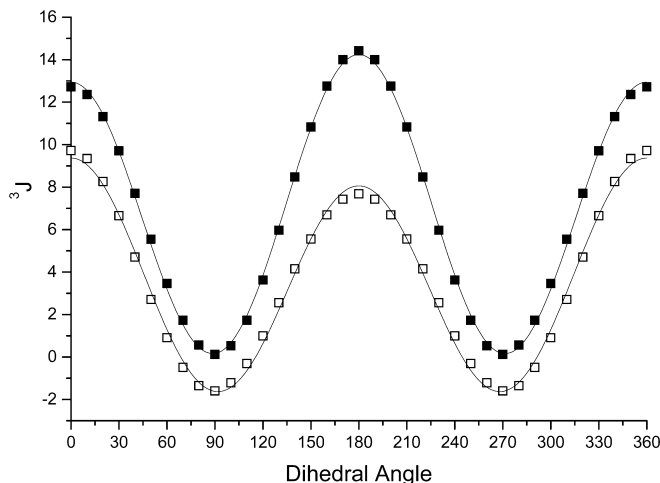
Table 4. Comparison of Karplus equations for methylamine and methanol

Author	Origin	a	b	c	Equation
Methylamine (2)					
This work	Calculated	6.85	-1.63	6.27	22
Fukui et al. [32]	Calculated	6.17	-0.99	4.60	23
Fukui et al. [28]	Calculated	6.35	-1.26	5.20	24
Govil [33]	Empirical	4.45	-1.80	5.35	25
Methanol (3)					
This work	Calculated	6.53	-1.79	5.41	26
Fukui et al. [32]	Calculated	5.82	-1.18	3.95	27
Fukui et al. [28]	Calculated	5.97	-1.23	4.15	28
Govil [33]	Empirical	5.20	-1.50	5.40	29

metically averaged results for the staggered conformation: **(2)** 6.21 (experiment 7.10 Hz [35]) and **(3)** 5.00 (experiment 5.0, 5.5 ± 1.5 Hz [36]). The results obtained in this work and displayed in Table 4 correspond to 6.57 and 5.53 Hz, respectively.

Owing to the presence of two exchangeable protons, there are no data on $^3J_{\text{HH}}$ coupling constants in hydrazine **(4)** (the degeneracy could have been removed using the $^{14}\text{N}/^{15}\text{N}$ derivative) or in hydroxylamine **(5)** or hydrogen peroxide **(6)**. The only related data are summarized in Scheme 1; they concern hydrazides **10** and **11** and one *N*-arylhydroxylamine **12** [37, 38, 39].

We optimized the geometries of these compounds **(12)** without the nitro group) at the B3LYP/6-31G* level. The corresponding dihedral angles are $\varphi = 110.5^\circ$ (**10**), 123.2° (**11**) and 76.7° (**12**). According to the equations of Table 4, these angles correspond to $^3J_{\text{HH}}$ values of 0.51, 3.10 and -0.96 Hz. Reciprocally, the $^3J_{\text{HH}}$ values of

**Scheme 1.** Experimental $^3J_{\text{HH}}$ couplings in hydrazine and hydroxylamine derivatives**Fig. 1.** Graphical representation of the Karplus equation for **1** (closed squares) and **6** (open squares)

Scheme 1 correspond to $\varphi = 107.4^\circ$ (**10**), 122.8° (**11**) and 55.9° (**12**). The agreement is satisfactory.

The case of hydrogen peroxide was studied theoretically by Galasso (SOS CI) [40]. He adjusted his calculated values to an extended Karplus-like equation:

$$^3J_{\text{HH}} = 8.71 + 0.59 \cos \varphi + 7.85 \cos 2\varphi + 0.89 \cos 3\varphi \quad (30)$$

This equation corresponds to values much larger than those provided by our Eq. (12) (e.g., for $\varphi = 0^\circ$, $J = 18.04$ Hz in place of 6.18 Hz).

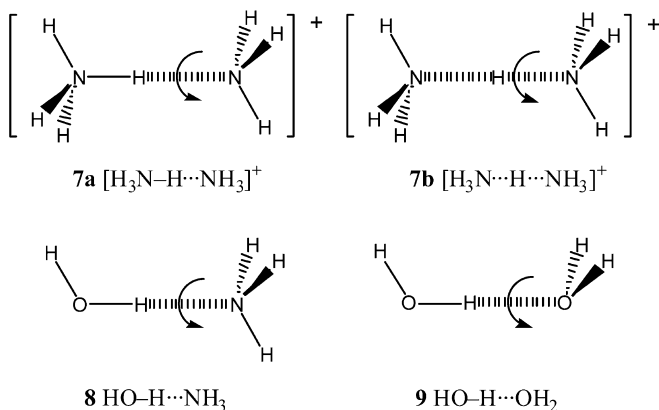
The shape of the Karplus equation depends on the coefficients a , b and c . The two maxima are for $\varphi = 0^\circ$, $J = a + b + c$ and for $\varphi = 180^\circ$, $J = a - b + c$; therefore, the difference (the asymmetry) is $-2b$. The minimum for $\varphi = 90^\circ$ corresponds to $J = -a + c$. We have illustrated in Fig. 1 the behavior of the two most extreme cases, ethane and hydrogen peroxide.

The coefficients of the Karplus equations reported in Table 2 (total J) show some regularities that deserve to be analyzed. A simple approach is to count the number of methyl, amino and hydroxy groups (0, 1 or 2) and try multiregressions Eqs. (31), (32) and (33):

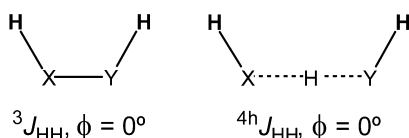
$$a = (3.48 \pm 0.12)n_{\text{Me}} + (3.32 \pm 0.12)n_{\text{NH}_2} + (2.65 \pm 0.12)n_{\text{OH}}, n = 6, r^2 = 0.999, \quad (31)$$

$$b = -(0.68 \pm 0.37)n_{\text{Me}} - (0.61 \pm 0.37)n_{\text{NH}_2} + (0.07 \pm 0.37)n_{\text{OH}}, n = 6, r^2 = 0.715, \quad (32)$$

$$c = (3.51 \pm 0.06)n_{\text{Me}} + (2.60 \pm 0.06)n_{\text{NH}_2} + (1.78 \pm 0.06)n_{\text{OH}}, n = 6, r^2 = 1.000. \quad (33)$$



Scheme 2. Schematic representation of the supermolecules studied



Scheme 3. Schematic representation of the $F=0^\circ$ geometries for the bonded and hydrogen bonded systems

Note: F corresponds to the greek letter shown in the scheme

In the case of b (which is smaller in absolute value than a and c) the results are not satisfactory. For a and c , the terms in the Karplus relationship reflect the decreasing importance of $\text{CH}_3 > \text{NH}_2 > \text{OH}$, roughly reciprocal to their electronegativities (Gordy's χ values C 2.55, N 2.98, O 3.45) [41, 42].

$$(a + c)/2 = (7.2 \pm 0.3) - (1.4 \pm 0.1)_\chi, n = 3, r^2 = 0.995 \quad (34)$$

The dependence of the ${}^3J_{\text{HH}}$ coupling constant of an $X-\text{CH}_2-\text{CH}_3$ fragment on the electronegativity of X is well known [43, 44]. But in the present case, the electronegativities of X and Y are those of $\text{H}-X-Y-\text{H}$ molecules, i.e., a very different situation.

Ammonia-ammonium (7), water-ammonia (8) and water dimer (9)

The molecules are shown in Scheme 2 and the results are shown in Fig. 2. These curves were adjusted to Karplus-

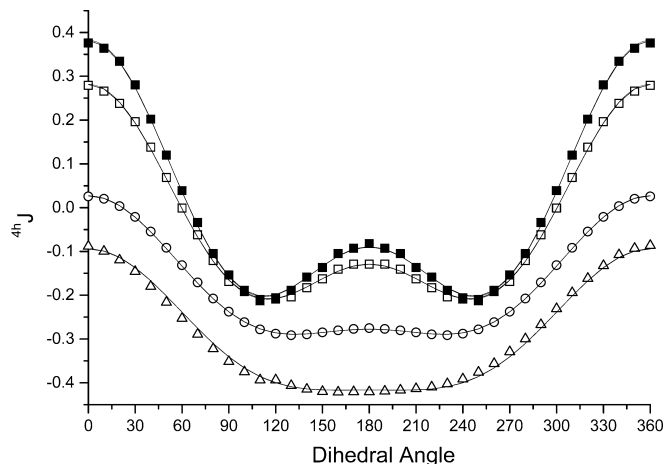


Fig. 2. Graphical representation of the Karplus equation for **7a** (closed squares), **7b** (open squares), **8** (circles) and **9** (triangles)

type relationships of the form ${}^4hJ_{\text{HH}} = a\cos 2\varphi + b\cos\varphi + c$. The corresponding equations are reported in Table 5.

With the exception of the FC term for the water dimer Eq. (41), the fitting is very good ($r^2 > 0.999$), proving that the Karplus relationship is also valid in supramolecular complexes. In the case of the water dimer (FC term), the addition of a fourth term slightly improves the fitting: ${}^4hJ_{\text{HH}} = (0.0308 \pm 0.0011)\cos 2\varphi + (0.0623 \pm 0.0021)\cos\varphi + (0.0024 \pm 0.0018)\cos\varphi/2 - (0.0097 \pm 0.0032)$, $r^2 = 0.994$. An attempt to use an equation similar to Eq. (1) (hydrogen peroxide) [40] does not improve the preceding one ($r^2 = 0.992$).

To compare with covalent models, ethane and hydrazine, we selected the calculated (at the same level) value of the coupling constant for $\varphi = 0^\circ$, ${}^3J_{\text{HH}} = 12.53$ Hz (H-H distance 2.356 Å) and ${}^3J_{\text{HH}} = 8.96$ Hz (H-H distance 2.116 Å), respectively. For the four examples of Table 3, the average H-H distance for $\varphi = 0^\circ$ is 3.492 Å. There is an effect of the non-hydrogen atoms involved (the heavier, the lower ${}^3J_{\text{HH}}$), while the effect of the distance is not so obvious (the H-H distance is shorter in hydrazine). Nevertheless, all the computational data indicate that, all other things being equal, a lengthening of the H-H distance will produce a decrease of J_{HH} . Therefore, the near 100-fold decrease from a covalent ${}^3J_{\text{HH}}$ to a hydrogen-bonded ${}^4hJ_{\text{HH}}$ should be related to the number of bonds (from 3 to 4) and to the bond order of 1

Table 5. Adjusted parameters for Karplus-type relationships between the FC term and total ${}^4hJ_{\text{HH}}$ versus the dihedral angle φ

System	Contribution	a	b	c	r^2	Equation
$[\text{H}_3\text{NH}\cdots\text{NH}_3]^+$	FC	0.0942 ± 0.0006	0.1202 ± 0.0006	0.1672 ± 0.0004	0.9994	(35)
	Total	0.12094 ± 0.0008	0.20555 ± 0.0008	-0.04464 ± 0.0006	0.9996	(36)
$[\text{H}_3\text{N}\cdots\text{H}\cdots\text{NH}_3]^+$	FC	0.1219 ± 0.0008	0.1449 ± 0.0008	0.2185 ± 0.0006	0.9992	(37)
	Total	0.15244 ± 0.001	0.23577 ± 0.001	-0.0051 ± 0.0008	0.9995	(38)
$\text{HOH}\cdots\text{NH}_3$	FC	0.0432 ± 0.0002	0.0624 ± 0.0002	0.0425 ± 0.0002	0.9996	(39)
	Total	0.05644 ± 0.0003	0.15237 ± 0.0003	-0.18139 ± 0.0002	0.9998	(40)
$\text{HOH}\cdots\text{OH}_2$	FC	0.0298 ± 0.001	0.0679 ± 0.001	0.0077 ± 0.0006	0.992	(41)
	Total	0.03707 ± 0.0008	0.16802 ± 0.0008	-0.28983 ± 0.0006	0.9992	(42)

in the case of covalent bonds and 0.5 for hydrogen bonds [45, 46].

Conclusion

Nearly 45 years after its discovery, the Karplus relationship appears to be very robust (in its statistical meaning) [47]. An examination of Figs 1 and 2 separately shows that molecular systems, on one hand, and supramolecular systems, on the other, behave very similarly; however, a cross-comparison of both figures leads to the conclusion that not only the supramolecular coupling constants are much weaker, but that the profile is rather different, in particular the $0^\circ/180^\circ$ values are inverted, and even the 180° maximum almost disappears in some cases (water dimer). The use of steep (high-exponent) basis functions in J -coupling computations appears to be justified on the basis of the good results obtained [48].

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References

- Alkorta I, Elguero J (2003) *Int J Mol Sci* 4:64
- Pecul M, Sadlej J (1999) *Chem Phys Lett* 308:486
- Czernek J, Brünschweiler R (2001) *J Am Chem Soc* 123:11079
- Barfield B (2002) *J Am Chem Soc* 124:4158
- Barfield M, Bergset JM, O'Leary DJ (2001) *Magn Reson Chem* 39:S115
- Perera SA, Bartlett RJ (2001) *Magn Reson Chem* 39:S183
- (a) Becke AD (1988) *Phys Rev A* 38:3098; (b) Becke AD (1993) *J Chem Phys* 98:5648; (c) Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785
- (a) Ditchfield R, Hehre WJ, Pople JA (1971) *J Chem Phys* 54:724; (b) Frisch MJ, Pople JA, Krishnam R, Binkley JS (1984) *J Chem Phys* 80:3265
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA (1998) *Gaussian 98*. Gaussian, Pittsburgh, PA
- Peralta JE, Ruiz de Azúa MC, Contreras RH (2000) *Theor Chem Acc* 105:165
- Peralta JE, Barone V, Ruiz de Azúa MC, Contreras RH (2001) *Mol Phys* 99:655
- Barone V, Peralta JE, Contreras RH, Sosnin AV, Krivdin LB (2001) *Magn Reson Chem* 39:600
- (a) Sychrovsky V, Grafenstein J, Cremer D (2000) *J Chem Phys* 113:3530; (b) Helgaker T, Watson M, Handy NC (2000) *J Chem Phys* 113:9402; (c) Peralta JE, Barone V, Contreras RH (2001) *J Am Chem Soc* 123:9162
- Helgaker T, Jensen HJA, Jørgensen P, Olsen J, Ruud K, Agren H, Andersen T, Bak KL, Bakken V, Christiansen O, Dahle P, Dalskov EK, Enevoldsen T, Fernandez B, Heiberg H, Hettema H, Jonsson D, Kirpekar S, Kabayashi R, Koch H, Mikkelsen KV, Norman P, Packer MJ, Sauer T, Taylor PR, Vahtras O (1997) *Dalton: an electronic structure program*, release 1.0
- Perera SA, Sekino H, Bartlett RJ (1994) *J Chem Phys* 101:2186
- Perera SA, Nooijen M, Bartlett RJ (1996) *J Chem Phys* 104:3290
- (a) Perera SA, Bartlett RJ (1995) *J Am Chem Soc* 117:8476; (b) Perera SA, Bartlett RJ (1996) *J Am Chem Soc* 118:7849
- Del Bene JE, Perera SA, Bartlett RJ, Elguero J, Alkorta I, López-Leonardo C, Alajarín M (2002) *J Am Chem Soc* 124:6393
- (a) Karplus M (1959) *J Chem Phys* 30:11; (b) Karplus M (1960) *J Phys Chem* 64:1793; (c) Karplus M (1963) *J Am Chem Soc* 85:2870
- Contreras RH, Peralta JE (2000) *Prog Nucl Magn Reson* 37:321
- Barfield M, Smith WB (1992) *J Am Chem Soc* 114:1574
- Sekino H, Bartlett RJ (1994) *Chem Phys Lett* 225:486
- Fukui H, Baba T (2001) *Nucl Magn Reson* 30:109
- Guilleme J, San Fabián J, Casanueva J, Díez E (1999) *Chem Phys Lett* 314:168
- Wigglesworth RD, Raynes WT, Sauer SPA, Oddershede J (1997) *Mol Phys* 92:77
- Provasi PF, Aucar GA, Sauer SPA (2000) *J Chem Phys* 112:6201
- Pecul M, Jaszunski M, Sadlej J (1999) *Chem Phys Lett* 305:139
- Fukui H, Baba T, Kurogi Y (2000) *J Chem Phys* 112:3532
- Pachler KGR (1972) *J Chem Soc Perkin Trans* 2 1936
- Imai K, Osawa E (1990) *Magn Reson Chem* 28:668
- San Fabián J, Guilleme J, Díez E, Lazzarotti P, Malogoli Zanasi MR, Esteban AL, Mora F (1994) *Mol Phys* 82:913
- Fukui H, Baba T, Inomata H, Miura K, Matsuda H (1997) *Mol Phys* 92:161
- Govil G (1971) *Indian J Chem* 9:824
- Pecul M, Sadlej J (2000) *J Chem Phys* 255:137
- Paolillo L, Becker ED (1970) *J Magn Reson* 3:200
- (a) Lazzarotti P (1979) *J Chem Phys* 71:2614; (b) Sandström C, Baumann H, Kenne L (1998) *J Chem Soc Perkin Trans* 2 2385
- Bouchet P, Elguero J, Jacquier R, Pereillo JM (1972) *Bull Soc Chim Fr* 2264
- Bouchet P, Coquelet C, Elguero J (1975) *Org Magn Reson* 7:247
- Elguero J, Johnson BL, Pereillo JM, Pouzard G, Rajzmann M, Randall EW (1977) *Org Magn Reson* 9:145
- Galasso V (1984) *Chem Phys Lett* 108:435
- Gordy W (1946) *J Chem Phys* 14:305. Gordy W (1946) *Phys Rev* 69:604
- Huggins ML (1953) *J Am Chem Soc* 75:4123
- Donders LA, de Leeuw FAAM, Altona C (1989) *Magn Reson Chem* 27:556
- Guilleme J, San-Fabián J, Díez E, Bermejo F, Esteban AL (1989) *Mol Phys* 68:65
- Alkorta I, Rozas I, J. Elguero J (1998) *Struct Chem* 9:243
- Alkorta I, Rozas I, Elguero J (1998) *THEOCHEM* 452:227
- Khuri AI, Cornell JA (1987) *Response surfaces. Designs and analyses*. Dekker, New York, p 276
- Helgaker T, Jaszunski M, Ruud K (1999) *Chem Rev* 99:293