Electric Field Effects on $^2J_{HH}$ Spin-Spin Coupling Constants

Martin Grayson

The Department of Chemistry, The University, Sheffield S3 7HF Tel. (+44 114 222 9527 Fax.
E-mail: m.grayson@shef.ac.uk

Abstract: Some calculations of the electric field derivative of the spin-spin coupling constant on molecules in the series CH_3F, CH_3Cl, CH_3Br, CH_3I, CH_4, CH_3Li, CH_3Na and CH_3K have been presented. The data is broken down into the 4 terms of the Ramsey theory: Fermi contact (FC); diamagnetic spin-orbit (DSO); paramagnetic spin-orbit (PSO) and spin-dipolar (SD). The FC term is seen to dominate all the calculated Js and their derivatives presented here. The situation where the FC term does not dominate in other molecules is discussed as a contrast.

Keywords: Spin-spin coupling; NMR; electric field; solvent shift.

1 Overview

When a molecule is in a non-gaseous environment, fields originating from localized charges and electric dipoles alter both the chemical shift and the spin-spin coupling constant. In terms of molecular properties these changes might be expressed by tensors describing the electric field strength derivatives of the magnetic property. The same property can be probed experimentally by pressure or temperature dependence of the spectra of a gaseous sample. The Buckingham Equation for magnetic shielding dates back to 1960 [1]. The current situation for shieldings has recently been reviewed by Raynes [2, 3].

The electric field derivatives of the magnetic shielding as used by Buckingham in 1960 were combined into single constants A and B for first and second electric field derivatives respectively. The minus sign was put in specifically because the field was expected usually to reduce the shielding by pulling electrons from *s*-type occupation into higher angular momentum orbitals. The Buckingham equation for the shielding of a nucleus in a diatomic is:

$$\sigma = \sigma_0 - A F_{\|bond} - B F^2 \tag{1}$$

where the direction of A, and therefore the sign of the parameter, has to be defined for each problem, as A is a vector like a bond dipole. B is analagous to a polarizability.

Raynes and Ratcliffe [4] worked out the number of unique derivatives in terms of the applied field for the nuclear shieldings. This problem still remains to be addressed for the spin-spin coupling, where the local symmetry of a two nucleus property has to be considered.

An attempt to follow on from this work with respect to J rather than the shielding has been begun here. (Small changes in the coupling constant's magnitude are much less important than the changes to the shielding so experimentalists have not required the numbers for the coupling constant's response to the environment so urgently. However the time is right to consider this problem.) The derivative $\partial J(iso)/\partial F_z$ where z is the principal axis of symmetry was calculated. For the molecules considered here there is then only one ^{2}J(H,H) to consider and only one 1st order field derivative is non zero. The C-X heteroatom bond has been placed in the positive z direction with the protons at negative z. (The water data quoted uses the same convention.)

The derivative can be used in the following formula

$$J = J_0 + \frac{\partial J}{\partial F_z} F_z \tag{2}$$

to first order. There are many surviving terms in F^2, but there is good evidence [5] that these terms contribute only about 5 percent of the field induced change in the case of the nuclear shielding. (In the above reference a selection of 80 liquid crystal molecules generated an average contribution

of 5.2% from terms involving the field squared. A small selection of 9 NLO molecules gave 4.2% and 20 amino acids, in the gas phase as neutral molecules gave 5.00% from the quadratic terms.)

The values for $\partial^2 J(iso)/\partial F_z^2$, which is only one of the second order contributions, from these calculations are for CH_3F, CH_3Cl, CH_3Br, CH_3Li and CH_3Na, (the molecules where the basis sets are largest), 475, 1025, 2175, 4450 and 8575 respectively. (The 25s, 50s and 75s show that the limit of the accuracy of the numerical differentiation has been reached for this second order derivative.) The numbers for this derivative form a monotonic series in both electronegativity and polarizability of the CH_3-X atom. The average for $\partial^2 \sigma(iso)/\partial F_z^2$ used in the parameter set of MolWeb [6], excluding any functional groups with atoms heavier than chlorine is 760. For σ these derivatives get large with increasing atomic number. MolWeb's estimation formula for the increase in Buckingham B on attaching a heavy atom is:

$$\mathrm{B} \;=\; \frac{1}{2}\frac{\partial^2 J(iso)}{\partial F_{(random)}^2} \;\approx\; 2n^2 + 21n + 157 \tag{3}$$

in units of ppm / au^2, where n is the atomic number. (This formula would not apply to very electropositive atoms like potassium, and might be better replaced by a function of polarizability.)

It can be seen from the above discussion of the magnitudes of the 2nd derivatives that it is reasonable to think there is a similar first order predominance in the perturbation of J.

2   Calculation Details

It is well known that the poor description of the triplet state in the SCF approximation means that SCF calculations of spin-spin coupling constants can be meaningless [7]. Despite this there are situations, such as calculating the Js for the Karplus equation [8], where SCF, whilst giving absolute values of J displaced by a large constant error, gives the right shape of the function of J over the potential surface [9]. However for the calculations presented here both SCF and the Second Order Polarization Propagator (SOPPA) [10-13] were used.

An attempt has been made to cover a significant area of chemistry rather than present a few definitive calculations. The definitive calculations with current technology would be a SOPPA-(CCSD) [13-18] calculation, perhaps using a specially optimised basis set for the spin-spin coupling calculations. The author did not have access to the relevant Coupled Cluster code at Sheffield. Special consideration might be needed for the different correlation in each group of molecules, especially for 1-bond couplings to heavier atoms such as S-H in H_2S [19, 7].

(The SOPPA(CCSD) method uses the SOPPA excitation energies, but replaces the MP2 coefficients with the Coupled Cluster amplitudes, which are the result of an iterative optimisation, and therefore might be expected to be more accurate than the pure SOPPA used here.)

For aliphatic systems the perturbation based SOPPA method is expected to give a better balance of correlation than a MCSCF calculation, where there are no obvious principal low lying excitations.

These calculations were performed using the ageing multiprocessor Ultra-Sparc at the Sheffield University Computer Centre for the SCF level calculations and the modern COMPAC system at the UK Computational Chemistry Facility at the Rutherford Appleton Laboratory for the SOPPA calculations. The field derivative $\partial J/\partial F$ was calculated with both SCF and SOPPA in order to test whether the errors in the SCF wavefunction subtract out for that particular derivative. $\partial J/\partial F$ was calculated using the the standard 2-point numerical differentiation formula which has been in reliable use long before computers [20]

$$\frac{\partial J}{\partial F} \approx \frac{J_+ - J_-}{2\Delta} \tag{4}$$

$$\frac{\partial^2 J}{\partial^2 F} \approx \frac{J_+ + J_- - 2J_0}{\Delta^2} \tag{5}$$

The applied field strength is a compromise between accuracy and contamination by higher derivatives and the optimum is potentially different for each perturbation. Experience has suggested ± 0.002 au is appropriate for this sort of perturbation. (Other examplse are the field effect on a distant functional group in a molecule caused by small changes to a nuclear charge elsewhere which requires a perturbation to the nuclear charge of ± 0.02 au, which causes a field of the order of 10^{-3} at typical intramolecular distances [21]. Where second derivatives of the energy with respect to atomic displacements are not available often a finite differencing procedure using displacements in atomic position of 0.001au is used.)

All the calculations were performed using the DALTON [22] program.

Experimental geometries were used where available (Table 1), supplemented by SCF calculations where necessary. Where possible a polarized triple zeta correlation consistent basis set was used. Some compromises were made for the heavy atom containing molecules.

Table 1. Table of Geometries and Basis Sets Used

Molecule	Geometry	Basis
CH_3F	experimental [23]	Dunning cc-pVTZ [27, 28]
CH_3Cl	experimental [24]	Dunning cc-pVTZ [27, 28]
CH_3Br	experimental [25]	Ahlrichs-VDZ [29]
CH_3I	experimental [26]	Pople 3-21G [30]
CH_3Li	SCF optimised	Pople 6-31G** [31]
CH_3Na	SCF optimised	Pople 6-31G** [31]
CH_3K	SCF optimised	Ahlrichs-VTZ [29]

3 The Terms in the Ramsey Theory

Much can be made of the 4-terms which contribute to the coupling constant in the Ramsey theory [32, 33], where the Fermi contact (FC) term is dominant, the diamagnetic spin-orbit (DSO) and the paramagnetic paramagnetic spin-orbit (PSO) terms often cancel and the spin-dipolar (SD) term is small. The prescence of large values in the other terms is perceived as being *novel*. However it must be remembered that these terms are not direct observables and can only be separated within the context of a model. (In the full relativistic formulation the coupling constant as calculated as an energy response function becomes only one term [34].) In the cases of N_2, CO [35] and F_2 the FC term is not dominant but this is interpreted as the FC term being a strong function of bond distance and happens coincidentally to pass through zero near the equilibrium bond length. In these 3 examples two have an unusually short bondlength because of the triple bond, and F_2 an unusually long bond because of the large number of lone pair to lone pair repulsions. In all 3 the equilibrium geometry is in an unusual electronic situation. Calculating J against bond length [35] seems to confirm this.

4 Results

There is both experimental and calculated data on intramolecular electric field effects on proton coupling constants and linear correlations to the electric field caused by the electronegativity difference of nearby substituents reported in reference [36].

One of the first calculations of the gradient of the spin-spin coupling constant with respect to a uniform electric field perturbation $\partial J/\partial F$ was presented by the author and Raynes [37] when then available computer resources did not allow detailed investigation at a correlated level of the sign change when going from SCF to MCSCF calculations. (The basis set used was the Sadlej Medium Polarized Set [38], which whilst not being particularly suited to spin-spin coupling calculations, was known to give good electron polarization properties at very modest cost.) The anecdotal observations at this time were that most of $\partial J/\partial F$ was coming from the FC derivative and the majority of this change was a correlation effect. For water $\partial J/\partial F$ actually changed sign from negative to positive when a SCF calculation was correlated by MCSCF. These observations are supported by the new data on the breakdown into terms presented here. The breakdown into the 4 components has been presented for the molecules CH_3F, CH_3Cl and CH_3Li, the 3 molecules with the largest basis sets, in Table 2.

Table 2. Table of the Breakdown into Terms FC, SD, DSO and PSO (All Js and components are in units of Hz, and derivatives in Hz / au. 1 au (Electric Field) = 5.14220 V m^{-1}.)

Molecule	J(SCF)	J(SOPPA)	$\partial J/\partial F$ (SCF)	$\partial J/\partial F$ (SOPPA)
CH$_3$F (Total)	-20.16	-10.71	79.23	56.33
FC	-20.42	-10.87	79.43	56.58
SD	0.62	0.49	-0.60	-0.60
DSO	-2.87	-2.87	0.75	0.70
PSO	2.53	2.54	-0.35	-0.33
CH$_3$Cl (Total)	-21.53	-11.62	73.40	56.78
FC	-22.18	-12.15	71.50	56.40
SD	0.61	0.48	-1.30	-1.30
DSO	-2.92	-2.92	1.65	1.55
PSO	2.97	2.97	0.10	0.18
CH$_3$Li (Total)	-23.54	-17.77	116.48	51.75
FC	-22.90	-17.61	122.48	49.90
SD	0.76	0.34	-13.03	-4.73
DSO	-2.71	-3.02	3.35	2.33
PSO	1.32	2.52	3.68	4.25
CH$_3$Na (Total)	-29.06	-16.01		32.83
FC	-30.22	-16.10		39.48
SD	2.47	0.45		-18.60
DSO	-2.64	-2.95		3.78
PSO	1.33	2.59		8.20
H$_2$O [37] (Total)	-23.42	-14.39	-5.45	34.15
FC	-24.46	-15.13	-22.60	16.65
SD	1.33	0.99	2.60	1.70
DSO	-7.09	-7.00	1.13	1.28
PSO	6.80	6.75	13.40	14.55

The CH$_3$Na SCF derivative values are not tabulated as the components have the same instability problem as the total. The components as calculated with SOPPA however have values in their expected ranges. The large SD derivative calculated with SOPPA is perhaps a sign of instability in the calculation. Note that for the water data the correlated calculation is MCSCF not SOPPA.

In general, as for the Karplus equation for ethane, the SCF values are about 10Hz too positive. The calculations on CH$_3$I, CH$_3$Na and CH$_3$K in particular require considerable basis improvement.

As can be seen from Table 3, the SCF method has not performed too badly with no change of sign between SCF and SOPPA, as has been seen in other calculations. The derivatives are in general too large, but by 30 percent on average, which could be much worse considering the poor desciption of the triplet state in the SCF RPA excitations. The correlation contributions are largely in the FC term, the contributions even to the derivative of J from SD, DSO and PSO being more or less equal between SCF and SOPPA. Polarizabilities and magnetizabilities have been calculated for calibration purposes as the ideal wavefunction for the derivate of J would also produce a good polarizability and magnetizability. Table 4 shows this has not been uniformly achieved, in particular the basis set used for the heavy atoms is not good enough to give the full polarizability.

Table 3. Table of Calculated J and their Field Derivatives (All Js are in units of Hz, and derivatives in Hz / au. 1 au (Electric Field) = 5.14220 V m^{-1}.)

Molecule	J(SCF)	J(SOPPA)	$\partial J/\partial F$ (SCF)	$\partial J/\partial F$ (SOPPA)
CH_3F	-20.16	-10.71	79.23	56.33
CH_3Cl	-21.53	-11.62	73.40	56.78
CH_3Br	-29.18	-20.81	44.00	56.68
CH_3I	-23.70	n.a.	30.55	n.a.
CH_3H	-23.84	-13.69	126.33	91.83
CH_3Li	-23.54	-17.77	116.48	51.75
CH_3Na	-29.06	-16.01	(†)-7311.83	32.83
CH_3K	-12.69	-19.04	(†)-4499.80	214.33
H_2O [37]	-23.42	-14.39	-5.45	34.15

(†) - these numbers are probably spurious due to SCF triplet instabilities, as a sequence of expected values, increasing with the increasing electropositive characteristics of the metal atom, is calculated with SOPPA.

Table 4. Some Calculated Polarizabilities and Magnetizabilities Compared to Experiment

Mol.	$\alpha_{(iso)}$ (calc.) x 10^{41} / $C^2m^2J^{-1}$	$\alpha_{(iso)}$ (exp.) x 10^{41} / $C^2m^2J^{-1}$ J	$\chi_{(iso)}$ (calc.) x 10^{30} / JT^{-2}	$\chi_{(iso)}$ (exp.) x 10^{30} / JT^{-2}
CH_3F	23.91	29.1 [39]	-317.02	-292.8 (†)
CH_3Cl	39.22	50.3 [40]	-567.30	-568.5 (†)
CH_3Br	35.96	62.2 [41]	-761.24	-722.9 (†)
CH_3I	43.07	88.7 [42]	-1070.96	-962.0 (†)
CH_3Li	44.27	49.78 (†)	-388.96	n.a.
CH_3Na	68.09	95.85 (†)	-510.14	n.a.
CH_3K	68.21	97.51 (†)	-708.54	n.a.

(†) - the magnetizabilities quoted here are estimated using the algorithm in the MolWeb program. The estimated polarizabilities are obtained by using the data of Guella *et al.* [43] on the gaseous dimers $(LiF)_2$, $(NaF)_2$ and $(KF)_2$ with a polarizability of F_2 from Jao *et al.* [44] to derive estimation contributions of 19.07 (CH_3-), 30.71 (Li), 76.78 (Na) and 78.44 (K) in the same SI units as above.

Experimental data for direct comparison has proved difficult to find. There is some folklore about perturbations to coupling constants among NMR experts, much of which is distributed throughout the multi-author *Encyclopedia of Nuclear Magnetic Resonance* and some is very coherently written about in Williams and Fleming [45]. It must be remembered that when J is positive, (for J(H,H), it means the antiparallel nuclear spin configuration is lower in energy and vice versa when J is negative [46]. The sign of J is also a function of the magnetogyric ratio of the nuclei involved and so in order to investigate the purely electronic features of bonding between the nuclei involved a reduced coupling constant, divided by the magnetogyric ratios might have to be used.

Most experimental methods can give only the relative signs of two Js. Electronegative attchments to $-CH_2-$ make the negatively signed ^2J coupling constant more negative, but electropositive attachments make them more positive. Hyperconjugation to a $sp^2\pi-$ system, *i.e.* something more electronegative than $C(sp^3)$, makes ^2J more negative. However hyperconjugation to a lone pair, *i.e.* a mesomeric electron donor, makes ^2J more positive. So even though experimentalists are largely interested in the absolute value of J it is necessary to know the sign if you are going to use estimation rules to predict changes.

The knowledge that electropositive attachments make J more postitve is entirely supported by the calculations here where the field along the principal axis could be expected to have the same effect as an electropositive substituent. All the values of $\partial J/\partial F$ are positive in sign.

In order to investigate perturbation effects on spin-spin coupling one possible source of verification of field derivative data is other high quality calculations on weakly bound molecular complexes. Pecul and Sadlej [47] have calculated the spin-spin coupling constants in the water dimer and used a dielectric polarization calculation on the monomer to extrapolate to the condensation changes. They have calculated ^{4}J(H,H) across the hydrogen bond and concluded that it is about 0.06Hz. Several unpublished calculations at Sheffield have come up with similar small values much less than 1 Hz. More work is needed to establish confidence levels for calculations of the different coupling constants ^{2}J, ^{3}J and ^{4}J.

5 Conclusions

A start has been made on extending the extensive data and understanding of field dependence of nuclear magnetic shieldings to spin-spin coupling constants. In this case the SCF wavefunction is insufficient but there are less problems of gauge invariance so a variety of correlated methods might be considered. Calculations have shown sensible chemical behaviour but a more extensive series of calculations over different basis sets and flavours of post Hartree-Fock methods are needed before the definitive numbers can be established.

However the derivatives here point to the values being consistently positive and of moderate magnitude, (about 50 Hz / au), corresponding to the perturbation reducing or increasing the FC term at the protons in question.

Acknowledgements

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