

Calculation of Chlorine Nuclear Quadrupole Coupling Constants

[GAMESS](#), [Dalton](#), [Gaussian](#)

W. C. Bailey
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Introduction

The nuclear quadrupole coupling constant (nqcc) tensor is the energy of interaction of the electric quadrupole moment (Q) of the atomic nucleus and the gradient of the electric field (efg) at the site of the nucleus. Components of the nqcc tensor χ are related to those of the efg tensor q by

$$\chi_{ij} = (eQ/h) q_{ij} \quad (1)$$

where subscripts i,j = a,b,c; which are principal axes of the molecular inertia tensor.

Thus, quantum chemistry calculation of the expectation values of the components of the efg tensor allows calculation of the components of the nqcc tensor¹. We report here the results of calculations made of chlorine nqcc tensors using the Gaussian 03M, Dalton 2.0, and GAMESS US (v. 7 Sept 06, R4) computational quantum chemistry packages.²

¹ A fortran program for conversion, if necessary, of calculated efg/nqcc tensors to efg/nqcc tensors in a,b,c coordinates is available [here](#).

² Calculations were made on a Mac G5/OS X 10.x system from [Apple Inc.](#)

Gaussian

The B1LYP/TZV(3df,2p) computational model as implemented in the Gaussian suite of programs has been shown effective for accurate calculation of nqcc tensors [[wcbailey](#)]. B1LYP is the one-parameter hybrid HF/DFT method of Barone and Adamo [1]. TZV(3df,2p) is Ahlrichs' TZV bases on heavy atoms and Ahlrichs' VTZ on hydrogen, with 3df,2p polarization functions obtained from Pople-type 6-311G(3df,2p) bases. (Information and references concerning these bases can be found at the online [EMSL basis set library](#).) Calculations were made using the "scf = tight" convergence criteria, and the program default integration grid.

Dalton

Dalton 2.0 does not contain B1LYP explicitly, but does provide a simple procedure for constructing linear combinations of DFT functionals with (or without) HF exchange [see Dalton 2.0 online manual, p 210]. The following combination is - I think³- B1LYP:

hf=0.25 slater=0.75 becke=0.75 lyp=1.00

So, in this case as with Gaussian, the model used is B1LYP/TZV(3df,2p). Polarization functions, which are not available in the package, were obtained from the EMSL basis set library. Calculations were made using the program default convergence criteria and integration grid. (Note: In the package that I have, there is an error in the Ahlrichs TZV basis file in one of the p exponents for boron. Dalton users should check this against the EMSL library.)

GAMESS

Documentation notwithstanding, the version of GAMESS US that I have contains only Becke's three-parameter method, B3LYP [2]. Therefore, the model used in this case is B3LYP/TZV(3df,2p). Calculations were made, as above, using the program default convergence criteria and integration grid.

³ Dear Reader: If I am mistaken, please correct me; if not, please inform me. wcbailey@mac.com. Thank you.

Results

Calculations were made of the efg's on 23 molecules for which experimental chlorine nqcc's and equilibrium molecular structures have been reported. These molecules are listed below in Table 2. Shown in Table 1 are the results of linear regression analysis of the calculated q_{ij} versus the experimental χ_{ij} -- that is, eq (1).

The slope of the linear regression line is designated eQ_{eff}/h , from which a nuclear quadrupole moment effective for conversion of the calculated q_{ij} to χ_{ij} is derived. The assumption that underlies this procedure is that errors inherent in the model used for calculation of the q_{ij} are systematic and can be corrected by use of an effective nuclear quadrupole moment. However, as can be seen in Table 1, for all three packages, $Q_{\text{eff}} \approx Q$, which is -81.65(80) mb for ^{35}Cl and -64.35(64) mb for ^{37}Cl [3]. Thus, the calculated χ_{ij} given in Table 2 for ^{35}Cl were derived using Q rather than Q_{eff} ; that is $eQ/h = -19.1849$ MHz/a.u. (and -15.1200 MHz/a.u. for ^{37}Cl . The results for ^{37}Cl parallel those for ^{35}Cl , and are not tabulated here.)

Table 1. Linear regression statistics for calculated q_{ij} versus experimental χ_{ij} .

		GAMESS US	Dalton	Gaussian
		B3LYP/TZV(3df,2p)	B1LYP/TZV(3df,2p)	B1LYP/TZV(3df,2p)
^{35}Cl	Number of Points	69	69	69
	Correlation Coefficient	0.99992	0.99996	0.99996
	Residual Standard Deviation (MHz)	0.68 (1.51 %) ^a	0.46 (1.03 %) ^a	0.47 (1.04 %) ^a
	Slope, eQ_{eff}/h (MHz/a.u.)	-19.1711(288)	-19.1763(196)	-19.1712(199)
	Q_{eff} (mb)	-81.59(12)	-81.61(8)	-81.59(8)

³⁷ Cl	Number of Points	48	48	48
	Correlation Coefficient	0.99992	0.99996	0.99996
	Residual Standard Deviation (MHz)	0.60 (1.57 %) ^a	0.41 (1.07 %) ^a	0.42 (1.09 %) ^a
	Slope, eQ _{eff} /h (MHz/a.u.)	-15.1233(290)	-15.1243(198)	-15.1193(201)
	Q _{eff} (mb)	-64.36(12)	-64.37(8)	-64.35(8)

^a Percent of the average of the magnitudes of the experimental χ_{ij} .

Table 2. Calculated and experimental ³⁵Cl nuclear quadrupole coupling constants, χ_{ij} (MHz). First reference is for the experimental χ_{ij} , second is for the molecular r_e structure on which calculation was made.

Molecule	ij	GAMESS	Dalton	Gaussian	Experimental	Ref.
		B3LYP/	B1LYP/	B1LYP/		
		TZV(3df,2p)	TZV(3df,2p)	TZV(3df,2p)		
HCl	aa	-68.07	-68.04	-68.04	-67.60916(30)	4, 4
BCl	aa	-16.61	-16.63	-16.63	-16.737(11)	5, 6
FCl	aa	-146.88	-146.40	-146.43	-145.87182(3)	7, 8

Cl ₂	aa	-112.88	-112.46	-112.48	-111.7902(38)	9, 10
CICN	aa	-82.65	-82.77	-82.77	-83.27519(40)	11, 12
CICP	aa	-71.20	-71.47	-71.47	-71.75(18)	13, 14
CIBS	aa	-42.38	-42.52	-42.53	-42.54(1)	15, 16
HCCCI	aa	-79.42	-79.60	-79.60	-79.7358(19)	17, 18
CH ₃ Cl	aa	-75.04	-74.86	-74.86	-74.7514(11)	19, 20
CH ₂ Cl ₂	aa	-41.87	-41.88	-41.88	-41.7418(11)	21, 22
	bb	1.71	1.81	1.81	1.8004(12)	
	cc	40.16	40.06	40.06	39.9414(12)	
CHCl ₃ ^a	uu	28.56	28.63	28.62	28.6436(4)	23, 24
	vv	-67.86	-67.89	-67.89	-67.8309(5)	
	ww	39.30	39.26	39.27	39.1872(5)	
SiH ₃ Cl	aa	-40.41	-40.03	-40.03	-39.689(5)	25, 25
SiH ₂ Cl ₂	aa	-20.83	-20.69	-20.69	-20.4150	26, 27
	bb	-0.32	-0.26	-0.26	-0.3095(19)	
	cc	21.15	20.95	20.95	20.7245(19)	
CH ₂ =CCl ₂	aa	-42.04	-42.12	-42.12	-42.48(10)	28, 29
	bb	8.20	8.09	8.09	8.12(18)	

	cc	33.84	34.03	34.03	34.36(15)	
c-CHF=CHCl	aa	-22.91	-23.07	-23.07	-22.719(14)	30, 31
	bb	-9.64	-9.75	-9.75	-10.600(13)	
	cc	32.55	32.82	32.82	33.319(17)	
ClF ₃	aa	-80.17	-81.40	-81.41	-82.0281(90)	32, 32
	bb	-66.40	-65.30	-65.33	-65.3590(101)	
	cc	146.57	146.70	146.74	147.3871(86)	
Cl ₂ O	aa	-71.91	-71.96	-71.96	-71.45	33, 34
	bb	6.90	7.03	7.02	6.86	
	cc	65.00	64.94	64.93	64.59	
ClO ₂	aa	-52.37	-52.27	-52.50	-52.086(102)	35, 36
	bb	1.97	2.93	2.68	2.808(66)	
	cc	50.39	49.35	49.82	49.278(66)	
FCIO ₂	aa	-33.84	-35.12	-35.12	-34.90065(43)	37, 38
	bb	-17.69	-17.51	-17.50	-17.10863(53)	
	cc	51.53	52.62	52.62	52.00928(39)	
HOCl	aa	-122.55	-122.30	-122.32	-121.958(8)	39, 40
	bb	59.96	59.82	59.83	59.519(10)	

	cc	62.59	62.48	62.48	62.439(10)	
O=C ³⁵ Cl ³⁷ Cl	aa	-35.52	-35.60	-35.60	-36.009(36)	41, 42
	bb	9.67	9.48	9.48	8.705(39)	
	cc	25.85	26.12	26.12	27.304(16)	
O=CHCl	aa	-50.46	-50.84	-50.84	-51.10(4)	43, 43
	bb	31.23	31.18	31.18	30.04	
	cc	19.22	19.65	19.65	21.06(6)	
O=CFCI	aa	-72.05	-72.20	-72.20	-73.0277(8)	44, 44
	bb	45.40	45.28	45.28	44.7073 ₅	
	cc	26.65	26.92	26.92	28.3203 ₅	
Average ^b		0.51	0.32	0.33		
RMS ^b		0.67	0.45	0.46		
BrCl		-103.66	---- ^c	-103.34	-102.378(1)	45, 46
GeH ₃ Cl		-47.47	---- ^c	-46.82	-46.9500(26)	47, 48

^a χ_{uu} is the component of the nqcc tensor along the threefold symmetry u-axis. χ_{vv} and χ_{ww} are the components along the v- and w- axes for the Cl atom in the uv-plane (C_s plane).

^b Average and root mean square (RMS) differences between calculated and experimental diagonal nqcc's for all 23 molecules.

^c Dalton calculation was not made for these molecules because 3df polarization functions for Ge and Br atoms are not available from the EMSL basis set library.

Discussion

Calculations have been made of chlorine nqcc tensors in 23 molecules using the B1LYP/TZV(3df,2p) model as implemented in the Gaussian 03M and Dalton 2.0 computational quantum chemistry packages, and B3LYP/TZV(3df,2p) as implemented in the GAMESS package (v. 7 Sept 06, R4).

The slopes of the linear regression lines given in Table 1 for Gaussian, Dalton, and GAMESS yield effective nuclear electric quadrupole moments Q_{eff} of -81.59(8), -81.61(8), and -81.59(12) mb respectively for ^{35}Cl ; and -64.35(8), -64.37(8), and -64.36(12) mb respectively for ^{37}Cl . For each isotope, these Q_{eff} are essentially the same, and well within the uncertainties in the currently recommended moments Q of -81.65(80) for ^{35}Cl and -64.35(64) for ^{37}Cl [3].

The major difference among the three calculations is the larger residual standard deviations for the B3LYP model of GAMESS compared the B1LYP models of Dalton and Gaussian: namely, for ^{35}Cl , 0.68 MHz compared with 0.46 and 0.47 MHz; and for ^{37}Cl , 0.60 Mz compared with 0.41 and 0.42 MHz.

In Table 2, calculated nqcc's are compared with each other and with the experimental nqcc's. These ^{35}Cl nqcc's were derived from calculated efg's using $eQ/h = -19.1849 \text{ MHz/a.u.}$ rather than eQ_{eff}/h . For 22 of the 23 molecules in this Table, nqcc's calculated with the B1LYP models of Dalton and Gaussian are "equal", the largest difference being 0.04 MHz for χ_{cc} for ClF_3 .

The lone exception is ClO_2 . In this case, Dalton and Gaussian nqcc's differ by 0.23, 0.25, and 0.47 MHz for χ_{aa} , χ_{bb} , and χ_{cc} respectively - the Dalton nqcc's being in better agreement with the experimental nqcc's.

As ClO_2 has a single unpaired valence electron and all other molecules in Table 2 are closed shell singlets, the obvious question arises: "Is the difference in ClO_2 due to spin multiplicity?" Thus, calculations were made of the nqcc's in the CCl , OCl , and SiCl radicals (all doublets). In both CCl and OCl - shown below - the difference between Dalton and Gaussian

nqcc's is 0.16 MHz - which is large compared with the closed shell molecules in Table 2, but not as large as the differences in ClO₂. In SiCl, the calculated nqcc's are "equal". This last notwithstanding, there are appreciable differences between the packages with respect to open shell calculations.

Molecule	Dalton	Gaussian	Experimental	Ref.
CCl	-34.76	-34.60	-34.26	49
OCl	-88.33	-88.17	-87.95(19)	50
SiCl	-22.94	-22.95	-23.13(96)	51

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