

Calculation of Deuterium 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.

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](#).

The B3LYP/6-31G(df,3p) computational model as implemented in the Gaussian suite of programs has been shown effective for efficient and accurate calculation of deuterium nqcc tensors [wcbaily]. We report here the results of calculations made of the nqcc tensors using this model as implemented in the Gaussian 03M, Dalton 2.0, and GAMESS US (v. 7 Sept 06, R4) computational quantum chemistry packages.²

B3LYP in the Gaussian package and B3LYP-G in Dalton is

hf=0.2 slater=0.8 becke=0.72 lyp=0.81 vwn3=0.19;

whereas B3LYP in the Dalton and GAMESS packages is

hf=0.2 slater=0.8 becke=0.72 lyp=0.81 vwn5=0.19.

The difference lies in the choice of VWN functional (see [1], and references therein). Comparison, therefore, is made not only of the different packages but also of the different implementations of the B3LYP method.

Calculations made with the GAMESS and Dalton packages were made using the default settings. With the Gaussian package, calculations were made using the "scf = tight" convergence criteria and the default integration grid.

Results

Calculations were made of the efg's on 8 molecules for which experimental deuterium nqcc's and equilibrium molecular structures have been reported. These molecules are listed below in Table 2. Also in this Table, results are given for calculations made on DCN, D₂O, and DBr which, for diverse reasons, are not included in the linear regression data.

The results of linear regression analysis of the calculated q_{ij} versus the experimental χ_{ij} -- that is, Eq (1) - are shown in Table 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. For comparison, the recommended Q for D is 2.860(15) mb [2].

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

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

	GAMESS US	Dalton		Gaussian
	B3LYP	B3LYP	B3LYP-G	B3LYP
Number of Points ^a	24	24	24	24
Correlation Coefficient	0.99991	0.99996	0.99996	0.99997
RSD ^b (kHz)	2.08 (1.58 %)	1.42(1.08 %)	1.44 (1.09 %)	1.14 (0.87 %)
Slope, eQ_{eff}/h (kHz/a.u.)	623.35(175)	635.74(122)	636.07(123)	637.348(980)
Q_{eff} (mb)	2.653(7)	2.706(5)	2.707(5)	2.712(4)

^a Includes all three diagonal components for the first 8 molecules given in Table 2. Excludes DCN, D₂O, and DBr.

^b Residual standard deviation. Percent of the average of the magnitudes of the experimental χ_{ij} .

Table 2. Calculated and experimental D nuclear quadrupole coupling constants, χ_{ij} (kHz). 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	B3LYP	B3LYP-G	B3LYP		

HD	aa	219.4	223.8	223.8	224.2	224.54(6)	3, 4
DF	aa	356.9	356.3	356.3	355.2	354.238(78)	5, 6
DCI	aa	185.6	187.0	187.0	186.8	187.46(30)	7, 7
CH ₃ D	aa	194.8	192.4	192.4	193.4	191.48(77)	8, 9
CF ₃ D	aa	167.6	166.4	166.4	167.6	170.8(20)	10, 11
D ₂ S	aa	52.4	52.7	52.7	52.8	51.84(17)	12, 13
	bb	36.5	36.5	36.6	36.6	36.54(13)	
	cc	-88.8	-89.3	-89.3	-89.4	-88.38(11)	
D ₂ CO	aa	-14.6	-13.8	-13.8	-13.9	-12.53(10)	14, 15
	bb	98.3	96.6	96.6	97.0	97.23(10)	
	cc	-83.8	-82.8	-82.8	-83.2	-84.70(10)	
HCOOD	aa	-119.8	-119.4	-119.4	-119.1	-119.3(20)	16, 17
	bb	268.7	267.9	267.9	267.5	267.5(30)	
	cc	-148.8	-148.5	-148.5	-148.4	-148.2(20)	
Average ^a		1.6	1.0	1.0	0.8		
RMS ^a		2.0	1.4	1.4	1.1		

DCN	aa	---- ^b	204.4	204.4	204.8	200.6(5)	18, 19
D ₂ O	aa	150.5	149.8	149.8	149.5	153.92(11)	20, 21
	bb	24.1	25.0	25.0	24.9	22.12(11)	
	cc	-174.6	-174.8	-174.8	-174.3	-175.037(11)	
DBr	aa	154.2 ^c	---- ^d	---- ^d	145.9 ^c	146.9(13)	22, 23

^a Average and root mean square (RMS) differences between calculated and experimental diagonal nqcc's for all 8 molecules.

^b Execution terminated abnormally with error message: "Roundoff error in bend - stop" ?

^c The 6-31G(df) basis for Br in the GAMESS package differs significantly from that in the Gaussian package. This explains, at least in part, the large difference in calculated nqcc's.

^d Dalton calculation was not made on DBr because 6-31G(df) basis for Br is not available from the EMSL basis set library.

Discussion

Calculations have been made of deuterium nqcc tensors in 8 molecules using the B3LYP/6-31G(df,3p) model as implemented in the Gaussian 03M, Dalton 2.0, and GAMESS (v. 7 Sept 06, R4) computational quantum chemistry packages.

As shown in Table 1, RSD for Gaussian (1.1 kHz) < RSD for Dalton (1.4 kHz) < RSD for GAMESS (2.1 kHz); and for Dalton, RSD for B3LYP-G (1.44 kHz) \approx RSD for B3LYP (1.42 kHz). Thus, Gaussian performs better than Dalton, which in turn performs better than GAMESS. And the results obtained for the different implementations of B3LYP in the Dalton package show no significant difference with respect to choice of VWN functional.

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