Calculation of Nitrogen Nuclear Quadrupole Coupling Constants

Dalton, Gaussian

W. C. Bailey
July 2007

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

$$\chi_{ij} = (eQ/h)\, q_{ij}. \qquad (1)$$

Subscripts i,j = a,b,c; where a,b,c 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 tensor[1].

Previously [1], the B3PW91/6-311+G(df,pd) computational model as implemented in the Gaussian 98 suite of programs has been shown effective for efficient and accurate calculation of nitrogen nqcc tensors.

Here, calculations were made of the efg tensors using this model as implemented in the Gaussian 03M and Dalton 2.0 computational quantum chemistry packages.[2] Methods and results - calibration of Eq (1) - are discussed in the following section.

Calibration

Dalton 2.0 does not contain B3PW91 explicitly, but does provide a simple procedure for constructing linear combinations of DFT functionals with (or without) HF exchange [see

[1] A fortran program for conversion, if necessary, of calculated efg tensors to efg 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.

Dalton 2.0 online manual, p 210]. The following combination is B3PW91:

hf=0.2 slater=0.8 becke=0.72 pw91c=0.81.

Furthermore, Dalton does not contain the 6-311+G(df,pd) bases. These are, however, easily generated from the 6-311++G(3df,3pd) bases, which are provided. (Incidentally, there is an error in the 6-311++G(3df,3pd) basis set for P in the version of Dalton 2.0 that I have recently downloaded.) Calculations made with the Dalton package were made using the default settings. With the Gaussian package, calculations were made using the "scf = tight" convergence criteria and the default integration grid.

Gaussian 03M calculations were made of the efg's at 50 nitrogen sites in 44 molecules for which experimental nqcc's and molecular structures (of various types) have been reported. These molecules, too many to report here, can be found at this link. Dalton 2.0 calculations were made on these same molecules except for BrCN and GeH_3CN, as 6-311++G(3df,3pd) bases for Br and Ge are not provided with the package or available at the EMSL basis set library. Dalton 2.0 calculation on the CN radical failed.

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 ^{14}N is 20.44(3) mb [2], and eQ/h is 4.803(5) MHz/a.u.

Table 1. Linear regression statistics for B3PW91/6-311+G(df,pd) calculated q_{ij} versus experimental χ_{ij}.

	Dalton 2.0	Gaussian 03M
Number of Points	141	150
Correlation Coefficient	0.99992	0.99994
RSD [a] (kHz)	0.034 (1.49 %)	0.030 (1.30 %)
Slope, eQ_{eff}/h (kHz/a.u.)	4.56689(479)	4.55852(404)
Q_{eff} (mb)	19.44(2)	19.40(2)

[a] Residual standard deviation. Percent of the average of the magnitudes of the experimental χ_{ij}.

Discussion

Calculations have been made of ^{14}N efg tensors using the B3PW91/6-311+G(df,pd) model as implemented in the Gaussian 03M and Dalton 2.0 computational quantum chemistry packages.

Conversion factors, eQ_{eff}/h for calculation of nqcc tensors have been derived by linear regression analyses of the calculated efg tensors versus the experimental nqcc tensors.

For the 41 molecules on which calculations were made with both packages, the average difference between Gaussian and Dalton calculated diagonal components of the nqcc tensors is 0.011 MHz. The largest difference is 0.042 MHz for χ_{cc} for BH_2NH_2. A few of the larger differences, including BH_2NH_2, are shown below in Table 2.

Finally, we note that differences between the Gaussian 03M calibration given here in Table 1 and the earlier Gaussian 98 calibration are not significant.

Table 2. Calculated and experimental ^{14}N nuclear quadrupole coupling constants, χ_{ij} (MHz). First reference is for the experimental χ_{ij}, second is for the molecular structure on which calculation was made.

Molecule	i j	Dalton	Gaussian	Experimental	Ref.
NH_3	aa	-4.047	-4.081	-4.08965	3, 4
$(CH_3)_3N$	aa	-5.486	-5.516	-5.5002(18)	5, 6
BH_2NH_2	aa	0.108	0.129	0.095(9)	7, 8
	bb	2.087	2.107	2.091(8)	
	cc	-2.194	-2.236	-2.186(8)	
CF_3NC	aa	-1.075	-1.103	-1.06(3)	9, 9
AlNC	aa	-2.216	-2.188	-2.1508(19)	10, 11
Pyrrole	aa	1.403	1.414	1.412(3)	12, 13
	bb	1.197	1.214	1.292(4)	
	cc	-2.600	-2.628	-2.704(4)	

References

[1] http://homepage.mac.com/wcbailey/nqcc/

[2] M. Tokman, D. Sundholm, P. Pyykkö, and J. Olsen, Chem. Phys. Lett. 265, 60 (1997).

[3] J. T. Hougen, J. Chem. Phys. 57, 4207 (1972).

[4] W. S. Benedict and E. K. Plyler, Canadian J. Phys. 35, 1235 (1957).

[5] X. L. Li, R. Bocquet, D. Petitprez, D. Boucher, L. Poteau, and J. Demaison, J. Mol. Spectrosc. 171, 449 (1995).

[6] J. E. Wollrab and V. W. Laurie, J. Chem. Phys. 51, 1580 (1969).

[7] K. Vormann, H. Dreizler, J. Doose, and A. Guarnieri, Z. Naturforsch. 46a, 770 (1991).

[8] M. Sugie, H. Takeo, and C. Matsumura, J. Mol. Spectrosc. 123, 286 (1987).

[9] D. Christen, K. Ramme, B. Haas, H. Oberhammer, and D. Lentz, J. Chem. Phys. 80, 4020 (1984).

[10] K. A. Walker and M. C. L. Gerry, Chem. Phys. Lett. 278, 9 (1997).

[11] J. S. Robinson, A. J. Apponi, and L. M. Ziurys, Chem. Phys. Lett. 278, 1 (1997).

[12] R. K. Bohm, K. W. Hillig II, and R. Kuczkowski, J. Phys. Chem. 93, 3456 (1989).

[13] L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sørensen, J. Mol. Struct. 3, 491 (1969).