JOURNAL OF MOLECULAR SPECTROSCOPY **185**, 403–407 (1997)
ARTICLE NO. MS977411

Prediction of ^{11}B Quadrupole Coupling Constants in Molecules

William C. Bailey

Department of Chemistry and Physics, Kean College of New Jersey, Union, New Jersey 07083

Received June 18, 1997

The B3LYP/6-31G(df, p) model is shown to be a viable alternative to the computationally demanding MP2/6-311G($3df$, $3pd$) model for the prediction of ^{11}B nuclear quadrupole coupling constants in molecules. Using eQ/h as a best fit parameter, coupling constants calculated with the B3LYP model show a root mean square (rms) deviation of 0.059 MHz from the experimental values for 11 molecules; those calculated with the MP2 model, 0.049 MHz. Comparison of coupling constants predicted by the two models for a sample size increased to 25 molecules yields a rms difference between models of 0.036 MHz. © 1997 Academic Press

INTRODUCTION

The energy of interaction of the electric quadrupole moment of the nucleus of an atom with the molecular electric field gradient (efg) at the site of the nucleus is determined experimentally by measurement of the nuclear quadrupole coupling constant (nqcc), the nqcc being proportional to the molecular efg.

Software packages for calculation of the molecular efg have been developed. These include the Gaussian 94 (*1*) package of programs, which was used for all calculations presented in this work.

For accurate calculation of the efg, the need to include correlation, at least at the level of second-order Moller–Plesset perturbation (MP2) theory, in conjunction with a fairly large basis set is generally acknowledged. This requirement, which is demanding of computer resources, places restrictions on the size of the molecule that may be investigated. To overcome these restrictions, Huber *et al.*, in a series of papers, have shown that the basis set must be of high quality principally in the area of the nucleus of interest, and that smaller bases may be used on atoms further removed. These authors have applied this method with good results to calculation of the molecular efg for ^{2}H (*2, 3*), ^{7}Li (*4*), ^{14}N (*5, 6*), and ^{17}O (*7*).

Another possibility is provided by a method developed by Becke (*8*) which combines Hartree–Fock theory with density functional theory. This method, known as Becke's three-parameter hybrid method (B3), permits calculations to be performed on fairly large molecules with computational cost considerably less than MP2 theory.

We report in this paper the results of calculations of the efg's at the site of the ^{11}B nucleus in a number of molecular environments carried out with MP2 theory and Becke's hybrid method. In an earlier paper, Palmer (*9*) reported the results of calculations at the self-consistent field (Hartree–Fock) level of theory using a large triple-zeta plus polarization basis.

NUCLEAR QUADRUPOLE COUPLING CONSTANTS

The components of the nqcc tensor χ_{ij} are related to those of the efg tensor q_{ij} by

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

where e is the proton charge, h is Planck's constant, and Q is the nuclear electric quadrupole moment. The q_{ij} are calculated in atomic units. The subscripts $ij = a, b, c$, where a, b, c are the principal axes of the moment of inertia tensor of the molecule. We have chosen molecular systems in which these axes are coincident with the principal axes of the nqcc tensor.

CALCULATIONS

Following a procedure similar, for example, to that of Eggenberger *et al.* (*7*), we take eQ/h in Eq. [1] as a best-fit parameter for least-squares, linear regression analysis of the calculated q_{ij} (efg's) versus the experimental χ_{ij} (nqcc's). In this way, the model (theory and basis set) is calibrated by the best-fit value of eQ/h, which may then be used for prediction of nqcc's in other molecules. This empirical procedure compensates somewhat for possible errors inherent in the model—namely, insufficient correlation and unsaturated basis; and for the effects of molecular vibrations, for which no correction is made in this work.

The molecules and experimental nqcc's (*10–20*) listed in

0022-2852/97 $25.00
Copyright © 1997 by Academic Press
All rights of reproduction in any form reserved.

TABLE 1
Nuclear Quadrupole Coupling Constants (MHz), Predicted and Experimental

Molecule	*ij*	MP2	B3LYP	Expt.	References nqcc	References struct.
BF	*aa*	−4.340	−4.284	−4.305 (2)	10	10
HBF^+	*aa*	−5.176	−5.196	−5.15 (26)	11	11
HBO	*aa*	−3.661	−3.635	−3.80 (10)	12	21
HBS	*aa*	−3.729	−3.761	−3.72 (3)	13	22
FBS	*aa*	−2.488	−2.492	−2.54 (4)	14	14
CH_3BS	*aa*	−3.757	−3.796	−3.714 (20)	15	15
BH_2NH_2	*aa*	−1.625	−1.604	−1.684 (14)	16	23
	bb	−2.249	−2.258	−2.212 (11)		
	cc	3.874	3.862	3.896 (11)		
BHF_2	*aa*	−0.787	−0.861	−0.75 (9)	17	24
	bb	−2.670	−2.590	-2.58_5[a]		
	cc	3.457	3.451	3.33_5[a]		
CH_3BF_2	*aa*	−2.669	−2.649	−2.713 (21)	18	25
	bb	−0.705	−0.735	−0.695 (27)		
	cc	3.374	3.383	3.408 (27)		
$C_6H_5BF_2$	*aa*	−2.621	−2.658	−2.589 (12)	19	26
	bb	−0.538	−0.534	−0.600 (15)		
	cc	3.160	3.192	3.189 (15)		
BH_3CO	*aa*	1.629	1.604	1.6619 (23)	20	27

[a] Derived from the reported data (*24*), $\chi_{aa} = -0.75$ and $\chi_{bb-cc} = -5.92$ MHz.

Table 1 were used for calibration of the calculated efg's. All calculations were performed on the experimental structures (*10, 11, 14, 15, 21–27*).

MP2/6-311G(3df, 3pd) efg's versus Experimental nqcc's

At the MP2 level of theory, a triple-split valence basis with three sets of *d*- and one set of *f*-polarization functions on all atoms other than hydrogen and three sets of *p*- and one set of *d*-polarization functions on hydrogen was used for calculation of the efg's. This model is denoted MP2/6-311G(3*df*, 3*pd*).

For phenyldifluoroborane, $C_6H_5BF_2$, following the lead of Huber *et al.*, the efg's were calculated with this large basis set on the boron atom and on the atoms with which it is bonded, namely the two flourines and one carbon; with 6-311G(*df*, *p*) bases on the adjacent carbons; and with double-split valence without polarization, 6-31G, on the remaining carbon and hydrogen atoms.

Figure 1a shows a plot of the calculated efg's versus the experimental nqcc's. Although not independent ($\Sigma\chi_{ii} = 0$), all three principal (diagonal) components of the nqcc tensor for all molecules are plotted, which assures that the least-squares line pass through the origin.

The slope of the best-fit, least-squares line is eQ/h = 9.088(31) MHz/a.u., with a correlation coefficient of 0.99982. The root mean square (rms) deviation of the calculated nqcc's from the experimental nqcc's is 0.049 MHz, which is 2.1% of the average absolute experimental nqcc of 2.347 MHz. These calculated nqcc's are shown in Table 1, along with the experimental values.

B3LYP/6-31G(df, p) efg's versus Experimental nqcc's

Calculations of the efg's were performed using Beck's three-parameter hybrid method in conjunction with the correlation functional of Lee *et al.* (*28, 29*), with a double-split valence basis having *d*- and *f*-polarization functions on atoms other than hydrogen and *p*-polarization functions on hydrogen. This model is denoted B3LYP/6-31G(*df*, *p*).

Numerical integration was performed over a spherical product grid having 96 radial shells around each atom with 32 θ points and 64 ϕ points per shell, for a total of 196 608 integration points per atom. This is a very fine grid that is found to be extreme for calculation of the efg's. This matter is addressed in the following section.

The slope of the best-fit, least-squares line for the efg's versus the experimental nqcc's, shown in Fig. 1b, is eQ/h = 9.673(40) MHz/a.u., with a correlation coefficient of 0.99974.

The calculated nqcc's are given in Table 1, along with the MP2 and experimental values. Comparison of these nqcc's with the experimental values shows a rms deviation of 0.059 MHz, which is 2.5% of the average absolute experimental nqcc. This result, although not quite as good as the MP2 result, is really not much different. The major difference between the two, aside from computational expense, is that the magnitude of the efg's calculated with the B3LYP model average about 6% less than those calculated with the MP2 model, as reflected by their respective values of eQ/h.

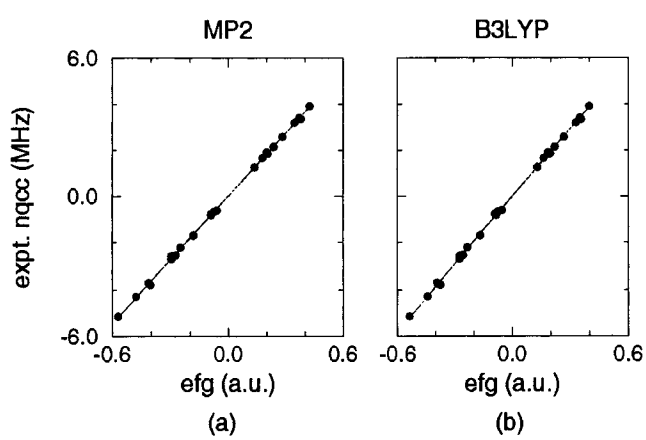

FIG. 1. Plots of calculated efg's versus experimental nqcc's. (a) MP2/6-311G(3*df*, 3*pd*). (b) B3LYP/6-31G(*df*, *p*).

Copyright © 1997 by Academic Press

TABLE 2
Predicted Nuclear Quadrupole Coupling Constants (MHz)

Molecule	*ij*	MP2	B3LYP	Ref.	Molecule	*ij*	MP2	B3LYP	Ref.
BCl[a]	*a*	−4.009	−3.981	*30*	$BHCl_2$[c]	*aa*	−0.641	−0.661	*38*
						bb	−2.896	−2.834	
ClBO	*aa*	−2.446	−2.440	*31*		*cc*	3.537	3.495	
ClBS	*aa*	−2.313	−2.303	*32*	BF_2Cl	*aa*	−1.305	−1.296	*39*
						bb	−1.348	−1.336	
BH_3	*cc*	5.859	5.991	*33*		*cc*	2.653	2.632	
BF_3	*cc*	2.685	2.691	*34*	$BH(NH_2)_2$	*aa*	−1.265	−1.257	*40*
						bb	−1.799	−1.733	
BCl_3	*cc*	2.557	2.496	*35*		*cc*	3.064	2.991	
BH_2F[b]	*aa*	−1.105	−1.143	*36*	BH_3NH_3	*aa*	2.521	2.576	*41*
	bb	−3.370	−3.376						
	cc	4.476	4.519		BF_2NH_2	*aa*	−1.932	−1.861	*42*
						bb	−0.491	−0.533	
BH_2Cl	*aa*	−0.966	−1.002	*37*		*cc*	2.424	2.394	
	bb	−3.635	−3.624						
	cc	4.601	4.627		$HCCBF_2$	*aa*	−2.172	−2.197	*43*
						bb	−0.908	−0.873	
						cc	3.080	3.070	

[a] An expt. value of −3.70 MHz for the nqcc, estimated from lineshape simulation, was reported by Y. Endo, S. Saito, and E. Hirota, *Bull. Chem. Soc. Jpn.* **56,** 3410–3414 (1983).
[b] Expt. values of the nqcc's are −1.34 (20), −3.37 (20), and 4.71 (20) MHz (Ref. (*36*)).
[c] Expt. values of the nqcc's are 0.4 (10), −3.3 (5), and 2.9 (11) MHz (Ref. (*38*)).

A more comprehensive comparison of the models is made in the following section.

B3LYP/6-31G(df, p) versus MP2/6-311G(3df, 3pd)

To increase both the sample size and variety, efg's were calculated on the experimental structures (*30–43*) of the molecules listed in Table 2. The nqcc's predicted, as discussed below, by both the MP2 and B3LYP models are also shown in this table.

Linear regression analysis of the B3LYP/6-31G(*df*, *p*) efg's versus the MP2/6-311G(3*df*, 3*pd*) efg's for all 25 molecules (Tables 1 and 2) yields a slope of 1.063—that is, the magnitudes of the B3LYP efg's average 6.3% less than the corresponding MP2 efg's, as was found above for the smaller sample size.

MP2 nqcc's were predicted from these efg's using Eq. [1] with eQ/h = 9.088(31) MHz/a.u. and B3LYP nqcc's with eQ/h = 9.673(40) MHz/a.u. Comparison of the predicted nqcc's for all 25 molecules shows a rms difference between the models of 0.036 MHz, which is 1.6% of the average absolute predicted nqcc of 2.263 MHz. The largest absolute difference is 0.132 MHz for BH_3, which is 2.3% of the MP2 value of 5.859 MHz for this molecule.

Figure 2 shows, for the convenience of visual comparison, a plot of the B3LYP nqcc's versus the MP2 nqcc's. The slope of the least-squares line is 0.99913, and the correlation coefficient is 0.99990.

As noted above, numerical integration was made over a grid having 196 608 integration points per atom. Integration over a grid consisting of 22 650 integration points per atom (75 radial shells with 302 angular points per shell) yields, to five figures, the same nqcc's as the finer grid.

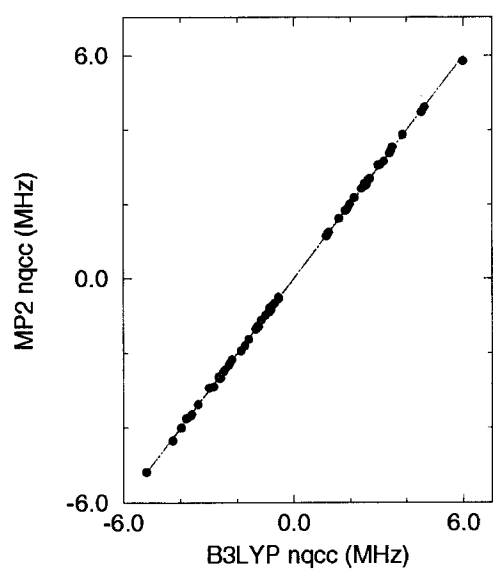

FIG. 2. Plot of MP2/6-311G(3*df*, 3*pd*) nqcc's versus B3LYP/6-31(*df*, *p*) nqcc's.

Copyright © 1997 by Academic Press

The default grid in the Gaussian 94/DFT (*1*) package is this 75 × 302 grid "pruned" to about 7000 integration points. In this case, the nqcc's are the same as the spherical product grid to four figures, which is the number of figures quoted in this work. These differences, therefore, are not significant.

DISCUSSION

It should be noted at this point that the choice of MP2/6-311G(3*df*, 3*pd*) and B3LYP/6-31G(*df*, *p*) models for this work was not arbitrary. A number of *ab initio* models, including Hartree–Fock and MP2, and a number of density functional models as well as Becke's hybrid forms, were investigated. From among the *ab initio* models, which were calibrated against the experimental nqcc's, the least rms deviation was obtained with the MP2/6-311G(3*df*, 3*pd*) model; while from among the density functional and hybrid models, which were calibrated against the experimental nqcc's and also compared with the MP2/6-311G(3*df*, 3*pd*) nqcc's, the best overall agreement was obtained with the B3LYP/6-31G(*df*, *p*) model.

A value of the nuclear electric quadrupole moment effective for calculation of the nqcc's, Q_{eff}, may be computed from the model dependent value of eQ/h. With Q in units of barns and the nqcc's in MHz, $eQ/h = 234.9649 \times Q$, where the numerical factor (units omitted) is a collection of the physical constants and the appropriate unit conversion factors. Thus, for the MP2/6-311G(3*df*, 3*pd*) model, $Q_{\text{eff}} = 0.03868(13)$ b and for the B3LYP/6-31G(*df*, *p*) model, 0.04117(17) b. Theoretical values of Q found in the literature (*44–50*) range from 0.03865 to 0.04196 b, with the most recent (*50*) being 0.04059 b. It is encouraging that the uncorrected Q_{eff} values found in this work lie within this range.

SUMMARY

In summary, nqcc's predicted by MP2/6-311G(3*df*, 3*pd*) efg's agree with the experimental nqcc's (for 11 molecules) with a rms difference of 0.049 MHz, which is 2.1% of the average absolute experimental nqcc; while nqcc's predicted by B3LYP/6-31G(*df*, *p*) efg's agree with the experimental nqcc's with a rms difference of 0.059 MHz, which is 2.5% of the average absolute experimental nqcc.

Furthermore, nqcc's predicted by the B3LYP efg's for a sample increased to 25 molecules agree with the MP2 nqcc's with a rms difference of 0.036 MHz, which is 1.6% of the average absolute predicted nqcc.

The B3LYP/6-31G(*df*, *p*) model is found to be a viable alternative to the computationally more expensive MP2/6-311G(3*df*, 3*pd*) model for the prediction of boron nqcc's in molecules.

REFERENCES

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gorden, C. Gonzalez, and J. A. Pople, "Gaussian 94, Revision B.1," Gaussian, Inc., Pittsburgh, PA, 1995.
2. H. Huber, *J. Chem. Phys.* **83,** 4591–4598 (1985).
3. S. Gerber and H. Huber, *J. Mol. Spectrosc.* **134,** 168–175 (1989).
4. S. Gerber and H. Huber, *J. Phys. Chem.* **93,** 545–549 (1989).
5. S. Gerber and H. Huber, *Z. Naturforsch. A* **42,** 753–760 (1987).
6. S. Gerber and H. Huber, *Chem. Phys.* **134,** 279–285 (1989).
7. R. Eggenberger, S. Gerber, H. Huber, D. Searles, and M. Welker, *J. Mol. Spectrosc.* **151,** 474–481 (1992).
8. A. Becke, *J. Chem. Phys.* **98,** 5648–5652 (1993).
9. M. Palmer, *Z. Naturforsch. A* **45,** 357–367 (1990).
10. G. Cazzoli, L. Cludi, C. Degli Esposti, and L. Dore, *J. Mol. Spectrosc.* **134,** 159–167 (1989).
11. S. Saito, S. Yamamoto, and K. Kawaguchi, *J. Chem. Phys.* **86,** 2597–2599 (1987).
12. Y. Kawashima, Y. Endo, K. Kawaguchi, and E. Hirota, *Chem. Phys. Lett.* **135,** 441–445 (1987).
13. E. F. Pearson, C. L. Norris, and W. H. Flygare, *J. Chem. Phys.* **60,** 1761–1764 (1974).
14. T. Cooper, S. Firth, and H. Kroto, *J. Chem. Soc. Faraday Trans.* **87,** 1499–1502 (1991).
15. C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.* **83,** 1–14 (1980).
16. K. Vormann, H. Dreizler, J. Doose, and A. Guarnieri, *Z. Naturforsch. A* **46,** 770–776 (1991).
17. N. Westwood, W. Lewis-Bevan, and M. Gerry, *J. Mol. Spectrosc.* **106,** 227–234 (1984).
18. L. Engelbrecht and D. Sutter, "Third European Microwave Spectroscopy Conference, Venice, 1974," paper D5.
19. K. Vormann and H. Dreizler, *Z. Naturforsch. A* **44,** 84–86 (1989).
20. A. Murray and S. Kukolich, *J. Chem. Phys.* **77,** 4312–4317 (1982).
21. Y. Kawashima, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **133,** 116–127 (1989).
22. E. Pearson and R. McCormick, *J. Chem. Phys.* **58,** 1619–1621 (1973).
23. M. Sugie, H. Takeo, and C. Matsumura, *J. Mol. Spectrosc.* **123,** 286–292 (1987).
24. A. Robiette and M. Gerry, *J. Mol. Spectrosc.* **80,** 403–410 (1980).
25. P. Langridge-Smith, R. Stevens, and A. Cox, *J. Chem. Soc. Faraday 2* **75,** 1620–1636 (1979).
26. D. Christen, D. Lister, and J. Sheridan, *J. Chem. Soc. Faraday Trans.* **70,** 1953–1958 (1974).
27. A. Venkatachar, R. Taylor, and R. Kuczkowski, *J. Mol. Struct.* **38,** 17–23 (1977).
28. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37,** 785–789 (1988).
29. B. Miehlich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.* **157,** 200–206 (1989).
30. A. G. Maki, F. J. Lovas, and R. D. Suenram, *J. Mol. Spectrosc.* **91,** 424–429 (1982).
31. K. Kawaguchi, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **93,** 381–388 (1982).
32. C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.* **83,** 130–147 (1980).
33. K. Kawaguchi, *J. Chem. Phys.* **96,** 3411–3415 (1992).
34. S. Yamamoto, R. Kuwabara, M. Takami, and K. Kuchitsu, *J. Mol. Spectrosc.* **115,** 333–352 (1986).

Copyright © 1997 by Academic Press

35. S. Konaka, Y. Murata, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.* **39,** 1134–1146 (1966).
36. H. Takeo, M. Sugie, and C. Matsumura, *J. Mol. Spectrosc.* **158,** 201–207 (1993).
37. Y. Kawashima, H. Takeo, M. Sugie, C. Matsumura, and E. Hirota, *J. Chem. Phys.* **99,** 820–826 (1993).
38. M. Sugie, H. Takeo, and C. Matsumura, *Spectrochim. Acta A* **50,** 1379–1387 (1994).
39. H. W. Kroto and M. Maier, *J. Mol. Spectrosc.* **65,** 280–288 (1977).
40. L. R. Thorne and W. D. Gwinn, *J. Am. Chem. Soc.* **104,** 3822–3827 (1982).
41. L. R. Thorne, R. D. Suenram, and F. J. Lovas, *J. Chem. Phys.* **78,** 167–171 (1983).
42. F. J. Lovas and D. R. Johnson, *J. Chem. Phys.* **59,** 2347–2353 (1973).
43. W. J. Lafferty and J. J. Ritter, *J. Mol. Spectrosc.* **38,** 181–194 (1971).
44. H. F. Schaefer III, R. A. Klemm, and F. E. Harris, *Phys. Rev.* **176,** 49–58 (1968).
45. H. F. Schaefer III, R. A. Klemm, and F. E. Harris, *Phys. Rev.* **181,** 137–143 (1969).
46. S. Larson, *Phys. Rev. A* **2,** 1248–1258 (1970).
47. R. K. Nesbet, *Phys. Rev. A* **2,** 1208–1216 (1970).
48. R. K. Nesbet, *Phys. Rev. Lett.* **24,** 1155–1157 (1970).
49. J. E. Rodgers and T. P. Das, *Phys. Rev. A* **12,** 353–361 (1975).
50. D. Sundholm and J. Olsen, *J. Chem. Phys.* **94,** 5051–5055 (1991).

Copyright © 1997 by Academic Press