The ab initio Calculation of Nuclear Quadrupole Coupling Constants and their Comparison with Experiment

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Ab initio calculations of electric field gradients (EFG) and conversion to nuclear quadrupole coupling constants (NQCC) are described, with particular reference to ^{14}N and ^{10,11}B. The correlation of EFG and NQCC for a series of boranes leads to the value 8.32 MHz/a.u. (0.0354 barn) for $Q(^{11}B)$.

The structural variations of these microwave and single molecule calculations of ^{10,11}B NQCC are discussed.

Introduction

In a previous paper we reviewed the ^{14}N nuclear quadrupole coupling constants (NQCC) obtained from microwave spectroscopy (MW) for a variety of small molecules [1], and compared the values with those computed by ab initio methods. The present paper falls into three parts: (i) it updates that review in a few selected cases and notes some of the difficulties associated with the calculation of NQCC in molecules where a highly polar or a cumulative bonded structure occurs; (ii) it discusses ^{10,11}B quadrupole coupling calculations in relation to MW data, leads to the evaluation of the ^{11}B nucleus quadrupole moment (Q_B), and discusses the variation of NQCC with structure; (iii) it is concerned with the correlation between calculated NQCC and nuclear quadrupole resonance data (NQR) in the poly-crystalline state. This in turn can be divided into two approaches: calculation of the molecule in question together with its local environment (say, molecule + nearest neighbours) or calculation of the wave-function in the unit cell framework and using the repeating structure in three dimensions to simulate the bulk.

Basic Concepts

For an isolated molecule of **C1** (zero elements) symmetry, the second rank NQCC tensor (χ_{ij}, MHz) has 6- non-zero elements related to the EFG (q_{ij}, a.u.) by

$$\chi_{ij} = e\,Q\,q_{ij}/h. \tag{1}$$

In the MW determination, (i, j) are the permutations of the inertial axes (IA; $i, j = a, b, c$) [2]. The theoretician computes the EFG and needs the appropriate quadrupole moment (Q) of the nuclear type under discussion. This aspect is discussed in detail below; when the χ_{ij} (or q_{ij}) tensor is diagonalised the principal axes (PA $i, j = x, y, z$ permutations) data are obtained. Because of the La Place relationship

$$q_{ii} + q_{jj} + q_{kk} = 0, \tag{2}$$

the trace of the tensor (i, j, k) is zero in both the non-diagonal and diagonalised forms. Up to this point the MW and NQR terminology is similar; however, the asymmetry parameter (η), (Eq. 3a)

$$\eta\,\chi_{zz} = \chi_{xx} - \chi_{yy}, \quad |\chi_{zz}| > |\chi_{yy}| > |\chi_{xx}|, \tag{3a}$$

is often differently defined by MW spectroscopists to have the identities $z = a$, $x = b$, $y = c$, irrespective of magnitudes, in the first part of 3a [3], and hence follows

$$\chi_+ = -\chi_{aa}, \eta\,\chi_{aa} = \chi_{bb} - \chi_{cc}. \tag{3b}$$

The EFG operator is evaluated over the full wavefunction (ψ_0) and has the form

$$q_{ij} = \langle \psi_0 | H_{ij} | \psi_0 \rangle, \tag{4}$$

where

$$H_{xx} = 3x^2 - r^2/r^5, \quad H_{xy} = 3xy/r^5.$$

It is a 1-electron operator, that is, it does not require the (2-electron) electron repulsion integrals (although these have been evaluated in the process of generating ψ_0). The form of the EFG operator (H_{ij}) is similar to that of the molecular quadrupole moment operator (Q_{ij}),

$$Q_{xx} = (3x^2 - r^2)/2, \quad Q_{xy} = (3/2)\,x\,y, \tag{5}$$

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a quantity which also can be determined by MW spectroscopy. Because of the x^2/r^5 dependence (etc.), it is clear that q_{xx} will decline with distance rather rapidly, so that the effect of neighbour molecules will be small beyond the nearest group. In the Townes-Dailey approach, the NQCC are evaluated purely from the atomic populations of the attached bonds at the centre [2, 4], although these are normally a function of a larger electronic structure calculation (usually at the semi-empirical level). In practice the method is frequently inverted, the χ_{ij} are used to evaluate the local bond populations.

Clearly the use of the ab initio wave-functions and full operator can be expected to yield better agreement with experiment if the atomic/molecular orbital basis is large enough and if the level of refinement of calculation (SCF, MC-SCF, CI) is sufficient. In the present study we describe various approaches. It should be noted that the electronic wave-function has no vibrational energy, and this effect may be significant in comparison with experiment when the magnitudes are small [5, 6]. Since the EFG and force constant are both second derivatives of a potential with respect to distance, correlations between q_{ij} and force constants (k) have been investigated [7]. One final dilemma surrounds the molecular structure, when comparing with MW data; NQCCs (in the IA frame) are frequently obtained in advance of a full r_s structure; even when the latter is available, the comparison is not always obvious, since strictly the EFG should be evaluated at the equilibrium structure (r_e). For most molecules, where a single Lewis structure can be written, there is a small difference between r_s and r_e (and this includes aromatic rings); for other compounds, the r_e structure may not be close to r_s, especially if a single configuration SCF wave-function is obtained.

Theoretical methods

The ab initio SCF/MC-SCF calculations were performed with GAMESS [8] and the CI by DIRECT [9], while the studies of full lattices utilised the 3-dimensional periodic systems program CRYSTAL [10]; all of these were mounted on Cray-1s or X-MP/48 computers. Basis sets used are derived from the Huzinaga sets [11], contracted to split valence (SV), double zeta (DZ) or triple zeta valence + polarisation (TZVP) according to the Dunning recipes [12].

Nuclear Quadrupole Moments (Q) at ^{14}N and ^{10,11}B

(a) Nitrogen-14

Although Q is known accurately for many nuclei [13], those for the more important nuclei in chemistry such as ^{14}N, ^{10,11}B, ^{33}S, ^{17}O are less certain; indeed, it was possible to assert that theoretical estimates even to $\pm 10\%$ accuracy [14] were more accurate than experiment. However, for ^{14}N nuclei two groups have reported Q_N as -17.4 ± 0.2 mb [15] and -19.4 ± 0.9 mb [16] (nb. 1 mb$=10^{-25}$ cm^2); although the apparent errors are larger, the latter has been widely accepted, being in line with the more exact theoretical calculations. These calculated values rely upon good/excellent quality calculations of the EFG for small molecules, such as NH_3 and NO^+, and use of (1). Since the computed EFGs depend on the basis set [17] and the method of calculating the wave-function (SCF, MC-SCF, CI etc.), this leads to values for Q_N between -13 and -20 mB, depending upon these methods as shown in Table 1 using NH_3 at is computed equilibrium geometry. In order to compute Q_N accurately a highly accurate χ_{zz} is required; the value for ammonia is known with extreme accuracy for a number of rotational states [18], and hence this is the most suitable molecule. Several estimates of Q_N arrive at values near -20.0 mB [19–24], usually after extensive CI with large basis sets. Probably the most accurate is the largest value -20.7 ± 0.4 mB [22] based on a calculation of the N^+ ($^1P_1$, 2p 3p) state, as in the Winter and Andrä experiment [16]. However, for most purposes, use of this value is not helpful in the assignment of NQR spectra, or getting a good fit with experimental values. If Q_N is treated as a scaling parameter, and a least squares fit over a set of compounds is used, then realistic χ_{ii} can be obtained from the q_{ii} (calc.), and have predictive and assignment value; such a procedure has been long used for SV and better basis sets;

Table 1. ^{14}N nuclear quadrupole moment from various basis sets for ammonia at the corresponding equilibrium structure (r_e).

Basis	Method	Structure	q_{zz}	Q_N
DZ	SCF	r_e	1.3283	13.1
DZ	CI	r_e	1.2049	14.4
TZV	SCF	r_e	1.2595	13.8
TZV	CI	r_e	1.2007	14.5
TZVP	SCF	r_e	1.0195	17.07
TZVP	CI	r_e	0.9825	17.71

this leads to scaling values of −15.0 (SV) [25], −16.7 (6−31 G) [26], −17.2 (DZ) [27, 28] and −17.7 mB (TZVP). These values are not exhaustive, and various other authors have proposed values appropriate for their basis set, while others have analysed the variation in q_{ii} with N−H etc. length, i.e. derivatives of the field gradient [29−32].

(b) Boron

The ^{11}B ($I = 3/2$) quadrupole coupling constant average value has been given as +41.0 mB, with that for ^{10}B ($I = 3$) 85.4 mB [13, 33], (but rather smaller values, such as (^{11}B) 35.5 mB have been used), together with the $^{10}B/^{11}B$ ratio of 2.84 [33]. In the following section we discuss the $^{10,11}B$ coupling in a series of boranes and borane complexes; at this point we refer to the clearly linear correlation of q_{ii} versus χ_{ii} obtained (Figure 1). The basis set was TZVP, and the calculations were at the SCF level, with equilibrium structure. The effective value for Q (^{11}B) is 8.32 MHz/a.u. or 35.4 mB; with only two exceptions (below), the fit is close; if the TZVP basis returns about the same proportions of the total Q as in the ^{14}N case (88%), then we arrive at 42.5 mB for the limiting value for Q (^{11}B), very close to that obtained by Rodgers and Das [33], but slightly larger than that calculated from polarisation wave-functions on the full atoms [34].

Structure and ^{11}B Coupling Constants

The principal results for the molecular total energy, calculated r_e and nuclear quadrupole coupling (q_{ii}) together with derived χ_{ii}, and experimental χ_{ii} with references are shown in Tables 2−5, and Figure 1. The relevant structures are shown in **1**−**17**.

The calculated values for q_{ii}/χ_{ii} (which include both EFG-PA and -IA data) (Table 5) use the TZVP basis correlation described above. The molecules studied are mostly neutral, closed shell molecules with the HBF cation included. The correlation diagram (Fig. 1) excludes HBF(+), but the computed χ_{zz} (−4.96 MHz) lies close to that from the MW data (−5.15 MHz). The worst discrepancies occur with $MeOBH_2$, NH_2BF_2 and H_3BCO at the SCF level; these and the other molecules are discussed below.

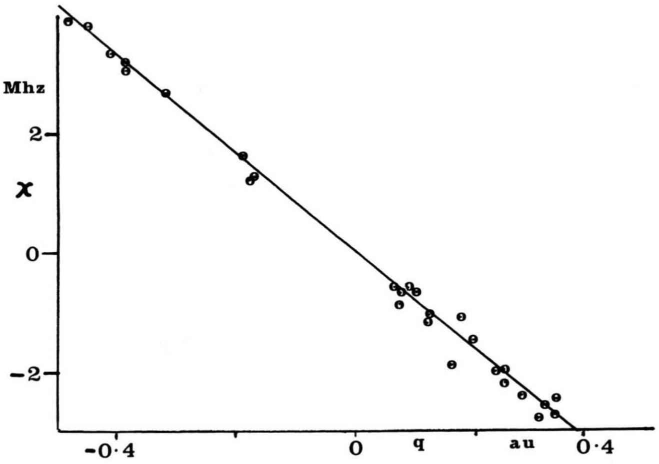
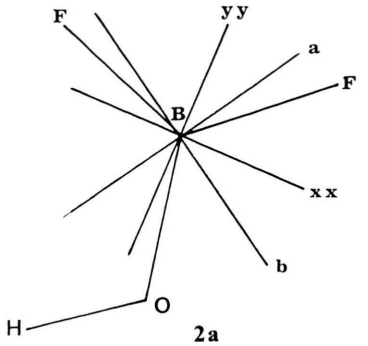


Fig. 1.

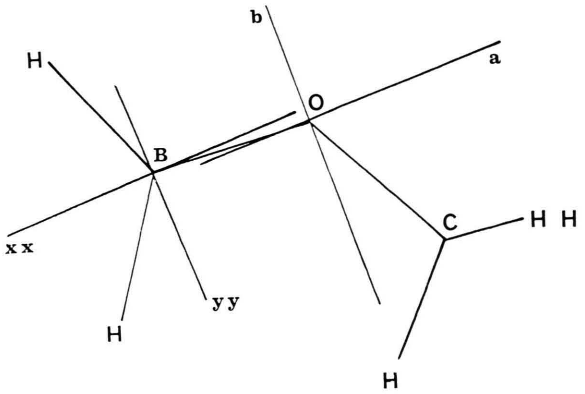
Table 2.1. Total energies (a.u.) of boranes studied with the TZVP basis set.

Molecule	Total energy	
	SCF	CI
BH_3	− 26.3992	− 26.5144
BF_3	−323.3244	−323.5792
HBF_2	−224.3527	
$MeBF_2$	−263.4204	−263.9900
$C_6H_5BF_2$	−453.8916	–
$HOBH_2$	−101.3641	–
$MeOBH_2$	−140.3959	–
$HOBF_2$	−299.3158	–
$HB(OCH_2)_2$	−253.2266	–
$H_2N\text{-}BH_2$	− 81.5245	−81.8063
$H_3N\text{-}BH_3$	− 82.6503	−82.9666
$Me_3N\text{-}BH_3$	−199.6719	–
$(NH_2)_2BH$	−136.6309	–
BF_2NH_2	−279.4694	−279.7324
$OC\text{-}BH_3$	−139.1889	−139.5650
$H_3P\text{-}BH_3$	−368.8824	–
$F_3P\text{-}BH_3$	−665.6753	–
$Me_3P\text{-}BH_3$	−485.9974	–
$B_3O_3H_3$	−300.7898	–
$B_3O_3(OH)_3$	−525.5958	–
$B_3O_3(OMe)_3$	−642.6098	–
HBF(+)	−124.4536	–
Boratrane ($C_6H_{12}BNO_3$)	−538.0835	–

Most of the 24 molecules of Tables 2−5 have planar (or near planar) trivalent boron; the two base molecules for discussion are BH_3 and BF_3; the present (r_e TZVP) q^{π}_{zz} are −0.63603 (BH_3, SCF) and −0.32675 a.u. (BF_3, SCF); both are little changed by CI. These are to be compared with earlier DZ values (with changed sign to fit the present convention) −0.5684 and −0.2218 a.u., respectively [35], while a larger basis yields (−) 0.3352 a.u. for BF_3 [36]. Neither BH_3 or BF_3 yield MW data, but the solid state BF_3



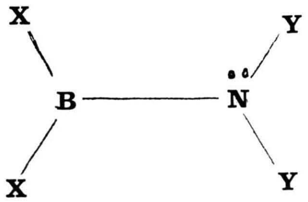
2a



2b

Fig. 2a.

Fig. 2b.



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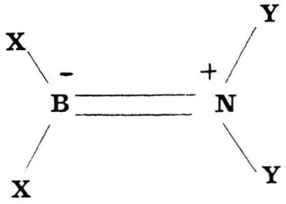

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Fig. 3.

Fig. 4.

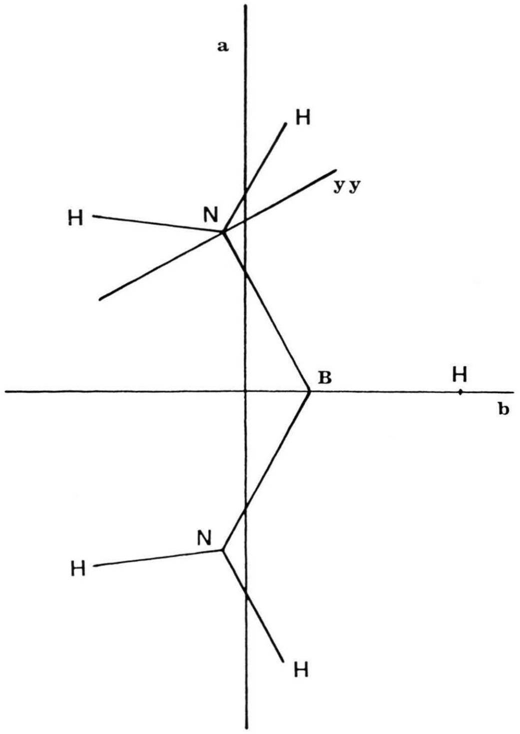


Fig. 5.

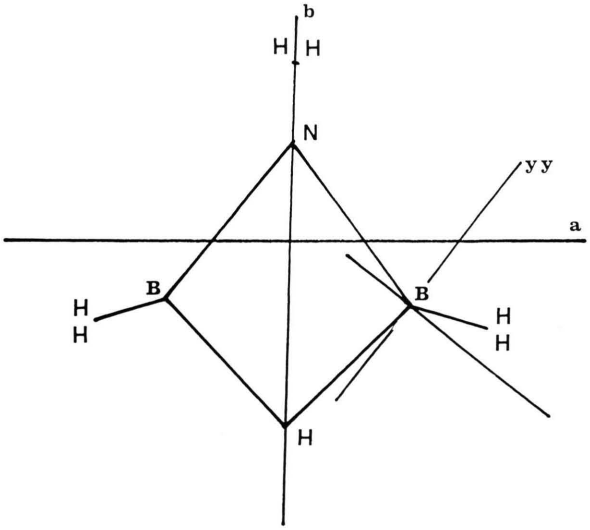


Fig. 6.

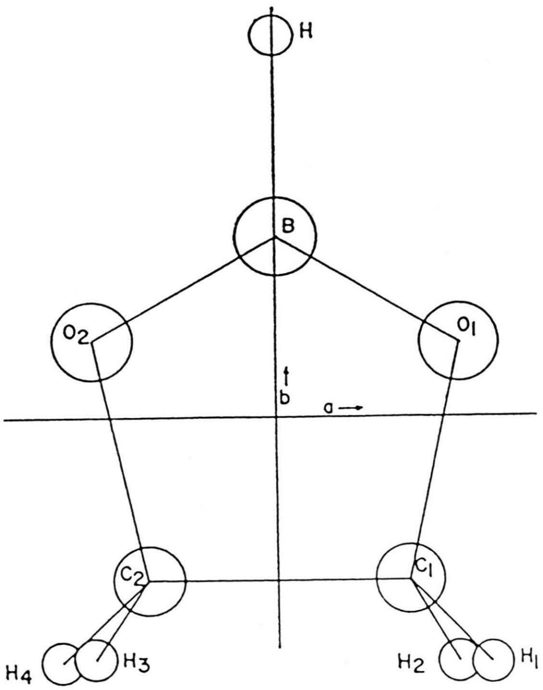
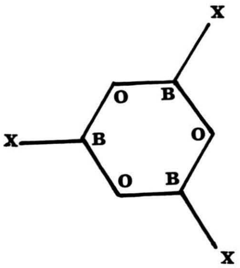


Fig. 7.



8 X = H

9 X = OMe

10 X = Ph

11 X = OH

Fig. 8.−11.

$O = C{-}BH_3$ Fig. 12.

12

$H_3B{-}NH_3$ Fig. 13.

13

$H_3B{-}NMe_3$ Fig. 14.

14

$H_3B{-}PX_3$

15 X = F Fig. 15.

16 X = H Fig. 16.

17 X = Me Fig. 17.

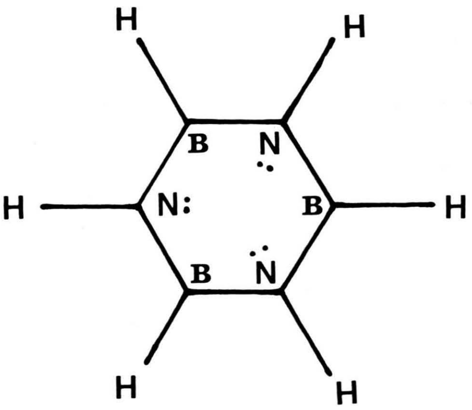


Fig. 18.

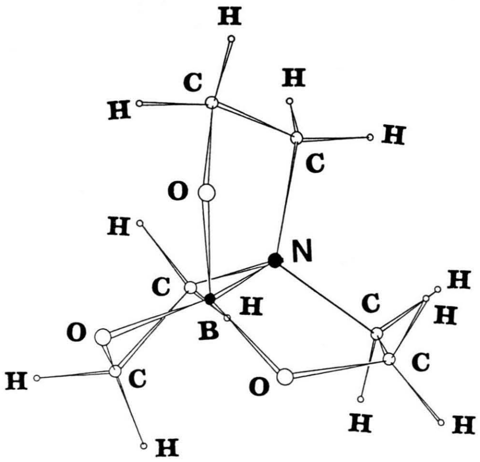


Fig. 19.

Table 3.1. Equilibrium structural data.

Molecule	Bond lengths (Å) and angles (degrees)
BH_3	BH 1.1874 HBH 120.0
BF_3	BF 1.2966 FBF 120.0
HBF_2	HB 1.1798 BF 1.3027 HBF 121.1
$MeBF_2$	BC 1.5655 BF 1.3109 CH 1.0849 HCB 110.8 FBC 122.1
$C_6H_5BF_2$	BC 1.5467 BF 1.3116 FBC 121.9 (CC 1.397, CH 1.085 ass.)
$HOBH_2$	HO 0.9404 OB 1.3439 $BH_{(c)}$ 1.1952 $BH_{(t)}$ 1,1880 HOB 115.3 $OBH_{(c)}$ 120.4 $OBH_{(t)}$ 117.6
$MeOBH_2$	CO 1.4057 CH 1.0825 BO 1.3345 $BH_{(c)}$ 1.1968 $BH_{(t)}$ 1.1896 COB 124.0 OCH 109.7 $HBO_{(c)}$ 120.6 $HBO_{(t)}$ 117.8
$HOBF_2$	$FB_{(c)}$ 1.3152 $FB_{(t)}$ 1.3030 BO 1.3344 OH 0.9408 $FBO_{(c)}$ 121.8 $FBO_{(t)}$ 120.1 HOB 115.6
$HB(OCH_2)_2$ (C_2 symm)	HB 1.1807 BO 1.3537 OC 1.4157 CH 1.0811 CC 1.5444 OBO 113.0 HBO 123.5 BOC 108.9 OCC 104.6

Table 3.2. Equilibrium structural data (continued).

Molecule	Bond lengths (Å) and angles (degrees)
H_2NBH_2	BN 1.3900 BH 1.1917 NH 0.9926 BNH 123.1 NBH 119.4
H_3NBH_3	BN 1.6839 BH 1.2090 NH 1.0013 BNH 110.6 NBH 104.6
Me_3NBH_3	BN 1.6820 BH1.2120 NC 1.5008 CH 1.0764 BNH 107.4 NBH 105.5 NCH 108.3 (Angle BN/C_{3v} axis 1.143°)
$HB(NH_2)_2$	HB 1.1942 BN 1.4126 $NH_{(i)}$ 0.9924 $NH_{(o)}$ 0.9905 HBN 118.7 NBN 122.6 $BNH_{(o)}$ 122.0 $BNH_{(i)}$ 124.2
BF_2NH_2	FB 1.3163 BN 1.3905 NH 0.9915 FBN 121.3 HNB 122.4
$OC.BH_3$	CO 1.1000 BC 1.6172 BH 1.2024 CBH 103.1
H_3PBH_3	HB 1.2054 BP 2.0255 PB 1.3992 HBP 103.2 HPB 117.4
F_3PBH_3	FP 1.5370 PB 1.9216 BH 1.2023 FPB 118.0 HBP 102.5

Table 3.3. Equilibrium structural data (continued).

Molecule	Bond lengths (Å) and angles (degrees)
Me_3PBH_3	PB 1.9648 BH 1.2128 CP 1.8453 CH 1.0803 BPC 112.6 HBP 105.2 HCP 107.5 (Angle PC/C_{3v} axis 1.920°)
$B_3O_3H_3$	HB 1.169 BO 1.388 BOB 123.5
$B_3O_3(OH)_3$ (C_{3h} symm)	$BO_{(r)}$ 1.3697 BO(H) 1.3399 OH 0.9485 HOB 119.9 O(H)BO(R) 122.1 BOB 122.5
$B_3O_3(OMe)_3$ (C_{3h} symm)	$BO_{(r)}$ 1.3730 BO(C) 1.3343 OH 1.4396 COB 125.5 O(C)BO(R) 122.2 BOB 122.7
HBF(+)	HB 1.1675 BF 1.2026 HBF 180.0

Table 4.1. ^{11}B SCF electric field gradients.

Molecule	q_{xx}	q_{yy}	q_{zz}
BH_3	0.3180	0.3180	−0.6360
BH_3(CI)	0.3231	0.3231	−0.6463
BF_3	0.1634	0.1634	−0.3268
BF_3(CI)	0.1434	0.1434	−0.2869
H_3N-BH_3	0.1495	0.1495	−0.2990
H_3N-BH_3(CI)	0.1498	0.1498	−0.2995
H_2N-BH_2	0.1989(BN)	0.2502	−0.4491(π)
$H_2N(B_2H_5)$	−0.1082	−0.1445	0.2527
Me_3N-BH_3	0.1222	0.1222	−0.2444
OC-BH_3	0.1370	0.1370	−0.2739
OC-BH_3(CI)	0.1339	0.1339	−0.2678
OC-BH_3(CASSCF)	0.0941	0.0941	−0.1882
$MeBF_2$	0.0771	0.3302(BC)	−0.4073(π)
$MeBF_2$(CI)	0.0742	0.3164	−0.3906
F_3P-BH_3	0.1312	0.1312	−0.2624
$HOBF_2$	0.1020	0.2134	−0.3154(π)
H_3PBH_3	0.1434	0.1434	−0.2868

Table 4.2. SCF electric field gradients (continued).

Molecule	q_{xx}	q_{yy}	q_{zz}
$C_6H_5BF_2$	0.0653	0.3206(BC)	−0.3858(π)
$HB(OCH_2)_2$	0.1054	0.2775(BH)	−0.3829(π)
$MeOBH_2$	0.1620	0.3013	−0.4634(π)
HBF_2	0.0955	0.3138	−0.4093(π)
Me_3PBH_3	0.0877	0.0877	−0.1755(π)
$HOBH_2$	0.1736	0.3073	−0.4809(π)
$B_3O_3H_3$	0.0888(BH)	0.3258	−0.4144(π)
$B_3O_3(OH_3)$	0.1234	0.1956	−0.3190(π)
$B_3O_3(OMe)_3$	0.1150	0.1979	−0.3128(π)
BF_2NH_2	0.0616	0.2361	−0.2978(π)
HBF(+)	−0.2983	−0.2983	0.5966(BF)

value is χ_{zz} 2.64 ± 0.04 MHz at 77 °K [37]; the present interpolated value from the correlation line is 2.69 MHz for BF_3 and 5.29 MHz for BH_3, the former being in excellent agreement with the experimental data. On this basis, the experimental χ_π for HBF_2 (3.34 MHz) [38] lies very close to the weighted average of the BH_3 and BF_3 calculated values. Replacement of H by Me [39] or Ph [40] leads to almost zero change both experimentally and theoretically.

Several of the substituted compounds X-BF_2 and X-BH_2 have only C_s symmetry so that the EFG-PA no longer lie along the bond axes; examples are X = OH, OMe (2a, b); the r_e structures computed are in excellent agreement with the MW data. In some cases the early MW studies did not resolve $^{10,11}B$ quadrupole coupling, but the advent of FT-MW has solved that problem.

Table 4.3. Derived ^{11}B quadrupole coupling constants and experimental data (MHz).

Molecule	Method	χ_{aa}	χ_{bb}	χ_{cc}	Ref.
BF_3	TZVP	−1.32	−1.32	2.64	–
	NQR	−1.34	−1.34	2.69	37
HBF_2	TZVP	−0.794	−2.611	3.405	–
	MW	−0.75	−2.58	3.33	38 b
$MeBF_2$	TZVP	−2.747	−0.641	3.389	–
	MW	−2.713	−0.695	3.408	39
$HOBF_2$	TZVP	−1.632	−0.993	2.625	–
	MW	−1.477	−1.195	2.672	41
$PhBF_2$	TZVP	−2.667	−0.543	3.210	–
	MW	−2.589	−0.600	3.189	40
NH_2BF_2	TZVP	−1.655	−2.081	3.736	–
	6-31G**	−1.81	−2.29	4.10	46
	MW	−1.6(ass)	−2.2(2)	3.8(2)	44
	MW	−1.995	−1.538	3.533	45
HBF(+)	TZVP	−4.964	2.482	2.482	–
	MW	−5.15	2.57	2.57	55
$HOBH_2$	TZVP	−1.474	−2.527	4.001	–
	MW	−1.1(7)	−2.8(4)	3.9(4)	42
$MePH_2$-BH_3	MW	0.975	−0.104	−0.872	72
F_3P-BH_3	TZVP	−0.745	−0.745	1.491	–
	MW	−0.739	−0.739	1.478	69
NH_3BH_3	TZVP	2.492	−1.246	−1.246	–
	NQR	1.253	(−)0.627	(−)0.627	60

Table 5. p_π and d_π boron populations in some boranes.

Molecule	p_π	d_π	π-Total
BH_3	0.0000	0.0000	0.0000
$HOBH_2$	0.1547	0.0265	0.1813
$MeBF_2$	0.1474	0.0670	0.2144
HBF_2	0.1957	0.0615	0.2572
NH_2BF_2	0.2249	0.0880	0.3130
$HOBF_2$	0.2980	0.0960	0.3940
BF_3	0.2783	0.1008	0.3791
NH_2BH_2	0.0957	0.0215	0.1172

The present calculations reproduce the differences between $HOBF_2$ (**1**) [40, 41], $HOBH_2$ [42], and $MeOBH_2$ (**2**) [43], but the smaller components show some scatter in the correlation; unfortunately the accuracy of the conventional CW-MW measurements is low, but a further feature is that the correlation relies on two assumptions, (a) that the r_e is the same as r_s, such that (b) the IA have similar directions. Neither of these will be strictly correct. In the series XBF_2, taking just the out-of-plane component (χ_π), we have the order (both experimentally and theoretically) for $|\chi_\pi|$: H, Me > Ph > F, OH; this series has increasing σ-attraction and π-donation from left to right. The resultant of these population trends (Table 5) shows that overall *B* is positive in character but with increasing π-electron release in the above series from H to F; thus, as in the Townes-Dailey requirement, the π-population is greatest where the π-coupling is least positive.

As mentioned above, some of the ^{11}B CW-MW values have high error bars; for example in BH_2OH, $\chi_{aa} = -1.1$ (7) [42], although the data fit the correlation line well. In practice, what is determined in structures such as the present is χ_+ $(= -\chi_{aa})$ and χ_- $(= \eta\chi_{aa} = \chi_{bb} - \chi_{cc})$, as in (3b); hence, if χ_+ $(-\chi_{aa})$ is small, $(\chi_{bb} - \chi_{cc})$ may still be large. Such a case is amino-borane (BH_2NH_2, **3**, **4**); both CW- [44] and FT-MW [45] yield $\chi_{bb} - \chi_{cc} = -6.0$ MHz, but different assumptions have been made with respect to χ_{aa}. Those based upon previous DZ [44] and DZ+ polarisation calculations [46] yield the best correlation with the present work. The FT-MW values χ_{ii} for BF_2NH_2 (**4**, X = F) [45] seem to be well-determined but do not lie close to the correlation with any of the calculated work (present, [46]); thus χ_π is smaller for X = H than X = F (**4**); this is contrary to the result for $HOBH_2$/$HOBF_2$ and indeed the calculated values for BH_3/BF_3; large scale CI on both molecules **4** does not indicate any significant change in χ_{ii}, and hence does not seem to imply that the molecules (**4**; (X = H, F) are very different in nature Clearly **4** (X = F) would be stabilised by electron acceptance from F relative to H. Comparison of the total atomic populations (e) and dipole moments for **3** (X = H) [44], **3** (X = F) [47] and the diaminoborane **5** [48] shows that the overall molecular dipole moments are accurate to ±0.2 D (Table 6), although, it is true, the error is in the reverse direction for the fluoro-compound. The charge distributions are likely to be realistic, and the placing of amino-borane between the HO and Me derivatives for both series **4** (X = H, F) is reasonable. The FT-MW result is curious in apparently making the boron coupling χ_{cc} larger for **4** (X = F) than **4** (X = H); since the ^{14}N (χ_{cc}) quadrupole coupling of **4** (X = H, −2.66 MHz) is smaller than **4** (X = F, −3.24 MHz), this implies that there is higher π-density on **4** (X = F) than **4** (X = H). This in turn can be understood as π-back-bonding in the X = F case, offsetting the high σ-acceptance. If the π-N density is higher (Table 5), in agreement with this, then the **4** (X = H) value for χ_{cc} should be more positive than that for **4** (X = F). The lengths of the B-N bonds in the two compounds are effectively identical (1.40 Å) [44, 47], as calculated. What does also seem clear is that the aminoboranes must lie a lot closer in electron distribution to **3** than **4**; this is evident both from the calculated electron

Table 6. Charge distributions in amino-boranes.

Molecule	Atomic population				Dipole moment (calc./exp.)
	H(N)	N	B	X(B)	
NH_2BH_2	0.7311	7.6633	4.7277	1.0731(H)	1.686/1.844
NH_2BF_2	0.7111	7.7185	4.1922	9.3334(F)	2.792/2.595
$(NH_2)_2BH$	0.7374	7.7408	4.4803	1.0824(H)	1.215/1.245

populations and also the experimental NQCC. If the B had a net negative charge as in **4**, then the χ_π would be much less positive than observed. The closely related molecule, amino-diborane (**6**) has not so far yielded ^{11}B quadrupole coupling, although ^{14}N data was obtained [49]; again we calculate the dipole moment (2.824 D) close to experiment (2.67 D), and the ^{14}N χ_{ii} are within about 0.25 MHz.

The cyclic 1,3,2,-dioxaborolane (**7**) has a slightly non-planar (C_2) structure. The magnitude of the χ_{cc} ^{11}B quadrupole coupling [50] is very close to several of the compounds with BF_2 groups (Table 4), and is well calculated, the dipole moment (and structure) again being close (2.39 D) to the MW value (2.28 D). Using the correlation line, this suggests that the ^{11}B quadrupole coupling for $FB(OH)_2$ should lie near 2.6 MHz (χ_{cc}), cf. [51].

The boroxine derivatives (**8**–**10**) are well known, and electron diffraction structures are available for **8** (X = H) [52] which shows a regular D_{3h} structure as the most probable. An early solid state NMR investigation of trimethoxyboroxine **9** (X = OMe) led [53] to the conclusion that $\chi_\pi = 2.14$ MHz, if the asymmetry parameter was assumed zero, which was not unreasonable for three neighbour oxygen atoms. The triphenyl derivative **10** (X = Ph), which should have NQCC values close to those for the parent ring (based upon $HBF_2/PhBF_2$) has been found to have χ_{zz} 3.148 MHz by NQR [54]. These values seemed reasonably consistent, but an investigation on each of **8** and **9** was performed. We thus optimised the structures for each of **8**, **9**, **11** (the latter pair being assumed to be C_{3h}), and obtained the NQCC; the values for boroxine (**8**, X = H) show that the largest component (χ_{zz}) lies in the π-direction, with the next largest (χ_{yy}) lying along the BH bonds, and the tangential value at the ring B atom being very small. This leads to a firm assignment to the NQR data for **8** (X = Ph), which can be expected to be similar to the parent molecule. Both of the derivatives **9** (X = OMe) and **11** (X = OH) show non zero asymmetry parameters, owing to the non-radial direction of the OH group, which leads to an oxygen lone pair lying in-plane on one side of the B-atom. If we presume a time average (both compounds acting the same) the present SCF values lie reasonably close to the early NMR data [53]. This method, or a modern equivalent, seems worthy of further action.

The HBF cation is linear [55] with r_s (BH) = 1.1735, r_s (BF) = 1.2103 Å; the present study (r_e) obtained 1.1674 and 1.2026 Å, a very satisfactory result. The ^{11}B quadrupole coupling as mentioned above (−4.96 calc./−5.15 MHz observed), seems very satisfactory. The calculated charge distribution shows H (+0.2345) B (+0.7478) F (−0.9823 e); the 2p orbital components along (z) and across (x, y) the molecular axis are 0.7672e and (2x) 0.1583e, respectively, so that the off-axis (π) density is very low. The highly positive χ_π is consistent with this and yields a value rather similar to that for BF_3.

As well as being one of the simplest adducts of borane, borane-carbonyl (BH_3-CO) is historically important; the nuclear spins of the isotopes of boron, ^{10}B ($I = 3$), ^{11}B ($I = 3/2$) were determined from the comparison of observed and calculated hyperfine structure for this molecule (**12**) [56]. The ^{11}B NQCC χ_{aa} 1.55 MHz was subsequently revised to 1.60 MHz [57], but still lies well off the correlation line (Figure 1). The critical point seems to be that the SCF optimisation leads to a rather weaker complex than observed; the CO bond is similar (1.100 calc./1.135 obs.), but the B-C length is rather longer (1.6172 calc./1.57 obs.) and HBH rather flatter. In consequence, the NQCC is more negative (a.u.), i.e. towards BH_3, leading to the point lying below the correlation.

A large scale CI (57975 configuration) and MC-SCF study at the single configuration structure failed to yield any improvement, so that the B-C length provides the only plausible explanation (see below). However, when the structure is at the MW values, and an MC-SCF calculation is performed, the EFG becomes q_{zz} −0.188 a.u. (χ_{zz} 1.566 MHz), which fits the correlation line exactly. This calculation used all permutations of 10 electrons in 10 MOs and generated 9772 configurations in the MC-SCF calculations.

The structure of the ethane analogue, ammonia-borane (**13**) is well known both theoretically and experimentally. The MW structure shows BN 1.6576, BH 1.2160, NH 1.0140 Å, with NBH 104° and BNH 110° [58]; again the tendency is to make the calculated BN (1.6839 Å) a little long, but this is not repeated in angle changes, so that the complex is not destabilised by the single configuration SCF calculation by much. An optimisation at the MP3 level (which mimics the CI process by introducing post-SCF effects via perturbation theory) leads to a shortening of the BN bond further [59]. The calculated EFG here suggests that the ^{11}B χ_{zz} should be near 2.4 MHz (with the ^{14}N χ_{zz} 2.0 MHz); these have not been observed by MW spectroscopy so far, but the ^{11}B NQCC has been investigated by NQR [60] at room temperature, which leads to a surprisingly low value of χ_{zz} 1.504 MHz. The fact that this agrees with an early SCF minimal basis set calculation is clearly fortuitous. The low ^{11}B NQCC appears to indicate a strong bond, on the basis that BH_3 is predicted to have a high positive value, and that the NH_3-BH_3 NQR value is also positive. Thus the ^{14}N NQR value should be low, because of the loss of lone pair character; this is observed with ^{14}N χ_{zz} 1.253 MHz [60], and the trend is reproduced by the calculation on ^{14}N (χ_{zz} 1.924 MHz). It seems that the same phenomenon as with borane-carbonyl is occurring, the complex is calculated slightly too weak at the SCF single configuration level. It is interesting to note that FT-MW has obtained rather larger couplings at both ^{11}B (+2.064 MHz) and ^{14}N (−2.832 MHz) for trimethylamine-borane (**14**) [61]. For NH_3BH_3 (**13**) the BN distance is 1.6576 Å [58], in the Me_3N adduct (**13**) it is variously described in the range 1.609–1.65 Å, but probably lies near 1.638 ± 0.01 Å [62], with angle NBH similar in **13** and **14**; this implies a slightly stronger BN bond in the Me_3N adduct, agreeing with its stronger basicity. On this ground, the ^{11}B and ^{14}N NQCC should both be smaller in magnitude (less positive and negative, respectively) for **14** than for **13**. This does not seem to be the case. However, the B-N lengths in various adducts of this type do not appear consistent [63, 64], and it has been suggested that they vary with temperature and perhaps phase [65]. The complexes of phosphines with boranes show a similar phenomenon, with very varying PB lengths; thus in **15**, **16** and **17** we find PB 1.836, 1.937, 1.901 [66–68]; this is an unexpected order, but it is interesting to note that the SCF r_e for this series yields 1.9216, 2.0255 and 1.9648 Å, respectively, mirroring the experiment. The ^{11}B NQCC is important in these studies, but so far CW/FT-MW data are inadequate with 1.478 MHz (**15**, X = F) [69], 1.198 MHz (**17**, X = Me) [70]. Since PMe_3 is presumably a stronger donor than PF_3, this suggests that we would expect χ_{zz} to be less positive in the Me than F case, as found.

Lastly, we comment upon the NQCC for borazine (**18**); NQR data yield (χ_{zz}/η) ^{11}B (3.249/0.133), ^{14}N (1.440 MHz/0.10) [71]. There exist electron diffraction structure data for this molecule which agree with various theoretical studies with values near BN 1.43 Å, with NBN 117.5° [73]. We obtain q_{zz} −0.3688 a.u. (3.068 MHz) for ^{11}B, with η 0.04; the radial component along BH is marginally larger (−1.596 MHz) than the tangential value at B (−1.473 MHz), and this appears to be in good agreement with the NQR data. On the other hand, at ^{14}N we obtain χ_π −1.514, $\chi_{NH(R)}$ 1.787 and χ_T −0.273 MHz, to be compared with magnitudes 1.44, 0.79, 0.65 MHz; it is clear that the magnitudes computed are in such strong disagreement, that we cannot be sure of the sign of χ_{zz}. The explanation is unclear, although NH/NH H-bonding in the solid remains a possibility.

Boratrane (**19**) is a typical case of the "atranes", the bridged rings with internal bonding, or at least complexing. The NQR of the parent compound, indexed as 2,8.9-trioxa-5-aza-1-bora-bicyclo[3,3,3]-undecane, has been obtained [54], while two crystal structures show the molecule to have C_3 symmetry [74, 75]. We have carried out an SCF calculation with the TZVP basis (only SV on H) at the more accurate structure [74]; the CH bonds were lengthened to the expected 1.085 Å along the observed X-ray vectors (where the usual shortening to ca. 1.0 Å was observed). The calculated EFG at B lies close to the correlation line with q_B −0.1872 a.u. (+1.558 MHz) and q_N 0.7749 a.u. (−3.107 MHz). The NQR χ_{zz} are 1.240 (^{11}B) and 2.880 MHz (^{14}N), with asymmetry zero at both centres [54], as required by C_3 symmetry.

Given the χ_π values for $HOBH_2$ (+3.9 MHz), $HOBF_2$ (+2.67 MHz) and Me_3N-BH_3 (+2.05 MHz), it seems probable that the dipolar structure $B^{(-)}-N^{(+)}$ is appropriate for boratrane (+1.240 MHz); O and F behave similarly here (BF_3 versus $HOBF_2$). The present level of agreement seems very acceptable at both centres; again this suggests that when H-bonding can be ignored, and a single configuration SCF is appropriate, agreement is to be expected. It further highlights the discrepancy with borazine [18].

Conclusions

There is now clear experimental and theoretical evidence that the atomic nuclear quadrupole moment

($Q_{^{14}N}$) is close to 20.5 mB. The value for $Q_{^{11}B}$ must be close to 42.0 mB. However, the calculated "effective Q_x" for nuclear X is quite definitely basis set dependent. Provided the basis set is DZ or better, we find the asymmetry reasonably stable with molecules of largely covalent nature; hence the Q_x can be used as a scaling parameter, leading to values for the NQCC reasonably close to experiment. This has long been practised, but means that the debate about the value of Q_x can be separated from the subject of assignment of NQR spectra.

For tri-covalent B, the NQCC are reasonably well determined from single configuration SCF r_e calculations, since r_e lies close to r_s, the correlation being with MW data. When the molecule is a clear donor-acceptor complex, it seems likely that single configuration (SC) SCF will not give r_e accurately enough to give good NQCC. This effect is likely to be worst with simple cases $X_3B\text{-}MY_3$ with C_{3V} symmetry; it is a further manifestation of the well-known deficiencies of the SC-SCF with di-atomics. Basically, too much emphasis is placed on σ-bonding in these cases, and only by introduction of doubly excited configurations with both $(\sigma^*)^2$ and $(\pi^*)^2$ can this be corrected. This is a function of the very high dominance of a single MO in the bonding; hence the problem is worst with small molecules, since larger, more complex, molecules have more delocalised MOs.

The advent of FT-MW seems likely to revolutionise the accurate evaluation of ^{11}B and ^{14}N NQCC, especially in cases where both elements, or several of each, are present.

In order to compare calculations of EFG with NQR data, it is clear that either the environment of the molecule in question must be included, or the molecule must have no strong interactions with its neighbours in the lattice. In recent papers we have shown that differences between MW and NQR data can be quite well reproduced in H-bonded situations, by study of small groups of molecules at the X-ray structure [76]. This approach will no doubt be widely applied, but a further, and more exciting prospect is the use of recently developed ab initio codes (CRYSTAL) for the calculation of the wave-function of a set of unit cells [10]; here the integrals are calculated in the repeating unit cell, until the values become smaller than a pre-set tolerance. The wave-function then is obtained per unit cell, but includes the effect of the bulk, out to some distance. In our hands, small molecule cases, such as N_2 and NH_3 give very good EFG agreement with NQR data. In the latter case of NH_3, the NQR value for ^{14}N is obtained from a study of one molecule with 12 neighbours in several shells, such that the full H-bonded environment of the probe molecule and its immediate neighbours is included. For small molecules, such as N_2 it can be difficult to obtain zero asymmetry in groups of molecules; the CRYSTAL approach solves this. The development of these codes to cope with systems of many atoms and many orbitals per unit cell, is eagerly awaited.

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