



Determining nuclear quadrupole moments of Bi and Sb from molecular data†

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An independent value of $-422(3)$ millibarn (mb) is obtained for the nuclear quadrupole moment $Q(^{209}\text{Bi})$ using experimental coupling constants for diatomic BiN, BiP, BiF, BiCl, and BiI, combined with full-Dirac CCSD-T calculations of the electric field gradient q . This value lies close to two other recently published molecular results, and a full-triplet CCSDT atomic result. Based on the same approach, we obtained $Q(^{121}\text{Sb}) = -541.7(0.8)$ mb and $Q(^{123}\text{Sb}) = -690.6(1.0)$ mb, in agreement with one recently published molecular result.

The nuclear quadrupole moment $Q(^{209}\text{Bi})$ was one of the first moments determined.¹ The value, in 1936, was -400 mb [1 mb = 10^{-31} m²]. Interest in the Q value of the neutron deficient isotopes continues, due to the nuclear physics.² A common way to determine Q is to measure a nuclear quadrupole coupling constant (NQCC), $B = eqQ/h$, and to combine it with a theoretical determination of the electric field gradient (EFG), q , on the nuclear site in the system studied. This can be done for atomic, molecular, or solid-state systems and the results usually agree with each other, and with the main alternative approach of muonic or pionic systems. For a recent review see Pyykkö.³

A notable exception is $Q(^{209}\text{Bi})$, where a 2001 atomic Q was $-516(15)$ mb⁴ but a molecular value using the BiN and BiP diatomics by Teodoro⁵ was $-420(8)$ mb. Both B experiments and both q calculations were expected to be quite accurate. Therefore the problem is still on the table (see below) and we want to have a further look at the ‘molecular’ $Q(^{209}\text{Bi})$. Note that we here consider two series of molecules, the pnictogens BiN and BiP and the monohalides BiX ($X = \text{Cl, F, I}$) and that these series have opposite signs of B (Table 1).

The case of antimony still remains difficult. The reference value has fluctuated widely over the years. The old, atomic

standard values for $^{121,123}\text{Sb}$ were $-360(40)$ mb and $-490(50)$ mb,⁶ respectively. Later, Voss *et al.* from an experimental and theoretical analysis of the configuration $5p^2 6s$ supported a value of $-440(30)$ mb for ^{121}Sb .⁷ Solid-state calculations by Svane⁸ first suggested that the ^{121}Sb value should be changed to -669 mb. Then molecular calculations by Demovič *et al.*⁹ and Haiduke *et al.*¹⁰ produced mutually consistent values of -556 mb and -543 mb, respectively. Both determinations were based on diatomic data for SbN, SbP, SbF and SbCl by Cooke and co-workers, reported in Table 1. This second series of four molecules has been studied in this work.

BiN, SbN, BiP and SbP are triple-bonded, closed-shell, short-bond systems with a substantial gap between the highest occupied and lowest empty molecular orbital. They are consequently easiest to describe with a single-configuration starting point. The monohalide BiX ($X = \text{F, Cl, I}$) and SbX ($X = \text{F, Cl}$) are, in a non-relativistic picture, open-shell $^3\Sigma^-$ states and were found to be a good example of Hund’s case (b). In the relativistic picture, due to strong spin-orbit coupling, they are very near the Hund’s case (c) limit, with the consequence of a $^1\Sigma^+$ ground state, that could be considered as a relativistic closed-shell.

Table 1 Available accurate experimental nuclear quadrupole coupling constants B_e at the equilibrium bond distance R_e in ^{209}Bi and ^{121}Sb diatomic molecules to lowest order

Molecule	B_e (MHz)	R_e (Å)	Ref.
BiN	905.066(88)	1.9349079(7)	11
BiP	903.031	2.2961520(80)	5 and 11
BiF	-1150.9632	2.034276(1)	12
BiCl	$-1027(12)^a$	2.47155(7)	13
BiI	$-909.5(20)^a$	2.80053(8)	14 and 15
SbN	649.669(9)	1.8356707(2)	16
SbP	620.35(1)	2.2054454(5)	16
SbF	$-586.802(1)$	1.917584(28)	17
SbCl	-515.124^b	2.335472(13)	17

^a Experimental B_0 given for BiCl and BiI. ^b This value of B has been calculated from the experimental results for $^{123}\text{Sb}^{35}\text{Cl}$ by using the ratio $B(^{123}\text{Sb})/B(^{121}\text{Sb}) = 1.27491(1)$.¹⁷

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In a diatomic molecule, the total electric-field gradient q at the nucleus X can be decomposed into nuclear and electronic contributions.

$$q(X) = q_{\text{nucl}}(X) + q_{\text{el}}(X)$$

In this work, the electronic contribution has been calculated with the DIRAC program package¹⁸ using a relativistic coupled-cluster approach (CCSD-T) and the density functional theory (DFT) using the long-range corrected hybrid CAM-B3LYP* functional¹⁹ with a 4-component Dirac-Coulomb (DC) Hamiltonian including spin-orbit coupling (see ESI† for details). CCSD-T was first introduced by Deegan and Knowles²⁰ and differs from the standard CCSD(T) correction by an inclusion of more disconnected triples terms up to fifth order. Haiduke *et al.*¹⁰ pointed out, for example, that for Sb compounds, there could be a non-negligible difference between CCSD(T) and CCSD-T for $Q(^{121}\text{Sb})$ and $Q(^{123}\text{Sb})$ and concluded that CCSD-T provided significantly better results.

All calculations were carried out applying CV3Z triple-zeta Dyall basis sets with core correlating functions (see ref. 21 and 22 and the appropriate references) in their fully uncontracted form. We used a Gaussian charge distribution model to describe the charge of nuclei. Furthermore, all the present calculations have been carried out at the experimental value of the equilibrium bond distances, R_e (Table 1). Note that the use of available experimental (B_e , R_e) takes care of the vibrational effects. Within the DFT framework, the electronic contribution to the q value is obtained from an analytic gradient formulation as implemented in the DIRAC program. For the CCSD-T approach, the electronic contribution to the q value is obtained by adding the q analytic HF value to the contribution of the electronic correlation to q ($q_{\text{el}}(X) = q_{\text{el, HF}}(X) + q_{\text{el, corr.}}(X)$). In order to get the correlation correction to q we used an approach proposed by Pernpointner *et al.*²³ fitting the correlation energy obtained at different field strengths (between $\pm 1.0 \times 10^{-6}$ a.u. and $\pm 1.0 \times 10^{-10}$ a.u.) to an n th order polynomial. The correlation correction to q is obtained from the first order response energy²³ (see ESI† for details). In a final step, Q was calculated from the indirect method introduced by Belpassi *et al.*²⁴ which corresponds to the calculation of slope from a least squares regression line through all (q, B) points of the Bi and Sb molecular series BIN, BiP, BiF, BiCl, BiI and SbN, SbP, SbF, SbCl according to: $(B/\text{MHz}) = 0.2349647 (q/\text{a.u.}) (Q/\text{mb})$ with B the experimental nuclear quadrupole coupling constant (see ESI† for details). This original approach combining on the one hand the polynomial determination of the correlation correction to q and on the other hand the indirect method to determine Q makes it possible to minimize the impact of errors in each stage of the evaluation of the Q value (see ESI† for details).

The graphs are reported in Fig. 1 and 2 for the Bi and Sb molecules, respectively, in a closed-shell ground-state picture.

For the Bi-containing molecules, we obtained a good agreement between CAM-B3LYP* functional and the CCSD-T value. The determined $Q(^{209}\text{Bi})$ value from the linear fit is $-405(9)$ mb from the DFT/CAM-B3LYP* calculations and $-422(3)$ mb from the CCSD-T calculation. Here the error limits are statistical standard errors. These values are in agreement with the recent determinations of Teodoro *et al.*⁵ at $-420(8)$ mb based on the

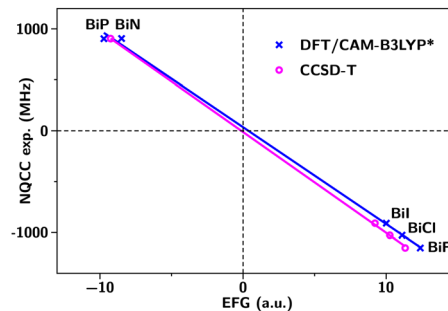


Fig. 1 The experimental NQCC in MHz as a function of the calculated EFG in atomic units for bismuth-based molecules.

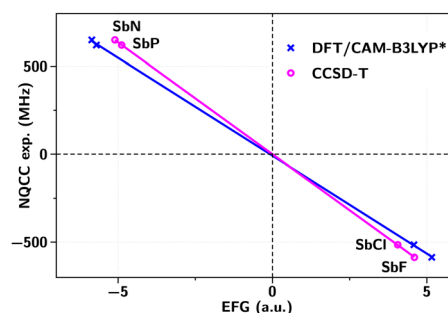


Fig. 2 The experimental NQCC in MHz as a function of the calculated EFG in atomic units for antimony-based molecules.

direct approach for each molecule BiN and BiP separately. Shee *et al.*²⁵ obtain from the same two molecules -415.1 mb. Skripnikov *et al.*²⁶ published a new ‘atomic’, FS-CCSDT $Q(^{209}\text{Bi})$ of $-418(6)$ mb. Our results are also consistent with recent work by Liu and Cheng²⁷ who obtained values in the range of -411 to -422 mb for the same five molecules using an atomic mean-field spin-orbit approach within the exact two-component theory (SOX2CAMF).

Commenting on the $Q(^{209}\text{Bi})$ of -516 mb by Bieroń and Pyykkö in 2001,⁴ it was obtained by about 20 000 Configuration State Functions (CSF), thought at the time to be adequate. Single, some double and no triple substitutions were included. Currently over 4 million CSFs are possible and still don’t provide a complete convergence for the 5-valence-electron system Bi.²⁸

We compare our $Q(\text{Bi})$ determination with the (previous) Group-15 case of $Q(\text{Sb})$. The B_e and R_e are listed in Table 1. Concerning the $Q(^{121}\text{Sb})$ we observed a significant deviation between the CAM-B3LYP* value at $-474(3)$ mb and the CCSD-T value at $-541.7(0.8)$ mb. In 2006, from a CCSD-T calculation, Haiduke *et al.*¹⁰ proposed a recommended value of $-543(11)$ mb for ^{121}Sb . Their values were calculated using only the SbN and SbP closed-shell molecule results due to too large errors in the SbF and SbCl open-shell calculations. In the same time, Demović *et al.*⁹ recommended the value of (-556 ± 24) mb from direct method on the SbN, SbP, SbF, SbCl series with IOTC CCSD(T) calculations. In closed-shell picture, the Haiduke *et al.*¹⁰ value is in good agreement with our new value. We can also notice the quality of calculated EFGs confirmed by an R^2 of 1 and the



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