

Supporting Information

Determining nuclear quadrupole moments of Bi and Sb from molecular data

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

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

$q_{nucl}(X)$ depends only on the nuclear charge and internuclear distance. The electronic contribution needs to be calculated by using computational methods of the electronic structure theory. Present electronic calculations were carried out with the DIRAC program package¹ using the 4-component relativistic Dirac-Coulomb (DC) Hamiltonian including spin-orbit coupling and taking two routes:

- DC-HF and Density functional theory (DC-DFT) using the long-range corrected hybrid CAM-B3LYP functional² as implemented³ in the DIRAC program. This is straightforward regarding the analytical implementation in DIRAC.
- Dirac-Coulomb Coupled Cluster based property calculations from numerical differentiation (analytical implementation is not yet available). CCSD-T is considered.

An analytic gradient formulation is used for DFT calculations. In Kohn-Sham calculations the open-shell molecules are treated in terms of fractional occupation. Thierfelder et al.⁴ noted that the CAM-B3LYP functional with the original parameter set does not perform well for EFG calculations. In this work, we employed the CAM-B3LYP*, a modified CAM-B3LYP functional explicitly optimised for EFG calculations with long-range correction parameters changed ($\alpha = 0.4$, $\beta = 0.179$ and $\mu = 0.99$) according to Thierfelder et al.⁴. All calculations were carried out applying CV3Z triple-zeta Dyall relativistic basis sets with core correlating functions (see^{5,6} and the appropriate references) in their fully uncontracted form to allow maximum flexibility of the one-particle density close to the nucleus. They are defined as Bi (30s26p17d12f1g), Sb(28s21p15d4f1g), N(14s8p3d1f), P(18s11p5d3f), F(14s8p3d1f), Cl(18s11p5d3f) and I(28s21p15d4f1g) for the large components. The small components are generated by the strict kinetic-balance. The active set of spinors is chosen according to the basis set correlating functions. The electronic contribution to the q value is obtained by adding the contribution of the electronic correlation to the analytic HF value ($q_{el}(X) = q_{el.,HF}(X) + q_{el.,corr.}(X)$). In most publications, this contribution is obtained numerically by differentiation of the correlation energy $E_{corr.}$ with respect to the perturbation strength λ :

$$\left(\frac{\partial E(\lambda)}{\partial \lambda}\right)_0 \approx \frac{E(+\lambda) - E(-\lambda)}{2\lambda} \quad (1)$$

This two points derivative method required a linear dependence of the correlation energy on λ that is satisfied only with small value of λ . As pointed out by Permpointer et al.⁷, this formulation can require to use very small λ values in order to obtain linear dependence on the perturbation strength, which however, can lead to numerical inaccuracies or to require too large values in order to obtain sufficient precision in the numerical differentiation of the total energy. In this work we used an alternative approach proposed by Permpointer et al.⁷ and whose accuracy has been shown by Arcisauskaite et al.⁸ expanding $E(\lambda)$ with respect to λ according to:

$$E(\lambda) = E_0 + \lambda \left(\frac{dE(\lambda)}{d\lambda}\right)_0 + \frac{1}{2}\lambda^2 \left(\frac{d^2E(\lambda)}{d\lambda^2}\right)_0 + \dots \quad (2)$$

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The correlation contribution to the EFG was obtained fitting the correlation energy obtained at different λ values (between $\pm 1.0 \times 10^{-6}$ a.u. and $\pm 1.0 \times 10^{-10}$ a.u.) to a 3rd order polynomial as shown in Figure 1, e.g., for BiX (X=F, Cl, I).

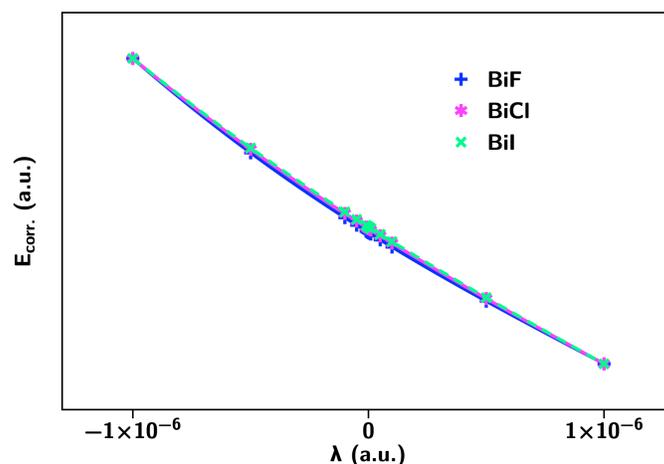


Fig. 1 CCSD-T correlation energy for different bismuth monohalides as a function of λ .

The resulting q values are given in Table 1.

Molecule	CAM-B3LYP*	CCSD-T
BiN	-8.491	-9.260
BiP	-9.728	-9.251
BiF	12.382	11.327
BiCl	11.109	10.251
BiI	10.009	9.217
SbN	-5.852	-5.102
SbP	-5.703	-4.884
SbF	5.158	4.596
SbCl	4.580	4.056

Table 1 Electric-field gradient calculated at the experimental values of the equilibrium bond distance. All data in a.u.

Notes and references

- 1 DIRAC, a relativistic ab initio electronic structure program, Release DIRAC19 (2019), written by A. S. P. Gomes, T. Saue, L. Visscher, H. J. Aa. Jensen, and R. Bast, with contributions from I. A. Aucar, V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, L. Halbert, E. D. Hedegård, B. Heimlich–Paris, T. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, J. K. Lærdahl, C. V. Larsen, Y. S. Lee, H. S. Nataraj, M. K. Nayak, P. Norman, G. Olejniczak, J. Olsen, J. M. H. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, R. di Remigio, K. Ruud, P. Sałek, B. Schimmelpfennig, B. Senjean, A. Shee, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, M. L. Vidal, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (available at <http://dx.doi.org/10.5281/zenodo.3572669>, see also <http://www.diracprogram.org>).
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