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Nuclear electric quadrupole moment of bismuth from the molecular method

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Electric-field gradients at bismuth nuclei in BiN and BiP molecules were determined from relativistic Dirac-Coulomb calculations by means of the coupled cluster approach with single and double substitutions with perturbative triple excitation corrections CCSD(T) and CCSD-T approaches. These theoretical values were combined with accurate experimental nuclear quadrupole coupling constants in order to obtain the nuclear electric quadrupole moment (NQM) of the ^{209}Bi nucleus. Our best results indicate an NQM of $-420(8)$ mb, which considerably deviates from the previously accepted standard value given by the atomic method $-516(15)$ mb.

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I. INTRODUCTION

The nuclear electric quadrupole moment (NQM) is an intrinsic feature of atomic nuclei with spin quantum number $I \geqslant 1$ [1]. This property is related to the shape of the nuclear ellipsoid charge distribution [2]. In other words, a non-null NQM value results in a distribution of nuclear charges that is not spherically symmetric.

Presently, according to Pyykkö [1], one of the most successful ways to obtain NQMs is the so-called molecular method where high level quantum chemical calculations of the electric-field gradient (EFG) at a given nucleus and nuclear quadrupole coupling constants (NQCCs), obtained from microwave spectra, are combined through the following relation:

$$Q(X) = \frac{\nu_Q(X)}{234.9647 q(X)}, \quad (1)$$

in which $Q(X)$, $\nu_Q(X)$, and $q(X)$, respectively, are the NQM (in barns), the NQCC (in megahertz), and the EFG [in atomic units (a.u.)] of an X nucleus in a linear molecule.

However, as can be seen in some recent compilations [1,3], accurate NQMs obtained by the molecular method are quite rare for heavy and superheavy elements. This is mainly caused by the scarceness of experimental data and the need for huge computational facilities to deal with such systems.

Hence, this paper uses high level relativistic calculations of electronic structures in BiN and BiP molecules to provide a new accurate estimate of the NQM value for the ^{209}Bi nucleus, which represents, as far as we know, the heaviest element ever treated at this level by the molecular method.

II. COMPUTATIONAL DETAILS

The general procedure performed here is similar to that used in previous studies [4–7]. Furthermore, all the calculations were carried out with the DIRAC12 package [8] by applying the relativistic four-component Dirac-Coulomb (DC) and Dirac-Coulomb-Gaunt (DG) Hamiltonians. The speed of light was assumed as 137.035 9998 a.u., and the Gaussian nuclear model was adopted. Also, small component integrals were replaced by an interatomic correction to reduce the computational cost [9]. The nonrelativistic correlation-consistent polarized valence triple-ζ (cc-pVTZ) and correlation-consistent polarized valence quadruple-ζ (cc-pVQZ) sets [10,11] were chosen for nitrogen and phosphorus, whereas, the relativistic adapted Gaussian basis set (RAGBS) [12] has been used for bismuth. All these sets were kept in their uncontracted forms. Moreover, these molecular calculations were performed for the $^1\Sigma^+$ ground state, with BiN and BiP equilibrium bond lengths (1.9349 and 2.2934 Å, respectively) taken from experimental data [13,14]. Hartree-Fock (HF) and density-functional-theory [Becke three-parameter Lee-Yang-Parr (B3LYP) and Becke-Perdew-Wang 91 (BPW91)] methods are used to furnish analytic EFG values.

Furthermore, in order to obtain estimates of electron correlation contributions to EFGs from methods lacking the implementation of analytic expressions in DIRAC12 as in the coupled cluster approach with single and double substitutions (CCSD) and its variations with perturbative triple excitation corrections [CCSD(T) and CCSD-T], the finite-difference technique was used in a two point form

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

where E is the total energy or the electronic correlation energy and λ is the field strength, which takes on the same absolute value successfully applied in earlier papers, 1×10^{-7} a.u. [5–7].

III. RESULTS AND DISCUSSION

A. Basis set increment study for bismuth

The first step of this paper consisted of an increment of the RAGBS for bismuth. At this stage, an investigation of analytic EFG results for the bismuth nucleus in the BiN molecule was performed by adding diffuse and tight s, p, d, and f functions to the original $30s27p17d11f$ set [12]. These calculations were performed at the DC-HF and DC-B3LYP levels along with the cc-pVTZ set for nitrogen. The exponents, shown in parentheses throughout this paper, were obtained by

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TABLE I. EFGs (a.u.) at the Bi nucleus in the BiN[a] molecule obtained during a basis set convergence study for bismuth.

Basis set	DC-HF		DC-B3LYP	
	q	Δq	q	Δq
RAGBS[b]	−5.647		−9.647	
+1 diffuse s[c]	−5.597	0.050	−9.533	0.114
+2 diffuse s	−5.596	0.001	−9.531	0.002
+3 diffuse s	−5.596	0.000	−9.531	0.000
+1 diffuse p[c]	−5.637	0.010	−9.631	0.016
+2 diffuse p	−5.636	0.001	−9.629	0.002
+3 diffuse p	−5.635	0.000	−9.628	0.000
+1 diffuse d[c]	−5.707	−0.060	−9.709	−0.061
+2 diffuse d	−5.705	0.002	−9.704	0.005
+3 diffuse d	−5.705	0.000	−9.703	0.000
+1 diffuse f[c]	−5.731	−0.084	−9.726	−0.078
+2 diffuse f	−5.729	0.002	−9.726	0.000
+3 diffuse f	−5.731	−0.002	−9.735	−0.009
+1 tight s	−5.645	0.001	−9.647	0.000
+2 tight s	−5.646	−0.001	−9.647	0.000
+1 tight p	−5.645	0.002	−9.649	−0.002
+2 tight p	−5.647	−0.002	−9.648	0.001
+1 tight d[c]	−5.657	−0.010	−9.654	−0.006
+2 tight d[c]	−5.669	−0.012	−9.662	−0.009
+3 tight d	−5.674	−0.004	−9.665	−0.003
+4 tight d	−5.679	−0.006	−9.670	−0.005
+1 tight f	−5.644	0.003	−9.645	0.003
+2 tight f	−5.644	0.000	−9.645	0.000
a-RAGBS[d]	−5.750		−9.655	
+1 g	−5.753	−0.003	−9.661	−0.005
+2 g[c]	−5.796	−0.043	−9.693	−0.032
+3 g[c]	−5.794	0.002	−9.683	0.010
+4 g	−5.791	0.003	−9.679	0.004
+5 g	−5.789	0.002	−9.676	0.003
a-RAGBS + 2g[e]	−5.791		−9.679	
+1 h	−5.798	−0.007	−9.685	−0.006
+2 h	−5.797	0.000	−9.685	0.001

[a] Calculations performed in combination with the cc-pVTZ set for nitrogen.
[b] Basis set size of $30s27p17d11f$ functions.
[c] Selected functions.
[d] Basis set size of $31s28p20d12f$ functions.
[e] Basis set size of $31s28p20d12f2g$ functions.

TABLE II. Analytic and finite-difference results of electronic contributions to EFGs (in a.u.) from DC-HF calculations for the Bi nucleus in the BiN[a] molecule during the sequential removal of tight p and d functions.

Basis set	Finite-difference results	Analytic results	$\|\Delta q\|$
$31s28p20d12f2g$	−235.297	−6.077	229.220
$31s27p20d12f2g$	−16.959	−6.077	10.882
$31s26p20d12f2g$	−7.063	−6.080	0.983
$31s25p20d12f2g$	−6.549	−6.090	0.458
$31s24p20d12f2g$	−6.529	−6.107	0.422
$31s24p19d12f2g$	−6.112	−6.095	0.017
$31s24p18d12f2g$	−6.087	−6.084	0.004

[a] Calculations performed in combination with the cc-pVTZ set for nitrogen.

extrapolations from polynomial generator coordinate Dirac-Fock parameters [12]. Such sequential augmentation was carried out individually for each angular momentum until only changes smaller than 0.01 a.u. in EFG values could be observed in further increments at both calculation levels. The obtained data are displayed in Table I.

As can be seen, both DC-HF and DC-B3LYP methods exhibit a nice agreement about the extra functions that present major relevance to the EFG (see Δq columns in Table I). Hence, one diffuse s (0.034 065 081 84), p (0.014 737 281 48), d (0.061 932 004 53), f (0.379 650 5458), and two tight d (70 373.400 43 and 15 316.499 80) functions had to be inserted into the set for bismuth, resulting in an augmented RAGBS (a-RAGBS).

Furthermore, a convergence study with polarization functions was performed by using the same criteria. Exponents for polarization functions of l angular momentum were selected from the most diffuse functions of the original RAGBS with angular momentum $l-2$. Two g functions (0.990 981 7718 and 0.435 838 9653) were added according to our threshold, whereas, no h function showed a relevant effect. Thus, the $31s28p20d12f2g$ set was applied in all the following calculations of analytic EFG values.

However, another aspect has to be taken into account for defining the basis set to be used with the finite-difference method. As more detailed, discussed by Haiduke *et al.* for antimony [5], p functions with large exponents may lead to huge perturbations in the EFG value due to small inaccuracies in molecular coefficients ascribed to these tight functions in core atomiclike orbitals. This failure can be detected by the comparison of analytic and finite-difference results of DC-HF calculations.

Hence, such an analysis was carried out for the Bi atom in the BiN molecule. The results are exhibited in Table II in which one can notice that the exclusion of only p functions does not seem enough to achieve deviations smaller than 0.01 a.u. (see the last column $|\Delta q|$) in a manner that, besides $4p$ functions, $2d$ tight functions also had to be taken out. This deletion led to a negligible variation of only −0.007 a.u. with respect to analytic EFG results from DC-HF calculations performed with the complete basis set for bismuth. Thus, the $31s24p18d12f2g$ set was adopted in the following studies of electron correlation contributions by means of the finite-difference method.

B. Electric-field gradients

Analytic EFG values obtained by means of DC-HF, DC-B3LYP, and DC-BPW91 calculations with the $31s28p20d12f2g$ set for bismuth and the cc-pVQZ basis set for the lighter elements are shown in Table III. The remaining results of this table, which refer to the electron correlation contribution calculations, were determined by using the aforementioned $31s24p18d12f2g$ set for bismuth along with the cc-pVTZ set for lighter atoms. More details on these later calculations are given in the next paragraph.

First, the active space was chosen in order to include all the spinors with energies between −6.0 and 20.0 a.u., which encloses a total of 26 and 32 valence electrons in BiN and BiP

TABLE III. Electric-field gradients and contributions from correlation treatments to these gradients (in a.u.) at the Bi nuclei in BiN and BiP molecules.

Method	BiN	BiP
DC-HF[a]	−5.782	−9.777
DG-HF[a]	−5.809	−9.777
DC-B3LYP[a]	−10.001	−9.341
DC-BPW91[a]	−9.675	−9.218
DC-MP2[b,c]	−8.194	−1.937
DC-MP2[c]	−8.229	−1.933
DC-CCSD[c]	−3.534	0.787
DC-CCSD(T)[c]	−3.258	0.620
DC-CCSD-T[c]	−3.358	0.621

[a] Analytic EFG values (the $31s28p20d12f2g$ set for bismuth and the cc-pVQZ set for the lighter elements).

[b] Electron correlation contribution obtained with a larger active space as explained in the text (the $31s24p18d12f2g$ set for bismuth and the cc-pVTZ set for the lighter elements).

[c] Electron correlation contribution determined by the finite-difference method (the $31s24p18d12f2g$ set for bismuth and the cc-pVTZ set for the lighter elements).

molecules, respectively. Furthermore, by means of calculations with the second-order Møller-Plesset method (DC-MP2), the reliability of such a limitation was tested by comparing EFG contributions from finite differences obtained with the selected active space and, likewise, with a larger one that encloses all electrons and spinors with energies up to 100 a.u.. The results from both active space alternatives showed absolute deviations of only 0.035 and 0.004 a.u. in BiN and BiP molecules, respectively. Hence, the restricted active space also was used in higher theoretical treatment levels, DC-CCSD, DC-CCSD(T), and DC-CCSD-T.

Moreover, as the full Breit term is not implemented in DIRAC12, an evaluation of higher-order relativistic effects associated with electron interactions had to be performed by analyzing the contribution of the Gaunt operator (DG-HF). It is important to mention that the lack of the gauge term (difference between full Breit and Gaunt Hamiltonians) does not seem, in general, crucial to EFGs. Even for elements as heavy as gold (in the AuF molecule), those contributions from the Gaunt part are the most relevant ones for EFGs [15]. Thus, as bismuth is an element just slightly heavier than gold and considering that the Gaunt term represents a contribution smaller than 0.5% of the total EFG (see the differences in EFG results from DC-HF and DG-HF in Table III), significant discrepancies are not expected when the gauge part is neglected.

Finally, one can obtain the total EFG at bismuth nuclei in each molecule either by the analytic values themselves or by summing the electron correlation contribution, given at different levels of calculation, with the analytic value provided by DG-HF calculations.

C. Nuclear quadrupole coupling constants

NQCCs for the ^{209}Bi nuclei in BiN and BiP molecules were obtained from the experimental work carried out by Cooke *et al.* [14]. However, although the equilibrium NQCC for BiN, 905.066 MHz, is given through a linear regression, the same cannot be performed for BiP as the NQCC is only measured at $\nu = 0$. This requires a correction obtained through an equation shown in Ref. [16], which needs the results for the first and second derivatives of EFGs with respect to changes in bond length around the equilibrium geometry. Hence, analytic EFGs were calculated at DC-B3LYP and DC-BPW91 levels with cc-pVTZ (for the P atom) and $31s28p20d12f2g$ (for the Bi atom) sets in four distorted geometries (± 0.005 and ± 0.01 Å) plus the equilibrium structure.

Finally, by means of the resulting polynomial regression along with the NQM given by BiN results and some experimental data [13], small corrections were obtained: 5.144 and 4.483 MHz from DC-B3LYP and DC-BPW91 levels, respectively. At last, the equilibrium NQCC for the ^{209}Bi atom in the BiP molecule was determined by summing the average of those corrections with the NQCC for $\nu = 0$, resulting in 903.031 MHz.

D. Nuclear quadrupole moment

The last step of this paper consists of the application of calculated EFGs and adjusted NQCCs in Eq. (1). The resulting NQMs are in Table IV. Through this data, one can see the enormous effect of the lacking electron correlation at DC-HF and DG-HF levels in results for the BiN molecule, which yields the largest mean absolute deviation (MAD) values (136 and 135 mb). Conversely, the inclusion of electron correlation at the DC-MP2 level clearly seems to overcorrect the electron correlation effect on EFGs (see Table III), leading to the lowest absolute values of NQMs in Table IV. Furthermore, both DFT functionals presented a nice concordance with respect to more reliable CC methods.

Finally, the lowest MAD values were obtained by including triple excitation perturbative corrections in coupled cluster calculations with the best results pointing to the DC-CCSD-T treatment, which is the same level chosen in previous studies for antimony, lutetium, and hafnium [5–7]. Hence, the NQM value indicated here for ^{209}Bi is −420 mb. Moreover, after considering some aspects that could aggregate any systematic error to the NQMs, as higher-order treatments of electron correlation or another quantum electrodynamical effect, a conservative deviation of 2% is suggested. See Refs. [4,5] for a detailed description of this error bar estimative.

TABLE IV. Nuclear quadrupole moments of the ^{209}Bi nucleus (in mbarn).

Method	BiN	BiP	Average	MAD[a]
DC-HF	−666	−393	−530	136
DG-HF	−663	−393	−528	135
DC-B3LYP	−385	−412	−398	13
DC-BPW91	−398	−417	−408	9
DC-MP2[b]	−275	−328	−302	26
DC-MP2	−274	−328	−301	27
DC-CCSD	−412	−428	−420	8
DC-CCSD(T)	−425	−420	−422	3
DC-CCSD-T	−420	−420	−420	0

[a] Mean absolute deviation.

[b] Values obtained by using a larger active space in EFG determinations as explained in the text.

IV. CONCLUSIONS

The NQM value of −420(8) mb, obtained here by the molecular method for the ^{209}Bi nucleus, is not in accordance with the currently accepted standard value determined by Bieron and Pyykkö [17] −516(15) mb. However, as can be seen from a summary in that paper, most of the previous studies that proposed alternative NQM values for this nucleus are in better agreement with our results, including the previously accepted standard value chosen by Pearson *et al*. [18] −370(26) mb.

Hence, our paper suggests that the standard NQM value for the ^{209}Bi nucleus should be reviewed once again given the known reliability of the molecular method in conjunction with DC-CCSD-T calculations of EFG values [5–7]. NQMs for other isotopes mentioned by Bieron and Pyykkö [17] also are changed proportionally.

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