

# Electric field gradients at the nuclei from all-electron four-component relativistic density functional theory using Gaussian-type orbitals

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We present an all-electron, four-component relativistic implementation of electric field gradients (EFGs) at the nuclei using Gaussian-type orbitals and periodic boundary conditions. This allows us to include relativistic effects variationally, which is important for compounds containing heavy elements and for a property dependent on the electronic structure close to the nuclei. The all-electron approach ensures an accurate treatment of both core and valence orbitals, as both are important in the evaluation of EFGs. Computational efficiency is achieved through the use of a recent implementation of density fitting in combination with quaternion algebra and restricted kinetic balance. We use the relativistic approach to calculate the EFGs in different arsenic, antimony, and bismuth halides and oxyhalides, and explore the importance of relativistic effects on EFGs in solids and compare these with results obtained for molecular species. Our calculations contribute to establishing a reliable estimate for the nuclear quadrupole moment of <sup>209</sup>Bi, for which our best estimate is  $-428(17)$  mb, in excellent agreement both with molecular data and a recent reevaluation of the nuclear quadrupole moment obtained from atomic data and *ab initio* calculations. Our results suggest that there is a need to revisit the experimental data for the EFGs of several bismuth oxyhalides.

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## I. INTRODUCTION

Nuclear electric quadrupole moments (NQMs) are important parameters providing fundamental information about nuclear structure, in particular whether the nuclear structure is spherically symmetric or not. A prerequisite for the existence of a nonvanishing NQM is a nuclear spin larger than  $1/2$ . The nuclear quadrupole moments interact with the electric field gradients (EFGs) at the nuclei, leading to a splitting of atomic or molecular energy levels that can be observed for instance in nuclear quadrupole resonance spectroscopy [1] or rotational spectroscopy [2,3] and correspond to excitation energies in the microwave region. Through measurements of the coupling of NQMs and EFGs, one can also obtain information about the electron density close to the nuclei, provided that accurate values of the NQMs are available. Much effort has therefore been devoted to determine NQMs [4].

One way of determining NQMs is to combine accurate *ab initio* calculations of EFGs with highly accurate transition energy data obtained from different experiments, and derive the NQMs using the relation between the EFGs and transition energies. A number of NQMs have been determined with very

high accuracy using this hybrid experimental/computational approach. For further information on various methods of determining NQMs, their expected accuracy, and the most up-to-date list of NQMs, we recommend the review by Pyykkö [4].

EFGs probe the electron density close to the nuclei, making relativistic effects crucial, particularly for heavier nuclei [5]. The calculation of EFGs is relatively straightforward, since the EFGs are first-order molecular properties. They can be evaluated either as expectation values for variational wave functions or by employing Z-matrix or Lagrangian techniques for highly correlated, nonvariational wave functions [6,7], such as coupled-cluster or configuration interaction methods. The incorporation of relativistic effects is also fairly straightforward, even at the fully relativistic level of theory using highly correlated wave functions [8,9]. However, when relativistic effects are approximated using a transformed Hamiltonian, significant picture-change effects must be accounted for [10]. We also note that special care must be taken if a finite-field approach is applied as an alternative way of calculating EFGs [11].

Compounds containing heavy elements often exist as solids. In the field of computational materials modeling, a plane-wave description of the valence electrons is often combined with the pseudopotential technique where the oscillatory core electronic orbitals are effectively substituted with pseudo-wavefunctions that mimic the effect of the core electrons on the valence electrons without the intricate oscillatory pattern. The use of pseudopotentials allows relativistic effects on the core electrons to easily be included, but the

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approximate description of the core electron density makes them unsuited for evaluating properties such as the EFGs. The projector augmented wave method allows for calculations of EFGs at the nuclei [12,13], but reaching accurate results can require that the EFGs are corrected using molecular calculations at a more advanced theory level (e.g., with a hybrid exchange-correlation functional) [14]. Alternative relativistic approaches include the use of four-component numerical [15–17] or two-component Slater-type atomic orbitals [5,18] or techniques that combine plane waves with auxiliary functions for explicit treatment of core electrons, while potentially also including relativistic effects [4,12,19]. Nevertheless, such hybrid approaches are inherently implementationally complex and computationally intensive, necessitating meticulous convergence settings and a profound understanding of the methods to ensure the accuracy of the calculated results in complex systems.

We have adopted an alternative, efficient all-electron approach that incorporates relativistic effects variationally at the four-component level of theory and which utilizes Gaussian-type basis sets with periodic boundary conditions, enabling systematic improvements in the results as the basis set is expanded. Computational efficiency is ensured by the use of quaternion algebra and restricted kinetic balance [20,21], as well as the resolution-of-the-identity approximation [22,23] for the Coulomb integrals in combination with multipole expansion of the far-field contributions [24]. Our previous study has shown that our method reliably achieves accurate band gaps already with double-zeta quality basis sets, and that smooth convergence of the density is assured without issues even when diffuse functions are incorporated into the basis set [21]. Indeed, we have established that retaining diffuse functions is essential for rapid basis set convergence; conversely, the more commonly employed “reduced” basis sets (where the diffuse functions are removed) [25–27] yield inferior results and slower basis set convergence.

We note here that the use of Gaussian-type orbitals (GTOs) for computational studies of periodic solids has an extensive history at the nonrelativistic level of theory, pioneered by the study of Pisani and Dovesi [28,29], followed by several more recent implementations [30–35]. Some of these GTO-based codes also reported calculations of EFGs for solid-state systems [36–40], albeit without the full consideration of relativistic effects.

Here, we extend our relativistic all-electron approach based on GTOs to the calculation of EFGs in solids and use the first-principles calculations in combination with experimental data to determine the NQM of As, Sb, and Bi from the EFGs in their halides and oxyhalides. Furthermore, we investigate the discrepancy between the atomic and molecular values of the NQM of  $^{209}\text{Bi}$  by using solid-state nuclear quadrupole resonance (NQR) data.

The remainder of the paper is organized as follows: In Sec. II, we provide the basic theory for the calculation of EFGs in solids at the four-component level of theory using Gaussian-type orbitals. In Sec. III, we give the computational details for the calculations presented in this paper. In Sec. IV, we explore the importance of relativistic effects and choice of basis sets on the EFGs in a series of pnictogen halides and oxyhalides, with a particular focus on bismuth-containing

systems. We obtain an estimate of the NQM of  $^{209}\text{Bi}$  and compare it with atomic and molecular data. Finally, in Sec. V, we give some concluding remarks and an outlook.

## II. THEORY

NQR utilizes the interaction of the nuclear charge density with the surrounding electric field. The quadrupole interaction is the leading contribution, i.e., the interaction between the nuclear quadrupole moment and the electric field gradient tensor. A detailed discussion can be found in Ref. [41]. This leads to the NQR Hamiltonian in the eigensystem of the EFG, given by

$$\begin{aligned} H_{\text{NQR}} &= \frac{Q}{2I(2I-1)} (V^{xx}I^x + V^{yy}I^y + V^{zz}I^z) \\ &= \frac{qQ}{4I(2I-1)} \left( 3I^z - I^2 + \frac{\eta}{2}(I_+^2 + I_-^2) \right). \end{aligned} \quad (2.1)$$

We have here introduced the eigenvalues of the electric field gradient components defined according to  $|V^{zz}| > |V^{yy}| > |V^{xx}|$ , the asymmetry parameter  $\eta = (V^{xx} - V^{yy})/V^{zz}$  and the nuclear spin  $I$ .  $Q$  denotes the nuclear quadrupole moment (NQM) and  $q$  is the largest eigenvalue  $V^{zz}$  and is often referred to as just the EFG. Diagonalization then leads to different spin energy levels, with the magnitude depending on  $q$  and  $Q$ , while the general structure depends on  $\eta$  and the total spin of the nucleus  $I$ . In the following, only the traceless part of the EFG is calculated; the traced part leads to a constant shift in the spectra [42] that is not considered in this paper.

The EFG tensor  $V^{ij}$  is defined as the second derivative of the electric potential at the position of the reference nucleus  $K$  (using the notation  $\partial^i \equiv \partial/\partial r^i$ ),

$$\begin{aligned} V_K^{ij} &= \partial^i \partial^j \int d\mathbf{r}' \rho(\mathbf{r}') \frac{1}{|\mathbf{r}' - \mathbf{r}|} \Big|_{\mathbf{r}=\mathbf{r}_K} \\ &= \int d\mathbf{r}' \rho(\mathbf{r}') v^{ij}(\mathbf{r}' - \mathbf{r}_K), \end{aligned} \quad (2.2)$$

with

$$v^{ij}(\mathbf{r}) = \frac{3r^i r^j - \delta^{ij} r^2}{r^5}, \quad (2.3)$$

and the total charge density of the infinite periodic system

$$\rho(\mathbf{r}) = \sum_{\mathbf{m}} \rho_{\mathbf{m}}(\mathbf{r}) = \sum_{\mathbf{m}} \rho_0(\mathbf{r} - \mathbf{r}_{\mathbf{m}}), \quad (2.4)$$

where  $\mathbf{m}$  labels the unit cell centered at  $\mathbf{r}_{\mathbf{m}}$ . In applying the derivative in Eq. (2.2), the Poisson term is neglected. This has no effect on the traceless part of  $V$  [42]. Equation (2.2) can be evaluated as stated by keeping the nucleus  $K$  fixed and summing over the charge densities of every unit cell. Alternatively, the summation can be shifted to the nucleus by using translation symmetry

$$\begin{aligned} V_K^{ij} &= \int d\mathbf{r}' \rho_0(\mathbf{r}') \sum_{\mathbf{m}} v^{ij}(\mathbf{r}' - \mathbf{r}_K + \mathbf{r}_{\mathbf{m}}) \\ &= \sum_{\mathbf{m}} \int d\mathbf{r}' \rho_0(\mathbf{r}') v_{\mathbf{m},K}^{ij}(\mathbf{r}'). \end{aligned} \quad (2.5)$$

The EFG consists of contributions from the electronic charge density and from all other nonreference nuclei.

Expressing the electron density using the one-electron reduced density matrix  $D$  and Gaussian-type basis functions  $\chi_{\mu\mathbf{n}}$  centered on each unit cell  $\mathbf{n}$ , the electronic part of the EFG tensor is obtained as

$$\begin{aligned} V_{e,K}^{ij} &= - \sum_{\mathbf{m}} \sum_{\mu\nu\mathbf{n}} \int d\mathbf{r} \text{Tr}[\chi_{\mu\mathbf{0}}^\dagger(\mathbf{r}) v_{\mathbf{m},K}^{ij}(\mathbf{r}) \chi_{\nu\mathbf{n}}(\mathbf{r}) D^{\nu\mathbf{n},\mu\mathbf{0}}] \\ &= - \sum_{\mathbf{m}u} \text{Tr}[I_{\mathbf{m},K,u}^{ij} D^{\bar{u}}], \end{aligned} \quad (2.6)$$

where  $u \equiv (\mu\nu\mathbf{n})$ ,  $\bar{u} \equiv (\nu\mathbf{n}\mu)$ , and the EFG integrals are labeled as  $I$ . Note here that the basis functions  $\chi_{\nu\mathbf{n}}$  are four-component Dirac bispinors, and the trace  $\text{Tr}$  needs to be introduced to sum over the four components, i.e., four diagonal matrix elements in the product of  $I$  and  $D$ . More details about the implementation of the calculation of the relativistic electronic structure of solids in the ReSpect program is found in Ref. [21]. Similarly, the nuclear part is given by

$$\begin{aligned} V_{n,K}^{ij} &= \sum_{\mathbf{m}} \sum_A Z_A \\ &\times \frac{3(\mathbf{r}_A - \mathbf{r}_{\mathbf{m},K})^i (\mathbf{r}_A - \mathbf{r}_{\mathbf{m},K})^j - |\mathbf{r}_A - \mathbf{r}_{\mathbf{m},K}|^2 \delta^{ij}}{|\mathbf{r}_A - \mathbf{r}_{\mathbf{m},K}|^5}. \end{aligned} \quad (2.7)$$

In the summations over all atoms  $A$  and unit cells  $\mathbf{m}$ , the reference nucleus term  $A = K$  must be excluded for  $\mathbf{m} = \mathbf{0}$ .

For sufficiently large values of  $\mathbf{m}$ , the charge density of the unit cell  $\mathbf{m} = \mathbf{0}$  has no significant overlap with the reference nuclei in the cell  $\mathbf{m}$  [43]. Therefore the lattice sum in Eq. (2.5) can be split into near and far-field (NF and FF) parts. The NF is calculated directly using Eqs. (2.6) and (2.7). The FF terms can be expanded using a multipole expansion. This is based on

$$\begin{aligned} &\partial^i \partial^j \frac{1}{|\mathbf{r}' - \mathbf{r}_K - \mathbf{r}_{\mathbf{m}}|} \\ &= \partial^i \partial^j \frac{1}{|(\mathbf{r}' - \mathbf{r}_C) - (\mathbf{r}_K + \mathbf{r}_{\mathbf{m}} - \mathbf{r}_C)|} \\ &= \sum_{lm} \partial^i \partial^j R_{lm}(\mathbf{r}' - \mathbf{r}_C) I_{lm}^*(\mathbf{r}_K + \mathbf{r}_{\mathbf{m}} - \mathbf{r}_C) \\ &= \sum_{lm} R_{lm}(\mathbf{r}' - \mathbf{r}_C) \partial^i \partial^j I_{lm}^*(\mathbf{r}_K + \mathbf{r}_{\mathbf{m}} - \mathbf{r}_C). \end{aligned} \quad (2.8)$$

The center of the unit cell is chosen as the center of the multipole expansion  $\mathbf{r}_C$  and  $R$  and  $I$  refer to the scaled regular and irregular solid harmonics as defined in Ref. [44]. The derivative in (2.8) acting on  $\mathbf{r}'$  is equivalent to a derivative on  $\mathbf{r}_{\mathbf{m}}$  up to a minus sign. This can be used to shift the derivatives between  $R$  and  $I$ . Recursive expressions for the derivatives are defined in Ref. [45], albeit using a different sign convention. The solid harmonics defined above are complex functions. However, in practical calculations, it is more convenient to use real harmonics [44]. Thus, the FF contribution to the EFG

becomes

$$\begin{aligned} V_{K,FF}^{ij} &= \sum_{lm} 2 \frac{1}{2^{\delta_{l0}}} Q_{lm}(\mathbf{r}_C) \partial^i \partial^j \sum_{\mathbf{m} \in FF} I_{lm}(\mathbf{r}_K + \mathbf{r}_{\mathbf{m}} - \mathbf{r}_C) \\ &= \sum_{lm} Q_{lm}(\mathbf{r}_C) I_{K,FF,lm}^{ij}(\mathbf{r}_C), \end{aligned} \quad (2.9)$$

with the total multipole moments of the unit cell defined as

$$Q_{lm}(\mathbf{r}_C) = \int d\mathbf{r} \rho_0(\mathbf{r}) R_{lm}(\mathbf{r} - \mathbf{r}_C). \quad (2.10)$$

Equation (2.9) contains both electronic and nuclear contributions and is evaluated in a similar manner as the NF terms in Eqs. (2.6) and (2.7). The additional factor compensates for the switch to real harmonics and is absorbed into  $I$ . The multipole moments are independent both of the lattice vector  $\mathbf{m}$  and the specific nucleus  $K$  and only need to be calculated once for a given system. To evaluate the lattice sum, the renormalization scheme from Ref. [46] is used, with additional details provided in Ref. [21]. This scheme only needs to be employed once per system as it can be shifted to the position of a different nucleus  $K'$  using the translation properties of  $I$ . Hence, the computational cost of evaluating the FF terms is negligible, and the entire computational effort comes from the direct calculation of the NF contributions in Eq. (2.6).

The calculation of EFGs for molecules is significantly simpler. Equations (2.6) and (2.7) can then be used directly by removing the lattice indices and the summation over  $\mathbf{m}$ . The NF-FF split is in this case not needed. Our implementation in ReSpect agrees for four-component molecular systems with DIRAC [47] and for one-component solids with CRYSTAL [48].

### III. COMPUTATIONAL DETAILS

We use the four-component Dirac–Coulomb Kohn–Sham level of theory together with the generalized gradient approximation (GGA) for the nonrelativistic exchange–correlation functional (PBE) [49]. The fully uncontracted triple- $\zeta$  (TZ) Dyall basis sets are used unless otherwise noted [50,51]. To accelerate the calculation of the Coulomb electrostatic interactions, we employed the resolution-of-the-identity approach for the Coulomb term (RI-J) [22–24]. A detailed discussion of the implementation and accuracy of the RI-J approximation used in this paper will be provided elsewhere [24], but calculations on BiOCl lead to errors of the order of  $10^{-3}$  V/m<sup>2</sup> in the EFG both at the nonrelativistic and relativistic levels of theory, a relative error that is less than 0.01%.

The momentum space was sampled with a  $9 \times 9 \times 9$  mesh of  $\mathbf{k}$  points for the bismuth oxyhalides and a  $5 \times 5 \times 5$  mesh for the other systems. The convergence with respect to the  $\mathbf{k}$ -point mesh was assessed by comparing the EFG results obtained from calculations across a progressively increasing sequence of meshes.

### IV. RESULTS AND DISCUSSION

In order to demonstrate the importance of relativistic effects for EFGs, we will have a particular focus on <sup>209</sup>Bi, as there until recently was a rather significant discrepancy

TABLE I. Basis set convergence of Bi EFGs. Results for a basis set  $X$  reported as  $\text{EFG}(X)/\text{EFG}(\text{QZ})$ . For details, see text.

System	tDz	DZ	tTz	TZ	tQZ	QZ
$\text{BiCl}_3$		0.979		0.997		1
$\text{BiOCl}$	0.879	0.938	0.984	0.986	1.0003	1

between the NQMs established based on comparing experimental and computed data between molecular [52] and atomic studies [53]. This discrepancy was, however, recently resolved [54,55], bringing the atomic NQMs into very good agreement with the molecular NQMs. We also note that nuclear calculations by Karayonchev *et al.* support the molecular NQM, with a NQM of  $-428$  mbarn [56]. It would be of interest to see whether our solid-state implementation would confirm these predictions.

In order to better assess the accuracy of our calculated results, we have performed benchmark calculations on molecular  $\text{BiCl}_3$  and solid  $\text{BiOCl}$  using Dyll's uncontracted double (DZ), triple (TZ), and quadrupole- $\zeta$  (QZ) basis sets [50,51]. We have also included truncated versions of these basis sets for the solid, in which we apply the commonly used approximation of removing all basis functions with exponents  $<0.1$  when calculating properties of periodic systems using GTOs [25–27].

The value of the Bi EFG for the different basis sets are reported in Table I relative to the Bi EFG obtained using the QZ basis set.  $\text{BiCl}_3$  uses the isolated molecular structure (*vide infra*), whereas for  $\text{BiOCl}$  we use the experimental solid-state structure of Ref. [57]. For the molecular system, both the DZ and TZ results are very close to the QZ value, being 97.9% and 99.7% of the QZ value, respectively. For the solid, convergence becomes worse, with the DZ results clearly being of inferior quality, with only 93.8% of the QZ value, whereas TZ is performing reasonably well with 98.6% of the QZ value. The Dyll basis sets are optimized for molecular calculations, and therefore a poorer basis set convergence in solids is not surprising. The truncated DZ basis set performed poorly, whereas for the TZ basis, the truncated result is only 0.2% off the full basis, and they are identical at the QZ level.

We recently demonstrated that the removal of diffuse functions is not necessary and inhibits basis-set convergence [21,58] and prevents convergence to the basis-set limit altogether for band gaps and structures. Even though EFGs are a core-electron property, this is not the reason for the reduced basis sets not affecting the quality of the calculated results. Instead, only two diffuse basis functions are removed on Bi, whereas in our previous paper, as many as six basis functions were removed in the case of tungsten. This highlights that truncation is highly dependent on the systems studied and the basis sets used, and should in general be applied with care and ideally not at all. In this paper, all exponents of the original basis set are retained.

For  $\text{BiOCl}$ , we have also performed test calculations with the BLYP functional [59–61]. The results are in good agreement with those obtained using the PBE functional, being less than 3% larger than the PBE results both at the nonrelativistic and relativistic levels of theory for the EFG at the Bi nucleus using the TZ basis set.

Considering the possible uncertainty in the NQM of the  $^{209}\text{Bi}$  nucleus, we have included a few arsenic and antimony halides and oxyhalides for which there exist experimental data, in order to benchmark our results against reliable experimental data. This also allows us to explore the relative importance of relativistic corrections as we go down in the periodic table. All our results are collected in Table II. We report, in addition to the calculated EFG value and the corresponding value for the asymmetry parameter  $\eta$ , also the derived value for the NQM using the experimental resonance frequencies. The reference values for the  $^{75}\text{As}$ ,  $^{121}\text{Sb}$ ,  $^{123}\text{Sb}$ , and  $^{209}\text{Bi}$  NQMs are  $-311$ ,  $-543$ ,  $-692$ , and  $-420$  mbarn, respectively [62–64], and we also report the ratio between the calculated and reference values for the NQM.

For all As and Sb compounds, we observe good agreement with experimental data. The differences are between 14 and 20% for the NQMs, which is in agreement with the error for DFT calculations on EFGs in the literature [12]. The error also includes temperature and other effects. For  $\beta$ - $^{121}\text{SbBr}_3$ , experimental data is only available at 300 K instead of at 77 K. If we assume a similar temperature behavior as  $\alpha$ - $^{121}\text{SbBr}_3$ , the ratio between theoretical and experimental NQMs should increase to about 1.15. The agreement for  $\eta$  is generally good, although this quantity potentially benefits more from error cancellation. The only exception is  $\alpha$ - $^{121}\text{SbBr}_3$ , with a measured value of 0.08 compared to the calculated value of 0.155.

Turning now to the bismuth compounds, the results for  $\text{BiCl}_3$  are in good agreement with experiment. An overshoot of 17% is within expectations and  $\eta$  differs by only 0.02. For  $\text{BiBr}_3$ , neither the calculated EFG nor the asymmetry parameter are in agreement with experiment. However, if we used a different assignment of the experimental data, as discussed below, the differences disappear and the agreement between theory and experiment is comparable to that of  $\text{BiCl}_3$ . Both  $\text{BiCl}_3$  and  $\text{BiBr}_3$ , assuming the different frequency assignment, support a value of  $-420$  mb [54,64] for the NQM of  $^{209}\text{Bi}$ .

The results for the bismuth oxyhalides are worse. The calculated EFGs decrease for the heavier halides, following the same trend as observed for the other systems. However, when combined with the experimental data, the resulting NQMs for  $^{209}\text{Bi}$  are erratic.  $\text{BiOF}$  yields an expected error of 10%, but the other three systems are much worse, without any discernible trend. Cl and Br have an overshoot of almost 50%, while I is only off by 36%. These are beyond expected variation both in relative accuracy as well as variation between the different oxyhalides, and we are currently unable to resolve these discrepancies. Whereas  $\text{BiOF}$  also supports a value of  $-420$  mb for the NQM, its reliability is questionable given the differences observed for the other three  $\text{BiOXs}$ . We note previously calculated EFGs of  $\text{BiOX}$  by Hamaed *et al.* [78]. Similarly, they also report no systematic behavior, when comparing calculated EFGs with measured frequencies. However, their calculated values also differ significantly and unsystematically from the ones reported here. This is likely caused by their use of pseudopotentials, which furthermore makes a direct comparison difficult.

As seen from Table II, the agreement between the calculated and experimental values for  $\eta$  is good for all compounds, except for  $\text{BiBr}_3$ , which shows a large disagreement. This general agreement may be due to error cancellation considering

TABLE II. Calculated EFGs [ $10^{21}$  V/m<sup>2</sup>], asymmetry parameters  $\eta$ , and resulting  $^{75}\text{As}$ ,  $^{121}\text{Sb}$ ,  $^{123}\text{Sb}$ , and  $^{209}\text{Bi}$  quadrupole moments  $Q$  [mb] for various solid-state compounds.

Compound	geom <sup>a</sup>	Nonrelativistic				Relativistic				Exp.	
		EFG	$\eta$	Q	$Q_{\text{calc}}/Q_{\text{ref}}$	EFG	$\eta$	Q	$Q_{\text{calc}}/Q_{\text{ref}}^b$	$\eta_{\text{exp}}$	Ref.
AsCl <sub>3</sub>	[65]	-19.11	0.0	-341.7	1.10	-18.47	0.0	-353.5	1.14	0 <sup>c</sup>	[66]
AsBr <sub>3</sub>	[67]	-14.47	0.076	-349.7	1.12	-13.65	0.082	-370.7	1.19	0 <sup>a</sup>	[66]
$^{121}\text{SbCl}_3$	[68]	-26.87	0.151	-590.6	1.09	-25.60	0.170	-619.9	1.14	0.184	[69]
$\alpha$ - $^{121}\text{SbBr}_3$	[70]	-22.63	0.114	-604.9	1.08	-20.76	0.155	-659.3	1.21	0.080	[71]
$\beta$ - $^{121}\text{SbBr}_3^d$	[72]	-23.31	0.178	-560.7	1.03	-21.50	0.202	-607.9	1.12	0.180	[71]
$^{123}\text{Sb}_4\text{O}_5\text{Cl}_2$	[73]	-32.81	0.261	-805.0	1.16	-33.37	0.302	-791.5	1.14	0.307	[57]
		-34.77	0.380	-805.0	1.16	-35.40	0.411	-791.4	1.14	0.396	[57]
BiCl <sub>3</sub>	[74]	-31.95	0.362	-421.3	1.00	-27.36	0.565	-492.1	1.17	0.583	[75]
BiBr <sub>3</sub>	[76]	-26.90	0.446	-523.5	1.25	-21.81	0.850	-645.8	1.54	0.553	[77]
BiBr <sub>3</sub> <sup>e</sup>	[76]			-387.1	0.92			-477.6	1.14	0.840	
BiOF	[57]	-29.90	0.000	-410.1	0.98	-26.70	0.000	-459.3	1.09	0	[57]
BiOCl	[57]	-15.39	0.000	-424.8	1.01	-10.62	0.001	-615.8	1.47	0	[57]
BiOBr	[57]	-12.56	0.001	-410.5	0.98	-8.22	0.002	-627.1	1.49	0	[57]
BiOI	[57]	-10.69	0.001	-372.5	0.89	-7.00	0.002	-569.4	1.36	0	[57]

<sup>a</sup>Experimental crystal structures.

<sup>b</sup>Reference values for the  $^{75}\text{As}$ ,  $^{121}\text{Sb}$ ,  $^{123}\text{Sb}$  and  $^{209}\text{Bi}$  NQMs are -311, -543, -692, and -420 mb, respectively.

<sup>c</sup>Assumed to be zero.

<sup>d</sup>Exp. data only available at 304 K.

<sup>e</sup>Refitted experimental data, see text.

that  $\eta$  involves a ratio between different EFG components. Furthermore, across all other compounds the EFG decreases for heavier halides. In contrast, the experimental data for BiBr<sub>3</sub> suggest a small increase in the EFG compared to BiCl<sub>3</sub>.

To investigate this conundrum, we have reoptimized the values for the nuclear quadrupole coupling constant and  $\eta$  from the experimentally measured frequencies. For most systems, we obtain a better agreement with the measured frequencies with a pure quadrupole spectrum from this refitting process. While the actual values of the EFGs do not change significantly, the refitting leads to a reduction in the experimental uncertainties. For example, for BiCl<sub>3</sub>, the agreement is below 0.1%. The only major change is for  $^{121}\text{Sb}$  in the  $\alpha$  structure, where the value changes from 343.95 MHz to 331.41 MHz, which appears to be due to a mistake in one of the tables of Ref. [71].

The agreement is also excellent for BiBr<sub>3</sub>, however, only three out of the four frequencies were observed. Therefore, the frequency assignment is ambiguous, and different choices are possible. We find a different assignment for  $\eta = 0.840$ . This value of  $\eta$  agrees with our calculated value for  $\eta$ , gives a good agreement for the NQM of  $^{209}\text{Bi}$  with the same overshoot as seen for the arsenic and antimony compounds, and follows the trend of lowering the EFG for heavier halides. However, this fit has a significantly higher  $\chi^2$  value of  $4 \times 10^{-1}$  compared to the experimental fit of  $6 \times 10^{-4}$ . For the other compounds, we obtain  $\chi^2$  values ranging from  $2 \times 10^{-2}$  to  $4 \times 10^{-6}$ , making this fit an outlier. We are at this point unable to provide an decisive conclusion on the origin of this discrepancy.

To estimate a value for the NQM of  $^{209}\text{Bi}$  based on the BiCl<sub>3</sub> data, we apply a scaling factor to the calculated value. The scaling factor is taken as the the average ratios of calculated and experimental NQMs for AsCl<sub>3</sub>, AsBr<sub>3</sub>,  $^{121}\text{SbCl}_3$ ,

and the two sites in  $^{123}\text{Sb}_4\text{O}_5\text{Cl}_2$ , as the temperature is the same for all these studies, and good agreement between calculated and measured  $\eta$  is observed. We then obtain a NQM of -428(17) mbarn, with the number in parenthesis representing the standard deviation, heavily influenced by the result for AsBr<sub>3</sub>.

We have also implemented the calculation of EFGs in the molecular ReSpect program. As we have a uniform level of theory for molecules and solids, and many of the pnictogen halides are molecular solids, we have also explored the effects of crystal packing as well as the geometry effects arising from differences in bond lengths and bond angles going from the gas-phase structure to the structure observed in the solid state. We have thus performed calculations on individual molecules by taking the positions of one pnictogen and its three nearest-bonding halides from the respective solid-state structures to study solid-state effects, as well as optimized the molecular structure in the gas phase to explore the relaxation effects. All computational details are the same, including XC functional and basis sets. The calculated EFGs and asymmetry parameters are collected in Table III.

There are significant effects both from changing the bond length going from gas phase to the isolated molecule retaining the solid-state structure, as well as due to neighboring atoms in the solid. Only the solid state calculations give results for both EFGs and  $\eta$  that are in agreement with experiment, illustrating the need to use both a proper geometry as well as include the solid-state effects. The increasing difference in EFGs from isolated solid-state structure molecules to the solid phase for the heavier compounds is not directly caused by relativity. This is rather due to the closer crystal packing, leading to larger crystal-packing effects. Both the pnictogen-pnictogen distances as well as the distance to the

TABLE III. Results for EFGs [ $10^{21}$  V/m<sup>2</sup>] and asymmetry parameters  $\eta$  in gas phase, for isolated molecular structures using solid-state geometries (“molecule”), as well as for solids. For details, see text.

Compound	EFG			$\eta$		
	gas	“molecule”	solid	gas	“molecule”	solid
AsCl <sub>3</sub>	-16.95	-19.22	-18.47	0	0.012	0.027
AsBr <sub>3</sub>	-13.86	-14.79	-13.65	0	0.048	0.082
SbCl <sub>3</sub>	-25.15	-28.71	-25.60	0	0.090	0.170
$\alpha$ -SbBr <sub>3</sub>	-21.36	-24.99	-20.76	0	0.100	0.155
$\beta$ -SbBr <sub>3</sub>	<sup>a</sup>	-24.61	-21.50		0.110	0.202
BiCl <sub>3</sub>	-30.95	-39.77	-27.36	0	0.229	0.565
BiBr <sub>3</sub>	-25.55	-32.67	-21.81	0	0.171	0.850

<sup>a</sup>Only one configuration in gas phase.

nearest nonbonding halides are for these heavier congeners smaller.  $\eta$  in the gas phase is zero due to the trigonal pyramidal geometry [79], whereas the value of  $\eta$  for isolated solid-state structures and the solids show that it depends strongly on the environment and is not only a results of the distorted trigonal pyramid in solids.

## V. CONCLUDING REMARKS

We have presented the theory for calculating EFGs in solids within the all-electron, four-component framework using GTOs as implemented in the RESPECT program. For As and Sb, these values are well established and we can use them to determine the accuracy of EFGs calculated using our approach, and in particular the inherent error of the DFT approximation applied in this paper. We have obtained good agreement for various systems, with errors in the range 14–20%, in line with other findings in the literature.

We have demonstrated that our solid-state approach for calculating electric field gradients is reliable enough to determine the nuclear quadrupole moment from observed nuclear quadrupole coupling constants. For  $Q(\text{Bi})$ , our current,

independent, result is  $-428(17)$  mb. It is comparable to the published “world average” of  $-420(17)$  mb of Barzakh *et al.* [64] or the “molecular” values of Teodoro and Haiduke [ $-420(8)$  mb] [52] or Dognon and Pyykkö [ $-422(3)$  mb] [54] and others, as well as with recent nuclear calculations by Karayonchev *et al.* ( $-428$  mb) [56]. Note that the old atomic value of Bieron and Pyykkö [ $-516(15)$  mb] [53] suffered from a too limited electron correlation space. Further values and a new world average  $Q(\text{Bi})$  should be proposed later. We see the main merit of the present paper, apart from the methodology, in providing a  $Q(\text{Bi})$  based on totally independent  $q$  calculations and totally independent measurements of the nuclear quadrupole coupling constant (NQCC) in solids. Although the error limit is slightly higher, the obtained  $Q$  agrees with the quoted recent atomic, molecular, and nuclear theory values.

However, the nuclear quadrupole moments derived from bismuth oxyhalides behave erratically, even though the calculated EFGs appear reasonable. Although the results for BiOF also supports the molecular value for the NQM of  $^{209}\text{Bi}$ , its reliability is in question until the disagreements for the other oxyhalides are resolved. We recommend that new experimental studies are performed for bismuth oxyhalides.

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