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Nuclear quadrupole moments for ^{27}Al and ^{69}Ga derived from four-component molecular coupled cluster calculations

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In this work we investigate different approaches for calculating electric field gradients in order to provide accurate theoretical values for the nuclear quadrupole moments (NQM) for aluminum and gallium. Electron correlation is included in a fully four-component framework at the CCSD(T) level. The resulting NQM for ^{27}Al (146.0 ± 0.4 mb) is in good agreement with earlier work, while the value for ^{69}Ga (171 ± 2 mb) is higher than suggested on basis of previous molecular calculations.

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INTRODUCTION

The determination of nuclear electric quadrupoles can be done directly using nuclear scattering experiments or nuclear structure theory. The accuracy of this procedure is, however, limited and indirect methods that combine theoretical electronic properties with precise spectroscopic data have become highly competitive.¹ In the so-called molecular method one relates very accurately measured nuclear quadrupole coupling constants, available from microwave spectroscopy, to the quadrupole moment (NQM) via a calculation of the electric field gradient (EFG) at the position of the nucleus.

Since this procedure will only work if the EFG can be calculated to a sufficient precision, it is essential to take both relativistic and electron correlation effects into account. This is most conveniently done in the Dirac picture, where one uses the relativistic Dirac equation and associated wave function to describe the coupling between the atomic nuclei and their surrounding electron cloud. This is the method that we employ in the current paper. Another well-established, more economical, method is to use either the Douglas–Kroll–Hess transformation^{2–5} or the ZORA method⁶ to derive an approximate, spin free, relativistic Hamiltonian that can be incorporated in a nonrelativistic quantum chemical computer code. This has been the method of choice for many recent calculations of EFGs.^{7–9} Although both methods give an accurate description of relativistic effects it is of utmost importance that the so-called picture change is taken into account.^{10–13} This can either be done by applying the Douglas–Kroll¹⁴ or ZORA transformation explicitly to the EFG operator, or by modelling the nuclear charge distribution with an array of point charges that is implicitly included in the standard transformation of the nuclear attraction integrals. The latter method is called the point charge model for nuclear quadrupole moments (PCNQM)¹⁵ and has become popular because it is readily used with any type of wave function or Hamiltonian. Since we use a four-component

wave function throughout we need not be concerned about possible picture change errors. Still, it is interesting to compare the PCNQM approach to the standard multipole expansion of the nuclear charge distribution, because the numerical stabilities of both methods may differ. We will study this by comparing results of both methods in the calculation of the EFG on Ga in the GaCl molecule.

THEORY

The experimentally measured nuclear quadrupole coupling constant (NQCC) can be represented as a first order correction to the electronic energy of the molecule caused by the perturbation

$$\hat{H}_1 = \frac{1}{2} \underline{\underline{Q}} \cdot \underline{\underline{q}}. \quad (1)$$

The expression for the EFG tensor operator $\underline{\underline{q}}$ is found by considering the interaction energy between the nucleus and its surrounding electronic cloud. In terms of the nuclear (ρ_N) and electronic (ρ_e) charge distributions the full interaction energy reads

$$E_{\text{int}} = \iint \frac{\rho_N(\mathbf{R})\rho_e(\mathbf{r})}{|\mathbf{R}-\mathbf{r}|} d\mathbf{R} d\mathbf{r} = \int \rho_N(\mathbf{R})\phi_e(\mathbf{R}) d\mathbf{R}. \quad (2)$$

Expansion of the electronic potential ϕ_e at the position \mathbf{R} around the center \mathbf{R}^0 of the nucleus gives as second order term the interaction between the NQM and the EFG:

$$E_{\text{int}}^{(2)} = \frac{1}{2} \sum_{\alpha\beta} \left(\frac{\partial^2 \phi_e}{\partial R_\alpha \partial R_\beta} \right)_{\mathbf{R}=\mathbf{R}^0} \times \int \rho_N(\mathbf{R})(\mathbf{R}-\mathbf{R}^0)_\alpha(\mathbf{R}-\mathbf{R}^0)_\beta d\mathbf{R} \\ = \frac{1}{2} \sum_{\alpha\beta} q_{\alpha\beta}(\mathbf{R}^0) Q_{\alpha\beta}(\mathbf{R}^0). \quad (3)$$

The EFG tensor is defined as

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$$\begin{aligned}
 q_{\alpha\beta}(\mathbf{R}) &= \frac{\partial^2 \phi_e}{\partial R_\alpha \partial R_\beta} \\
 &= \frac{1}{\partial R_\alpha \partial R_\beta} \left\langle \frac{-1}{|\mathbf{r}-\mathbf{R}|} \right\rangle \\
 &= \left\langle \frac{3(r_\alpha - R_\alpha)(r_\beta - R_\beta) - \delta_{\alpha\beta} |\mathbf{r}-\mathbf{R}|^2}{|\mathbf{r}-\mathbf{R}|^5} \right\rangle
 \end{aligned} \quad (4)$$

and gives the well-known expression

$$\hat{q}_{\alpha\beta}(\mathbf{R}^0) = \frac{3(r_\alpha - R_\alpha^0)(r_\beta - R_\beta^0) - \delta_{\alpha\beta} |\mathbf{r}-\mathbf{R}^0|^2}{|\mathbf{r}-\mathbf{R}^0|^5} \quad (5)$$

for the EFG operator. A problematic feature of this operator is the inverse cubic dependence on the electron–nucleus distance. This gives rise to large matrix elements if the basis set contains tight functions and may lead to numerical instabilities in the calculation.

An alternative operator is used in the PCNQM¹⁵ method. In its six-charge form one assumes that the finite extent of a nucleus can be modeled by an octahedral array of six point charges ζ_i placed at a distance d from the nucleus

$$\rho_N(\mathbf{R}) = Z_N \delta(\mathbf{R}-\mathbf{R}^0) + \sum_{i=1}^6 \zeta_i \delta(\mathbf{R}-\mathbf{R}^i). \quad (6)$$

Equation (2) then gives

$$E_{\text{int}} = \left\langle \frac{-Z_N}{|\mathbf{r}-\mathbf{R}^0|} \right\rangle + \sum_{i=1}^6 \left\langle \frac{-\zeta_i}{|\mathbf{r}-\mathbf{R}^i|} \right\rangle \quad (7)$$

which is related to the EFG via

$$E_{\text{int}}^{(2)} \approx \sum_{i=1}^6 \left\langle \frac{-\zeta_i}{|\mathbf{r}-\mathbf{R}^i|} \right\rangle = \frac{1}{2} \zeta d^2 (2q_{zz} - q_{xx} - q_{yy}) \quad (8)$$

if we neglect the terms of fourth and higher order that are contained in expression (7). For linear molecules where the z axis is the molecular axis we end up with two alternative expressions for the operator \hat{q}_{zz}

$$\hat{q}_{zz}^{\text{PCNQM}} = \frac{1}{3d^2} \sum_{i=1}^6 \frac{1}{|\mathbf{r}-\mathbf{R}^i|}, \quad \hat{q}_{zz}^{\text{PQ}} = \frac{3(z-Z)^2 - |\mathbf{r}-\mathbf{R}|^2}{|\mathbf{r}-\mathbf{R}|^5}. \quad (9)$$

The EFG can now be determined by taking the first derivative of the total electronic energy to the λ -dependent Hamiltonian

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{q}_{zz}. \quad (10)$$

This differentiation can be done analytically by realizing that the presence of $\lambda \hat{H}_1$ in the Hamiltonian causes a λ dependence of the wave function $\Psi(\lambda)$ and total energy $E(\lambda)$

$$E(\lambda) = \langle \Psi(\lambda) | \hat{H}(\lambda) | \Psi(\lambda) \rangle. \quad (11)$$

After the expansion of $E(\lambda)$ with respect to λ according to

$$E(\lambda) = E_0 + \lambda \left(\frac{dE(\lambda)}{d\lambda} \right)_0 + \frac{1}{2} \lambda^2 \left(\frac{d^2E(\lambda)}{d\lambda^2} \right)_0 + \dots \quad (12)$$

the first order response energy is given by

$$E_1 = (dE(\lambda)/d\lambda)_0. \quad (13)$$

It should be noted that all components in Eq. (11) that contain a λ dependence should be differentiated. For variational wave functions the Hellmann–Feynman theorem holds^{16–18} and the determination of the first order response energy simplifies according to

$$E_1 = \left(\frac{\partial E(\lambda)}{\partial \lambda} \right)_0 = \langle \Psi(0) | \hat{q}_{zz} | \Psi(0) \rangle. \quad (14)$$

For nonvariational wave functions we also have to consider a term involving the first order response of the wave function to the perturbation

$$\begin{aligned}
 E_1 &= \left(\frac{dE(\lambda)}{d\lambda} \right)_0 \\
 &= \langle \Psi(0) | \hat{H}_1 | \Psi(0) \rangle + 2 \langle (d\Psi(\lambda)/d\lambda)_0 | \hat{H}_0 - E_0 | \Psi(0) \rangle
 \end{aligned} \quad (15)$$

which can be done via a coupled perturbed Hartree–Fock (CPHF) step. This means that the response of the MO coefficients with respect to λ has to be determined according to the response equation¹⁹

$$c_{\mu p}(\lambda) = \sum_{q=1}^N c_{\mu q}(0) U_{qp}(\lambda), \quad (16)$$

where N includes all occupied and virtual spinors. The summation over all spinors is an important point if one evaluates this equation in the molecular orbital basis as is currently done in the implementation of the MP2 first energy derivative in the DIRAC program system.²⁰ Since the active space in general contains only a subset of all MOs, contributions possibly important for the response are left out. This incompleteness can in principle be solved by including all spinors in the active space. In the relativistic case the problem is enhanced by the fact that contributions from negative energy states—that should not be included in the calculation of the correlation energy—are in principle to be included in the CPHF procedure in order to obtain the complete orbital response. This contribution should be small for first order properties because it only concerns the correlation–NQM cross term. The major error will come from the truncation of the orbital space in the positive energy region. For higher order properties, in particular if perturbations concern magnetic fields, contributions from negative energy states do, however, play a significant role^{21,22} and should also be included in actual response calculations.

Both problems in calculating the full response do not occur if we differentiate Eq. (13) by a finite-difference method. In that case we include contributions from negative energy states in the orbitals during the SCF iterations and get the full relaxation under the influence of the perturbation. A disadvantage of this procedure is, however, the fact that the observed λ dependence may be higher than linear because the field strength has to be chosen rather large (about a factor of 10 000 larger than the actual strength) in order to get sufficient precision in the numerical differentiation of the total energy.

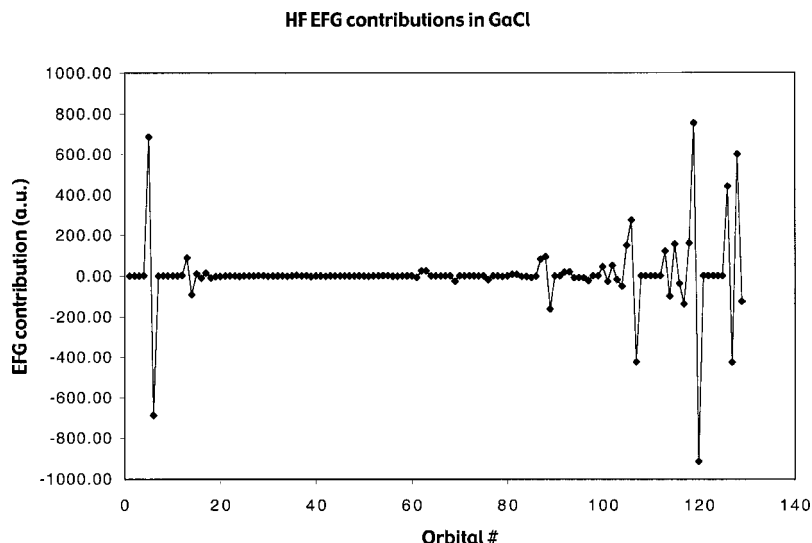


FIG. 1. HF EFG contributions (in a.u.) for the individual MO's in GaCl.

COMPUTATIONAL DETAILS

The calculations of the six different metal halides were done at the equilibrium geometries taken from Huber.²³ The experimental nuclear quadrupole coupling constants (NQCCs) were taken from Lucken²⁴ ($^{27}\text{Al}^{19}\text{F}$, $^{69}\text{Ga}^{19}\text{F}$, $^{69}\text{Ga}^{79}\text{Br}$), Hensel *et al.*²⁵ ($^{27}\text{Al}^{35}\text{Cl}$), Walker²⁶ ($^{27}\text{Al}^{79}\text{Br}$), and Gordy²⁷ ($^{69}\text{Ga}^{35}\text{Cl}$).

In all our calculations the Dirac–Coulomb Hamiltonian was used and integrals of the (SS|SS) type were neglected.²⁸ Since a pronounced dependence of the EFG on the contraction length in the p -function space^{15,29} was found we chose to avoid basis set contractions in all reported calculations.

For aluminum a (16s/10p/2d/1f) cc-pVTZ nondual basis³⁰ was used with one hard s and p function (exponents 1372.002, 924 and 1080.87, respectively) added to account for a good relativistic description. In the case of Al the exponents were not reoptimized. For Ga we employed two sets in order to determine the effect of a nonrelativistic and relativistically optimized basis on the EFG. The nonrelativistic basis was taken from Wilson *et al.*³¹ augmented by one hard s and p (exponents 43796.668, 35 and 33981.4, respectively) and one soft p function (exponent 0.01) resulting in a nondual (21s/15p/9d/1f) basis (B1). The second (19s/16p/11d/3f) Ga basis (B2) was optimized under the constraint of duality³² using the relativistic four-component Hamiltonian. Since we wanted to keep the f -space dual we chose these exponents according to the maximum weights of the d functions rather than optimizing them freely. The large d and f space should allow for a good correlation description and compensate the fact that those exponents were not individually optimized at the correlated level.

The fluorine basis was taken from Dunning³³ and augmented by one hard (exponent 128.1854) and one soft p (exponent 0.07361) function resulting in a nondual cc-pVTZ (11s/7p/2d/1f) set. For chlorine we used the nondual cc-pVTZ basis³⁰ augmented by one hard s function (exponent 3044.449, 0) and one hard p function (exponent 2691.50) leading to a (16s/10p/2d/1f) primitive set and for bromine the nondual (21s/15p/9d/1f) cc-pVTZ basis.³¹

We found that the choice of active space was nontrivial

in the case of the gallium halides, because inclusion of the mainly atom-centered inner-lying p functions made the correlated results numerically unstable. To investigate this problem we looked at the individual orbital contributions to the EFG at the Hartree–Fock level. For atoms we know that fully occupied shells in the absence of polarization give cancelling EFG contributions. The nonlocal orbitals found in the molecule yield a nonvanishing contribution but for the inner shells the atomic picture still holds to a good approximation. As one can see in Fig. 1 for GaCl those nearly cancelling contributions from inner orbitals have large values and are prone to give rise to numerical inaccuracies. A strongly oscillating behavior is observed again beyond orbital #87 in the virtual space and inclusion of these corelike highly virtuals causes also significant numerical noise. Exclusion of both critical orbital ranges gave stable results. A similar problem was observed in the case of AlBr where the virtual space showed stronger oscillations. We therefore had to restrict the active space to orbitals with a small (absolute) orbital energy value in order to avoid numerical problems. This restriction may cause some underestimation of core correlation effects but is the best we could do with the present methodology. For AlF and AlCl we ended up excluding the $1s$ functions at Al and the halides from the active space, whereas in AlBr the Al $1s$ and Br $1s2s2p3s3p$ orbitals were kept frozen. To freeze the Br $3s3p$ while including the Br $3d$ might seem a bit unphysical, but the energetic splitting of approximately 4.2 atomic units between the Br $3p$ and $3d$ levels justifies this approach. In the selection of virtual orbitals we applied energy thresholds of 4.5 a.u. (AlF and AlCl), 4.4 a.u. (AlBr), 5.1 a.u. (GaF), 4.0 a.u. (GaCl), and 3.5 a.u. (GaBr) to exclude corelike virtuals.

The total electronic contribution to the EFG can either be obtained by differentiating the total CCSD(T) energy directly or by differentiating the correlation energy separately and adding this contribution to the Hartree–Fock value. The latter procedure has advantages if the methods show a different behavior relative to the applied field strength. This is indeed the case because we found that the dependence of the correlation energy to the applied field strength was almost

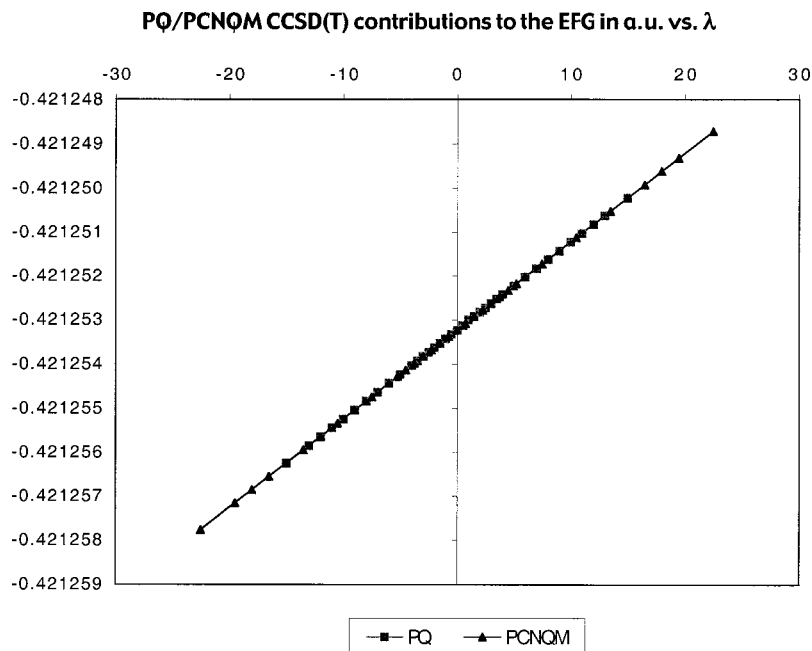


FIG. 2. Correlation contributions to the EFG at the CCSD(T) level for both perturbation Hamiltonians. λ in units of 10^{-5} a.u.

perfectly linear (see Fig. 2) in both the PQ and the PCNQM model. This means that the correlation contribution can be obtained via a simple two-point approximation

$$\left(\frac{\partial E(\lambda)}{\partial \lambda}\right)_0 \approx \frac{E(+\lambda) - E(-\lambda)}{2\lambda} \quad (17)$$

using a suitable value of λ (see below). The Hartree–Fock contribution, however, readily shows nonlinear contributions upon increasing the perturbation strength and use of a two-point approximation for this contribution can lead to significant errors. In order to analyze the size of these errors we fitted the GaCl HF curve (Fig. 3) to the polynomial

$$E_{\text{HF}}(\lambda) = E(\lambda=0) + c_1\lambda + c_2\lambda^2 + c_3\lambda^3 \quad (18)$$

using 20 data points. This gave the coefficient $c_1 = -2.955\,9647$ which is in good agreement with the analytical value of $-2.955\,9651$ a.u. but also large $c_2 = -157\,107.995\,68$ and $c_3 = -2\,340\,087.090\,57$ coefficients. The simple two-point approximation based on the smallest perturbation strengths gave $-2.956\,1985$ a.u., which is not accurate enough for our purposes. We therefore used the analytic Hartree–Fock value as the starting point for the total value of the EFG and combined this value with a finite-difference correlation contribution for the MP2, CCSD, and

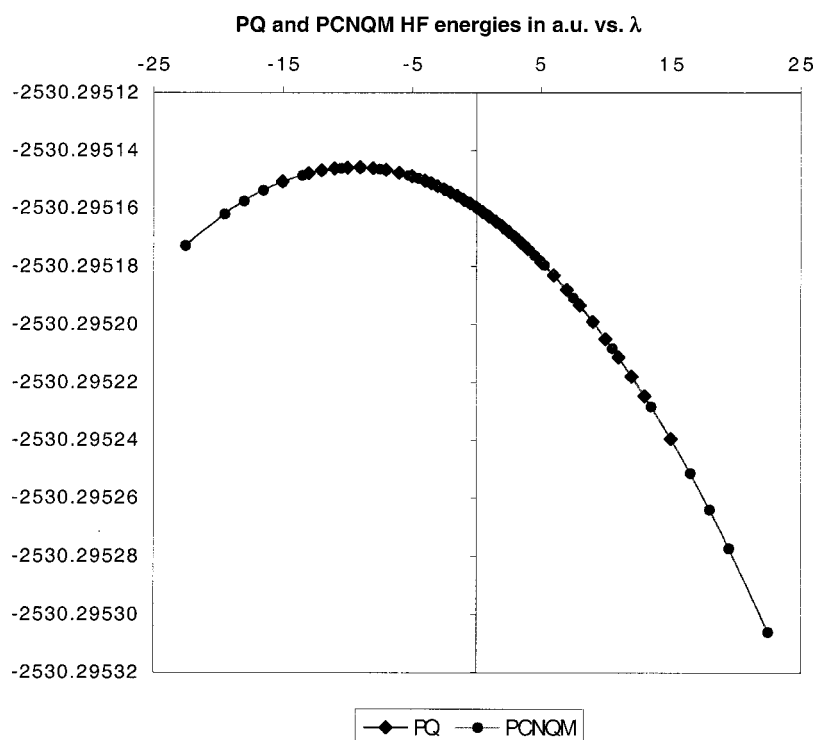


FIG. 3. HF energies for both perturbation Hamiltonians (PQ and PCNQM) over a large range of λ (in units of 10^{-5} a.u.).

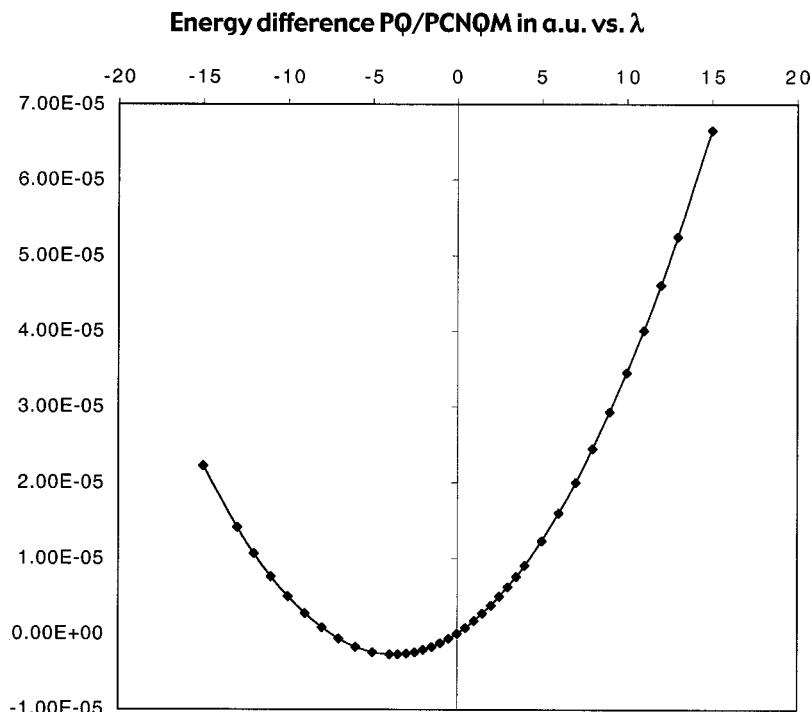


FIG. 4. HF energy differences between the two perturbation Hamiltonians over a large range of λ (in units of 10^{-5} a.u.).

CCSD(T) levels of theory. At the MP2 level of theory we also used a completely analytic procedure formulated in the MO basis as an extra check on the correctness of the results.

We performed various test calculations to determine the appropriate perturbation strength λ for the finite-difference calculations and found that a value of $\lambda = \pm 10^{-5}$ was suitable.

RESULTS AND DISCUSSION

With an appropriate choice of the point-charge-nucleus distance d , the PCNQM and the point quadrupole (PQ) perturbations should give nearly the same energy dependence on λ . In picture 2 one can see that GaCl SCF perturbed energies indeed match accurately for an extended λ range. One has to plot the differences of these energies (Fig. 4) to notice the deviation caused by the higher order terms in the PCNQM operator. Looking more closely at the cause of this difference one easily understands that for diffuse functions it does not matter much whether the EFG matrix element is calculated via an array of point charges placed closely around the nucleus (PCNQM) or with the PQ operator of Eq. (5). For tight functions significant discrepancies will arise, however, because they probe the region of space where the electron-nucleus distance is of comparable size or smaller than the point-charge-nucleus distance. Kellö and Sadlej determined a hydrogenic correction formula for the error that arises and found that its leading term has a $Z^5 d^2$ dependence.³⁴ With the value of $d = 10^{-3}$ a.u. that we used the difference between the PQ and PCNQM SCF energies becomes important only in the region where the absolute magnitude of the perturbation is such that the linear approximation fails. Since this region should be avoided anyway, we conclude that both models are equally well applicable in ac-

tual calculations and that the choice for one or the other will depend more on computational efficiency than on numerical stability.

For ^{27}Al we observe good agreement between the various molecular NQM results given in Table IV. Here we recalculated the DFT EFG and NQM values from the reported NQCC values given by van Lenthe and Baerends.⁷ Their best results should be the ZORA-4 values that range from 141.9 mb (AlBr) to 145.0 mb (AlF). A recent value of the ^{27}Al NQM (146.6 ± 1.0 mb) was suggested by Kellö *et al.*⁸ on basis of Douglas-Kroll CCSD(T) calculations on AlF and AlCl and an atomic MCHF calculation. The discrepancy between their separate calculations is only 1.0 mb. These high-level calculations have as weakest point probably only the neglect of the small second-order spin-orbit coupling effects. In our calculations all relativistic effects are taken into account at the expense of using a smaller active space and basis set. We find that the deviation between the calculated ^{27}Al s NQMs derived from different molecular data is 3 mb for the Hartree-Fock method and reduces to 1 mb or less for all correlated methods. The numerical and analytical MP2 results show a good agreement that is probably due to the

TABLE I. EFG values (a.u.) for the aluminum halides using $\lambda = 0.00001$ a.u. The results marked (A) were obtained via analytic differentiation of the electronic energy expression. The constant nuclear contributions (not included) are Al(AlF), 0.5891 a.u.; Al(AlCl), 0.5214 a.u.; Al(AlBr), 0.8581 a.u.; F, 0.8509 a.u.; Cl, 0.3987 a.u.; Br, 0.3187 a.u.

Method	Al (AlF)	Al (AlCl)	Al (AlBr)	F	Cl	Br
HF (A)	-1.7952	-1.5142	-1.7759	-0.6754	0.0993	0.8510
MP2 (A)	-1.7348	-1.4497	-1.7142	-0.8037	0.0193	0.6792
MP2	-1.7303	-1.4426	-1.7083	-0.8108	0.0064	0.6505
CCSD	-1.7069	-1.4271	-1.6954	-0.7715	0.0642	0.7726
CCSD(T)	-1.6866	-1.4072	-1.6760	-0.7850	0.0386	0.7154

TABLE II. EFG values (a.u.) for the gallium halides using basis B1 for Ga and $\lambda=0.00001$ a.u. The results marked (A) were obtained via analytic differentiation of the electronic energy expression. The constant nuclear contributions (not included) are Ga(GaF), 0.4778 a.u.; Ga(GaCl), 0.4719 a.u.; Ga(GaBr), 0.7968 a.u.; F, 1.6456 a.u.; Cl, 0.8605 a.u.; Br, 0.7057 a.u.

Method	Ga (GaF)	Ga (GaCl)	Ga (GaBr)	F	Cl	Br
HF (A)	-3.3358	-2.9560	-3.1317	-1.1118	-0.1142	0.8532
MP2 (A)	-3.2674	-2.9134	-3.0750	-1.2243	-0.1626	0.7461
MP2	-3.2467	-2.8001	-2.9325	-1.2185	-0.1605	0.7167
CCSD	-3.1710	-2.7539	-2.8955	-1.1764	-0.1199	0.8160
CCSD(T)	-3.1154	-2.7070	-2.8535	-1.1969	-0.1489	0.7537

fact that for these smaller systems the active space could be kept reasonably complete. Based on the spread of values at the highest level of theory [CCSD(T)] and the experimental error bars in the NQCCs we therefore suggest an ^{27}Al NQM value of 146.0 ± 0.4 mb. This value falls within the error bars of the value suggested by Kellö *et al.*⁸

There exist two ^{69}Ga reference values: A molecular value of 165 mb determined in GaF by Pernpointner and Schwerdtfeger³⁵ and an atomic value of 173(3) mb obtained from an atomic MCHF wave function in combination with relativistic corrections by Tokman *et al.*³⁶ In addition one can calculate DFT molecular values ranging from 165.3 mb (GaBr) to 168.1 mb (GaF) from the results of van Lenthe and Baerends.⁷ This means that the spread in NQM values is considerably larger than the one for Al which is mostly due to the precision of the EFG calculations.

Upon using basis B1 we find a spread of the Hartree–Fock values of 1.6 mb and 6.6 mb in the numerical CCSD(T). The analytical and finite difference MP2 values are now less close which is probably due to the smaller active space used in the solution of the CPHF equations (see theory section). This means that the numerical MP2 results are to be preferred unless the finite size perturbation gives rise to numerical problems. After switching to basis B2 and enlarging the correlation space the maximum spread in the NQMs reduced to 2 mb (SCF), 4 mb (numerical MP2), 2.9 mb (numerical CCSD), and 3.1 mb [numerical CCSD(T)]

TABLE III. EFG value (a.u.) for the gallium halides using basis B2 for Ga and $\lambda=0.00001$ a.u. The results marked (A) were obtained via analytic differentiation of the electronic energy. The constant nuclear contributions (not included) are given in Table II.

Method	Ga (GaF)	Ga (GaCl)	Ga (GaBr)	F	Cl	Br
HF (A)	-3.3806	-3.0011	-3.1680	-1.1167	-0.1114	0.8336
MP2 (A)	-3.3014	-2.9741	-3.0951	-1.1944	-0.1526	0.7380
MP2	-3.2781	-2.8226	-3.0241	-1.1950	-0.1517	0.7205
CCSD	-3.2315	-2.8077	-2.9878	-1.1570	-0.1098	0.8128
CCSD(T)	-3.1749	-2.7593	-2.9403	-1.1755	-0.1366	0.7525

which strongly favors the relativistic basis B2 to serve as a reference basis.

The trend in the NQMs is the same as for Al: the NQM value increases with the level of sophistication in the correlation calculations and all correlated calculations suggest that the ^{69}Ga NQM value lies above 170 mb. This favors the value suggested by Tokman *et al.*³⁶ above the molecular value by Pernpointner and Schwerdtfeger. The deviations in the Ga DFT results amount to a maximum of 2.8 mb which is lower than the deviation of 3.1 mb at the CCSD(T) level. On this basis one cannot decide whether the DFT or the *ab initio* EFG values should be preferred. Taking into account the deviation of the three gallium halide results at the highest level of theory [CCSD(T)] and adding the error in the NQCC measurements we suggest a ^{69}Ga NQM value of 171 ± 2 mb.

In Tables I–IV we also give the halide EFG and NQM values for the sake of completeness. Since we have not performed a specific optimization of the halide basis sets for the EFG property these values will be less accurate than the metal EFGs. This is one reason for the considerable spreads in the corresponding NQM values. A thorough basis set optimization and active space analysis would be necessary in order to recommend NQM values for the halide atoms. It can be assumed that the halide basis is nevertheless suitable for a good valence description of the molecule but not adapted well enough for the halide EFG. A detailed investigation of the halide EFGs at the Dirac–Fock CCSD(T) level of theory is underway.

TABLE IV. Experimental hyperfine coupling constants (NQCC in MHz) and calculated quadrupole moments (NQM in mb) for the different methods. The results marked (A) were obtained via analytic differentiation of the electronic energy expression. The GaX results were obtained with the EFGs from Table III (Ga B2 basis).

	NQCC	HF(A)	MP2(A)	MP2	CCSD	CCSD(T)	DFT ^a
AlF(^{27}Al)	-37.75 ^b	133.2	140.2	140.8	143.7	146.4	145.0
AlCl(^{27}Al)	-30.4081(27) ^c	130.4	139.4	140.5	142.9	146.1	142.1
AlBr(^{27}Al)	-28.0059(35) ^d	129.9	139.2	140.2	142.4	145.7	141.9
GaF(^{69}Ga)	-107.07 ^b	157.0	161.4	162.7	165.5	169.0	168.1
GaCl(^{69}Ga)	-92.10(14) ^e	155.0	156.7	166.7	167.8	171.4	165.9
GaBr(^{69}Ga)	-86.68 ^b	155.6	160.5	165.6	168.4	172.1	165.3
AlCl(^{35}Cl)	-8.8290(35) ^c	-75.4	-89.9	-92.8	-81.2	-85.9	-89.4
GaCl(^{35}Cl)	-13.30(13) ^e	-75.0	-79.4	-79.3	-74.8	-77.6	-84.3
AlBr(^{79}Br)	78.7064(14) ^d	286.4	335.7	345.6	306.9	323.9	320.2
GaBr(^{79}Br)	105.78 ^b	292.5	311.8	315.7	296.5	308.7	313.9

^aReference 7.

^bReference 24.

^cReference 25.

^dReference 26.

^eReference 27.

It is somewhat disconcerting to see that the reported results were so sensitive to the choice of the active orbital space, a sensitivity that was not found in corresponding non-relativistic calculations. The origin of this increased sensitivity in four-component calculations is not entirely clear, it may be due to diagonalization of the Dirac–Fock matrix for which the spread of eigenvalues is larger than in nonrelativistic calculations and can cause inaccuracies in the calculated eigenvectors. We have not analyzed this in detail because we intend to implement an analytic procedure that solves the CPHF equations in the AO basis so that both the problems with the finite difference and the analytic approach may be solved.

CONCLUSION

In this paper we have investigated the difference between the point quadrupole and the PCNQM approaches for calculating the EFG. Both methods showed problems for high field strengths and large active spaces but were in good agreement for smaller field strengths. The correlation contributions to the EFG behaved linearly so that a separate treatment and combination with analytic Hartree–Fock values was found to be the most reliable and economical procedure.

In order to achieve the most accurate correlation results coupled cluster gradients should include the relaxation with respect to the full orbital space including the negative energy solutions. So far this relaxation can be incorporated only in a finite field approach. The next step increasing the accuracy of the correlated results therefore will be the complete implementation of CCSD gradients in a four-component setting. Work in this direction is underway.

A word of caution may be in place as our recommended values for the nuclear quadrupole moments of ^{27}Al (146.0 ± 0.4 mb) and ^{69}Ga (171 ± 2 mb) have error bars that are solely based on the consistency between the calculated molecular results for different molecules and the accuracy of the measured NQCCs. It would be interesting to do an intrinsic check of the basis set convergence and importance of higher order relativistic effects on the EFG but this is not yet feasible at the four-component CCSD(T) level of theory.

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