Nuclear quadrupole moment of ^{139}La from relativistic electronic structure calculations of the electric field gradients in LaF, LaCl, LaBr, and LaI

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Relativistic coupled cluster theory is used to determine accurate electric field gradients in order to provide a theoretical value for the nuclear quadrupole moment of ^{139}La. Here we used the diatomic lanthanum monohalides LaF, LaCl, LaBr, and LaI as accurate nuclear quadrupole coupling constants are available from rotational spectroscopy by Rubinoff *et al.* [J. Mol. Spectrosc. **218**, 169 (2003)]. The resulting nuclear quadrupole moment for ^{139}La (0.200 ± 0.006 barn) is in excellent agreement with earlier work using atomic hyperfine spectroscopy [0.20(1) barn]. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2787000]

I. INTRODUCTION

Molecular microwave data combined with calculated nuclear electric field gradients (EFGs) are one of the most reliable source for obtaining accurate spectroscopic nuclear quadrupole moments (NQMs).[1] This method is based on the well-known relation between the experimentally determined nuclear quadrupole coupling constant (NQCC), the NQM, and the EFG at a specific nucleus. For a linear molecule the NQM $Q(X)$ at nucleus X can be calculated from

$$Q(X)[b] = \frac{\mathrm{NQCC}(X)[\mathrm{MHz}]}{234.9647 q_{zz}(X)[\mathrm{a.u.}]}. \tag{1}$$

Over the last ten years highly accurate relativistic coupled cluster calculations have led to the refinement of a number of NQMs for various isotopes, i.e., ^{27}Al, ^{45}Sc, ^{69}Ga, ^{85,87}Rb, ^{91}Zr, and ^{179}Au, to name a few.[2–6]

The first estimate for the ^{139}La NQM with nuclear spin $I = +7/2$ came from the hyperfine structure measurement of the $5d^2 6s^1\ {}^4F_{3/2}$ state of La(I) by Murakawa and Kamei in 1957,[7,8] who recommended $Q = 0.35 \pm 0.1$ b using atomic structure theory including the contribution from Sternheimer shielding. The hyperfine states of La(I) have been refined later by Gangrsky *et al.*[9] Shortly after Murakawa's paper Ting observed the hyperfine structure of the $5d^1 6s^2\ {}^4D_{3/2,5/2}$ states of La(I) and recommended $Q = 0.268 \pm 0.010$ b for ^{139}La.[10] The currently accepted value comes from high-resolution spectroscopy of the hyperfine structure of the $5d^2$ and $5d^1 6s^1$ levels of La(II) in a collinear laser-ion beam by Höhle *et al.*[11] together with nonrelativistic multiconfiguration Hartree-Fock calculations including Sternheimer corrections by Bauche *et al.*[12] In this work a NQM of $Q = 0.20(1)$ b was obtained. This value was recently used to determine the NQMs of ^{135}La, ^{137}La, and ^{138}La from collinear laser spectroscopic measurements of the hyperfine splitting in the $6s^2\ {}^1S_0 \rightarrow 5d^1 6p^1\ {}^3D_1$ and $5d^2\ {}^3P_2 \rightarrow 5d^1 6p^1\ {}^1D_2$ transitions of La(II).[13]

The atomic structure calculations used in these previous works are not of sufficient accuracy, as, for example, relativistic effects were not considered.[14] It is therefore desirable to obtain a more accurate value for the ^{139}La NQM. As accurate measurements of isotope effects from the hyperfine structure of La (Ref. 13) are already available, the NQMs of the other important isotopes of La can also be determined accurately. To obtain an accurate value for the ^{139}La NQM will also be important for future theoretical work on lanthanum containing compounds. Electric field gradient calculations are already available for the bulk metal of lanthanum,[15–17] for high-T_c systems containing La,[18,19] and most recently for coordination compounds of La^{3+}.[20]

Recently, Rubinoff *et al.* measured the pure rotational spectra of the lanthanum monohalides from LaF to LaI,[21] which gave the corresponding NQCCs for ^{139}La to relatively high precision. We mention that the diatomic lanthanum monohalides are well characterized.[21–25] We therefore decided to perform accurate relativistic coupled cluster calculations for the electric field gradient of LaF, LaCl, LaBr, and LaI.

II. METHODS AND COMPUTATIONAL DETAILS

All molecular calculations have been carried out for the $^1\Sigma^+$ ground state[26] of LaX (X=F, Cl, Br, and I) at the experimentally determined equilibrium bond distance,[21] i.e.,

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2.023 38 Å for LaF, 2.498 04 Å for LaCl, 2.652 08 Å for LaCl, and 2.878 85 Å for LaI. The components of the electronic and nuclear field gradient tensor $q_{\alpha\beta}^{\mathrm{el}}$ and $q_{\alpha\beta}^{nuc}$ at nucleus X are the expectation values over the corresponding operators[27]

$$\hat{q}_{\alpha\beta}^{\mathrm{el}}(\mathbf{R}_X) = -\sum_i^n \frac{3(r_{i\alpha}-R_{X\alpha})(r_{i\beta}-R_{X\beta})-\delta_{\alpha\beta}|\mathbf{r}_i-\mathbf{R}_X|^2}{|\mathbf{r}_i-\mathbf{R}_X|^5} \tag{2}$$

and

$$\hat{q}_{\alpha\beta}^{\mathrm{nuc}}(\mathbf{R}_X) = \sum_{Y\neq X} \frac{Z_Y[3(R_{Y\alpha}-R_{X\alpha})(R_{Y\beta}-R_{X\beta})-\delta_{\alpha\beta}|\mathbf{R}_X-\mathbf{R}_Y|^2]}{|\mathbf{R}_X-\mathbf{R}_Y|^5}. \tag{3}$$

Here α and β stand for x,y, or z, $(x,y,z)=\mathbf{r}_\alpha$ and $(X,Y,Z)=\mathbf{R}_\alpha$; the summation in Eq. (2) runs over all electrons i, and the summation in Eq. (3) runs over all nuclei Y. The nuclear part [Eq. (3)] is a simple constant addition to the electronic field gradient tensor. In the HF case, which is the main contribution to the EFG tensor, the expectation can be written as a sum of one-particle integrals of the form

$$q_{\alpha\beta}^{\mathrm{el}}(\mathbf{R}_X,\phi_i) = \sum_i^n \langle\phi_i(\mathbf{r})|\frac{\partial^2}{\partial R_{X\alpha}\partial R_{X\beta}}\frac{1}{|\mathbf{r}-\mathbf{R}_X|}|\phi_i(\mathbf{r})\rangle, \tag{4}$$

where the ϕ_i represent the canonical HF orbitals.

Electron correlation has been accounted for by using coupled cluster calculations with full iterative treatment of single and double excitations (CCSD) and perturbative correction for triple excitations (CCSD(T)). This method has been successfully used in previous calculations of EFGs,[28–30] and should be suitable for the description of the electronic structure of the lanthanum monohalides. The only question which may arise is whether the use of a single determinant reference is sufficient. Although low lying triplet states have been observed, these states do not mix with the singlet ground state. For example, for LaF and LaI excited electronic states have been investigated spectroscopically and the lowest excited singlet state observed was 1.45 eV (Ref. 26) and 0.65 eV (Ref. 23) above the ground state, respectively. This separation seems to be sufficiently large for a single reference treatment. The use of a single determinant reference is further justified by the t_1 diagnostics[31,32] for the importance of single excitations in the CCSD approximation, which is less than 0.014 for all the lanthanum monohalides investigated.

Since the EFG scales $\sim r^{-3}$, it is an inner shell property and one may therefore expect significant contributions from relativistic effects and electron correlation[28–30] already for the lighter elements. Since we found that all lanthanum monohalides are closed shell in the ground state ($^1\Sigma^+$), the relativistic contributions clearly are dominated by scalar-relativistic effects, and spin-orbit contributions are expected to be rather small. Scalar-relativistic effects can effectively be treated by using the Douglas-Kroll-Hess (DKH) transformation.[33–35] Here we used the second-order DKH Hamiltonian as implemented in the MOLCAS 5.4 program package.[36,37] Finite size Gaussian nuclei were used to avoid singularities of the wave function arising in scalar relativistic calculations with point nuclei. For the nuclear exponents the recommended values by Vischer and Dyall were used.[38]

All calculations were carried out using atom-centered Gaussian-type orbitals. These basis sets were generated by Nakajima and Hirao[39] starting from an all-electron atomic natural orbital (ANO) set by an energy optimization of the neutral atom using the DKH Hamiltonian within a finite-nucleus model. For our molecular calculations these basis sets needed to be supplemented by diffuse and higher angular momentum functions. For lanthanum the original $(23s23p15d)$ basis set was used in its uncontracted form and extended by one diffuse s function ($\zeta=0.02$), two diffuse p functions ($\zeta=0.08$ and 0.0251), one diffuse d function ($\zeta=0.051\,275\,503$), five f functions ($\zeta=8.4893$, 3.7672, 1.5902, 0.6098, and 0.1973), and three g functions ($\zeta=1.5902$, 0.6098, and 0.1973), resulting in an uncontracted $(24s25p16d5f3g)$ basis set.

However, to make the calculations computationally feasible the basis sets for the halides had to be contracted. Contractions were only used in the inner core region which is not relevant for the EFG at the lanthanum nucleus, as only the outer tail of the density will influence the EFG at the neighboring La atom. In the valence region the basis sets were therefore left completely uncontracted to offer sufficient flexibility for a proper description of the polarization of the electron distribution around the La nucleus. For fluorine the tightest nine s functions and five p functions of the original $(12s8p)$ basis set were contracted to two s functions and one p function using the contraction coefficients given by Nakajima and Hirao[39] (general contraction scheme). To this we added one diffuse s function ($\zeta=0.085\,94$), one diffuse p function ($\zeta=0.065\,68$), three d functions ($\zeta=5.014$, 1.725, and 0.586), and two f functions ($\zeta=3.562$ and 1.148). This results in a contracted $(13s9p3d1f)/[6s5p3d1f]$ basis set. The basis sets for the other halides were contracted in a similar way. For chlorine we contracted the ten tightest s and the seven tightest p functions to two s and one p function and added one diffuse s function ($\zeta=0.0519$), one diffuse p function ($\zeta=0.0376$), three d functions ($\zeta=1.551$, 0.628, and 0.254), and two f functions ($\zeta=1.089$ and 0.423) to obtain a contracted $(17s12p3d2f)/[9s7p3d2f]$ basis set. For bromine the 13 tightest s, the 10 tightest p, and the 6 tightest d functions were contracted to two contracted s functions, two contracted p functions, and one contracted d function. One diffuse s function ($\zeta=0.044\,27$), one diffuse p function ($\zeta=0.030\,513$), three diffuse d functions ($\zeta=0.423\,13$, 0.1779, and 0.0829), three f functions ($\zeta=0.3407$, 0.8257, and 0.1748), and one g function ($\zeta=0.6491$) were added, yielding a $(21s16p12d3f1g)/[10s8p7d3f1g]$ basis set for Br. Finally, for iodine the 14 tightest s functions, the 12 tightest p functions, and the 6 tightest d functions were contracted to three contracted s functions, two contracted p functions, and one contracted d function. We added one diffuse s function ($\zeta=0.058\,108$), one diffuse p function ($\zeta=0.037\,653$), two diffuse d functions ($\zeta=0.186\,597$ and 0.074 797), three f

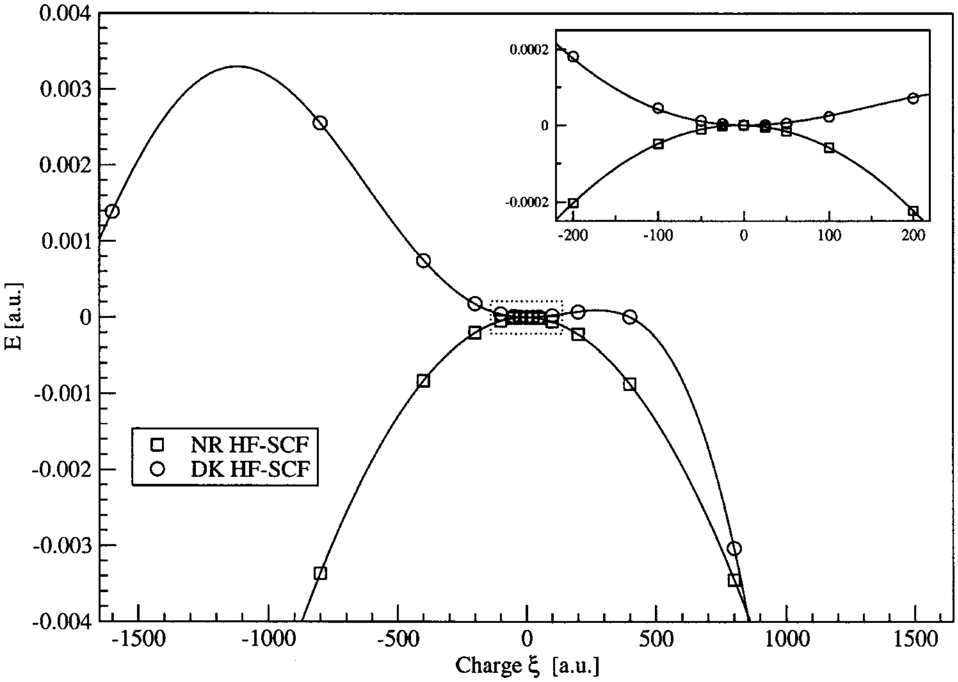

FIG. 1. Response of the total electronic energy E to size of point charges ξ used in the PCNQM model for nonrelativistic (NR) and DKH scalar-relativistic HF calculations on LaF. A distance of $d=10^{-4}$ a.u. was chosen for the distribution of the charges around the La nucleus. The solid lines show the interpolating polynomials.

functions (ζ=0.701 216, 0.272 850, and 0.150 736), and one g function (0.479 874), resulting in a $(22s20p14d3f1g)/[11s10p9d3f1g]$ basis set.

Because CCSD(T) calculations with a fully active orbital space were not feasible with the large basis sets used, some inner core orbitals were kept frozen and all virtual orbitals with energies larger than 500 a.u. were omitted. In the calculations on LaF and LaCl the La $1s2s2p$ orbitals were kept frozen. For LaBr we also froze the Br $1s$ orbital, and finally for LaI the La $1s2s2p$ and I $1s2s2p$ orbitals were frozen. This corresponds to correlating 56 electrons in LaF, 64 electrons in LaCl, 80 electrons in LaBr, and 90 electrons in LaI. We performed additional calculations using Møller-Plesset second-order perturbation theory (MP2) to make sure that this choice of the active orbital space does not lead to large deviations in the calculated EFGs. The error arising through this treatment was estimated from MP2 calculations correlating all electrons, and the calculated EFGs were corrected accordingly.

The determination of the EFG tensor as the expectation value of a well known EFG operator is nontrivial in one-(scalar) or two-component relativistic calculations. As the DKH transformation involves a unitary transformation of the Dirac four-component wave function to eliminate the small component, an appropriate transformation of the EFG operator is also required.[40,41] The evaluation of the expectation value of the original untransformed EFG using transformed wave functions can lead to significant errors in the EFG tensor, which is termed the picture change error (PCE).[40,42,43] The DKH transformation of the EFG operator has recently been performed by Malkin *et al.*[44]

A method which entirely avoids the PCE in relativistic calculation of EFGs is the use of a quadrupolar point charge distribution around the nucleus [the point-charge NQM (PCNQM) model].[45] In the PCNQM method used here the nuclear quadrupole moment is modeled by placing six point charges (two of size ξ at distance d from the nucleus in z-direction along the molecular axis and four of size $-\xi/2$) at distance d in x- and y-direction. These point charges lead to additional terms to the potential energy operator which are automatically included in the DKH transformation through the transformation of the corresponding nuclear attraction integrals. This introduced perturbation Q leads to a quadrupolar perturbation Hamiltonian

$$\hat{H}' = Q\hat{q}_{zz}, \tag{5}$$

where the perturbation strength $Q=\frac{2}{3}\xi d^2$ depends on the size of the point charges ξ and their distance d from the nucleus. Variations of Q therefore result in changes in the total electronic energy E and the expectation value of the EFG can be obtained from

$$q_{zz} = \left.\frac{dE(Q)}{dQ}\right|_{Q=0}. \tag{6}$$

This differentiation of the total electronic energy with respect to the perturbation strength is performed numerically by varying the charge ξ at fixed distance d.

For the optimal choice of d we have performed numerous test calculations on LaF using different distances d. We obtained numerically accurate results using a distance of $d=10^{-4}$ a.u. In the numerical differentiation, the EFG contributions at the HF level and at the correlated level are treated separately as they show a very different response to the quadrupolar perturbation. While the electron correlation contribution shows a nearly linear dependence on the perturbation strength Q, in the HF case the higher derivatives give significant contributions.[45] Furthermore, we observe that the behavior of the total electronic energy with varying perturbation strength is quite different in the nonrelativistic compared to the DKH relativistic calculations, and the choice of the point charges has to be carefully adjusted to this different

TABLE I. Parameters used in the PCNQM calculations for the nonrelativistic (NR) and DKH scalar-relativistic HF calculations.

		Point charges[a]	Order of approximation[b]
LaF	NR	$\pm 3200 - \pm 200$	5
	DKH	$\pm 1600 - \pm 50$	6
LaCl	NR	$\pm 3200 - \pm 400$	4
	DKH	$\pm 3200 - \pm 50$	7
LaBr	NR	$\pm 400 - \pm 100$	3
	DKH	$\pm 400 - \pm 12.5$	6
LaI	NR	$\pm 400 - \pm 50$	4
	DKH	$\pm 25 - \pm 6.25$	3

[a]Range of the point charges used in the PCNQM method. Point charges of sizes $\pm 100 \times 2^n$ a.u. in this range are used.
[b]Number of pairs of point charges. If the order of approximation is n, the total electronic energy is calculated at $2n$ points and an interpolating polynomial of degree $2n-1$ is used to approximate the first derivative.

behavior. For example, for LaF, Fig. 1 shows the total electronic energy as a function of the size of the point charges in the nonrelativistic and in the DKH scalar relativistic HF case. It can be clearly seen that in the relativistic calculations the behavior of the electronic energy is more irregular. The coefficients of the interpolating polynomials show that in the relativistic case the higher order contributions are larger than in the nonrelativistic case. Even in the region of quite small point charges, where a finite difference method works well in the nonrelativistic case, the higher order contributions are significant in the relativistic case.

In our calculations the algorithm used for the numerical differentiation is able to adapt to these different behaviors. The parameters resulting from this algorithm that were finally used for the numerical differentiation in the HF calculations is given in Table I. For all four molecules we had to use much smaller charges in the relativistic calculations than in the nonrelativistic case. For the numerical differentiation in the HF calculations we used the algorithm of Ridders as described in Ref. 46. Briefly, this algorithm starts with calculating the total electronic energy at two points corresponding to rather large perturbations of opposite sign (we used charges of $\xi = \pm 3200$ a.u.), and from that one calculates a first approximation to the first derivative. In the following steps the charges used are repeatedly divided by two and the total electronic energy is calculated for two more points. Using these additional points new approximations to the derivative (of higher order and of lower order but taking only the smaller charges into account) are calculated using the Neville interpolation scheme. The quality of each approximation is estimated from the difference to the approximation of lower order. The algorithm terminates when this estimated error increases due to the numerical inaccuracies in the calculated energies when very small perturbations are used.

The main advantage of using this algorithm instead of using a fixed number of charges and constructing the interpolating polynomial for the energies calculated at these points is that it can adapt to the different response behavior of the total electronic energy in different molecules and in nonrelativistic and DKH scalar relativistic calculations. The parameters and orders of interpolation that were actually used for the calculation of the field gradients are discussed below. In any cases the errors of the calculated field gradients estimated by the algorithm are smaller than 10^{-4} a.u. This error can be regarded as a measure for the importance of the higher order contributions, but it does not include the intrinsic errors of the PCNQM method. These are believed to be equally small because of the excellent agreement of the PCNQM result and the expectation value obtained in our nonrelativistic calculations.

For the electron correlation contribution in the CCSD(T) calculations four different points ($\xi = \pm 800, \pm 400$ a.u.) and in the MP2 calculations six different points ($\xi = \pm 800, \pm 400, \pm 200$ a.u.) have been used. In both cases the derivative was obtained from differentiating the corresponding interpolating polynomial. Because of the very close to linear behavior, the higher order contributions are rather small (below 0.05) and the field gradients obtained are believed to be accurate through at least three decimals.

We also carried out four-component relativistic (Dirac-Coulomb) HF (DC-HF) and density functional theory (DFT) calculations using the DIRAC program package[47] with the same basis sets but in completely uncontracted form. Here we used the hybrid-GGA B3LYP containing exact exchange,[48] and the recently developed Coulomb-attenuated B3LYP functional (CAM-B3LYP),[49] with modified parameters adjusted to accurately describe EFGs (denoted as CAM-B3LYP* for the following using the parameters $\alpha = 0.4$, $\beta = 0.179$, and $\mu = 0.99$; see Refs. 49 and 50 for details). In order to study the influence of spin-orbit effects we also employed Dyall's spin-free (SF) Hamiltonian[51] in our relativistic HF and DFT calculations. The influence of the Gaunt term of the Breit interaction was investigated at the DHF level only, as such effects can become important for the heavier elements.[52–54] We note that the inclusion of the Breit term in the DFT formalism requires the accurate description of the electron self-interaction correction.[55] For all four-component calculations we used an extended basis set for La (denoted as EB for the following). This $(26s16p20d11f9g)$ set for La has been ontained by adding additional two diffuse s functions ($\zeta = 0.10$ and 0.05), one diffuse p function ($\zeta = 0.078\,75$), three tight ($\zeta = 230\,100.0$, $747\,76.0$, and $242\,91.1$) and one diffuse ($\zeta = 0.024\,56$) d functions, six tight f functions ($\zeta = 1111.7, 493.33, 218.92, 97.147, 4.311, 1.913$), and five tight ($\zeta = 96.388\,764$, $46.482\,627$, $22.421\,27$, $10.813\,77$, and 4.1468) and one diffuse ($\zeta = 0.063\,836\,16$) g functions in an even-tempered manner. This basis set was applied in its fully uncontracted form and, in addition, the halogen basis sets were fully uncontracted. The results obtained with this basis set should be close to the DC-HF limit. We note that we neglected the two-electron integrals arising solely from the Dirac small component.[56] A DC-HF test calculation for LaF including all (SS|SS) integrals changed the EFG of La by only 0.0013 a.u.

Vibrational corrections can be derived using the Buckingham formula.[57–59] This formula is derived from perturbation theory and in its most general form is expressed in a polynomial form[59] for a specific property P,

TABLE II. Electric field gradients at La for the lanthanum monohalides at the experimental equilibrium bond distance. All values are in a.u.

	LaF	LaCl	LaBr	LaI
Nuclear contribution	+0.3220	+0.3232	+0.5561	+0.6583
Electronic contributions				
DC-HF (EB)[a]	−4.0704	−4.0213	−4.1484	−4.1591
DKH-HF	−4.1106	−4.0640	−4.1977	−4.2303
DKH-MP2 (frozen)[b,c]	+0.7838	+0.9279	+0.9679	+1.0219
DKH-MP2 (full)[d,c]	+0.7828	+0.9275	+0.9676	+1.0219
Inner core correlation[e]	−0.0010	−0.0004	−0.0003	0.0000
DKH-CCSD[c]	+0.5799	+0.6664	+0.6778	+0.7040
DKH-CCSD(T)[c]	+0.7396	+0.8603	+0.8824	+0.9277
Gaunt[f]	+0.0217	+0.0305	+0.0095	+0.0062
Total[g]	−2.9881	−2.8077	−2.7007	−2.5669

[a]Extended basis set used in the Dirac-Coulomb HF calculations.
[b]Frozen core used and high virtual orbitals deleted, see text for details.
[c]Electron correlation contribution only.
[d]Fully active orbital space for correlation.
[e]Correction for inner core correlation estimated using MP2.
[f]Gaunt contribution see Table IV.
[g]DC-HF+CCSD(T)+core correlation+Gaunt+nuclear contribution.

$$P_n = P(r_e) + \sum_{k=1} c_i \left(n + \frac{1}{2} \right)^k . \tag{7}$$

Here we take a different approach. Instead of calculating the vibrational corrections to the EFGs, which requires accurate knowledge of the potential energy curve and the corresponding EFG curve, we use the vibrationally resolved NQCCs of Rubinoff *et al.*[21] to obtain the equilibrium NQCCs from a fit to Eq. (7). A good test will be if these NQCCs are identical for the two isotopes ^{35}Cl and ^{37}Cl in LaCl. Only for LaF vibrational NQCC values are available up to the vibrational quantum number $n=2$. However, the quadratic term in the polynomial [Eq. (7)] was found to be very small and a linear fit is justified.

III. RESULTS AND DISCUSSION

The calculated lanthanum electric field gradients for the lanthanum monohalides are summarized in Table II. We note that the core correlation contribution is rather small for all molecules, but was nevertheless used to correct the EFGs calculated using CCSD(T). Interestingly this correction decreases from LaF to LaI as one may expect larger contributions from electronegative ligands polarizing the core. The noniterative triple contributions are rather large for the La EFG, ranging from 22% to 24% of the total electron correlation contribution and 5.3% to 8.7% of the total electric field gradient. Hence, the nonperturbative treatment of the triples and the neglect of the quadruples in the coupled cluster procedure represent one source of error in our calculations.

In order to examine the importance of relativistic effects we have carried out nonrelativistic HF and MP2 calculations. The field gradients obtained from these calculations are compared to the corresponding relativistic results in Table III. First we note that the nonrelativistic La EFGs obtained from the expectation value according to Eq. (4) and the PCNQM model according to Eqs. (5) and (6) are in perfect agreement. This again points at the high numerical accuracy of the PCNQM model. Second, scalar-relativistic effects cannot be neglected. Including electron correlation they range from 1.2% of the total EFG for LaI to 14% for LaF. Interestingly, they diminish with decreasing electronegativity of the ligand. Third, the results clearly demonstrate that electron correlation and relativistic effects are not additive. Fourth, the picture change error is rather large and from LaCl onwards is even larger than the scalar-relativistic effects. This has been pointed out before by Pernpointner *et al.*[43]

TABLE III. Comparison of scalar-relativistic (DKH) and nonrelativistic (NR) results for the electric field gradients at La in the lanthanum monohalides at the experimental equilibrium bond distances (electronic contribution only). All values are in a.u.

	LaF	LaCl	LaBr	LaI
HF (NR)[a]	−3.4785	−3.7032	−3.9652	−4.1684
HF (NR) PCNQM[b]	−3.4785	−3.7031	−3.9651	−4.1683
HF (DKH)[a]	−4.5628	−4.5902	−4.7302	−4.7774
HF (DKH) PCNQM[b]	−4.1106	−4.0640	−4.1977	−4.2303
HF relativistic contribution	−0.6321	−0.3608	−0.2325	−0.0619
DKH picture change error	−0.4522	−0.5262	−0.5325	−0.5471
MP2 (NR) PCNQM[b,c]	+0.5756	+0.7654	+0.8298	+0.9298
MP2 (DKH) PCNQM[b,c]	+0.7828	+0.9275	+0.9676	+1.0219
MP2 relativistic contribution	+0.2072	+0.2022	+0.1378	+0.0921
Total relativistic contribution[d]	−0.4249	−0.1586	−0.0947	+0.0302

[a]Calculated as the expectation value of the EFG operator in Eq. (2).
[b]Calculated using the PCNQM method.
[c]Electron correlation contribution only using MP2 with full active orbital space.
[d]HF+MP2.

Table IV lists DC-HF and DC-DFT EFGs for lanthanum. We also include results from Dyall's spin-free approach to obtain the influence of spin-orbit coupling. We find that the

TABLE IV. Contributions of spin-orbit coupling and the Gaunt term (HF level only) to the electronic component of the electric field gradients at La in the lanthanum monohalides at various levels of theory using the extended basis sets as described in the text. All values are given in a.u.

	LaF	LaCl	LaBr	LaI
HF (DKH)[a]	−4.1106	−4.0640	−4.1977	−4.2303
HF (SF)[a]	−4.1134	−4.0660	−4.1989	−4.2320
HF (4*c* DC)[a]	−4.1352	−4.0760	−4.2017	−4.2083
HF Δ_{SO}[a]	−0.0218	−0.0100	−0.0028	+0.0236
HF (SF)	−4.0484	−4.0106	−4.1446	−4.1804
HF (4*c* DC)	−4.0704	−4.0213	−4.1484	−4.1591
HF Δ_{SO}	−0.0220	−0.0107	−0.0038	+0.0213
HF (4*c* DC+Gaunt)	−4.0487	−4.0092	−4.1389	−4.1529
HF Δ_{Gaunt}	+0.0217	+0.0305	+0.0095	+0.0062
B3LYP (SF)	−3.2799	−3.0063	−3.0871	−3.0742
B3LYP (4*c* DC)	−3.2872	−3.0033	−3.0812	−3.0579
B3LYP Δ_{SO}	−0.0073	+0.0033	+0.0059	+0.0169
CAM-B3LYP (SF)	−3.4623	−3.2634	−3.3576	−3.3626
CAM-B3LYP (4*c* DC)	−3.4711	−3.2591	−3.3484	−3.3364
CAM-B3LYP Δ_{SO}	−0.0088	+0.0043	+0.0092	+0.0262
CAM-B3LYP* (SF)	−3.6833	−3.5110	−3.6092	−3.6107
CAM-B3LYP* (4*c* DC)	−3.6953	−3.5076	−3.5989	−3.5779
CAM-B3LYP* Δ_{SO}	−0.0120	+0.0034	+0.0103	+0.0328

[a]Using the smaller $(24s25p16d5f3g)$ basis set for La.

TABLE V. Effect of extending the La basis set in LaF in the DC-HF calculations, starting from the extended ANO basis set described above (electronic contribution only). All values are in a.u.

	EFG	ΔEFG
Original (24*s*15*p*16*d*5*f*3*g*)	−4.1354	
Uncontracted F basis set	−4.1352	+0.0001
B1 (24*s*15*p*19*d*8*f*9*g*)[a]	−4.0684	+0.0668
EB (26*s*16*p*20*d*11*f*9*g*)[b]	−4.0704	−0.0020
EB+tight set[c] (27*s*17*p*21*d*12*f*10*g*)	−4.0720	−0.0016
EB+diffuse set[d] (27*s*17*p*21*d*12*f*10*g*)	−4.0707	−0.0004
EB+extended F[e]	−4.0742	−0.0038
EB+extended F[f]	−4.0762	−0.0058

[a]original+added two tight *d*, one diffuse *d*, three tight *f*, five tight *g*, and one diffuse *g*.
[b]B1+added two diffuse *s*, one diffuse *p*, one tight *d*, and three tight *f*.
[c]EB+added one tight *s*,*p*,*d*,*f*,*g*.
[d]EB+added one diffuse *s*,*p*,*d*,*f*,*g*.
[e]extended F basis set by one set of diffuse and one set of tight functions.
[f]extended F basis set by two sets of diffuse and one set of tight functions.

second-order DKH results are almost identical to the spin-free calculations, and higher order terms in DKH transformation are therefore small. We note that for the treatment of these higher order contributions, there are efficient infinite order schemes by Reiher and Wolf[60] as well as Iliaš and Saue.[61] The spin-orbit contributions are quite small but non-negligible and decrease from LaF to LaI in both the HF and DFT calculations. DFT gives somewhat smaller values than HF. Nevertheless, spin-orbit effects remain small even when using the CAM-B3LYP* functional, which was recently used in field gradient calculations of copper and gold halides and was found to produce excellent results.[50] However, the Gaunt contribution to the La EFG in LaF is opposite in sign and therefore almost completely cancels the spin-orbit contribution. Nevertheless, the data in Table IV give an indication of the error introduced by not correctly taking the spin-orbit and Breit interactions at the correlated level into account.

As a further possible error we checked the error due to basis set incompleteness for LaF as detailed in Table V. We systematically extended the original basis set by adding both tight and diffuse functions in an even tempered way. Uncontracting and extending the F basis set do not change the EFG significantly, but going to the large La basis set (especially adding tight *f* and *g* functions) leads to a significant contribution (≈0.07 a.u.) to the EFG. Nevertheless, the large basis set EB we used in our Dirac-Coulomb calculations already gives stable results. We also ran tests constructing a completely new basis set. Starting from the even-tempered (dual family) basis set by Fægri,[62] which is (33*s*31*p*24*d*3*f*1*g*), we added tight and diffuse functions one by one and checked the effect on the La EFG (in combination with an uncontracted aug-cc-pVTZ basis set for F) using DC-HF. This leads to a very large (28*s*29*p*22*d*10*f*9*g*) basis set, and an EFG for LaF of 4.0718, which should be the HF basis set limit. This is very close to the DC-HF value calculated using the EB set. Also adding one tight and one diffuse function set for iodine in LaI using the EB basis set changes the EFG by only −0.0019 a.u. We therefore conclude that our EB basis set is sufficiently large (at least for the HF part).

Table VI shows the equilibrium NQCCs obtained from Eq. (7) together with the total EFGs from Table II and the resulting NQMs from Eq. (1). First we note that the equilibrium NQCCs obtained for the two different chlorine isotopes are virtually identical and do not change significantly the NQM. However, the spread of the calculated NQMs is quite large, 10.9 mb. If we take the average over the four different NQMs we obtain 200±6 mb, which lies within error bar of the currently accepted value of 200(10) mb. Assuming an accuracy of 0.01 a.u. for the calculated EFG due to the different spin-orbit values, one obtains for $\Delta Q \approx 1$ mb which is not consistent with the spread of the calculated NQMs. Hence we conclude that the level of electron correlation applied is not sufficient to obtain a more accurate value compared to the recommended literature value. Moreover, if we plot the NQCC against the EFGs shown in Table VI, the values are lying nicely on a straight line with a correlation coefficient of 0.9992, but the intercept deviates substantially from exact zero with 48.7 MHz. Even worse, from this line we obtain a NQM of 274 mb. This points towards a systematic error in our calculations which we believe comes from the correlation treatment which requires at least nonperturbative triples and quadruples to obtain more accurate results. Another possible source of error is the basis set used in the coupled cluster calculations, which for the DC-HF part yields results close to the basis set limit, but which could nevertheless be not sufficiently large for the correlation treatment. However, employing a larger basis set would turn the coupled cluster calculations infeasible. Finally, one has to consider spin-orbit effects at the correlated level although the DFT calculations might suggest that this is not the largest source of error. We point out that the performance of the four-component density functionals varies widely with B3LYP giving the best results. From a linear fit we obtain a NQM of 199 mb and a small intercept of −6.6 MHz. The CAM-B3LYP method in contrast does not perform so well with 240 mb and +32.6 MHz for the NQM and intercept, respectively. Even the modified CAM-B3LYP* method adjusted to describe the field gradients well for the notoriously

TABLE VI. Calculated nuclear quadrupole moments for ^{139}La.

	LaF	La^{35}Cl	La^{37}Cl	LaBr	LaI
NQCC (MHz)[a]	−144.52	−132.96	−132.92	−125.49	−117.60
Total EFG (a.u.)[b]	−2.9881	−2.8077	−2.8077	−2.7007	−2.5669
NQM (mb)	205.8	201.5	201.5	197.8	194.9

[a]From Ref. 21 and extrapolated to r_e using Eq. (7).
[b]See Table II.

difficult cases of copper and gold halides[50] does not perform well with a NQM of 250 mb and an intercept of +53.6 MHz.

IV. CONCLUSION

We used state-of-the-art *ab initio* methods including relativistic effects (scalar relativity, spin-orbit, and Gaunt interactions) together with coupled cluster theory at the CCSD(T) level to obtain the EFGs of the lanthanum halides. Our final recommended value for the NQM of ^{139}La is 200 ± 6 mb in good agreement with the currently recommended value of Bauche *et al.*[12] In order to improve on this value four-component coupled cluster calculations beyond nonperturbative triples are required and possible including the Breit term in the Coulomb gauge,[63] which will be computationally demanding. Alternatively, microwave data for LaH would be ideal for this purpose as it would reduce the computational costs significantly.

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