

# The quadrupole moment of the $3/2^+$ nuclear ground state of $^{197}\text{Au}$ from electric field gradient relativistic coupled cluster and density-functional theory of small molecules and the solid state

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An attempt is made to improve the currently accepted muonic value for the  $^{197}\text{Au}$  nuclear quadrupole moment [ $+0.547(16) \times 10^{-28} \text{ m}^2$ ] for the  $3/2^+$  nuclear ground state obtained by Powers *et al.* [Nucl. Phys. **A230**, 413 (1974)]. From both measured Mössbauer electric quadrupole splittings and solid-state density-functional calculations for a large number of gold compounds a nuclear quadrupole moment of  $+0.60 \times 10^{-28} \text{ m}^2$  is obtained. Recent Fourier transform microwave measurements for gas-phase AuF, AuCl, AuBr, and AuI give accurate bond distances and nuclear quadrupole coupling constants for the  $^{197}\text{Au}$  isotope. However, four-component relativistic density-functional calculations for these molecules yield unreliable results for the  $^{197}\text{Au}$  nuclear quadrupole moment. Relativistic singles-doubles coupled cluster calculations including perturbative triples [CCSD(T) level of theory] for these diatomic systems are also inaccurate because of large cancellation effects between different field gradient contributions subsequently leading to very small field gradients. Here one needs very large basis sets and has to go beyond the standard CCSD(T) procedure to obtain any reliable field gradients for gold. From recent microwave experiments by Gerry and co-workers [Inorg. Chem. **40**, 6123 (2001)] a significantly enhanced  $^{197}\text{Au}$  nuclear quadrupole coupling constant in (CO)AuF compared to free AuF is observed. Here, these cancellation effects are less important, and relativistic CCSD(T) calculations finally give a nuclear quadrupole moment of  $+0.64 \times 10^{-28} \text{ m}^2$  for  $^{197}\text{Au}$ . It is argued that it is currently very difficult to improve on the already published muonic value for the  $^{197}\text{Au}$  nuclear quadrupole moment. © 2005 American Institute of Physics. [DOI: 10.1063/1.1869975]

## I. INTRODUCTION

The precise determination of spectroscopic nuclear quadrupole moments (NQM),  $Q_s$ , relies on both the precise measurement of the nuclear quadrupole coupling constant (NQCC),  $C_{\text{NQC}} = eqQ_s$ , from spectroscopic methods and the accurate calculation of the electric field gradient  $q$  for atoms, molecules, or the solid state.<sup>1,2</sup> First-principle nuclear structure calculations to determine directly  $Q_s$ , or alternatively the intrinsic nuclear quadrupole moment  $Q_0$ , do not give very reliable results at present, especially for isotopes of the heavier elements.<sup>3</sup> For the most abundant isotope of gold,  $^{197}\text{Au}$ , a value of  $+0.547(16)b$  ( $1b = 10^{-28} \text{ m}^2$ ) has been determined from both muonic hyperfine measurements and corresponding relativistic electric field gradient calculations using the Dirac equation.<sup>4</sup> These calculations include quantum electrodynamic, nuclear size and deformation, muon magnetic moment, and electron screening effects. This value is supported by an earlier atomic-beam magnetic resonance measurement of the  $^{197}\text{Au}$  NQCC from the  $^2D_{5/2}$  hyperfine splitting of atomic gold by Childs and Goodman.<sup>5</sup> Using atomic  $\langle r^{-3} \rangle_{5d_{3/2}}$  values from magnetic hyperfine interactions, the NQM of  $^{197}\text{Au}$  was determined as  $+0.59(12)b$ , with most of the uncertainty coming from the Sternheimer correction. A similar conclusion comes from hyperfine measurements of the  $^2D_{5/2}$  and  $^4F_{9/2}$  states of  $^{197}\text{Au}$  by Blachmann, Landman, and Lurio<sup>6</sup> who estimated the NQM as  $0.604b$ . More recently, Mössbauer studies together with linearized augmented plane-wave solid-state density-functional calculations for gold-aluminium alloys by Wagner and co-workers<sup>7</sup> gave a NQM of  $0.56(3)b$ . The current muonic  $^{197}\text{Au}$  value is used as a basis for the determination of NQMs from atomic hyperfine splitting for a number of different gold isotopes.<sup>8</sup>

NQMs derived from muonic values are assumed to be very accurate. However, Sundholm and Olsen compared muonic NQM data with values derived from atomic hyperfine spectra in electronic transitions of  $^{23}\text{Na}$ ,  $^{25}\text{Mg}$ , and  $^{27}\text{Al}$ .<sup>9</sup> They performed accurate finite-element multiconfiguration Hartree–Fock calculations and concluded that muonic values contain noticeable errors originating from both the experimental measurements and the theoretical treatment. We also mention a very recent publication by Bieron, Pyykkö, and Jönsson on the NQM of  $^{201}\text{Hg}$  obtained from hyperfine structure calculations of the excited  $^3P_1$  state of neutral Hg, which differs from the latest muonic value.<sup>10</sup> The question therefore remains if a more accurate NQM for  $^{197}\text{Au}$  can be obtained from either Mössbauer spectra of solid state gold compounds<sup>11,12</sup> or from microwave spectra of small diatomic<sup>13–15</sup> or polyatomic<sup>16–19</sup> gold compounds. This, however, involves the accurate determination of the electric field gradient tensor from theory.

For atoms and small molecules electric field gradients can be calculated to relatively high accuracy applying relativistic coupled cluster or multireference configuration interaction methods.<sup>1</sup> Recent applications improved on existing NQM values for  $^{23}\text{Na}$ ,  $^{25}\text{Mg}$ , and  $^{27}\text{Al}$ ,<sup>9</sup> for  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$ ,<sup>20</sup> for  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ ,<sup>21</sup> for  $^{201}\text{Hg}$ ,<sup>10</sup> and for  $^{209}\text{Bi}$  to name a few.<sup>22</sup> For solid-state Mössbauer measurements usually a large number of measured NQCCs is plotted against calcu-

lated electric field gradients obtained from density-functional theory (DFT) to deduce the NQM of the target isotope from a linear fit according to the simple relation

$$C_{\text{NQC}} \text{ (MHz)} = 234.9647 Q_s [b] q \text{ [a. u.]} \quad (1)$$

This was used for the determination of the  $^{100}\text{Rh}$ ,  $^{57}\text{Fe}$ , and  $^{199}\text{Hg}$  NQMs, for example.<sup>23–26</sup> However, while it is widely assumed that DFT performs reasonably well in electric field gradient calculations,<sup>27–35</sup> for transition elements there seem to be serious problems with DFT leading to significant errors.<sup>36–39</sup> The question therefore arises whether or not density functionals currently in use are sufficiently accurate for the determination of the nuclear quadrupole moment of  $^{197}\text{Au}$ . We therefore decided to investigate if an accurate NQM for  $^{197}\text{Au}$  can be obtained from solid-state DFT calculations together with Mössbauer measurements, testing the DFT approximation for a variety of diatomic gold compounds in the gas phase using microwave data, and from relativistic *ab initio* calculations for AuF, AuCl, AuBr, and AuI, and finally for (CO)AuF in connection with accurate microwave data.<sup>13,14,18</sup>

## II. THEORY

Relativistic solid-state DFT calculations<sup>40</sup> for a number of gold compounds were performed using the projector augmented wave method (PAW) of Blöchl,<sup>41</sup> together with the local density approximation (LDA) and the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional.<sup>42,43</sup> The crystal structure data were taken from x-ray diffraction studies (for details see Sec. III). Relativistic effects were included using the method of Koelling and Harmon,<sup>44</sup> i.e., the core states are treated relativistically<sup>45</sup> and the valence states in a scalar relativistic fashion. In this formalism the contribution of the small component is accounted for, and picture change effects<sup>46–48</sup> are avoided for the calculation of electric field gradients. The electric field gradient tensor  $V^{\alpha\beta}$  is obtained directly as the expectation value of the field gradient operator,  $V^{\alpha\beta} = +\langle \Psi | \hat{V}^{\alpha\beta} | \Psi \rangle$ , where  $\hat{V}^{\alpha\beta}$  located at center  $\vec{R}_X$  can be decomposed into the electronic and nuclear contribution,

$$\hat{V}_{\text{el}}^{\alpha\beta}(\vec{r}_i; \vec{R}_X) = - \frac{3(\vec{r}_i - \vec{R}_X)_\alpha (\vec{r}_i - \vec{R}_X)_\beta - |\vec{r}_i - \vec{R}_X|^2 \delta_{\alpha\beta}}{|\vec{r}_i - \vec{R}_X|^5}, \quad (2)$$

$$\hat{V}_{\text{nuc}}^{\alpha\beta}(\vec{R}_X) = \sum_{Y \neq X} Z_Y \frac{3(\vec{R}_Y - \vec{R}_X)_\alpha (\vec{R}_Y - \vec{R}_X)_\beta - |\vec{R}_Y - \vec{R}_X|^2 \delta_{\alpha\beta}}{|\vec{R}_Y - \vec{R}_X|^5}. \quad (3)$$

The letters  $\alpha, \beta$  hereby denote the Cartesian components  $x, y, z$  and  $X, Y, Z$  of the electronic or nuclear coordinates. The technical details are given in Ref. 49.

In Mössbauer experiments the energy levels are perturbed by the nuclear quadrupole deformation

$$\Delta E_{\text{NQC}}(I, m_I) = \frac{eQ_s q [3m_I^2 - I(I+1)] (1 + \eta^2/3)^{1/2}}{4I(2I-1)}, \quad (4)$$

where  $I$  and  $m_I$  are the well-known nuclear spin quantum numbers, and the nuclear quadrupole coupling is related to the measured quadrupole splitting  $\nu_{\text{QS}}$  by

$$\nu_{\text{QS}} = \frac{c}{E_\gamma} \frac{eQ_s q}{2} (1 + \eta^2/3)^{1/2} \quad (5)$$

with the asymmetry parameter  $\eta$ ,

$$\eta = (V^{xx} - V^{yy})/V^{zz}, \quad |V^{xx}| \leq |V^{yy}| \leq |V^{zz}|, \quad (6)$$

and  $q = V_{zz}$ .  $c$  is the velocity of light and  $E_\gamma = 77$  keV is the energy of the emitted  $\gamma$  radiation of the  $^{197}\text{Au}$  nucleus.

To test the reliability of DFT we carried out four-component relativistic Hartree–Fock (HF) and DFT calculations for AuF, AuCl, AuBr, and AuI using the Dirac–Coulomb–Hamiltonian (in atomic units),

$$D = \sum_i \{c\tilde{\alpha}_i \vec{p}_i + c^2 \beta_i + V_{\text{ext}}(i)\} + \sum_{i < j} r_{ij}^{-1} \quad (7)$$

within the program package DIRAC.<sup>50</sup>  $\tilde{\alpha}$  and  $\beta$  are the Dirac matrices in the usual standard representation. An isotropic nuclear charge distribution for all elements was used.<sup>51</sup> (SS|SS) type two-electron integrals were omitted in all HF type calculations as such contributions can safely be neglected. Four-component Kramers-restricted density-functional theory was used within a Kohn–Sham formalism.<sup>52–55</sup> In Kohn–Sham theory the field gradient is obtained simply from the evaluation of the matrix elements over the field gradient operator (2).<sup>56,57</sup> Nonrelativistic functionals that were used as relativistic corrections in the functional do not lead to significant changes in properties.<sup>58</sup> Here we used the local density approximation (LDA) to compare with the solid-state results,<sup>59</sup> the generalized gradient approximations of Becke–Lee–Yang–Parr (BLYP),<sup>60,61</sup> Perdew–Wang (PW86),<sup>62</sup> and the hybrid functional B3LYP.<sup>63</sup> The basis set for Au is of dual family type (26s24p16d12f) (see Table I). For F and Cl we used an uncontracted version of Dunning's correlation-consistent aug-cc-pVTZ basis set without the  $f$  and  $g$  functions, i.e., (13s7p4d) and (17s12p4d) for F and Cl, respectively,<sup>64,65</sup> as these are not so important in DFT calculations.<sup>36</sup> For Br and I we took the dual basis sets of Faegri<sup>66</sup> extended by a diffuse  $p$  function, i.e., (19s17p9d) and (20s19p11d). The geometries for the diatomic gold halides were taken from the work of Evans and Gerry.<sup>13–15</sup>

For the two smaller diatomic gold molecules, AuF and AuCl, we carried out Dirac–Coulomb (DC) coupled cluster calculations including singles and doubles with triples treated perturbatively, CCSD(T), using the basis sets as described above. Here we could only apply a small active space with 40 electrons correlated for both AuF and AuCl, and all virtual orbitals above 10 a.u. were discarded. Here the Dirac-HF contribution is determined directly through the expectation value of Eq. (2). For the coupled cluster calculations we used a point-charge nuclear quadrupole moment (PCNQM) model shown in Fig. 1.<sup>67</sup> For the correlation con-

TABLE I. (26s24p16d12f) dual family basis set for Au. The  $s$  and  $p$  exponents are explicitly given, whereas the  $d$  and  $f$  exponents are indicated with ( $d$ ) and ( $f$ ) after the  $s$  and  $p$  exponents, respectively.

No.	$s$ exponent	Dual	$p$ exponent	Dual
1	88 087 000.0		58 592 500.0	
2	22 021 800.0		14 648 100.0	
3	5 505 440.00		3 662 030.00	
4	1 376 359.95		915 508.000	
5	389 821.512		228 877.000	
6	127 125.247		57 219.300 0	
7	45 806.447 5		14 304.813 9	
8	17 736.109 3		4 640.219 19	
9	7 209.377 28	( $d$ )	1 767.014 64	
10	3 026.147 48	( $d$ )	742.207 018	( $f$ )
11	1 308.488 72	( $d$ )	331.722 681	( $f$ )
12	582.871 920	( $d$ )	154.856 063	( $f$ )
13	259.343 171	( $d$ )	74.215 333 0	( $f$ )
14	122.675 842	( $d$ )	35.853 679 2	( $f$ )
15	59.682 322 1	( $d$ )	17.372 511 4	( $f$ )
16	29.637 468 1	( $d$ )	8.312 760 28	( $f$ )
17	14.507 742 1	( $d$ )	3.898 304 37	( $f$ )
18	6.980 440 78	( $d$ )	1.612 321 51	( $f$ )
19	3.299 458 65	( $d$ )	0.685 303 12	( $f$ )
20	1.405 592 51	( $d$ )	0.268 43664	( $f$ )
21	0.554 811 83	( $d$ )	0.107 370 00	( $f$ )
22	0.221 925 00	( $d$ )	0.042 950 00	
23	0.088 769 90	( $d$ )	0.017 180 00	
24	0.035 508 00	( $d$ )	0.006 872 00	
25	0.014 203 00			
26	0.005 680 00			

tribution only two single point calculations are required since the dependence is linear in the applied charge  $e$ .<sup>67</sup>

Since correlated Dirac calculations are computationally most demanding limiting the use of large and extended basis sets and the active space in the correlated calculations, we carried out scalar relativistic calculations for AuF, AuCl, AuBr, and AuI by modifying the one-electron integrals in the Hartree–Fock scheme<sup>68</sup> according to the so-called spin-free (SF) Douglas–Kroll (DK) approximation.<sup>69</sup> The explicit Fou-

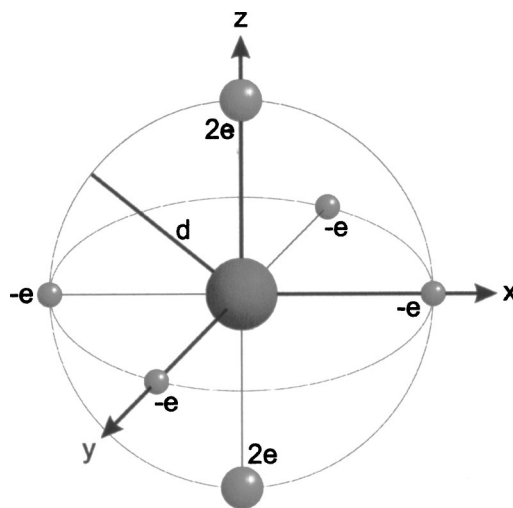


FIG. 1. The nuclear quadrupole point charge model used in all correlated *ab initio* calculations.

rier transform of the DK formalism is avoided by the use of the identity resolution based on eigenvectors of the kinetic energy operator.<sup>70,71</sup> Details of this very successful numerical implementation of the DK method including applications can be found in Refs. 72–75. The scalar DK Hamiltonian is the result of the approximate reduction of the four-component to the two-component formalism followed by the removal of all spin-dependent terms. This involves simultaneous change of all operators<sup>46,76,77</sup> and in particular of the electric field gradient operator.<sup>47</sup> The neglect of the change of picture contribution is far from being negligible.<sup>47,48</sup> This is one of the advantages of PCNQM (Refs. 47,48,67,78) that the change of picture for the electric field gradient operator can be easily taken into account and replaced by the numerical differentiation of the calculated DK energies. We therefore used the PCNQM model as shown in Fig. 1 within the spin-free relativistic DK approximation as implemented in MOLCAS5 [the nonrelativistic value is obtained through the expectation value of Eq. (2)].<sup>68</sup> For the correlation contribution to the electric field gradient we used well-tempered Huzinaga–Klobukowski basis sets<sup>79</sup> for all atoms, i.e., for Au an uncontracted (25s20p16d12f) set, for F, Cl, and Br generally contracted (15s11p4d)/[7s7p2d], (18s14p6d)/[10s8p3d], and (21s15p10d)/[8s8p4d] sets, respectively. In order to obtain near HF limit results at the nonrelativistic and relativistic DK level of theory, we used uncontracted basis sets for all atoms, and further extended them by additional hard, diffuse, and polarization functions. These basis sets contain *f* and *g* functions for all atoms, i.e., the basis sets are (26s25p18d13f4g) for Au, (15s11p5d3f2g) for F, (19s16p10d5f4g) for Cl, (22s18p14d5f4g) for Br, and (25s21p13d5f4g) for I.

As we will discuss below in detail, the gold NQCC and corresponding field gradients for AuF, AuCl, AuBr, and AuI are too small to accurately determine the nuclear quadrupole moment of <sup>197</sup>Au and we did not investigate these systems further with larger basis sets. Instead we searched for a simple linear gold compound with a very large NQCC. The coordinated (CO)AuX (X=F, Cl, Br) compounds have NQCCs of around 1 GHz,<sup>18</sup> more than an order of magnitude larger compared to the corresponding uncoordinated compounds AuX. We therefore investigated (CO)AuF in detail. For these calculations we used the well-tempered Huzinaga–Klobukowski basis sets,<sup>79</sup> i.e., an uncontracted (24s20p16d12f2g) set for Au, and contracted (13s7p4d)/[6s5p4d] sets for C and O, and a (15s11p4d)/[7s7p2d] set for F. Because of the high computational demand of the coupled cluster procedure, we had to freeze the orbitals below –20 a.u. [first 20 low lying orbitals for (CO)AuF] and above +1000 a.u. [last 48 high lying orbitals for (CO)AuF]. The structural data were taken from Ref. 18 (in detail: for (CO)AuF  $r(\text{CO})=1.336$  Å,  $r(\text{AuC})=1.847$  Å,  $r(\text{AuF})=1.909$  Å). Note that these distances are not ideal  $r_e$  values. For the determination of the electric field gradient, we again used the PCNQM model, for example, for (CO)AuF we applied a range of different charges ( $e=\pm 4.0$ ,  $\pm 2.0$ ,  $\pm 1.0$ ,  $\pm 0.5$ ,  $\pm 0.25$ , and  $0.0$  a.u. along the *z* axis) at a distance  $d=10^{-3}$  a.u. around the gold nucleus. Again, at the CCSD(T) level of theory only two single point calculations are necessary because of the linear behavior of the correla-

TABLE II. Measured Mössbauer electric quadrupole splitting  $\nu_{\text{QS}}$ (mm/s), calculated DFT electric field gradient  $q$  (in atomic units), and asymmetry parameter  $\eta$  of the field gradient tensor [see Eq. (5)] using the LDA and PBE functionals.

Compounds	Expt.	LDA		PBE	
	$\nu_{\text{QS}}$	$q$	$\eta$	$q$	$\eta$
Au(I) compounds					
AuCl	–4.65 <sup>a</sup>	–3.396	0.1104	–3.658	0.1137
AuBr-I <sup>f</sup>	...	–3.708	0.0023	–3.962	0.0062
AuBr-P <sup>f</sup>	–4.23 <sup>a</sup>	–3.010	0.3578	–3.252	0.3227
AuT	–3.98 <sup>a</sup>	–3.280	0.2810	–3.483	0.2567
CsAuO	–6.11 <sup>b</sup>	–3.485	0.2896	–3.851	0.2795
RbAuO	–5.88 <sup>b</sup>	–4.459	0.1213	–4.834	0.1266
KAuS	–6.694 <sup>c</sup>	–5.915	0.0941	–6.171	0.0542
KAuSe	–6.21 <sup>c</sup>	–5.300	0.1277	–5.572	0.0847
KAuTe	4.82 <sup>c</sup>	4.021	0.3449	4.184	0.3221
CsAuTe	–5.63 <sup>c</sup>	–5.038	0.1653	–5.201	0.1735
Cs <sub>2</sub> Au <sub>2</sub> Cl <sub>6</sub>	–5.04 <sup>d</sup>	–4.631	0	–4.866	0
Na <sub>3</sub> AuO <sub>2</sub>	–6.7 <sup>b</sup>	–4.904	0.0633	–5.292	0.1396
Na <sub>3</sub> AuS <sub>2</sub>	–7.70 <sup>c</sup>	–6.315	0	–6.568	0
K <sub>4</sub> Au <sub>6</sub> S <sub>5</sub>	–5.97 <sup>c</sup>	–5.254	0.1615	–5.586	0.1556
Au(III) compounds					
Au <sub>2</sub> O <sub>3</sub>	0.70 <sup>b</sup>	1.127	0.3437	1.454	0.2882
Li <sub>3</sub> AuO <sub>3</sub>	2.27 <sup>b</sup>	1.265	0.5535	1.594	0.4670
Na <sub>3</sub> AuO <sub>3</sub>	3.016 <sup>b</sup>	3.489	0.3615	3.926	0.3563
RbAuF <sub>4</sub>	0.17 <sup>e</sup>	–0.961	0.3787	0.337	0.0285
Cs <sub>2</sub> Au <sub>2</sub> Cl <sub>6</sub>	1.17 <sup>d</sup>	2.098	0	2.153	0
Intermetallic compounds					
NaAu <sub>2</sub>	–3.743 <sup>b</sup>	–3.330	0	–3.403	0
LiAu <sub>3</sub>	–1.53 <sup>b</sup>	–1.268	0	–1.303	0
Au(I) in KAu <sub>5</sub>	–3.23 <sup>b</sup>	–2.928	0.0335	–2.930	0.0385
Au(II) in KAu <sub>5</sub>	3.23 <sup>b</sup>	2.797	0.7362	2.833	0.7484
Au(I) in K <sub>2</sub> Au <sub>3</sub>	–3.09 <sup>b</sup>	–2.814	0.7788	–2.917	0.7693
Au(II) in K <sub>2</sub> Au <sub>3</sub>	4.18 <sup>b</sup>	3.402	0.6973	3.508	0.7046

<sup>a</sup>Reference 103.

<sup>b</sup>Reference 104.

<sup>c</sup>Reference 105.

<sup>d</sup>Reference 106.

<sup>e</sup>Reference 107.

<sup>f</sup>I and P denote different chain modifications of AuBr.

tion energy with changing NQM. We mention that other numerical schemes are available as well all leading to numerically stable results.<sup>80</sup>

### III. EXPERIMENTAL DETAILS

*Compound preparation.* The gold halides AuCl (Ref. 81) and AuI,<sup>82</sup> Cs<sub>2</sub>Au<sub>2</sub>Cl<sub>6</sub>,<sup>83</sup> and RbAuF<sub>4</sub> (Ref. 84) were prepared according to the literature. Crystalline gold (III) oxide Au<sub>2</sub>O<sub>3</sub> was obtained by dehydration of hydrous Au<sub>2</sub>O<sub>3</sub> under hydrothermal conditions<sup>85</sup> and subsequent tempering at 300 °C and 300 MPa for two weeks.<sup>86</sup> The oxoaurates RbAuO,<sup>87</sup> CsAuO,<sup>88</sup> and Li<sub>3</sub>AuO<sub>3</sub> (Ref. 89) were synthesized by careful oxidation of the aurides RbAu, CsAu, and Li<sub>3</sub>Au with elemental oxygen. In the case of the oxoaurate Na<sub>3</sub>AuO<sub>2</sub> a preprepared intermetallic of the composition NaAu was oxidized with sodium peroxide Na<sub>2</sub>O<sub>2</sub>.<sup>90</sup> KAuS, KAuSe,<sup>91</sup> KAuTe,<sup>92</sup> CsAuTe,<sup>93</sup> and Na<sub>3</sub>AuS<sub>2</sub> (Ref. 94) were synthesized as described by Bronger and co-workers. The

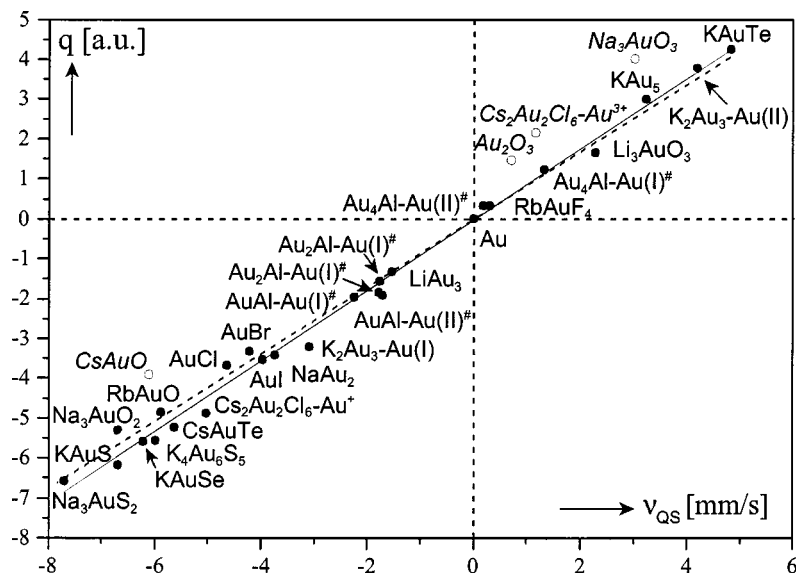


FIG. 2. Calculated electric field gradients for gold (corrected by the asymmetry factor) against the Mössbauer electric quadrupole splitting. Solid line, PBE; dashed line, LDA. The compounds set in italics (open circles) are outside of the error analysis test and are not used in the linear fit procedure (see text). The # symbol denotes data taken from Wagner and co-workers (Ref. 7).

intermetallics  $\text{LiAu}_3$  (Ref. 95) and  $\text{NaAu}_2$  (Refs. 96–98) were prepared directly from the elements.

**Sample preparation.** As all substances are either moisture and/or oxygen sensitive the samples were prepared under an argon atmosphere in Pyrex glass tubes (diameter 4–6 mm, length about 2 cm, flat bottom).

**Mössbauer spectroscopy.** The Mössbauer spectra were measured in a liquid He bath cryostat with both the source and the absorber at 4.2 K. Sources of  $^{197}\text{Pt}$  ( $T_{1/2}=19$  h) were obtained by neutron irradiation of isotopically enriched  $^{196}\text{Pt}$  metal in the Munich Research Reactor. The spectra were fitted with appropriate superpositions of Lorentzian lines.

## IV. DISCUSSION

### A. Solid-state relativistic density-functional calculations

Previous Mössbauer studies<sup>7</sup> for the determination of the  $^{197}\text{Au}$  NQM focused on intermetallic gold-aluminium compounds in a rather limited range of quadrupole splittings. Here we extend this study to a large range of gold compounds in different oxidation states. Table II shows the Mössbauer electric quadrupole splitting and calculated field gradients for a number of different gold compounds in the solid state. The field gradients range from  $-6.5(\text{Na}_3\text{AuS}_2)$  to  $+4.2$  a.u. ( $\text{KAuTe}$ ) at the DFT level of theory using the PBE functional. Figure 2 shows the experimentally measured electric quadrupole splitting against the calculated field gradient [which includes the correction for the asymmetry parameter in Eq. (4)] from which we determine from the slope a NQM of  $0.637(13)b$  (LDA) and  $0.603(9)b$  (PBE) in reasonable agreement with the muonic value of  $+0.547(16)b$ .<sup>4</sup> The points shown in Fig. 2 are from the PBE calculations (which include the calculations and Mössbauer data for the gold-aluminium alloys by Wagner and co-workers<sup>7</sup>). The LDA linear fit, however, is also shown in Fig. 2 and the corresponding values are listed in Table II. Both functionals give similar results, and one might conclude that density-functional theory produces reliable results for field gradients, at least for the compounds investigated here. However, it was

pointed out before that for transition elements there seems to be a serious problem with DFT in general leading to significant errors in field gradients.<sup>38,39</sup> This is also supported by the fact that some compounds clearly have field gradients outside the expected range (e.g.,  $\text{Na}_3\text{AuO}_3$ , see Fig. 2) and were therefore left out in the linear fit procedure. We therefore decided to look at different DFT approximations for simple diatomic gold compounds as discussed in the following.

### B. Four-component relativistic density-functional calculations for AuF, AuCl, AuBr, and AuI

The calculated relativistic DFT and HF electric field gradients  $q$  for the diatomic gold halides are shown in Table III derived at the experimental bond distances. It is clear that there is a large variation in the results with different approximations applied. Figure 3 shows the calculated field gradients plotted against the experimental NQCCs. One immediately notices that the straight lines are not going through the origin as they should. Table IV shows the linear fit parameters with large deviations from the ideal intercept at the origin. Hence DFT shifts the linear curve away from the origin introducing an unphysical systematic error. Moreover, from the slope one determines the NQM also shown in Table IV. The DFT values not only substantially deviate from the proposed muonic value, but for some functionals also give the wrong sign. Hence one can conclude that DFT is not appropriate for obtaining even reasonable values for electric field gradients. This does not explain, however, why the solid-state values lead to a reasonable NQM for gold. Here, however, one chooses a wider range of compounds from field gradients of  $-6.6(\text{Na}_3\text{AuS}_2)$ – $+4.2$  a.u. ( $\text{KAuTe}$ ) in different oxidation states of gold. Obviously, errors cancel out here. Also in the solid state the gold atom is surrounded by a number of atoms which in most cases leads to much larger polarization of the Au(5d) core.<sup>99</sup> This even changes the sign in the electric field gradient as a comparison between the LDA values for the gold halides at the PAW level shows, Tables II and III. For the PAW results in Table III we ex-

TABLE III. Calculated Dirac–Coulomb HF and DFT electric field gradients  $q$  (in atomic units). Experimental bond distances  $r_e$  from experimental work of Gerry and co-workers (Refs. 13–15) and the constant nuclear contribution to the field gradient,  $q_{\text{nuc}}$ , are also listed.

Molecule	Method	$q$
AuF $r_e=1.918\,449\text{ \AA}$ $q_{\text{nuc}}=0.377\,768\text{ a.u.}$	HF	-4.610
	LDA	4.074
	PW86	4.263
	BLYP	4.005
	B3LYP	2.190
	LDA/PAW	2.658
	PBE/PAW	2.207
AuCl $r_e=2.199\,029\text{ \AA}$ $q_{\text{nuc}}=0.473\,793\text{ a.u.}$	HF	-3.428
	LDA	3.746
	PW86	3.818
	BLYP	3.659
	B3LYP	2.206
	LDA/PAW	2.297
	PBE/PAW	1.912
AuBr $r_e=2.318\,41\text{ \AA}$ $q_{\text{nuc}}=0.832\,397\text{ a.u.}$	HF	-2.903
	LDA	3.700
	PW86	3.789
	BLYP	3.625
	B3LYP	2.280
	LDA/PAW	2.180
	PBE/PAW	1.866
AuI $r_e=2.471\,102\text{ \AA}$ $q_{\text{nuc}}=1.040\,967\text{ a.u.}$	HF	-2.240
	LDA	3.514
	PW86	3.571
	BLYP	3.445
	B3LYP	2.310
	LDA/PAW	1.766
PBE/PAW	1.483	

tended the lattice such that in each unit cell we basically obtain a free molecule with little interactions with nearest neighbors. We mention that the PAW results are below the more accurate DC value, which shows the sensitivity of the field gradient to the electron density obtained in the two different methods (the DC-LDA being the more accurate). In Fig. 3 we include both DFT PAW results (dashed line). Again, we derive NQMs not in agreement with the muonic value. We therefore decided to carry out more accurate coupled cluster calculations for the diatomic gold compounds.

### C. Relativistic Douglas–Kroll and Dirac–Coulomb calculations for AuF, AuCl, AuBr, and AuI

The calculated electric field gradients and derived quadrupole moments for  $^{197}\text{Au}$  are shown in Table V. The total field gradient is calculated by adding the following terms to the nonrelativistic (purely electronic) HF value [ $q_{\text{NRHF}}$  according to Eq. (2)]:

$$q = q_{\text{NRHF}} + q_{\text{rel}} + q_{\text{cor}} + q_{\text{nuc}}, \quad (8)$$

where  $q_{\text{nuc}}$  is the nuclear contribution [Eq. (3)],  $q_{\text{rel}}$  is the relativistic contribution at the HF level, and  $q_{\text{cor}}$  is the correlation contribution at the relativistic level of theory using

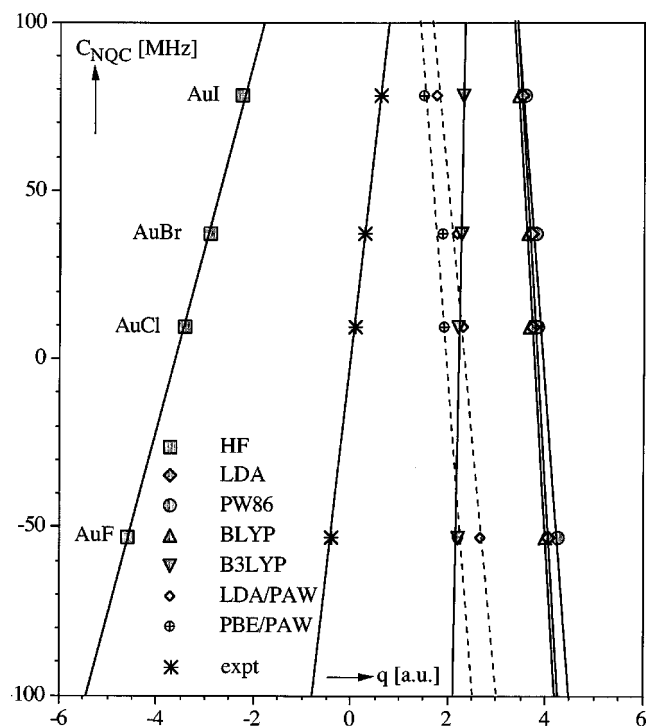


FIG. 3. Calculated Dirac HF and DFT electric field gradients for gold plotted against the experimentally determined nuclear quadrupole coupling constants from Refs. 13–15. The line marked “expt” refers to the muonic value.

coupled cluster theory. The  $q_{\text{NRHF}}$  and  $q_{\text{rel}}$  DK terms should be of near HF limit quality.

The results in Table V show that the derived spectroscopic nuclear quadrupole moments differ substantially between the molecules AuF, AuCl, and AuBr and are critically dependent on the level of approximation applied. Furthermore, for AuF the sign is not even correct compared to the muonic value of  $+0.547b$ . The problem is clearly the strong cancellation of the large HF contribution with the correlation contribution, which requires very precise calculations in order to get correct results. Nevertheless, we extended the active virtual space in our coupled cluster DC calculations for AuF to  $<100\text{ a.u.}$ , which further lowers the field gradient by  $0.021\text{ a.u.}$  The calculated vibrational contribution for AuF is only  $-0.019\text{ a.u.}$  obtained from a numerical treatment of the vibrational Schrödinger equation, and gives a final field gra-

TABLE IV. Slope  $a$  and intercept  $b$  from a linear fit  $C_{\text{NQC}}=aq+b$  ( $C_{\text{NQC}}$  in MHz and  $q$  in a.u.) of the calculated electric field gradients against the experimental  $C_{\text{NQC}}$  (from Refs. 13–15). From the slope  $a$  the NQM  $Q_s$  (in barn) is obtained according to Eq. (1). The experimental muonic value is from Ref. 4.

Method	$a$	$b$	$Q_s$
HF	55.06	199.41	+0.234
LDA	-234.43	898.85	-0.998
PW86	-186.54	738.12	-0.794
BLYP	-232.46	874.20	-0.989
B3LYP	883.11	-1966.01	+3.758
LDA/PAW	-147.95	347.23	-0.630
PBE/PAW	-180.17	354.37	-0.767
muonic	129(4)	0.0	+0.547

TABLE V. Nonrelativistic HF and relativistic Dirac–Coulomb (DC) and Douglas–Kroll (DK) HF and coupled cluster [CCSD(T)] Au electric field gradients for AuF, AuCl, and AuBr (in atomic units). Different style of basis sets are used for the DC and DK calculations, see the text.

Molecule	Method	$q_{\text{NRHF}}$	$q_{\text{rel}}$	$q_{\text{cor}}$	$q_{\text{nuc}}$	$q$	$C_{\text{NQC}}(\text{exp})^{\text{a}}$	$Q_s^{\text{b}}$
AuF	DC	−5.636	+0.643	+4.765	+0.378	+0.150	−53.2344(67)	−1.51
	DK	−5.605	+0.809	+4.848	+0.378	+0.430	−53.2344(67)	−0.53
AuCl	DC	−4.353	+0.443	+3.062	+0.474	−0.374	9.63312(13)	−0.11
	DK	−4.397	+0.593	+4.076	+0.474	+0.746	9.63312(13)	+0.05
AuBr	DK	−4.196	+0.491	+3.118	+0.832	+0.245	37.2669(14)	+0.65
AuI	DK	−3.713	+0.418	...	+1.041	...	78.273(11)	...

<sup>a</sup>Experimental nuclear quadrupole coupling constants (in megahertz) for the vibrational ground state (from Refs. 13–15). The results for the  $^{19}\text{F}$ ,  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ , and  $^{127}\text{I}$  isotopes are used.

<sup>b</sup>Calculated nuclear quadrupole moments (in barn) using Eq. (1).

dient close to zero. It is therefore clear that a much larger active space in our correlated calculations is needed which was beyond our computational resources. Also, the basis sets used in our DC coupled cluster calculations were limited. We therefore decided to perform DK coupled cluster calculations with larger basis sets since for a number of heavy element systems it was shown that spin-orbit effects in field gradients are quite small compared to the basis set incompleteness and correlation error. The results are also shown in Table V.

We first note that the picture change error is quite large for these molecules, i.e., taking the untransformed operator (2) and the DK wave function for the expectation value,  $\langle \psi^{\text{DK}} | q^{\text{NR}} | \psi^{\text{DK}} \rangle$ , we get  $q_{\text{rel}} = -3.469$  a.u. for AuF,  $-2.706$  a.u. for AuCl,  $-2.412$  a.u. for AuBr, and  $-1.313$  a.u. for AuI at the corresponding equilibrium distances. Hence even the sign is wrong compared to the exact DK contribution as shown in Table V. We therefore used the PCNQM model as described in detail in Ref. 67.

The DK calculations show exactly the same pattern compared to the four-component results. Here we basically have near Hartree–Fock values for the field gradients, but the coupled cluster procedure is not precise enough to obtain reliable field gradients. For example, the correlation contribution for AuF changes from  $q_{\text{cor}} = 4.235$  at the CCSD level to 4.848 upon perturbative inclusion of triple contributions. Hence we expect that one needs at least CCSDTQ in order to get converged correlated results. Increasing the active space cannot be completely neglected as the difference between the full active space and the one used in our coupled cluster calculations changes the field gradient by  $-0.049$  a.u. at the second-order Møller–Plesset (MP2) level of theory. We note that correlating the  $5s^2$  shell already contributes about  $-0.05$  a.u. Moreover, spin-orbit effects are not small either as usually assumed. Using the DC basis set in the DK calculations gives (approximately) the spin-orbit contribution for the field gradient at the HF level of theory,  $q_{\text{SO}} = -0.226$  a.u. for AuF, which goes into the right direc-

tion. However, the spin-orbit contribution is already 55% of the expected total electric field gradient ( $-0.412$  a.u. using the muonic nuclear quadrupole moment and the data  $C_{\text{NQC}}$  values in Table V), and this value might change significantly at the correlated level. The situation does not improve for AuCl. Interestingly, for AuBr we get approximately the right value for the nuclear quadrupole moment (Table V), which we believe is rather fortuitous. Even here the perturbative triples contributions in the coupled cluster procedure are quite large with  $+0.402$  a.u. Moreover, including all inner core levels in the correlation procedure at the MP2 level of theory changes the field gradient by  $+0.102$  a.u. Spin-orbit effects are also neglected. We therefore decided not to investigate AuI in more detail, which has the largest nuclear quadrupole coupling constant, because of similar difficulties expected here.<sup>100</sup>

It is interesting to compare the individual contributions to the field gradient between the different molecules. We see a clear trend of decreasing HF contribution, relativistic and electron correlation effects with increasing nuclear charge of the halide ligand.

To conclude this section, the field gradients for the gold halides are too small to obtain an accurate nuclear quadrupole moment for  $^{197}\text{Au}$ . This is also evident from Fig. 3 where the curve labeled “expt” shows field gradients close to the zero value. In these molecules the HF value is almost completely canceled by the correlation effect. Hence it is of no surprise that similar difficulties were encountered before using the simple Townes–Dailey approximation.<sup>13</sup> We therefore turn to (CO)AuF, a molecule with a rather large  $^{197}\text{Au}$  nuclear quadrupole coupling constant where such cancellation effects should be less significant.

## D. Relativistic Douglas–Kroll coupled cluster calculations for (CO)AuF

It is well known that the electric field gradients are quite sensitive to small changes in the electron density, e.g., weak

TABLE VI. Nonrelativistic HF and relativistic DC and DK HF, second-order Møller–Plesset MP2, and CCSD(T) Au electric field gradient contributions for (CO)AuF.

Molecule	$q_{\text{NRHF}}$	$q_{\text{nuc}}$	$q_{\text{rel}}^{\text{DK}}$	$q_{\text{rel}}^{\text{DC}}$	$q_{\text{cor}}^{\text{MP2}}$	$q_{\text{cor}}^{\text{CCSD(T)}}$	$q$
(CO)AuF	−10.099	+0.755	−1.846	−1.897	+5.305	+4.457	−6.784

interactions with other atoms (such as rare gas atoms) or molecules can easily be seen in a shift in the NQCC. For the gold halides, the interaction with rare gas atoms is not small and of the order of 50 kJ/mol for both Kr and Ar<sup>16,19</sup> and 100 kJ/mol for Xe.<sup>101</sup> In these cases a large enhancement of the NQCC is observed, e.g., for AuF the <sup>197</sup>Au NQCC changes dramatically from -53.2 MHz for free AuF to -333.4 MHz for ArAuF, -404.8 MHz for KrAuF, and -527.6 MHz for XeAuF. For the CO interaction with AuF Gerry and co-workers obtained from accurate microwave measurements a factor of twenty times (!) larger <sup>197</sup>Au NQCC of -1025.975 MHz compared to free AuF.<sup>18</sup> Similar large effects are observed for (CO)AuCl.<sup>18</sup> Here earlier relativistic coupled cluster calculations already gave a substantial interaction energy of 182 kJ/mol between CO and AuCl.<sup>102</sup> This rather large interaction energy is relativistically enhanced as nonrelativistic calculations only give 63 kJ/mol.<sup>102</sup> Hence, these triatomic and four-atomic linear molecules with strongly enhanced electric field gradients are ideal for our theoretical studies.

The results for (CO)AuF are presented in Table VI. The nonrelativistic Au electric field gradient is already very large with -10.099 a.u. Interestingly, relativistic effects have the same sign as the nonrelativistic HF value and therefore, there are no cancellation effects. Spin-orbit effects are also small as a comparison between the DK and DC results shows, i.e.,  $q_{so} = -0.051$  a.u. This value is smaller compared to AuF as expected since it is well known that spin-orbit effects are quenched in a ligand field. The largest uncertainty lies in the correlation contribution obtained at the CCSD(T) level of theory. Nevertheless, the total field gradient is now -6.748 a.u., which translates into a <sup>197</sup>Au NQM of 0.644*b* using the experimental NQCC, slightly larger than the NQM estimated from our Mössbauer studies. Beside missing important electron correlation terms in the coupled cluster procedure, another uncertainty may come from the bond distances used as  $r_e$  values and from the sensitivity of the electric field gradient to CO coordination, which could lead to non-negligible vibrational effects. We mention that second-order Møller-Plesset theory does not lead to reliable results as the comparison with the coupled cluster value in Table VI shows.

## V. CONCLUSION

Our calculations demonstrate that it is currently a non-trivial task to obtain a better NQM for <sup>197</sup>Au besides the already existing muonic value. Both the solid-state DFT calculations using Mössbauer electric quadrupole splitting and the relativistic coupled cluster calculations for (CO)AuF give NQMs for <sup>197</sup>Au of 0.60*b* and 0.64*b*, respectively, in qualitative agreement with the muonic value of 0.55*b*. However, the problems in using DFT for electric field gradients were addressed in detail for the gold halides. Although accurate nuclear quadrupole coupling constants are available for the simple diatomics from AuF to AuI, the rather small resulting electric field gradient for all of these compounds does not allow an accurate determination of the <sup>197</sup>Au NQM. Here, the large nonrelativistic or relativistic HF value is almost

completely canceled out by the electron correlation contribution, and very precise relativistic coupled cluster calculations going beyond the CCSD(T) model would be required to obtain accurate field gradients. This is currently not feasible at the four-component relativistic level of theory. We conclude that the best chance to improve the existing muonic <sup>197</sup>Au NQM is to perform more precise calculations for the molecules (CO)AuX (X=F, Cl, and Br),<sup>18</sup> or perhaps to investigate the hyperfine structure for the  $5d^9 6s^2 \ ^2D_{3/2}$  and  $\ ^2D_{5/2}$  states of atomic Au (Ref. 5) by using multireference Dirac-Fock calculations, as this has been done recently for <sup>201</sup>Hg.<sup>10</sup>

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