Nuclear electric quadrupole moment of gold

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The nuclear quadrupole moment for ^{197}Au has been determined on the base of the state-of-art relativistic molecular calculations. The experimental shifts in the nuclear coupling constants in the series of molecules AuF, XeAuF, KrAuF, ArAuF, (OC)AuF, and AuH have been combined with highly accurate determinations of the electric field gradient (EFG) at the gold nucleus, obtained by molecular relativistic Dirac-Coulomb-Gaunt Hartree-Fock calculations. The electronic correlation contribution to the EFG is included with the CCSD(T) and CCSD-T approaches, also in the four-component framework, using a finite-difference method. In order to estimate the accuracy of their approach the authors have thoroughly investigated the convergence of the results with respect to the basis set employed and the size of the correlated orbital space. The effect of the full Breit electron-electron interaction on the nuclear quadrupole moment of gold has also been considered explicitly for the AuF molecule. They obtain for ^{197}Au a nuclear quadrupole moment of 510 ± 15 mb, which deviates by about 7% from the currently accepted muonic value. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2436881]

I. INTRODUCTION

The nuclear quadrupole moment (NQM) is the parameter that describes the nonspherical distribution of the nuclear charge[1] and accurate knowledge of NQMs is thus of fundamental importance in many fields of nuclear physics and chemical spectroscopy. The direct determination of NQM values by experimental measurement is, however, particularly complicated[2] and, at present, the most usual way to obtain the NQM, $Q(\mathrm{X})$, of an atom X is based on the combination of a theoretical prediction of the electric field gradient (EFG) at the nucleus of interest with the experimental determination of the nuclear quadrupole coupling constant (NQCC) obtained by high resolution spectroscopy,[2,3] according to the formula

$$Q(\mathrm{X}) = k\frac{\nu_Q(\mathrm{X})}{q(\mathrm{X})}, \tag{1}$$

where ν_Q is the NQCC in megahertz, $q(\mathrm{X})$ is the EFG at the nucleus X in a.u., and $k=1/0.234\,964\,7$ is the conversion factor to obtain Q in millibarns. A simple but more useful variant of this equation will be proposed in this paper.

If accurate NQCCs are available, Eq. (1) shows that the accuracy of the NQM obtained is determined entirely by the quality of the calculation of the EFG. Using this approach NQM values have been calculated for a number of light and moderately heavy atoms,[2] but its application in the case of heavier nuclei still poses a formidable challenge owing to the sensitivity of the calculated EFG to electron correlation and relativistic effects. In these cases, not only can the predicted NQMs be affected by large uncertainties due to the approximations necessarily adopted in the calculations but it is also rather difficult to estimate the magnitude of such errors.

The NQM is an inherently nuclear property that is not affected by molecular structure and therefore, provided that NQCC values are available, one may either carry out EFG calculations on atoms (in an open shell state) or on molecules containing the isotope of interest.[4] Due to the open shell nature of the problem, atomic calculations of the EFG of heavy nuclei are usually based on multiconfigurational Dirac-Hartree-Fock methods, possibly including Breit and QED corrections.[5,6] Bierón and Pyykkö presented the first successful application of this approach for the calculations of the NQM of bismuth[7] and, more recently, of ^{201}Hg.[8] One of the basic problems in such calculations is to assess the convergence of the EFG result with respect to the size of the configuration space, but computational cost almost always impedes or severely limits such assessment.[8] The determination of NQMs based on molecular calculations is an effective alternative, and complementary to the atomic, approach. In small closed shell molecules, the static electron correlation problem may be somewhat mitigated compared to open shell atomic states and, in addition, the possible availability of NQCC data for several such molecules may provide for a much more exhaustive comparison and accuracy assessment

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of the results. Here one of the most effective methods to introduce relativistic effects, often essential also for the EFG of relatively light atoms, is the four-component Dirac-Coulomb (DC) method, followed by coupled-cluster calculations to introduce dynamic correlation effects. The molecular method has been applied with success for moderately heavy atoms.[2] Recent examples are ^{127}I (Ref. 9) and $^{121-123}$Sb (Ref. 10) nuclei. In all cases, obtaining accurate EFG requires special care in the selection of appropriate atomic basis sets affording, in particular, a good description of the atomic core region. Again, convergence of the results with respect to the basis should be assessed, but this task also rapidly goes beyond feasibility for many-electron systems. Finally, relativistic effects beyond the DC model Hamiltonian, such as especially the Breit electron-electron interaction, may affect the computed EFG values for heavy atoms but only few investigations of this problem in molecular calculations have been carried out so far.[11]

As a result of the problems recalled above, to the best of our knowledge, no truly reliable determination of the NQM of a very heavy nucleus by EFG calculations has been carried out so far. A particularly relevant case illustrating these difficulties is that of gold. Its accepted NQM value[2] is 547 ± 16 mb, determined by Powers *et al.*[12] from muonic hyperfine measurements. Recently, based on atomic calculations on the $5d^9 6s^2\ ^2D_{3/2,5/2}$ excited states of Au, Itano[13] proposed a NQM of 587(29) mb, with an error bar barely overlapping that of the spectroscopic value. On the molecular side efforts have been made by Schwerdfeger *et al.*,[14] through relativistic DFT and coupled-cluster calculations on several molecules, to ascertain this value, but the variance of the results obtained led the authors to conclude that "it is currently very difficult to improve on the already published muonic value."[14] A more optimistic conclusion was reached by Lantto and Vaara[15] who very recently published nonrelativistic HF, MP2, CCSD(T), and relativistic DC-HF and DC-MP2 calculations on the whole family of noble-gas coinage metal fluorides. They found that qualitatively correct trends for the gold NQCCs are obtained at their highest level of theory DC-MP2 and conclude that DC-CCSD(T) calculations "would be expected to be very accurate, but they are beyond our current resources."

In the present work, we have taken up this challenge of determining the NQM of ^{197}Au through extensive relativistic four-component molecular calculations. Our specific aim was to assess, in as much detail as is currently feasible, the impact of various factors on the computed NQM value, in order to put a small and reliable error bar on the computed value. We have therefore carried out a great number of large-scale calculations on several gold molecules, paying particular attention to establish the convergence of our results with respect to the atomic basis set, electron correlation method, active space, and relativistic effects included. In this last respect, we performed calculations beyond the DC model by including the magnetic (Gaunt) term in the self-consistent field. This term is reputed to account for a large fraction of the effects due the full Breit interaction and we have duly checked this assumption by performing small basis-set calculations including the full two-electron Breit operator. To our knowledge, this is the first study of Breit interaction effects on the EFG in molecular calculations. We have thus performed calculations on six linear gold molecules, including AuF and its complexes XeAuF, KrAuF, ArAuF, and (OC)AuF. The latter systems, in contrast to the first, have particularly high NQCCs. To these systems we have added AuH because its NQCC has been recently determined.[16]

One additional significant aspect of the present work, as mentioned above, is the proposal and analysis of a different approach to the determination of the NQM via EFG calculations, which one can adopt in molecular calculations. When computing the nuclear EFG in several different molecules, it may be more rewarding, rather than using the absolute value of the EFG $q(\mathrm{X})$ in Eq. (1) (which we shall refer to as the "direct" method), to concentrate only on its *variation* along the molecular series, due to changes in the chemical environment of the atom of interest. This leads immediately to the use of the alternative "indirect" formula

$$Q(\mathrm{X}) = k\frac{\Delta\nu_Q(\mathrm{X})}{\Delta q(\mathrm{X})}, \tag{2}$$

employing the *shifts* $\Delta\nu_Q(\mathrm{X})$ and $\Delta q(\mathrm{X})$ in the NQCC and EFG, respectively, with respect to a reference molecule. This procedure resembles the calculation of chemical shifts instead of absolute shieldings in the analysis of nuclear magnetic resonance spectroscopy.

II. THEORY AND COMPUTATIONAL DETAILS

All the EFG calculations have been carried out in the relativistic four-component framework.[17] At the Hartree-Fock level of theory, the calculations have been carried out using both the DC and Dirac-Coulomb-Gaunt (DCG) Hamiltonians and computing the expectation value of the corresponding property operator,[17] using the electronic structure code DIRAC.[18] A benchmark calculation employing the program BERTHA (Ref. 19) has been carried out on AuF in order to estimate the effect on the EFG of the full relativistic low-frequency two-electron interaction described by the Breit operator. The nuclear charges have been modeled by a finite Gaussian distribution.[20]

For hydrogen, carbon, oxygen and argon atoms the aug-cc-pVTZ basis of Dunning[21,22] has been chosen. For xenon a $(28s/21p/15d/1f)$ and for krypton a $(23s/16p/10d/1f)$ basis set, both of triple zeta qualities, as optimized by Dyall,[23] have been employed. Clearly, the choice of the basis set on the heavy atom where the EFG is computed is of special importance in the present work. We have extensively studied this aspect by employing three different relativistic fully uncontracted basis sets for Au, recently optimized by Dyall:[24] $(22s/19p/12d/8f)$, $(29s/24p/15d/10f/1g)$, and $(34s/30p/19d/13f/4g/2h)$ of double, triple, and quadruple zeta qualities, respectively. Accordingly, in this work we shall refer to the three basis sets as VDZ, VTZ, and VQZ, respectively. In all cases the small component part of the basis set has been obtained by the kinetic balance prescription.[25]

Due to its linear behavior, first observed in Refs. 26 and 27, the electron correlation contribution to the EFG has been

TABLE I. Experimental geometries (Å) and NQCCs (MHz).

Molecule	r_e(AuF)	r_e(XAu)	r_e(OC)	ν_Q
AuF	1.918[a,b]	⋯	⋯	−53.2344
XeAuF	1.918[a]	2.548[c]	⋯	−527.4513
KrAuF	1.918[a]	2.463[d]	⋯	−404.5734
ArAuF	1.918[a]	2.391[e]	⋯	−323.3558
(OC)AuF	1.909[f]	1.847[f]	1.1336[f]	−1006.2852
AuH	⋯	1.524[g]	⋯	187.116[h]

[a]Reference 29.
[b]Reference 30.
[c]Reference 31.
[d]Reference 32.
[e]Reference 33.
[f]Reference 34.
[g]Reference 35.
[h]Reference 16.

determined by the finite-difference method (see Ref. 17) and has been computed at the MP2, CCSD, CCSD(T), and CCSD-T levels, again in the four-component framework. The finite-difference method has a major limitation in the finite-field strength that can be used.[10,17] This strength should be small enough to remain in the linear regime, while at the same time it should be large enough to prevent numerical inaccuracies due incomplete convergence of the iterative procedures and other sources of numerical noise. A particular problem lies in the fact that high basis function exponents create large perturbations even with rather small field strengths.[10] We found EFG instabilities also in our series of molecules but, based on a series of tests, we have been able to reach stable EFG results using an absolute field strength of 1×10^{-8} a.u. and deleting the first and the first two tight p functions of the gold basis sets VTZ and VQZ, respectively. The deletion of these functions and the use of the finite-field method resulted in only a negligible ($<0.1\%$) change of the DC-HF analytic EFG values, indicating that they do not contribute significantly to the EFG.

The active space of interacting orbitals in the correlation calculations has been taken to be in the orbital energy range from −3.4 to 10 hartree. This includes the $5p$, $5d$, and $6s$ electrons of gold, the valence electrons of C, O, and F, the $3s3p$ shell of Ar, $3d$, $4s$, and $4p$ for Kr, and $4d$, $5s$, and $5p$ of Xe. In the case of the AuF and ArAuF molecules it has been possible to extend the active space from −9.0 to 40 hartree, thus including the $5s$ and $4f$ electrons of gold. These computations are exceptionally demanding.[28] For instance, in the case of (OC)AuF, the active space comprises 34 electrons in 520 orbitals, and the calculations required about 100 Gbytes of disk storage and about ten days of computation on a 1.3 GHz Itanium-2 processor for the four-index transformation.

For each molecule, the calculations were done for a single geometry with bond lengths taken from the analysis of the experimental microwave data, summarized in Table I. The limited number of lines and isotopic data from the microwave spectra prohibits accurate determination of r_e distances, so that r_0 values had to be used for this purpose. For the three-atomic systems the AuF bond length was furthermore kept fixed at the monomer distance.[31–33]

III. RESULTS AND DISCUSSION

In this section we present the results we obtained for the EFG and the resulting NQMs using both the direct and indirect formulas discussed in the Introduction. An extensive basis set study allowed us to make an estimate of the error on the NQM due to the basis set. We will show clearly that the NQM obtained by the indirect method presents a particularly low basis set error. Investigating other possible error sources we will finally estimate the total error bar on the NQM result.

The computed EFGs obtained with the large VQZ basis for the different molecules are reported in Table II. The DC-MP2 values agree well with the values reported by Lantto and Vaara.[15] In agreement with their work we also find that an accurate account of electron correlation effects is mandatory to obtain meaningful results. In all molecules studied, electron correlation gives a substantial positive contribution the value of the EFGs. In the AuF molecule this contribution is nearly as large as, and opposite to, the DC-HF EFG value, leading to a very small final result. For AuH, the correlation correction is even found to exceed the negative DC-HF EFG, leading to a change of sign. The effect of the Gaunt interaction (DCG-HF) is to reduce the computed EFG value by an amount ranging from 0.002 a.u. for (OC)AuF to 0.068 a.u. for ArAuF. This is in contrast with what has been found recently by Pernpointner[11] for the TlH molecule, where the Gaunt interaction produces an increase of the EFG. By taking the Gaunt effect as a correction to be added "as is" to the final correlated EFG value, we see that for the present series of molecules, with the exception of AuF, this correction is less than 2.6%. The AuF molecule represents an exception

TABLE II. EFGs at the gold nucleus (in a.u.) in different gold compounds using VQZ basis set.

Method	AuF	XeAuF	KrAuF	ArAuF	(OC)AuF	AuH
DC-HF	−4.921	−7.912	−7.052	−6.488	−12.292	−2.269
DCG-HF	−4.981	−7.956	−7.101	−6.556	−12.294	−2.292
DC-MP2	−0.144	−3.896	−2.884	−2.155	−7.482	2.510
DC-MP2[a]	⋯	−3.832	−2.897	−2.125	⋯	⋯
DC-CCSD	−1.054	−4.916	−3.904	−3.200	−8.872	1.150
DC-CCSD(T)	−0.374	−4.376	−3.354	−2.640	−8.232	1.600
DC-CCSD-T	−0.394	−4.396	−3.374	−2.655	−8.242	1.610
DC-CCSD-T_{Gaunt}	−0.454	−4.440	−3.424	−2.724	−8.245	1.587

[a]Computed from the NQCCs and ^{179}Au NQM given in Ref. 15.

TABLE III. Computed NQM (mb) of gold obtained using the direct method and the VQZ basis set. The error on the average values is the standard deviation of the data.

Method	AuF	XeAuF	KrAuF	ArAuF	(OC)AuF	AuH	Average
DC-HF	46.0	283.7	244.2	212.1	348.4	−351.0	131±257
DCG-HF	45.5	282.1	242.5	209.9	348.4	−347.5	130±255
DC-MP2	1574.4	576.2	597.0	638.6	572.4	317.3	713±437
DC-CCSD	215.0	456.6	441.0	430.0	482.7	692.5	453±152
DC-CCSD(T)	606.1	513.0	513.3	521.2	520.2	497.7	529±39
DC-CCSD-T	575.3	510.6	510.3	518.3	519.6	494.6	522±28
DC-CCSD-T_{Gaunt}	499.4	505.6	502.9	505.3	519.4	501.0	506±7

due to its very small EFG value, which even small perturbations may affect significantly. In this case the Gaunt effect is more than 15%.

For the AuF molecule a benchmark calculation adding the full Breit electron-electron interaction to the DC Hamiltonian has been carried out, using the VDZ basis set, with the relativistic molecular program BERTHA. The effect of the retardation contribution of the electron-electron interaction is found to decrease the magnetic (Gaunt) contribution, reducing the effect, with respect to DC-HF calculation, from 0.065 to 0.050 a.u. By analyzing the orbital contributions we have found that not only the core orbitals but also the valence and subvalence orbitals contribute to some extent to the Gaunt-Breit effect. This means that the simple additive approximation mentioned above is not rigorously applicable and that the fully optimized Gaunt-Breit orbitals should be correlated. It is reasonable to assume, however, that correlation effects modify the Gaunt correction by a relatively small fraction.[11]

In Table III, we report the NQM results obtained by the direct method. The table emphasizes again that direct NQM results obtained without consideration of electron correlation in the EFG calculation may easily be useless. The average NQM over the various molecules is hugely underestimated at the DC-HF and DCG-HF levels, and even excluding the two most differing results (for AuF and AuH) the average of 272 and 270 (at the DC-HF and DCG-HF levels, respectively) is still roughly half the value obtained at a higher level of theory. In the AuH case the NQM has even the wrong sign and for AuF it is more than ten times smaller than the correlated values. The introduction of electron correlation leads to NQM values lying very much closer to the currently accepted muonic value and, very important, their variance over the various molecules drops very rapidly. At the DC-CCSD-T level we find an average value of 521.5 mb which appears converged to within 11%. Note again that if one excludes AuF and AuH from the data, the average NQM moves by 7 to 515 mb but the standard deviation drops to only 5 mb. The further addition of the Gaunt effect alters the average NQM value by about 3%, largely due to its impact in the AuF case. Excluding AuF, the average impact of the Gaunt effect reduces to 0.7%. Accidentally, the inclusion of the Gaunt correction brings the NQM value extracted from the AuF case much closer to the correct value.

We turn now to a discussion of the results obtained by using the indirect method, Eq. (2), which are shown in Table IV. Since we have a significant number of molecules under study, it turns out to be particularly insightful to compare the mean results obtained by taking each molecule in turn as reference system. In the table we thus report, for each theoretical method and each reference molecule a, the NQM of gold computed by averaging over the various EFG differences,

$$Q(\mathrm{Au}) = \frac{k}{N-1}\sum_{i\neq a}\frac{\nu_{Q_i}(\mathrm{Au}) - \nu_{Q_a}(\mathrm{Au})}{q_i(\mathrm{Au}) - q_a(\mathrm{Au})}. \tag{3}$$

The first of the two columns labeled "Average" reports the average over the various reference molecules. As ± error bar, we have conservatively reported the maximal standard deviation found for any one reference system. Note that the latter is systematically several times larger than the spread of the average values. It is immediately eye catching that, in sharp contrast to the results of the direct formula, all the NQM results obtained by taking relative values fall roughly in the correct range: even at the uncorrelated level the error in the average results is of the order of 10%. This testifies to the ability of the indirect method in diminishing the impact

TABLE IV. NQM (mb) of gold computed by the indirect method with the VQZ basis set using the various molecules as reference system. The second average in each row is calculated by excluding the (OC)AuF column and the result obtained by the EFG difference between ArAuF and KrAuF (see text).

Method	AuF	XeAuF	KrAuF	ArAuF	(OC)AuF	AuH	Average	
DC-HF	609.2	579.4	587.6	594.4	502.4	494.6	561±143	571±143
DCG-HF	609.7	583.4	593.6	600.1	506.4	491.7	564±145	572±145
DC-MP2	518.7	519.3	512.1	511.2	546.4	460.2	511±76	508±76
DC-CCSD	513.2	512.4	509.2	509.0	513.7	494.0	509±28	509±28
DC-CCSD(T)	509.6	510.8	506.2	504.8	521.2	512.9	511±15	511±11
DC-CCSD-T	508.4	510.2	505.1	503.5	521.7	509.4	510±16	510±12
DC-CCSD-T_{Gaunt}	507.6	513.5	509.1	507.4	526.1	505.8	512±14	510±13

of large systematic errors in the evaluation of the EFG. The variance of the data again drops dramatically upon introducing correlation effects, so that the average CCSD(T) and CCSD-T agree very well and appear to converge to within little more than 3%.

As we have just pointed out, the indirect approach has the useful advantage of minimizing the impact of systematic errors in the evaluation of the EFG, because only differences in the EFG of various molecules enter the equation. For the same reason, however, the indirect formula cannot be used blindly, as it may yield meaningless results when the difference between the EFG in a pair of molecules is not larger than the inaccuracy in the EFG evaluation itself. Closer analysis of the NQM results obtained by using various molecule pairs shows, in fact, that the difference in EFG between ArAuF and KrAuF is too small to be reliably considered. Furthermore, as will become evident later, the NQM results obtained from the calculations on (OC)AuF appear affected by some systematic anomaly. By excluding the corresponding data from the calculation, one arrives at the average results shown in the last column of Table IV. As is evident, the estimated NQM is essentially unchanged in this modified statistics, but the variance of the data decreases somewhat for the CCSD(T) and CCSD-T results. We note that the direct and indirect CCSD-T NQM estimates coincide within the respective error bars and that the agreement improves by excluding the "problematic" AuF and AuH cases from the direct data.

It is interesting to note that, in the indirect results of Table IV, inclusion of the Gaunt effect leads on average to a slight increase of the NQM, while we have seen that the opposite is true in the direct determination (see Table III). The reason for the latter result is simple: the Gaunt contribution is found to systematically reduce the negative EFG (see Table II). In the indirect approach, the mean result emerges in a more complicated way by a balance of the differences in the Gaunt effect on the EFG in different molecules in relation to the corresponding changes in NQCC. As we have mentioned earlier, at the orbital level we find that both the core and the valence orbitals contribute to the Gaunt effect on the EFG. It turns out that the two contributions have generally opposite sign, and the core portion is roughly of the same magnitude in all molecules. Thus the core contribution approximately cancels in the indirect method and the net effect is an average of the balance of the valence contributions. Since the latter obviously interferes with the effects of electron correlation, and we neglect this interference, the true impact of the Gaunt effect should be considered to lie beyond our model. We may estimate an upper bound of 4 mb for the Gaunt effect on the NQM by taking the average from Table III after excluding the anomalous AuF case.

Before arriving at a final estimate of the NQM of gold, we must yet briefly discuss the convergence of our results with respect to the basis set. We performed an explicit convergence study at DC-CCSD-T level with respect to the size of the basis set employed, using the basis sets VDZ, VTZ, and VQZ on gold. The NQM results of this study using the direct and indirect approaches are shown in Figs. 1 and 2,

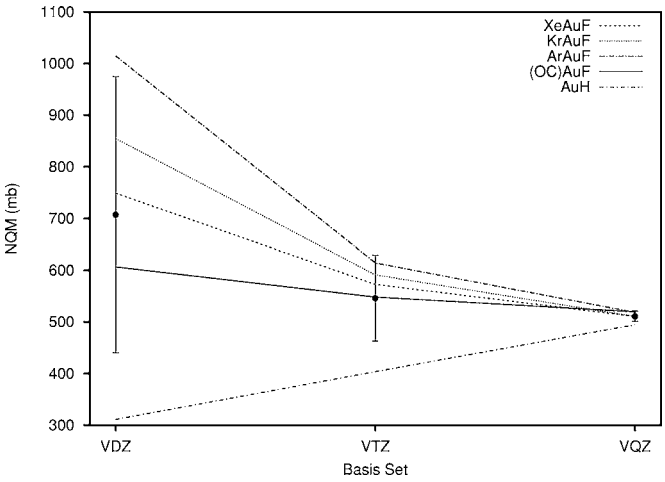

FIG. 1. NQM of gold in a series of molecules computed by the direct method as a function of basis set. The average value and associated standard deviation are shown for each basis set as a dot with error bar.

respectively. In the direct method, the lines plotted show, as a function of basis set, the NQM values obtained from the calculations on the various molecules. In the indirect case, the molecular label of the curves refers to the system chosen as reference. For each basis set, the mean NQM and associated standard deviation are shown in the figures as dots with error bars. In Fig. 1, the curve for AuF has been omitted because the results obtained with the VDZ and VTZ basis sets, due to the small value of the EFG in this molecule, turn out to be wildly off target: with the VDZ basis the computed EFG is 0.610 a.u., yielding a *negative* NQM of −371 mb, while in the VTZ basis the EFG is −0.032 a.u., corresponding to a NQM of about 7 b. The computed NQMs in the remaining molecules appear to converge satisfactorily both in the absolute result and, except for AuH, in terms of the difference between progressively larger basis sets. Using the indirect approach leads to further substantial enhancement, by more than one order of magnitude, in the convergence of the results, as is evident from Fig. 2, with the eye-catching

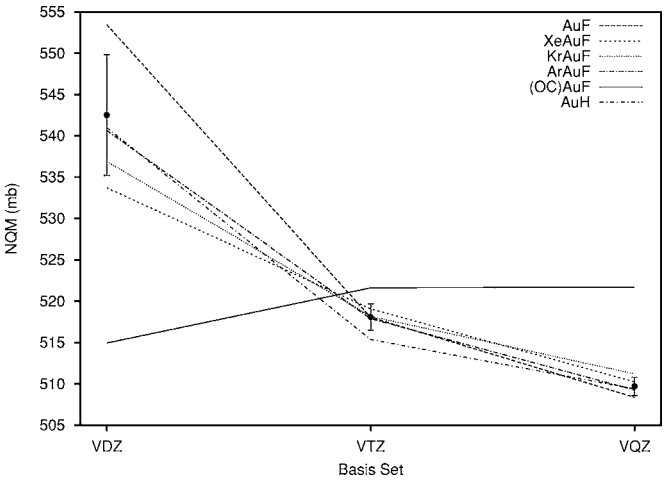

FIG. 2. NQM of gold computed by the indirect method and taking various molecules as reference system, as a function of basis set. The average and standard deviation over the various reference systems, for each basis set, is shown as a dot with error bar and does not include the results obtained for the (OC)AuF reference system (solid line).

exception of the NQM data obtained by taking (OC)AuF as reference system. The (OC)AuF line is clearly diverging both in position and slope from the others, suggesting some kind of systematic error in the calculations on this molecule and, for this reason, it has been excluded from the calculation of the average and error bars shown in Fig. 2. We shall return to this point later.

In order to arrive at a final value for the NQM of gold, we first estimate the uncertainty component due to the basis set. The good convergence of our results, as just discussed, enables us to do this with confidence and we adopt the simple and conservative approach of taking as error the absolute difference between the average NQM results obtained with the VTZ and VQZ basis sets. Using the direct method this is 35 mb but, as we have seen, the use of the indirect approach enables us to put this error bar down to only 8 mb.

Besides the basis set error, we can further quantify other sources of error in our calculations. As we have mentioned earlier, we may conservatively estimate an error due to the Gaunt effect of about 4 mb. This arises by incorporating into the correlated results the EFG change due to the Gaunt effect obtained at the DC-HF level (the Gaunt effect on the DC-HF results themselves turns out to be somewhat smaller, see Table III), which is an approximation of the effect one would obtain by using Gaunt-corrected orbitals in the correlated calculations. To date, the only published work,[11] where the orbitals obtained by DCG-HF procedure have been used for correlated calculations, appears to indicate that this indeed modifies only fractionally the Gaunt contribution to the final EFG. We have further shown in this work that, in the case of the AuF molecule, the retardation part of the full Breit interaction reduces the Gaunt effect by about a quarter. Although these findings represent only partial indications obtained in special cases, it seems safe to assume that, overall, the Gaunt-Breit effect on the NQM of gold amounts to not more than a few millibarns.

The error in our results introduced by limiting the number of active orbitals in the correlated calculations can in principle be explicitly considered by extending the active space in a few calculations. An exhaustive study of the convergence of the results with the active space is not feasible when so many electrons are involved, and in addition one should not neglect that there is a strong interplay between the impact of the active space restrictions and of the basis set employed. Nevertheless, to gain some insight into this problem, we did manage to carry out two additional VQZ calculations on AuF and ArAuF by extending the correlated space from −9.0 to 40 hartree orbital energy, thus including the 5 s and 4f electrons of gold besides enlarging the virtual space. This extension changes the NQM of gold computed by Eq. (2) from 508.5 to 514.3 mb.

Finally, we discuss the significance of the fact that the (OC)AuF results appear to be approaching a limiting value that is at variance with the average of the other molecules by more than ten times the corresponding estimated error bar. A likely cause of this discrepancy are uncertainties in the equilibrium bond lengths that were employed. Since the experimental data refers to r_0 values, we implicitly assume that vibrational corrections are small. Since all complexes are reported to be rigid[31] this should be a good approximation, but a full theoretical treatment with explicit calculation of vibrational corrections could test this assumption and supply an appropriate error bar. It seems likely that such an analysis, that is currently computationally infeasible, would give relatively larger corrections for the four-atomic (OC)AuF than for the three-atomic rare gas complexes. Another (related) explanation for the anomaly found in the (OC)AuF-based NMQs is that the shortening of the AuF bond length in (OC)AuF could be overestimated due to inaccuracies in the experimental fitting procedure.

Summarizing all of the above considerations on the various sources of error into a single completely reliable error bar on our best average CCSD-T result of 510 mb is obviously impossible but it would seem that 15 mb, obtained by summing the main uncertainties we have been able to verify, is a safe estimate.

IV. SUMMARY AND CONCLUSIONS

By extensive state-of-the art *ab initio* calculations in the four-component relativistic framework, including electron correlation, on a series of gold-containing molecules, we have been able to arrive at a well converged and validated estimate of the nuclear quadrupole moment of ^{197}Au at the DC-HF-CCSD-T level, equal to 510±15 mb. We have explored the impact on the estimated value of several factors, besides electron correlation, including the Breit interaction, basis set extension, and the truncation of the correlated orbital space. The use of an *indirect* formula, computing the NQM by employing the *differences* in electric field gradient in various molecules, turned out to be a key aspect for the success of our investigation. Not only does the indirect method improve significantly the convergence of the results by implicitly minimizing the impact of systematic errors but it also explicitly unmasks them, as in the case of (OC)AuF, permitting to discard unreliable results.

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