PHYSICAL REVIEW A **91**, 042516 (2015)

Nuclear electric quadrupole moment of gold from the molecular method

Régis Tadeu Santiago and Roberto Luiz Andrade Haiduke[*]

Departamento de Química e Física Molecular, Instituto de Química de São Carlos, Universidade de São Paulo,
Avenida Trabalhador São-Carlense, 400-CP 780, 13560-970 São Carlos, São Paulo, Brazil

(Received 20 March 2015; published 30 April 2015)

The nuclear electric quadrupole moment (NQM) of gold is reviewed by means of the molecular method and data from as many as 15 linear systems. The electric-field gradients (EFGs) used to this end were obtained with the Dirac-Coulomb Hamiltonian and coupled-cluster theory, CCSD(T) and CCSD-T, by means of an augmented relativistic basis set for gold. The direct approach was found to be inadequate for the diatomic molecules investigated, which is probably due to improper treatment of the static electron correlation. However, these effects are much less relevant for OCAuX (X = F, Cl, Br, and I) complexes. Thus, the indirect version of the molecular method is preferred in this case. Hence, a NQM value of 515(15) mb is determined for ^{197}Au from linear regressions performed with the best EFGs determined for ten of these systems.

DOI: 10.1103/PhysRevA.91.042516 PACS number(s): 31.15.aj, 21.10.Ft

I. INTRODUCTION

The nuclear electric quadrupole moment (NQM) of gold has been subjected to many investigations over the years, as discussed in a compilation published in 2008 [1]. The standard value selected at that time for ^{197}Au was 547(16) mb, which was obtained in 1974 from muonic measurements [2]. However, recent studies based on the application of so-called “atomic” or “molecular” methods provided strong evidence in favor of a smaller NQM for this nuclide. For instance, the atomic results now indicate 521(7) and 521.5(5.0) mb [3,4].

Two variants of the molecular method can be used. The direct version relies on the calculation of electric-field gradients (EFGs) and their prompt combination with experimental nuclear quadrupole coupling constants (NQCCs) through the equation

$$Q\,(X) = \frac{\nu_Q\,(X)}{234.9647 q\,(X)}, \tag{1}$$

in which the labels $Q(X)$, $\nu_Q(X)$, and $q(X)$ respectively stand for NQMs (barns), NQCCs (MHz), and EFGs (a.u.) at the nucleus X in linear molecules. On the other hand, the indirect molecular method requires one to obtain the EFG and NQCC changes from a group of compounds containing the element X [5]. Hence, this indirect proposal is much less susceptible to systematic EFG errors [6], which is advantageous during the determination of accurate NQMs.

The two most recent values derived for gold by means of the molecular method follow from the indirect approach. Thus, a NQM of 510(15) mb was proposed for ^{197}Au on the basis of EFG calculations done with the Dirac-Coulomb (DC) Hamiltonian, with a Gaunt correction estimated at the Hartree-Fock (HF) level (the treatment labeled here as DC + G), and the coupled-cluster theory including iterative single and double substitutions together with perturbative corrections for triple excitations, CCSD(T) and CCSD-T, for AuH, AuF, XeAuF, KrAuF, ArAuF, and OCAuF [6]. Moreover, the other molecular result of 526 mb is obtained with EFGs given by the density functional theory (DFT) for AuH, AuX, and OCAuX systems (X = F, Cl, Br, and I) [7].

The objective pursued here is to provide another determination of the NQM for ^{197}Au by means of the molecular method. However, this work is concerned with an improvement of the results in two main aspects. First, the EFG calculations are also performed at the most advanced DC + G-CCSD(T) and DC + G-CCSD-T levels, but the basis set used for gold is now especially augmented for this kind of property. Second, the group of molecules investigated is larger than those selected in both of the previous studies mentioned above: AuH, AuF, AuCl, AuBr, AuI, ArAuF, ArAuCl, ArAuBr, KrAuF, KrAuCl, XeAuF, OCAuF, OCAuCl, OCAuBr, and OCAuI. This large number of linear systems will allow one to judge the reliability of EFGs for individual members.

II. COMPUTATIONAL DETAILS

The calculations were done within the DIRAC12 package [8]. The Dirac-Coulomb (DC) and Dirac-Coulomb-Gaunt (DG) Hamiltonians were considered. A standard speed-of-light value of 137.035 999 8 a.u. is employed together with the Gaussian nuclear model. The substitution of two-electron integrals involving only small component functions (SS|SS) by an approximated treatment is also explored here [9]. Gold is represented by means of the relativistic adapted Gaussian basis set (RAGBS) of the [Xe]$6s^1 4f^{14} 5d^{10}$ ground-state configuration, which presents a size of the $30s22p17d11f$ functions [10] before an augmentation stage is performed, as discussed in the following section. Basis sets selected for the remaining elements in each molecule are listed in Table I [11–16]. Such sets have always been used in their uncontracted form. The geometries and NQCCs adopted in our calculations are taken from experiment [17–27] and the first ones can be found in Table II.

Analytical expressions were employed to obtain EFGs at the theory levels of HF and DFT, using the Becke and Perdew-Wang (BPW91) and Becke, three-parameter, Lee-Yang-Parr (B3LYP) exchange-correlation functionals. However, a numerical two-point approach in terms of the parameter λ is used to attain electron correlation contributions at the Møller-Plesset second-order perturbation (MP2) and coupled-cluster

---

[*] haiduke@iqsc.usp.br

TABLE I. Basis sets selected for EFG calculations.

$(Y-\text{Au}-X)$[a]	Y	X
AuH		cc-pVTZ
AuF		cc-pVTZ
AuCl		cc-pVTZ
AuBr		dyall.v3z
AuI		dyall.av2z
ArAuF	cc-pVDZ	cc-pVDZ
ArAuCl	cc-pVDZ	cc-pVDZ
ArAuBr	cc-pVDZ	dyall.v2z
KrAuF	dyall.v2z	cc-pVDZ
KrAuCl	dyall.v2z	cc-pVDZ
XeAuF	dyall.v2z	cc-pVDZ
OCAuF	cc-pVDZ	cc-pVDZ
OCAuCl	cc-pVDZ	cc-pVDZ
OCAuBr	cc-pVDZ	dyall.v2z
OCAuI	cc-pVDZ	dyall.v2z

[a] X refers to hydrogen or an halogen while Y is a noble gas or the C,O pair of atoms.

[CCSD, CCSD(T), and CCSD-T] theories, as discussed in previous studies [28]. The strength of λ is set to 1×10^{-7} a.u. Moreover, the threshold for writing transformed two-electron integrals was reduced to 1×10^{-17}, seeking an increase in accuracy. The smallest active space considered includes all the spinors between −3.3 and 20 a.u., with a minimum gap of 0.5 a.u., except for OCAuBr and OCAuI, in which cases the upper limit was decreased to 12 a.u. due to computational limitations. Hence, the number of correlated electrons varies from 18 to 44, including the $5p$, $5d$, and $6s$ electrons of gold (see Table II). Alternative calculations done at the DC-MP2 level are performed with a much larger active space that encloses all electrons and virtual spinors with an energy up to 100 a.u.

TABLE II. Bond lengths (Å), T_1 diagnostic values obtained during our coupled-cluster calculations, and the number of electrons in the smallest active space considered.

Molecules	r(O-C)	$r(Y-\text{Au})$[a]	$r(\text{Au}-X)$[a]	T_1[b]	Electrons[c]
AuH[d]			1.5239	0.0424	18
AuF[e]			1.918 449	0.0463	24
AuCl[f]			2.199 029	0.0395	24
AuBr[f]			2.318 410	0.0333	34
AuI[g]			2.471 102	0.0345	34
ArAuF[h]		2.391	1.918	0.0298	32
ArAuCl[i]		2.4693	2.1983	0.0274	32
ArAuBr[h]		2.502	2.316	0.0247	42
KrAuF[j]		2.4597	1.918	0.0295	32
KrAuCl[i]		2.5225	2.2044	0.0268	32
XeAuF[k]		2.5435	1.918	0.0253	42
OCAuF[l]	1.134	1.847	1.909	0.0285	34
OCAuCl[l]	1.1265	1.8859	2.2125	0.0257	34
OCAuBr[l]	1.1341	1.8886	2.3364	0.0235	44
OCAuI[m]	1.131	1.908	2.501	0.0238	44

[a] X refers to hydrogen or a halogen while Y is a noble gas or the carbon atom.
[b] CCSD calculations with the smallest active space.
[c] Number of electrons included in the smallest active space.
[d] Reference [17].
[e] Reference [19].
[f] Reference [20].
[g] Reference [21].
[h] Reference [22].
[i] Reference [23].
[j] Reference [24].
[k] Reference [25].
[l] Reference [26].
[m] Reference [27].

III. RESULTS AND DISCUSSION

A. Gold basis set increment

First of all, it is necessary to investigate if the basis set of gold should be complemented to accurate EFG determinations at such a nucleus. This step is carried out with DC-HF and DC-B3LYP calculations for AuH, following a strategy outlined in our previous studies [28]. We noticed in Table III that some tighter functions are required since they cause EFG variations of at least 0.002 a.u. (roughly 0.1%) at the DC-HF or DC-B3LYP levels (the exponents are shown between parentheses): $2p$ (1.4816×10^8 and 9.7217×10^8), $5d$ (1.1198×10^5, 5.0391×10^5, 2.7299×10^6, 1.8113×10^7, and 1.4974×10^8), and $1f$ (2.5317×10^3). Moreover, tighter p Gaussians than the ones mentioned here are not considered because they lead to numerical oscillations in analytical EFG

TABLE III. EFGs (a.u.) at the Au nucleus in the AuH (cc-pVTZ basis set for the H atom) molecule obtained during a basis set convergence study with the addition of tight and diffuse functions.

	DC-HF		DC-B3LYP	
Basis set	q	Δq	q	Δq
$30s22p17d11f$[a]	−1.9127		2.8405	
+1 tight s	−1.9126	0.0001	2.8406	0.0001
+2 tight s	−1.9126	−0.0001	2.8406	−0.0001
+1 tight p[b]	−1.9077	0.0050	2.8443	0.0038
+2 tight p[b]	−1.9125	−0.0048	2.8409	−0.0034
+1 tight d[b]	−1.9785	−0.0658	2.7830	−0.0575
+2 tight d[b]	−2.0237	−0.0453	2.7435	−0.0395
+3 tight d[b]	−2.0532	−0.0295	2.7177	−0.0258
+4 tight d[b]	−2.0704	−0.0171	2.7028	−0.0150
+5 tight d[b]	−2.0741	−0.0037	2.6996	−0.0032
+6 tight d	−2.0737	0.0003	2.6999	0.0003
+1 tight f[b]	−1.9127	0.0000	2.8378	−0.0027
+2 tight f	−1.9135	−0.0009	2.8372	−0.0006
+1 diffuse s	−1.9132	−0.0005	2.8400	−0.0005
+1 diffuse p[b]	−1.9831	−0.0704	2.8187	−0.0218
+2 diffuse p[b]	−1.9914	−0.0083	2.8153	−0.0034
+3 diffuse p	−1.9914	0.0000	2.8150	−0.0003
+1 diffuse d[b]	−1.9216	−0.0090	2.8313	−0.0093
+2 diffuse d	−1.9224	−0.0008	2.8310	−0.0002
+1 diffuse f[b]	−2.0225	−0.1098	2.7824	−0.0582
+2 diffuse f[b]	−2.0368	−0.0143	2.7813	−0.0011
+3 diffuse f	−2.0368	0.0000	2.7812	0.0000
$30s26p23d14f$[c]	−2.2607		2.5960	

[a] Original RAGBS for the gold atom.
[b] Selected functions.
[c] RAGBS incremented with the selected functions.

TABLE IV. EFGs (a.u.) at the Au nucleus in the AuH (cc-pVTZ basis set for the H atom) molecule obtained during a basis set convergence study with the addition of polarization functions.

	DC-HF		DC-B3LYP	
Basis set	q	Δq	q	Δq
$30s26p23d14f$	−2.2607		2.5960	
$+1g$	−2.2608	−0.0001	2.5958	−0.0002
$+2g$[a]	−2.2638	−0.0031	2.5908	−0.0052
$+3g$[a]	−2.3025	−0.0386	2.5428	−0.0480
$+4g$[a]	−2.3655	−0.0631	2.4686	−0.0741
$+5g$[a]	−2.3789	−0.0134	2.4549	−0.0137
$+6g$[a]	−2.3863	−0.0074	2.4489	−0.0060
$+7g$[a]	−2.3889	−0.0026	2.4466	−0.0023
$+8g$	−2.3884	0.0005	2.4462	−0.0004
$+9g$	−2.3872	0.0012	2.4462	0.0000
$30s26p23d14f6g$	−2.3889		2.4466	
$+1h$	−2.3889	0.0000	2.4466	0.0000
$+2h$	−2.3887	0.0002	2.4467	0.0001
$+3h$	−2.3883	0.0003	2.4469	0.0003
$+4h$[a]	−2.3900	−0.0017	2.4450	−0.0020
$+5h$[a]	−2.3915	−0.0015	2.4421	−0.0029
$+6h$	−2.3913	0.0001	2.4408	−0.0013
$+7h$	−2.3906	0.0007	2.4405	−0.0003
$30s26p23d14f6g2h$[b]	−2.3918		2.4420	

[a] Selected functions.

[b] Basis set obtained after the polarization study.

values that are probably associated with small imprecisions in coefficients for these functions in deep core spinors. In addition, as presented in Table III, more diffuse functions were also included based on the same threshold: $2p$ (0.0463 and 0.1306), $1d$ (0.0383), and $2f$ (0.0851 and 0.2440). This gave the origin to an intermediate basis set for gold consisting of $30s26p23d14f$ functions. Next, Table IV shows that this last set should be augmented with six polarization g functions (0.1147, 0.3034, 0.7221, 1.5723, 3.1870, and 6.1172), which were relevant to EFG calculations at the gold nucleus, again according to our threshold. Finally, two polarization h functions (1.3687 and 2.8180) also have to be added to the previous $30s26p23d14f6g$ set, resulting in an extended $30s26p23d14f6g2h$ basis set for gold that is used in all analytical EFG determinations.

However, those p and d Gaussian functions with the largest exponents may also be the cause of significant inaccuracies in the electron correlation contributions derived from the two-point numerical approach [28]. Thus, a comparison of the analytical and finite difference DC-HF values obtained for the EFG at gold in AuH indicated that the four tightest p and d functions must be removed from the basis of this element to provide stable numerical results. Hence, these particular numerical calculations used a smaller $30s22p19d14f6g2h$ basis set for gold.

B. Electric-field gradients

The EFGs at the gold nucleus are found in Table V. First of all, it is possible to notice that the Gaunt term, as considered at the HF level, almost always leads to a slight decrease of these values, except for OCAuX complexes, which present negligible negative or positive EFG variations due to this effect. Nevertheless, the largest relative contribution of this factor is only 1.1% (AuF). Higher-order relativistic two-electron corrections beyond the DG Hamiltonian such as those from the full Breit expression are expected to be much less important, according to literature results found for AuF [6]. As one can see, electron correlation tends to increase these EFG values. However, the MP2 treatment leads to a significant overestimation of the correlation effects on this

TABLE V. EFGs (in a.u.) at the Au nuclei given by different theoretical treatments.

Molecule	DC-HF[a]	DG-HF[a]	DC-BPW91[a]	DC-B3LYP[a]	DC + G-MP2[b]	DC + G-MP2[c]	DC + G-CCSD[d]	DC + G-CCSD(T)[d]	DC + G-CCSD-T[d]
AuH	−2.392	−2.415	3.368	2.442	2.706	2.311	1.117	1.646	1.655
AuF	−5.088	−5.146	3.351	1.774	0.126	−0.474	−1.142	−0.318	−0.347
AuCl	−3.885	−3.921	3.005	1.791	0.695	0.210	−0.458	0.191	0.180
AuBr	−3.358	−3.386	2.978	1.869	0.892	0.442	−0.184	0.418	0.408
AuI	−2.687	−2.707	2.825	1.895	1.271	0.882	0.224	0.764	0.761
ArAuF	−6.645	−6.702	0.844	−0.524	−1.861	−2.473	−3.291	−2.606	−2.631
ArAuCl	−5.688	−5.723	0.719	−0.405	−1.387	−1.893	−2.642	−2.070	−2.084
ArAuBr	−5.139	−5.168	0.871	−0.173	−1.073	−1.542	−2.242	−1.694	−1.707
KrAuF	−7.227	−7.279	0.091	−1.265	−2.586	−3.194	−4.005	−3.335	−3.361
KrAuCl	−6.330	−6.362	−0.065	−1.179	−2.189	−2.696	−3.429	−2.870	−2.886
XeAuF	−8.095	−8.136	−1.018	−2.358	−3.656	−4.193	−5.028	−4.385	−4.411
OCAuF	−12.483	−12.494	−4.925	−6.341	−7.226	−7.744	−8.965	−8.223	−8.246
OCAuCl	−12.277	−12.275	−5.438	−6.683	−7.565	−8.013	−9.041	−8.387	−8.402
OCAuBr	−12.027	−12.022	−5.382	−6.590	−7.427	−7.895	−8.904	−8.251	−8.269
OCAuI	−11.696	−11.688	−5.378	−6.532	−7.317	−7.750	−8.711	−8.070	−8.086

[a] Analytical EFG values.

[b] Sum of the DG-HF EFG value with the electron correlation contribution obtained with a larger active space.

[c] Sum of the DG-HF EFG value with the electron correlation contribution obtained by the respective method.

[d] Sum of the DG-HF EFG value with the electron correlation contribution obtained by the respective method and a full active space correction (see text).

property. In addition, the DFT methods such as B3LYP and BPW91 provide even EFGs with wrong signs.

The EFGs at the gold nucleus encountered in our work can also be compared with the ones obtained in Ref. [6] for AuH, AuF, XeAuF, KrAuF, ArAuF, and OCAuF. Thus, the DC-HF and DG-HF values found here are always smaller than those calculated by Belpassi *et al.* by 0.12–0.20 a.u. Hence, according to an analysis of the basis sets employed in both investigations, we believe that this discrepancy is almost entirely caused by the use of insufficient tight d functions to properly deal with the core polarization in that previous work. The Dyall's quadruple-zeta (dyall.v4z) basis set chosen for gold in Ref. [6] ($34s30p19d13f4g2h$) does not contain enough tight d functions to guarantee convergence in these EFG values. One can see that all five tight d functions added during our basis set augmentation study, which result in a decrease of DC-HF EFGs at gold (Table III), have larger exponents than the ones found in this dyall.v4z set. Another DC-HF calculation done for AuH with the basis sets used in Ref. [6] augmented by four extrapolated tighter d functions for gold showed an EFG of −2.385 a.u., which is virtually the same as our respective value (−2.392 a.u.). Thus, apart from other basis set differences, this single factor seems to explain almost all of the decrease observed in our DC-HF and DG-HF EFGs with respect to those from Belpassi *et al.*

Next, the comparison of electron correlation contributions obtained at the DC-CCSD-T level from Ref. [6] with our respective original values (without full active space corrections) results in an excellent agreement, with deviations smaller than 1% (0.03 a.u.). These almost negligible differences are not surprising if one takes into account the fact that the active spaces are similar, although we considered more virtual spinors than those chosen by Belpassi *et al.* Furthermore, an increase of the smallest active space used in this work in order to include all electrons and virtual spinors up to 100 a.u. resulted in large EFG increments at gold according to our DC-MP2 calculations, as one can see in Table V (from 0.39 to 0.61 a.u.). However, we believe that the MP2 treatment is also overestimating such a correction, and additional calculations were done with an active space from −15 to 20 a.u. for AuH (44 electrons) to better investigate this hypothesis. Thus, the DC-MP2, DC-CCSD, DC-CCSD(T), and DC-CCSD-T correlation contributions to EFGs obtained at the gold nucleus were 5.034, 3.511, 4.022, and 4.032 a.u., respectively. First, one can notice that this DC-MP2 result is slightly smaller than the one from full electron calculations (5.120 a.u.), which implies that the effect of lower-lying electrons compared to those in the 4d subshell of gold and upper virtual spinors beyond 20 a.u. is almost negligible. Moreover, the MP2 treatment provides a difference to the value from our smaller active space (4.725 a.u.) of 0.309 a.u., which is obviously not in agreement with findings from the most advanced methods, since EFG increments at gold of 0.075, 0.139, and 0.137 a.u. were obtained respectively from these DC-CCSD, DC-CCSD(T), and DC-CCSD-T calculations. Hence, given the relevance of such factor and considering the data mentioned, we suggest a full active space correction that is evaluated by taking the electron correlation contribution differences from DC-MP2 calculations scaled according to the AuH values [the scaling factors are given as 0.2415, 0.4515, and 0.4431 for the DC-CCSD, DC-CCSD(T), and DC-CCSD-T methods, respectively]. Other similar calculations performed with an active space from −15 to 20 a.u. for AuF (50 electrons) also supported the main findings discussed here.

TABLE VI. NQCCs (in MHz) at the ^{197}Au nuclei.

Molecule	NQCC
AuH[a,b]	191.591 (4.474)
AuF[c,d]	−52.966
AuCl[c,e]	9.991
AuBr[c,e]	37.572
AuI[c,f]	78.300
ArAuF[g]	−323.356
ArAuCl[h]	−259.835
ArAuBr[g]	−216.709
KrAuF[i]	−404.775
KrAuCl[h]	−349.857
XeAuF[j]	−527.704
OCAuF[k]	−1006.285
OCAuCl[c,k]	−1027.600
OCAuBr[k]	−999.119
OCAuI[l]	−981.038

[a] Equilibrium value estimated in this work (the vibrational correction is between parentheses).
[b] Reference [18].
[c] Extrapolated values from linear regressions.
[d] Reference [19].
[e] Reference [20].
[f] Reference [21].
[g] Reference [22].
[h] Reference [23].
[i] Reference [24].
[j] Reference [25].
[k] Reference [26].
[l] Reference [27].

C. Nuclear quadrupole coupling constants

The experimental NQCCs [18–27] are considered in Table VI. The values for diatomic molecules refer to the equilibrium condition and were extrapolated from linear regression of NQCCs for the ground vibrational state ($\upsilon = 0$) and other excited levels, except for AuH. This last molecule required additional DC-B3LYP and DC-BPW91 calculations for the evaluation of the first and second derivatives of EFGs at gold in terms of bond length changes with respect to the equilibrium value (±0.005 and ±0.010 Å) and their further combination with some experimental values [17] and the accepted NQM [1], as done previously for copper-containing diatomic systems [28]. The NQCC for OCAuCl was also obtained by linear regressions.

D. Nuclear quadrupole moments

First, a discussion is presented in terms of NQMs obtained for ^{197}Au by means of the direct method. These values are given in Table VII. One can notice that the best results from the direct approach are those for OCAuX complexes. All

TABLE VII. NQMs of the ^{197}Au nuclei (in mb) determined through various theoretical treatment levels.

Molecule	DC-HF	DG-HF	DC-BPW91	DC-B3LYP	DC + G-MP2[a]	DC + G-MP2	DC + G-CCSD	DC + G-CCSD(T)	DC + G-CCSD-T
AuH	−340.9	−337.7	242.1	333.9	301.3	352.9	730.0	495.4	492.6
AuF	44.3	43.8	−67.3	−127.1	−1783.7	475.4	197.5	708.4	649.9
AuCl	−10.9	−10.8	14.2	23.7	61.2	202.9	−92.9	222.6	235.7
AuBr	−47.6	−47.2	53.7	85.5	179.2	362.1	−869.6	382.8	391.6
AuI	−124.0	−123.1	118.0	175.8	262.2	377.9	1489.4	435.9	438.1
ArAuF	207.1	205.3	−1629.7	2625.8	739.3	556.4	418.2	528.0	523.1
ArAuCl	194.4	193.2	−1538.3	2733.0	797.3	584.1	418.5	534.3	530.5
ArAuBr	179.5	178.5	−1059.4	5316.4	859.9	598.2	411.5	544.3	540.2
KrAuF	238.4	236.7	−18898.5	1361.3	666.1	539.4	430.1	516.5	512.6
KrAuCl	235.2	234.0	23002.6	1262.7	680.3	552.3	434.2	518.8	515.9
XeAuF	277.5	276.0	2205.3	952.4	614.3	535.6	446.7	512.2	509.2
OCAuF	343.1	342.8	869.6	675.4	592.7	553.0	477.7	520.8	519.4
OCAuCl	356.2	356.3	804.2	654.4	578.1	545.8	483.7	521.5	520.5
OCAuBr	353.6	353.7	790.0	645.2	572.5	538.6	477.6	515.3	514.3
OCAuI	357.0	357.2	776.4	639.2	570.6	538.8	479.3	517.4	516.4
Average[b]	**274.2**	**273.4**	**532.2**	**1686.6**	**667.1**	**554.2**	**447.7**	**522.9**	**520.2**
MAD[b,c]	63.3	63.8	5050.9	1123.1	81.7	15.2	25.5	7.6	6.7
Regression plot[b,d]	**493.0**	**496.1**	**508.0**	**505.8**	**529.7**	**535.9**	**508.8**	**515.3**	**515.3**
R^2[b,d]	0.994	0.994	0.988	0.995	0.999	0.999	1.000	1.000	1.000
Intercept (MHz)[b,d]	405.3	414.4	−374.7	−228.7	−83.3	−12.8	62.9	−5.6	−3.2

[a] Results directly calculated from EFGs attained with the largest active space.

[b] These values do not include results for AuH, AuF, AuCl, AuBr, and AuI molecules.

[c] Mean absolute deviation.

[d] Results determined through an indirect approach.

the treatments point to positive NQMs for such molecules, and the electron correlation tends to increase these values, although MP2 clearly leads to an overcorrection. The effect of perturbative triple substitutions is not higher than 8% in these cases. As expected, common DFT functionals are unable to provide accurate EFG values for this element [7], even in these cases. On the other hand, the complexes with noble gases (Ng) belong to an intermediate category, in which the effect of perturbative triple excitations can be as high as 24%. DFT EFGs furnish totally unreliable NQMs for ^{197}Au in such NgAuX systems and DC-HF values are now smaller than the ones for OCAuX, while MP2 again predicts overestimated electron correlation contributions.

Finally, the direct results for diatomic molecules are not satisfactory, even at the most advanced theory levels considered here (except perhaps for AuH). We suspect that this inadequacy is caused by static electron correlation effects since the respective values for the T_1 diagnostic [29] are the largest found in this study, that is, from 0.033 to 0.046 (see Table II), and the perturbative triples result in a change of at least 48% in these NQMs. Thus, the satisfactory direct NQM obtained for this nuclide in AuF by Belpassi *et al.*(Q[DC + G-CCSD-T] = 499 mb) is probably due to a fortuitous error cancellation in the EFG that occurs mainly among basis set incompleteness (−0.17 a.u.), and deep core (0.27 a.u.) plus static correlation contributions (probably around −0.10 a.u. for gold halides). Furthermore, it is worth mentioning that some diatomic molecules containing copper also exhibited similar static correlation problems [28].

Fortunately, the indirect method can be used to better determine the NQM for ^{197}Au. However, for precaution, the data from these diatomic systems will not be considered in the regressions performed here. As expected, the NQMs determined from the indirect version are more robust, and even HF or DFT levels now provide much more reliable estimates, although their significant intercept values indicate that there are large systematic errors in the respective EFGs. The Gaunt term, the electron correlation at the CCSD level, and perturbative triple excitations result in NQM increments of 3.1, 12.7, and 6.5 mb, respectively. Moreover, the deficiencies previously observed in the MP2 treatment are manifested again in larger NQMs for ^{197}Au and systematic errors with opposite signs with respect to the HF ones. Nevertheless, one could take the difference between both DC-MP2 indirect values to attain an upper estimate of full active space effects, which point to a NQM reduction of up to 6.2 mb. Hence, considering our indirect data obtained for ^{197}Au at the most advanced levels employed here [DC + G-CCSD(T) and DC + G-CCSD-T], we notice that the full active space correction suggested in this work, which is scaled as mentioned before, causes a smaller NQM decrease of 2.5 mb and reduces significantly the systematic error presented in the original EFGs. The respective intercepts are decreased by 31 MHz due to this correction and the final values (−5.6 and −3.2 MHz) are much closer to zero.

Finally, the best NQM estimate obtained from the indirect method for ^{197}Au is 515 mb. Another argument in favor of this determination is that the most reliable direct NQMs for ^{197}Au obtained from OCAuX complexes agree to within 1% of this indicated value. Thus, an error bar of 3% is proposed because of higher-order effects than the ones already taken into account here, following the suggestion of Ref. [6].

IV. CONCLUSION

The analysis of our results indicated that the electron structure treatment employed in this work is not adequate for diatomic gold-containing systems, which is attributed to static electron correlation effects. Thus, these molecules were excluded from the remaining investigations. The best EFG values at the gold nucleus from the direct molecular method are found for OCAuX (X = F, Cl, Br, and I) complexes and point to an average NQM for ^{197}Au of 518–519 mb.

On the other hand, the indirect version of the molecular method based on DC + G-CCSD(T) and DC + G-CCSD-T EFG calculations at gold, which is not significantly affected by the remaining systematic errors in EFGs [6], furnished a NQM for ^{197}Au of 515(15) mb. This value is in excellent accordance with recent atomic and molecular results. Finally, considering that this determination is also farther away from the standard NQM accepted for this nuclide [1], 547(16) mb, our work reinforces that a revision of this quantity is necessary.

ACKNOWLEDGMENTS

The authors thank FAPESP for financial support (Grant No. 2010/18743-1). R.T.S. also thanks CNPq for support from a doctoral fellowship.

---

[1] P. Pyykkö, Mol. Phys. **106**, 1965 (2008).

[2] R. J. Powers, P. Martin, G. H. Miller, R. E. Welsh, and D. A. Jenkins, Nucl. Phys. A **230**, 413 (1974).

[3] H. Yakobi, E. Eliav, and U. Kaldor, J. Chem. Phys. **126**, 184305 (2007).

[4] J. Bieroń, C. Froese Fischer, P. Indelicato, P. Jönsson, and P. Pyykkö, Phys. Rev. A **79**, 052502 (2009).

[5] P. Dufek, P. Blaha, and K. Schwarz, Phys. Rev. Lett. **75**, 3545 (1995).

[6] L. Belpassi, F. Tarantelli, A. Sgamellotti, H. M. Quiney, J. N. P. van Stralen, and L. Visscher, J. Chem. Phys. **126**, 064314 (2007).

[7] C. Thierfelder, P. Schwerdtfeger, and T. Saue, Phys. Rev. A **76**, 034502 (2007).

[8] DIRAC, a relativistic *ab initio* electronic structure program, Release DIRAC12 (2012), written by H. J. Aa. Jensen, R. Bast, T. Saue, and L. Visscher, with contributions from V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. K. Lærdahl, Y. S. Lee, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kullie, C. V. Larsen, H. S. Nataraj, P. Norman, G. Olejniczak, J. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, K. Ruud, P. Sałek, B. Schimmelpfennig, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (see http://www.diracprogram.org).

[9] L. Visscher, Theor. Chem. Acc. **98**, 68 (1997).

[10] R. L. A. Haiduke and A. B. F. da Silva, J. Comput. Chem. **27**, 1970 (2006).

[11] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[12] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).

[13] K. G. Dyall, Theor. Chem. Acc. **108**, 335 (2002).

[14] K. G. Dyall, Theor. Chem. Acc. **115**, 441 (2006).

[15] K. G. Dyall, Theor. Chem. Acc. **99**, 366 (1998).

[16] K. G. Dyall, Theor. Chem. Acc. **108**, 365 (2002).

[17] D. R. Lide, in *CRC Handbook of Chemistry and Physics*, edited by V. M. Haynes, 94th ed. (CRC Press/Taylor and Francis, Boca Raton, FL, 2014), http://www.hbcpnetbase.com/

[18] T. Okabayashi, E. Y. Okabayashi, M. Tanimoto, T. Furuya, and S. Saito, Chem. Phys. Lett. **422**, 58 (2006).

[19] C. J. Evans and M. C. L. Gerry, J. Am. Chem. Soc. **122**, 1560 (2000).

[20] C. J. Evans and M. C. L. Gerry, J. Mol. Spectrosc. **203**, 105 (2000).

[21] L. M. Reynard, C. J. Evans, and M. C. L. Gerry, J. Mol. Spectrosc. **205**, 344 (2001).

[22] C. J. Evans, D. S. Rubinoff, and M. C. L. Gerry, Phys. Chem. Chem. Phys. **2**, 3943 (2000).

[23] C. J. Evans, A. Lesarri, and M. C. L. Gerry, J. Am. Chem. Soc. **122**, 6100 (2000).

[24] J. M. Thomas, N. R. Walker, S. A. Cooke, and M. C. L. Gerry, J. Am. Chem. Soc. **126**, 1235 (2004).

[25] S. A. Cooke and M. C. L. Gerry, J. Am. Chem. Soc. **126**, 17000 (2004).

[26] C. J. Evans, L. M. Reynard, and M. C. L. Gerry, Inorg. Chem. **40**, 6123 (2001).

[27] N. R. Walker, S. G. Francis, S. L. Matthews, J. J. Rowlands, and A. C. Legon, Mol. Phys. **104**, 3329 (2006).

[28] R. T. Santiago, T. Q. Teodoro, and R. L. A. Haiduke, Phys. Chem. Chem. Phys. **16**, 11590 (2014).

[29] T. J. Lee and P. R. Taylor, Int. J. Quantum Chem. **36**, 199 (1989).