

Effect of Basis Set Superposition Error on the MP2 Relative Energies of Gold Cluster Au₆

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We have studied the structures and stabilities of Au₆ to explore the origin of the large discrepancy between relative energies obtained from the density functional theory (DFT) and ab initio correlated levels of theory. The MP2 methods significantly overestimate the stability of the non-planar isomer when the double- ζ polarization quality of basis sets, such as LANL2DZ+1f and CEP31G+1f, are used. However, we show that such preference for the non-planar structure at the MP2 level mainly originates from the large basis set superposition error.

Key Words: Gold clusters. Density functional calculation. Coupled-cluster calculation. Basis set superposition error. Effective core potential

Introduction

Clusters and nanoparticles of gold have received considerable attention during the past few years.¹⁻⁴ The exceptional catalytic properties of small gold aggregates^{5,6} have motivated research aimed at providing insights into the molecular origins of this unexpected reactivity of gold.⁷ The experimental observations have stimulated many theoretical studies of the electronic, structural, and chemical properties of neutral and charged gold clusters,⁸⁻²³ in which one of the most intriguing results is the tendency of small Au clusters to adopt planar structures. A preference of two-dimensional (2D) structures up to Au₁₂⁺ has also been experimentally indicated by ion mobility measurements¹³ and photoelectron spectroscopy¹⁵ in combination with density functional theory (DFT) calculations. In view of the present knowledge of stable structures for small noble-metal clusters, the preference for 2D structures for sizes larger than the hexamer is unique for gold. The 2D stability of gold clusters was explained by strong relativistic effects in gold that reduce the *s-d* energy gap, thus inducing hybridization of the atomic 5*d*-6*s* levels and causing overlap of the 5*d* shells of neighboring atoms in the clusters.¹⁰

Over the past decade, there have been a number of papers dedicated to the structure of neutral gold clusters in order to determine the value of *n* at which nonplanar structures begin.^{12,16-19,22,23} We note that the DFT results indicate that the turn-over point is in the range of *n* = 11-14. Actually, DFT methods have been recognized to favor planar structures for gold clusters.^{12,14,18,22}

However, we now show that the DFT methods do not overestimate the stabilities of the planar isomer for gold clusters Au₆. The observed overestimation in the DFT results is ascribable to the fact that the basis set superposition error (BSSE) values in the correlated ab initio results are large.

Computation Details

Kohn-Sham DFT calculations were performed with two

Table 1. Relativistic effective core potentials (RECP),^a valence basis sets, and number of basis sets (NBS) for Au

	RECP	Basis set ^b	NBS
Basis1	Stevens <i>et al.</i> (SKBJ) CEP ^c	(7s7p5d1f)[4s4p3d1f]	228
Basis2		7s7p5d2f	402
Basis3		7s7p5d3f2g	552
Basis4	Hay and Wadt (HW)	(5s6p3d1f)[3s3p2d1f] ^d	174
Basis5		5s6p3d2f	312
Basis6	Andre <i>et al.</i> (Stuttgart)	(8s7p6d1f)[6s5p3d1f]	258
Basis7		8s7p6d2f	438

^a19 valence electrons ^b1f exponent = 0.89; 2f exponents = 0.84, 0.31; 3f exponents = 2.0, 0.84, 0.31; 2g exponent = 1.90, 0.69. The polarization sets were employed in Ref. [18]. ^cCompact effective potential ^dLos Alamos RECP plus double- ζ basis set (LANL2DZ) - 1f exponent

different exchange-correlation functionals, namely, pure gradient-corrected Perdew-Wang's 1991 (PW91)^{24,25} and hybrid Becke's three-parameter hybrid exchange with the nonlocal correlation of Lee-Yang-Parr (B3LYP)²⁶ functionals. We summarize three relativistic effective core potentials (RECP) and valence basis sets employed here in Table 1 and give brief descriptions in the footnote of the table.²⁷⁻²⁹ Moller-Plesset second-order perturbation (MP2)³⁰ and coupled-cluster singles, doubles, and perturbative triples [CCSD(T)]^{31,32} methods were employed. The CCSD(T) calculations were performed at the MP2 geometries. For Au₂, the BSSE was accounted for by counterpoise³³ optimization correction.³⁴ All the calculations were carried out with the program package GAUSSIAN03.³⁵

Results and Discussion

The structures of three isomers are depicted in Figure 1, and the relative energies at the PW91, B3LYP, MP2, and CCSD(T) levels of theory are listed in Table 2. The optimized geometries are given in the Supporting Information. It is widely known that the A1 and A2 isomers are the most stable planar and nonplanar forms, respectively. It should be men-

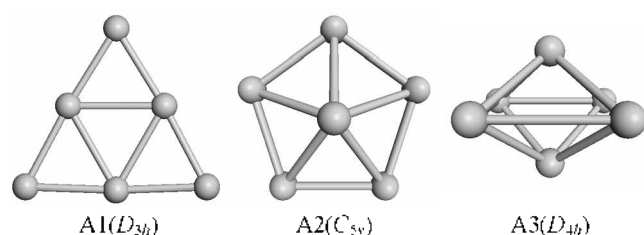


Figure 1. Optimized structures of Au₆ isomers.

Table 2. Relative energies in kcal/mol for Au₆ isomers.

		Δ1	Δ2	Δ3
Basis1 (SKBJ)	PW91	0.0	18.6	38.4
	B3LYP	0.0	19.8	44.1
	MP2	0.0	11.1	29.8
	CCSD(T)	0.0	15.9	34.2
Basis2 (SKBJ)	PW91	0.0	20.5	40.5
	B3LYP	0.0	21.3	45.9
	MP2	0.0	18.6	40.6
	CCSD(T)	0.0	22.5	43.3
Basis3 (SKBJ)	PW91	0.0	21.2	41.3
	B3LYP	0.0	21.9	46.5
	MP2	0.0	18.2	39.7
Basis4 (IIW)	PW91	0.0	21.6	38.5
	B3LYP	0.0	22.0	44.4
	MP2	0.0	7.2	21.3
	CCSD(T)	0.0	12.2	27.6
Basis5 (HW)	PW91	0.0	22.4	41.2
	B3LYP	0.0	23.0	46.5
	MP2	0.0	20.1	40.3
	CCSD(T)	0.0	23.6	42.1
Basis6 (Stuttgart)	PW91	0.0	19.8	39.4
	B3LYP	0.0	20.6	45.2
	MP2	0.0	14.9	35.2
	CCSD(T)	0.0	17.9	36.9
Basis7 (Stuttgart)	PW91	0.0	20.7	40.5
	B3LYP	0.0	21.6	46.2
	MP2	0.0	17.5	39.2
	CCSD(T)	0.0	21.3	42.6

tioned that the nonplanar A3 isomer is very unstable energetically, but it is selected as a proper model structure for our purposes. To assess the accuracy of the CCSD(T) data, T₁ diagnostic values were computed for the CCSD wavefunctions. The T₁ values are found to be about 0.02 for all the cases, indicating that a single reference treatment is quite adequate.³⁶ All the methods agree that the lowest-energy isomer for Au₆ is the planar A1 structure, but the relative energies significantly vary for the methods and the basis sets.

First, we used the RECPs derived by Stevens *et al.* and valence basis sets,²⁷ which were employed in Ref. [18]. We note that the DFT methods indeed overestimate the stability of planar structure, relative to *ab initio* MP2 and CCSD(T) methods, when CEP31G+1f (Basis1) was used. The ΔE(A1–A2) values of 18.6 and 19.8 kcal/mol at the PW91 and B3LYP levels, respectively, are quite larger than those of 11.1 and 15.9 kcal/mol at the MP2 and CCSD(T) levels of theory.

However, using the uncontracted CEP *spd*+2*f* basis set (Basis2), we obtained a bit smaller DFT values, 20.5 (PW91) and 21.3 kcal/mol (B3LYP), than the CCSD(T) value of 22.5 kcal/mol. Employing the 3/2*g* polarization basis sets (Basis3) instead of the 2*f* exponents only slightly affected the relative energies at the MP2 level. We observed a similar trend in the case of the ΔE(A1–A3) values, as shown in Table 2.

Secondly, we used another popular HW RECPs and valence basis sets.²⁸ The ΔE(A1–A2) values of about 22 kcal/mol at the DFT levels are much larger than those of 7.2 and 12.2 kcal/mol at the MP2 and CCSD(T) levels, respectively, when the LANL2DZ+1*f* (Basis4) is employed for Au. Similarly with the Stevens *et al.*'s RECP case, the difference between the DFT and CCSD(T) values became small, *i.e.*, 23.0 (B3LYP) vs. 23.6 kcal/mol [CCSD(T)], provided the uncontracted LANL2DZ *spd*+2*f* (Basis5) is used. For ΔE(A1–A3), the PW91 value is in good agreement with the MP2 and CCSD(T) results within 1 kcal/mol in the Basis5 results, while there are large discrepancies between DFT and correlated *ab initio* values in the Basis4 results.

Finally, we tested the Stuttgart RECP and valence basis sets.²⁹ (8*s*7*p*6*d*1*f*)/[6*s*5*p*3*d*1*f*] (Basis6). The differences between DFT and correlated *ab initio* results are insignificant in the Basis6 results, relative to the cases of LANL2DZ+1*f* (Basis4) and CEP31G+1*f* (Basis1) results. However, it is clear that the uncontraction of *spd* basis set (Basis7) also reduces the differences between DFT and correlated *ab initio* results.

It is noteworthy that the DFT methods do not overestimate the stability of the planar isomer of Au₆, provided that the uncontracted *spd*+2*f* basis sets are used, irrespective of the RECPs chosen. We found that the relative energy is strongly sensitive to the basis sets in the correlated *ab initio* results, which is ascribable to different intramolecular BSSE³⁷ for the different isomers. The BSSE seems to stabilize the 3D isomers preferentially, because the 3D isomers are geometrically more compact than the 2D isomers.

In Table 3, we list the bond lengths and dissociation energies³⁸ of Au₂ with or without counterpoise BSSE corrections at the MP2 level of theory. The BSSE values obtained by the counterpoise procedure may be less reliable for strong covalent interaction than for weak interaction. However, we believe that the counterpoise correction is very useful to estimate the quality of basis sets employed. We mention that the counterpoise procedure was applied to evaluate the spectroscopic constants - R_e, ω_e, and D_e - of Au₂.^{39,40} We would like to repeat that the differences between DFT and CCSD(T) relative energies are the largest for the Basis4 case, followed by Basis1. The BSSE values also have the same trend for Au₂, *i.e.*, the BSSE values are 13.4 and 9.2 kcal/mol for Basis4 and Basis1, respectively. The BSSE values for Au₂ are relatively insignificant, 3.2–4.4 kcal/mol, for Basis 2, Basis5, and Basis7. As expected, the BSSE is the smallest (2.1 kcal/mol) for the largest basis set, Basis3. It is known that basis set convergence and elimination of the BSSE are achieved much earlier for DFT than for correlated *ab initio* methods.⁴¹ The BSSE values are only 2.3 and 1.8 kcal/mol for the PW91 and B3LYP results, respectively, despite using Basis4, confirming that the DFT methods are relatively free of BSSE. Our results

Table 3. BSSE-uncorrected and BSSE corrected bond lengths (R_e in Å) and binding energies (BE in kcal/mol) of Au_2 computed at the MP2 level of theory

	R_e	R_e (BSSE corrected)	BSSE (R_e)	BE	BE (BSSE corrected)	BSSE (BE)
Basis1	2.474	2.515	+0.041	56.0	46.8	-9.2
Basis2	2.457	2.470	+0.013	57.9	54.7	-3.2
Basis3	2.437	2.444	+0.007	60.0	57.9	-2.1
Basis4	2.555	2.576	+0.021	51.0	37.6	-13.4
Basis5	2.441	2.458	+0.017	60.2	55.8	-4.4
Basis6	2.482	2.511	+0.029	53.5	45.9	-7.6
Basis7	2.457	2.470	+0.013	56.5	53.3	-3.2

The experimental R_e and BE values are 2.47 Å and 53.3 kcal/mol for Au_2 , respectively.³⁸

clearly show that the MP2 and CCSD(T) relative energies are heavily contaminated by BSSE for the CEP31G+1f (Basis1) and LANL2DZ+1f (Basis4) cases for Au_6 . Conclusively, both a high-level CCSD(T) method and high-quality basis set are necessary to precisely determine the relative energies of gold cluster isomers. For instance, Han⁴² demonstrated that the CCSD(T)/small basis+[MP2/large basis-MP2/small basis] calculations provide similar results to the DFT results for the relative energies of Au_8 .

To summarize, we demonstrated that the large intramolecular BSSE can be a nonnegligible error for determining the relative energies of gold cluster isomers in *ab initio* correlated calculations. Our results clearly show that the DFT methods do not overestimate the stability of the planar isomer of Au_6 . Therefore, DFT still appears as a practical and useful method, with a small BSSE, to explore the potential energy surface of gold clusters.

Supporting Information. The Supplementary optimized geometries mentioned in the text is available at the bkcs website (<http://www.kcsnet.or.kr/bkcs>).

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