Performance of Density Functionals for the Calculation of Gold Clusters

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Clusters and nanoparticles of gold have received considerable attention during the past decade.[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.[7] The experimental observations have stimulated many theoretical studies of the electronic, structural, and chemical properties of gold clusters.[8-13]

Since it is not practical to calculate gold clusters using high-level ab initio correlation methods, density functional theory (DFT)-based approaches have usually been employed in such calculations, but it is not clear which functionals provide the best performance. Herein we report the results of calculations on the structure and stability of Au_2 and Au_8, as a model study, using various density functionals. To the best of our knowledge, there has been no previous systematic study for DFT performance on the structure and stability of gold clusters. Although the performance of density functionals is widely known for light element systems,[14-16] certain functionals successful in light element chemistry may not work effectively in heavy element chemistry. This is due to the strikingly different bonding nature of heavy element systems from their light element analogues.[17] Thus, the results of this work may be useful for future work in choosing the most appropriate density functional for gold clusters when performing DFT calculations.

Kohn-Sham DFT calculations were performed with 16 different exchange correlation functionals, namely, the local density approximation (LDA:SVWN),[18] the generalized gradient approximation (GGA:BLYP, BP86, BPW91, PW91, PBE, HCTH, tHCTH, LC-BPW91, LC-PW91 and LC-PBE),[18] and the hybrid GGA functionals (B3LYP, B3PW91, mPW1PW91, PBE0 and X3LYP).[18] We used the relativistic effective core potentials derived by Stevens *et al.* and valence basis sets[19] employed in previous works.[9,10] All the calculations were carried out using the program package GAUSSIAN 09.[18]

Au_2 Cluster. We compare the calculated spectroscopic constants, bond length (R_e), vibrational frequency (ω_e), and dissociation energy (D_e) with the experimental data[20] in Table 1. Overall, the LDA and several GGA functionals provide good performance for bond length (and vibrational frequency) and dissociation energy, respectively. The use of hybrid GGA functionals, i.e., the inclusion of Hartree-Fock

exchange, does not improve the pure GGA results. These observations are in contrast to the known performance of functionals in light element chemistry: in general, LDA < GGA < hybrid GGA. It was reported, for instance, that the performance of the pure BP86 functional is very poor for light element systems,[21,22] but its performance is observed to be one of the most effective for Au_2. It is evident from our calculations that any one functional could not provide reliable spectroscopic constants of Au_2. The poor performance of hybrid GGA functionals may be partly ascribed to the functional parameterization optimal to light-element systems only. Intriguingly, the long range correction to the GGA functionals (LC-GGA) improves the performance for bond lengths.

Au_8 Cluster. There are no experimental data for the structures and energies of Au_8. Han[10] reported the relative

Table 1. Bond lengths, vibrational frequencies, and dissociation energies of Au_2

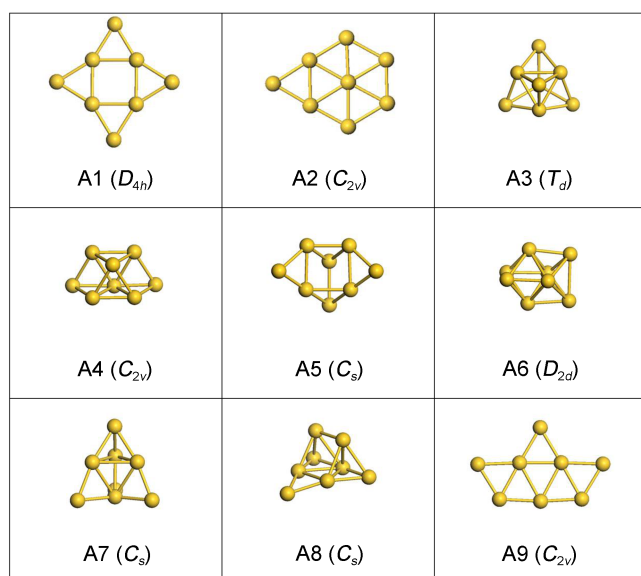|	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
Local density approximation			
SVWN	2.454	195.9	3.04
Generalized gradient approximation			
BLYP	2.556	164.7	2.17
BP86	2.519	174.8	2.33
BPW91	2.522	173.5	2.23
PW91	2.518	175.2	2.38
PBE	2.519	174.2	2.36
HCTH	2.537	163.4	2.08
tHCTH	2.510	173.5	2.26
LC-BPW91	2.463	199.0	2.09
LC-PW91	2.463	199.1	2.09
LC-PBE	2.461	199.6	2.10
Hybrid GGA			
B3LYP	2.545	169.0	2.02
B3PW91	2.519	175.8	2.06
mPW1PW91	2.517	177.0	2.05
PBE0	2.515	177.1	2.10
X3LYP	2.543	169.6	2.04
Exp.*a*	2.476	190.0	2.24

*a*Reference [20]

Figure 1. Optimized structures of Au8 isomers.

energies of nine isomers of Au_8 (see Figure 1) computed at the CCSD(T)/small basis + [MP2/large basis – MP2/small basis] level of theory. We compare the relative energies of Au_8 using various DFT functionals with the more elaborate ab initio results in Table 2. Overall the performance of density functionals is found to be GGA ~ hybrid GGA >> LDA. The PW91 and PBE functionals, in particular, provide

better performance than other functionals including the most popular B3LYP. Long range correction to the GGA functionals does not improve the performance.

The GGA and hybrid functionals correctly predict the lowest energy isomer, i.e., the planar A1 isomer. However, the LDA functionals indicate that one of the compact isomers, A4, has the lowest energy. It is worth noting that these observations for Au_8 are related to the dissociation of energies of Au_2. The severe overbinding Au-Au interaction in LDA results makes the LDA calculations overestimate the stability of compact structures such as A3, A4, and A6 significantly, because much more Au-Au bonding exists in the compact structures than in the planar isomers.

The gist of our DFT calculations is as follows:

1. Pure GGA functionals provide overall better performance than the LDA and hybrid GGA functionals for the structures and energies of gold clusters.

2. The LDA functionals can be employed for only the structural optimization of gold clusters. We suggest a GGA// LDA procedure, a GGA energy evaluation at the LDA optimized structure, for a practical method of choice. The PW91//SVWN calculations provided similar results with the PW91 results for Au_8 (see Table 2).

Many theoreticians have tried to develop well-behaved density functionals for certain purposes, such as evaluation of reaction barrier height.[23-25] If no panacea can be found, it is urgent to develop specific density functionals optimal for heavy element systems.

Table 2. Relative energies in kcal/mol for Au8 isomers

	A1	A2	A3	A4	A5	A6	A7	A8	A9	RMS[a]
Local density approximation										
SVWN	0.0	2.1	−1.4	−3.1	3.2	−1.2	5.5	2.8	10.5	5.7
Generalized gradient approximation										
BLYP	0.0	10.4	21.3	20.0	14.4	24.7	14.6	18.4	13.2	11.5
BP86	0.0	7.8	13.9	13.3	11.1	16.8	11.9	13.9	12.4	6.5
BPW91	0.0	8.1	14.4	14.0	11.6	17.6	12.3	14.4	12.4	7.0
PW91	0.0	6.9	11.0	10.4	9.6	13.5	10.6	11.9	12.0	4.5
PW91//SVWN	0.0	7.2	11.8	11.5	10.1	14.6	11.0	12.6	12.0	5.2
PBE	0.0	6.9	10.8	10.5	9.7	13.6	10.6	11.9	11.9	4.5
HCTH	0.0	11.0	21.4	22.5	15.4	27.1	15.1	19.8	13.3	12.7
tHCTH	0.0	10.8	21.7	21.6	15.5	26.3	15.5	19.8	13.7	12.4
LC-BPW91	0.0	12.4	7.4	10.8	11.2	15.5	13.2	13.9	21.7	5.8
LC-PW91	0.0	12.4	7.3	10.7	11.2	15.5	13.2	13.9	21.7	5.7
LC-PBE	0.0	12.2	6.6	10.1	10.9	14.9	12.9	13.5	21.6	5.4
Hybrid GGA										
B3LYP	0.0	11.2	19.6	19.1	14.3	23.4	14.6	18.6	15.4	10.8
B3PW91	0.0	9.5	13.9	14.3	12.1	17.8	12.8	15.5	14.8	7.1
mPW1PW91	0.0	9.2	11.8	12.5	11.3	15.7	12.0	14.4	15.0	5.8
PBE0	0.0	8.7	10.0	10.9	10.4	13.8	11.2	13.2	14.8	4.6
X3LYP	0.0	11.0	18.7	18.3	13.9	22.4	14.2	18.0	15.5	10.2
CCSD(T)est[b]	0.0	6.7	4.6	4.1	8.6	6.0	9.0	9.0	15.3	0.0

[a]Root-mean-square deviation with respect to the CCSD(T)est results. [b]Reference [10].

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