A density functional theory study of the Au$_7$H$_n$ (n = 1–10) clusters

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The geometries, electronic, and magnetic properties of the Au$_7$H$_n$ (n = 1–10) clusters have been systematically investigated by using relativistic all-electron density functional theory with generalized gradient approximation. It is found that the Au$_7$ on the whole retains its triangle structure after hydrogen atoms adsorption and adsorbing hydrogen atoms can stabilize the Au$_7$ structure. The Au$_7$H$_7$ cluster is much higher stability than the neighboring clusters. The pronounced even–odd alternation of the magnetic moments is observed in the Au$_7$H$_n$ systems indicating Au$_7$H$_n$ clusters possess tunable magnetic properties by adding even or odd number of H atoms.

1. Introduction

Gold is an element in that it has the atomic configuration $4f^{14}$ $5d^{10}$ $6s^1$, and shows properties similar to alkali metals due to its single valence s electron. On the other hand, gold has very large relativistic effects, larger than any other element with $Z < 100$ in the periodic table. The strong relativistic effect leads to reduced $5d$–$6s$ energy gap and strong s–d hybridization. During the past two decades, small gold clusters have been intensively studied by both experiment [1–13] and various theoretical methods [14–48] due to their unique catalytic, electronic, and optical properties. Hydrogen is the first element in the periodic table with the atomic configuration $1s^1$. Thus, it is very interesting to study the interaction of the small gold clusters with hydrogen atoms because both Au atom and H atom have one single valence s electron. In 1978, Hay et al. [49] performed the ab initio studies on diatomic gold hydride using relativistic effective core potentials. Later, a number of experimental and theoretical studies have been reported about the interaction of the gold clusters with hydrogen [50–68]. In 2003, the photoelectron spectra of bare Au$_n^-$ and Au$_{n-1}$H$^-$ clusters were presented by Buckart et al. [68], and the spectra of Au$_n^-$ and Au$_{n-1}$H$^-$ clusters showed almost identical features for $n > 2$ suggesting that hydrogen behaved as a protonated species by contrib-

uting one electron to the valence pool of the Au$_n^-$ cluster. Although there are already many studies in the literature, most of these work are concerned with the adsorption of one hydrogen atom or one hydrogen molecule onto small gold clusters. To our knowledge, a systematically theoretical study of a number of hydrogen atoms (nH with n = 1–10) interaction with gold clusters is still lacking.

Very recently, an edge-capped triangle with C_s symmetry structure for neutral Au$_7$ was unambiguously assigned in the gas phase [13]. Thus, motivated by the experiment [13] of the neutral Au$_7$ cluster, we perform a first-principles study on the Au$_7$H$_n$ (n = 1–10) clusters. The main aim of this paper is to study multi-hydrogen atoms adsorption and their effect on the electronic and magnetic properties of small gold clusters. We hope that this study can help people to understand the interaction of small gold clusters with hydrogen atoms better. We describe details of our computational scheme in Section 2 and present our results and discussion in Section 3. Finally, the conclusion is given in Section 4.

2. Computational methods

The calculations in this work are carried out by using density functional theory (DFT) [69,70] implemented in the DMOL3 package [71]. The electron density functional is treated by the generalized gradient approximation (GGA) with the PW91 exchange-correlation functional parametrized by Perdew and Wang [72]. All-electron spin-unrestricted calculations with scalar relativity

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Table 1

Calculated bond distance d (Å), vibrational frequency ω_e (cm^{-1}), binding energies per atom E_b (eV), vertical electron detachment energies VDE (eV), adiabatic electron detachment energies ADE (eV), and ionization potential IP (eV) of the AuH, Au$_2$, Au$_2^-$, Au$_7$, and Au$_7^-$ clusters.

System	Property	This work	Experiment [1–7,13]
AuH	d	1.532	1.524
	ω_e	2330	2305
	E_b	1.67	1.68
Au$_2$	d	2.49	2.47
	ω_e	178	191
	E_b	1.18	1.15, 1.18
	IP	9.43	9.50, 9.22
Au$_2^-$	d	2.587	2.582
	VDE	2.08	2.01
Au$_7$	ω_{e1}	168.2	165
	ω_{e2}	190.0	185
	ω_{e3}	205.5	203
Au$_7^-$	VDE	3.45	3.46
	ADE	3.28	3.40

(via VPSR tag) and double-numerical basis set that included d polarization functions (DND) [73] are employed in this work. The direct inversion in iterative subspace (DIIS) [74,75] approach is used to speed up SCF convergence. Hirshfeld charge analysis is made to obtain the net spin populations on each atom. The Global orbital cutoff quality is set as "fine" to describe the electronic wave functions. Self-consistent field calculations were done with a convergence criterion of 2×10^{-5} hartree on total energy in our calculation. We confirm the stability of the lowest-energy structures as minima of the potential energy surface by considering vibrational frequency. There is no imaginary frequency for structures reported here. In addition, for geometry optimization of each isomer, the spin multiplicity (M) was considered at least 1, 3, and 5 for even-electron clusters Au$_7$H$_n$ (n = 1, 3, 5, 7, 9) and 2, 4, and 6 for odd-electron clusters Au$_7$H$_n$ (n = 2, 4, 6, 8, 10). If the total energy decreases with increasing M, we will consider higher spin state until the energy minimum with respect to M is reached.

In order to check the validity of the computational method used for the Au$_7$H$_n$ clusters, we perform the calculations on AuH, Au$_2$, Au$_2^-$, Au$_7$, and Au$_7^-$ clusters, respectively, and the results are summarized in Table 1. All of the properties of these clusters are in excellent agreement with available experimental data. For pure Au$_2$ dimer, the computed bond length, binding energies per atom E_b and ionization potential IP are 2.49 Å, 1.18 eV and 9.43 eV, respectively. These results are well consistent with the experimental data [1,5] of 2.47 Å, 1.18 eV and 9.50 eV, respectively. For AuH dimer,
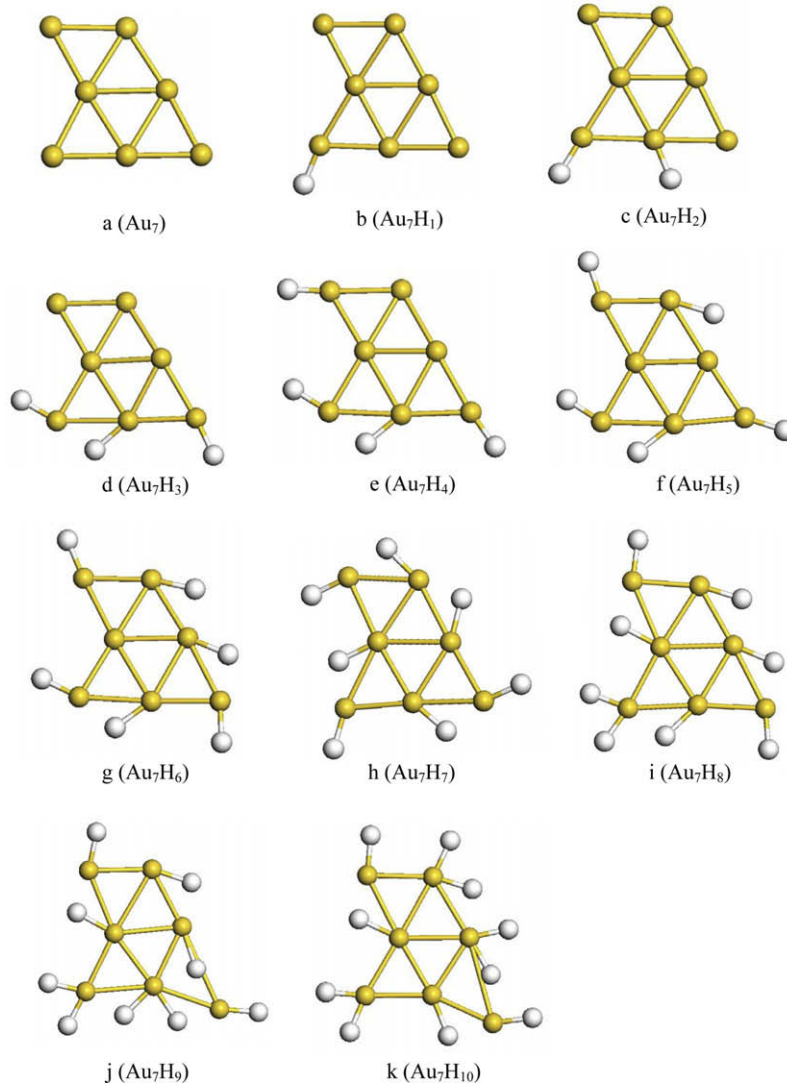

Fig. 1. Optimized structures of the pure Au$_7$ cluster and Au$_7$H$_n$ (n = 1–10) clusters using density functional theory with the PW91 functional, DND basis, and VPSR pseudopotential (see text for details). The H atom is represented by white sphere.

the bond length, binding energies per atom E_b and vibrational frequency ω_e by 1.532 Å, 1.67 eV and 2330 cm^{-1}, respectively, are in good agreement with the experimental data [1] of 1.524 Å, 1.68 eV and 2303 cm^{-1}, respectively. For Au$_7$, the calculated vertical electron detachment energies (VDE) and adiabatic electron detachment energies (ADE) by 3.45 and 3.28 eV, also agrees well with the available experimental value [7] of 3.46 and 3.40 eV, respectively. These indicate that our methods are reliable and accurate enough to describe the structures and properties of Au$_7$H$_n$ clusters.

3. Results and discussion

3.1. Geometric structure

We first present theoretical studies on the geometrical and electronic properties of the pure Au$_7$ cluster using the computation scheme described in Section 2. An extensive structural search was performed. We found a planar edge-capped triangle with C_s symmetry (Fig. 1a) to be lowest in energy for pure Au$_7$ cluster. This structure has been recently unambiguously assigned by Gruene et al. [13] by comparing the experimental spectrum (Far-IR multiple-photon dissociation (FIR-MPD) spectroscopy in the gas phase) with the calculated vibrational spectra for multiple isomers. The calculated vibrational frequency ω_e in our work is in excellent agreement with the result of the experiment [13] (see Table 1). Then, based on the optimized ground-state geometries of Au$_7$, we perform an extensive minimum energy structural search for a number of hydrogen atoms binding on Au$_7$ cluster. We found that all the Au$_7$H$_n$ (n = 1–10) structures prefer low spin multiplicity (M = 1 for odd number n and M = 2 for even number n). The lowest-energy structure of the Au$_7$H$_n$ (n = 1–10) are displayed in Fig. 1. From the Fig. 1 we can clearly see that the Au–Au bond length of the Au$_7$H$_n$ system has slightly changed and the triangle structure of Au$_7$ becomes slightly distorted after the adsorption of H atoms. This distortion becomes more obvious as the number of H atoms increases, indicating that the interaction between the gold and hydrogen becomes stronger.

Table 2 gives structural and electronic characteristics of Au$_7$H$_n$ (n = 1–10) clusters. Generally, the binding energy (E_b) of a given cluster is a measure of its thermodynamic stability. The average binding energies are calculated in this work as the following formulas:

$$E_b^a = [7E(\text{Au}) + nE(\text{H}) - E(\text{Au}_7\text{H}_n)]/(n+7), \qquad (1)$$

$$E_b^b = [E(\text{Au}_7) + nE(\text{H}) - E(\text{Au}_7\text{H}_n)]/n, \qquad (2)$$

$$E_b^c = [E(\text{Au}_7) + \frac{n}{2}E(\text{H}_2) - E(\text{Au}_7\text{H}_n)]/n, \qquad (3)$$

where E_b^a, E_b^b, and E_b^c are defined as the difference between the energy sum of all the free atoms (7Au and nH) constituting the cluster and the total energy of the cluster (Au$_7$H$_n$), the energy sum of the Au$_7$ and the nH minus the total energy of Au$_7$H$_n$, and the energy sum of the Au$_7$ and the $\frac{n}{2}$ H$_2$ minus the total energy of Au$_7$H$_n$, respectively.

The binding energy per atom (E_b^a) for the ground-state of Au$_7$H$_n$ (n = 2–10) clusters, except for Au$_7$H, is obviously higher than that for pure Au$_7$, indicating that adsorbing H atoms can stabilize the Au$_7$ structure. It can be seen from the Table that the binding energy (E_b^a) becomes increasingly large as the number of H atoms increases, and reaches a maximum at Au$_7$H$_7$ with 2.50 eV. Subsequently, it decreases as the number of H atoms increases from n = 8 to n = 10. Additionally, Au$_7$H$_7$ also has the largest binding energy per H-atom (E_b^b) and the binding energy per H-atom (E_b^c) with 2.79 and 0.49 eV, respectively. The HOMO–LUMO energy gap is another useful quantity for examining the kinetic stability of clusters. A large energy gap corresponds to a high strength required to perturb the electronic structure. We compare the E_{gap} of all Au$_7$H$_n$ clusters and find the E_{gap} of the Au$_7$H$_7$ is the largest one with 1.51 eV, and larger than the E_{gap} of the pure Au$_7$ cluster. This suggests that Au$_7$H$_7$ is relatively more chemically stable than the neighboring clusters. From the discussion above, it seems that the interaction between gold atoms and hydrogen atoms is strongest in the case that one hydrogen atom is adsorbed on each gold atom correspondingly.

3.2. Magnetic moment

In what follows, we will discuss the magnetic moments of Au$_7$H$_n$ (n = 2–10) clusters in this work and they are listed in Table 3. It is worthy to note certain trends of the magnetic moments of Au$_7$H$_n$ as follows. (1) Table 3 shows that all the even-numbered Au$_7$H$_n$ clusters are fount to exhibit magnetic with the same value 1 μ_B. This indicated that the nonmagnetic hydrogen and nonmagnetic gold can combine as a magnetic cluster. On the other hand, the odd-numbered Au$_7$H$_n$ clusters are fount to exhibit no magnetic with the value 0 μ_B. (2) The pronounced even–odd alternation of the magnetic moments is observed in the Au$_7$H$_n$ systems as Table 3 shows. In other words, the Au$_7$H$_n$ systems maybe can serve as the material with tunable code capacity of "0" and "1" by adding even or odd number of the H atoms. This odd–even alternation behavior can be very simply understood by considering the electron pairing effect. As some H atoms are adsorbed on Au$_7$ cluster, the half-filled 6s shell of Au atom and half-filled 1s shell of H atom in Au$_7$H$_n$ clusters prefer to form a closed electronic structure with the Hund's rule. And hence the odd-numbered Au$_7$H$_n$ clusters show nonmagnetic according to Pauli repulsion in the case of the s electron pair-

Table 2
The spin multiplicity (M), symmetry type, binding energy per atom E_b^a, binding energy per H-atom E_b^b, binding energy per H-atom E_b^c, and HOMO–LUMO energy gap E_{gap} of the Au$_7$H$_n$ (n = 1–10) clusters (for details see the text).

Cluster	M	Symmetry	E_b^a (eV)	E_b^b (eV)	E_b^c (eV)	E_{gap} (eV)
Au$_7$	2	C_s	2.21	-	–	1.08
Au$_7$H	1	C_s	2.20	2.09	−0.20	0.35
Au$_7$H$_2$	2	C_1	2.22	2.25	−0.05	0.62
Au$_7$H$_3$	1	C_1	2.33	2.61	0.32	1.17
Au$_7$H$_4$	2	C_1	2.35	2.58	0.28	0.87
Au$_7$H$_5$	1	C_1	2.40	2.66	0.37	0.67
Au$_7$H$_6$	2	C_1	2.44	2.71	0.42	1.07
Au$_7$H$_7$	1	C_1	2.50	2.79	0.49	1.51
Au$_7$H$_8$	2	C_1	2.48	2.70	0.41	0.93
Au$_7$H$_9$	1	C_1	2.47	2.67	0.38	1.49
Au$_7$H$_{10}$	2	C_1	2.42	2.56	0.26	0.62

Table 3
Magnetic moment (μ_B) of the H atoms and Au atoms, total magnetic moment of the Au$_7$H$_n$ (n = 1–10) clusters, and atomic averaged charges on H atom by Hirshfeld method.

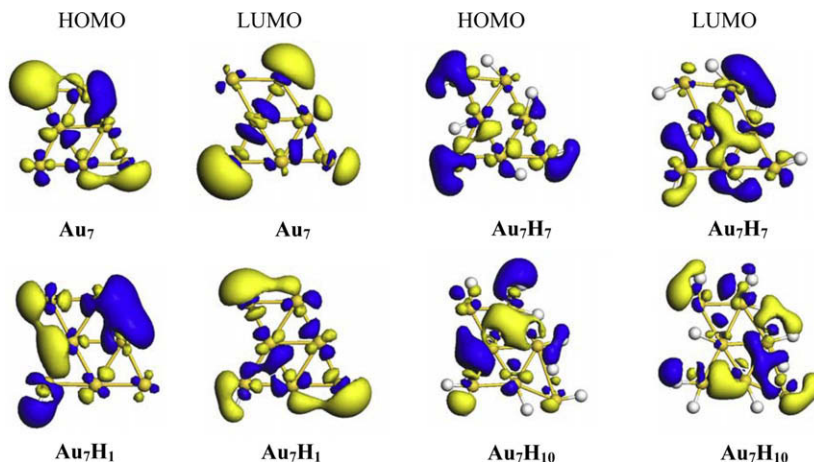| System	Charge (a.u.)	Moment (μ_B)		
		Au$_7$	H$_n$	total
Au$_7$	–	0	0	0
Au$_7$H$_1$	0.082	0	0	0
Au$_7$H$_2$	0.070	0.920	0.080	1
Au$_7$H$_3$	0.082	0	0	0
Au$_7$H$_4$	0.073	0.853	0.147	1
Au$_7$H$_5$	0.076	0	0	0
Au$_7$H$_6$	0.075	0.862	0.138	1
Au$_7$H$_7$	0.074	0	0	0
Au$_7$H$_8$	0.066	0.807	0.193	1
Au$_7$H$_9$	0.067	0	0	0
Au$_7$H$_{10}$	0.052	0.649	0.351	1

Fig. 2. The HOMO and LUMO orbitals of the pure Au_7, Au_7H_1, Au_7H_7, and Au_7H_{10} clusters, yellow indicates that the wave function has a positive sign, while blue indicates a negative sign. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ing. While the even-numbered Au_7H_n clusters has 1 μ_B with one unpaired *s*-electron. Janssens et al. [76] reported that with the delicate energy balance between Hund's rule and electronic shell closing, the quenching of magnetic moments of a transition metal dopant in silver clusters was likely induced by the gain in energy related with the 18-electron shell closing. It is similar to the situation of our results.

It is also worthy to note that there are strong interactions between Au and hydrogen through the charge transfers. We perform Hirshfeld charge analysis for the Au_7H_n clusters and the atomic averaged charges on H atom are listed in Table 3. Hirshfeld charge analysis indicates that H atoms entail a small negative charge to the Au atoms in all Au_7H_n clusters. Which suggests that Au is slightly more electronegative than H, so Au_7 cluster can easily attract electrons from the H adsorption atoms to become negatively charged. These transfers are favorable for electron pairing and adsorption.

Finally, we have performed a detailed analysis of molecular orbitals by examining the electron density of HOMO and LUMO states. Fig. 2 depicts the HOMO and LUMO pictures of the pure Au_7, Au_7H_1, Au_7H_7, and the Au_7H_{10} clusters. From Fig. 2, we can easily see that there is strong *s–d* orbital hybridization in the pure Au_7 cluster. Then the distribution of electron density of the HOMO and LUMO states changes a lot after different number of hydrogen atoms adsorption. For the Au_7H_1, Au_7H_7, and Au_7H_{10} clusters, both the HOMO and the LUMO states are mainly localized around Au atoms, while there is some distribution around H atoms. This indicates that besides the strong hybridization of *s–d* orbital in Au atoms, a degree of hybridization between the *s* orbitals of Au and the s orbitals of H also exists.

4. Conclusion

The geometric structures and magnetic properties of the Au_7H_n ($n = 1$–10) clusters have been systematically studied by using relativistic all-electron density functional theory with generalized gradient approximation. The results are summarized as follows.

(1) Preliminary theoretical results show that the binding energy per atom (E_b^a) of Au_7H_n ($n = 2$–10) clusters is obviously higher than that for pure Au_7, and the Au_7 with seven hydrogen atoms shows much higher stability than the neighboring clusters. This indicates that adsorbing H atoms can stabilize the Au_7 structure. Furthermore, the value of the HOMO– LUMO gap of the Au_7H_7 cluster is much larger than those of the other clusters.

(2) The pronounced even–odd alternation of the magnetic moments is observed in the Au_7H_n systems. All the even-numbered Au_7H_n clusters are found to exhibit magnetic with the same value 1 μ_B. This indicated that the nonmagnetic hydrogen and nonmagnetic gold can combine as a magnetic cluster and the Au_7H_n clusters possess tunable magnetic properties by adding even or odd number of H atoms.

(3) The Hirshfeld charge analysis on the Au_7H_n clusters shows that the H atoms donate a small amount of charge to the Au atoms. The HOMO and LUMO pictures indicate that there are some hybridization between the H atoms and Au_7 in the Au_7H_n clusters.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2009.06.041.

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