Theoretical investigation on structural evolution, energetic stability trend and electronic properties of $Au_nCd(n=1–12)$

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Abstract.   We systematically studied the geometrical structures, relative stabilities, electronic properties and chemical hardness of Au_nCd ($n=1–12$) clusters based on the framework of the density functional theory using relativistic all-electron methods. Low-lying energy structures include two-dimensional and three-dimensional geometries. Especially, all the lowest-energy structures of Au_nCd ($n=1–12$) clusters are inclined to be planar geometries with slight distortion, in which the dopant Cd atom has higher coordination at $n=2–6$, but lower coordination at $n=7–12$. The fragmentation energies, second-order difference of energies, the highest occupied–lowest unoccupied molecular orbital gaps and chemical hardness of Au_nCd and Au_{n+1} exhibit a pronounced even–odd alternations phenomenon in the reverse order This result indicates that the geometrical, electronic and chemical stabilities of Au_nCd with even number of valence electrons are higher than those of the neighbouring Au_nCd with odd number of valence electrons and corresponding Au_{n+1} with odd number of valence electrons. Additionally, $4d$ valence electrons orbital of impurity Cd atom in Au_nCd hardly joins in the orbital interactions compared with $5d$ valence electrons of corresponding Au atom in Au_{n+1}. Au–Cd bonds of Au_nCd clusters are weaker and have more obviously ionic-like characteristics than the corresponding Au–Au bonds of Au_{n+1}.

Keywords. Au_nCd cluster; stability pattern; electronic property; population analysis; ionic-like characteristic

1. Introduction

Heteroatomic nanoclusters have received much attention due to their distinctive catalytic, structural, electronic, magnetic and optical properties.[1–3] There is a growing interest in transition metal-doped gold clusters because transition metal elements can strongly influence the chemical and physical properties of host gold clusters.[4–8] For instance, Bonačić-Koutecký *et al.*[9] studied the structure and electronic properties of bimetallic $Ag_mAu_n(3<(m+n)<5)$ clusters, and found that the charge transfer from Ag to Au plays a dominant role in the structure of the bimetallic clusters. The ground geometric structures, the stability and electronic properties of the small Au_nM ($n = 1–7$, M = Ni, Pd, Pt) clusters were researched,[10] and it was found that the stability of Pd- and Pt-doped gold clusters is evidently changed due to the relative strong bonding interaction contributed by d-electrons, and the d–d and s–d interactions between impurities and gold atoms can markedly modify the electronic properties of doped

gold clusters. The theoretical study[11] of Au_nM^+ clusters (M=Sc, Ti, V, Cr, Mn, Fe, Au; $n\leq9$) discovered that the positive charge of the cationic Au_nM^+ clusters, which is localized mainly in the impurity, and the magnetic and geometrical configurations are strongly correlated with cluster sizes. The geometric and electronic properties of neutral and anionic bimetallic vanadium–gold clusters $Au_nV(n=1–14)$ were theoretically studied,[6] which found that the smaller ground-state clusters of Au_nV prefer 2D geometries up to Au_8V involving a weak charge transfer, but the larger systems bear 3D conformations with a more effective electron transfer from Au to V. Neukermans *et al.*[12] studied element-dependent $3d$ electron delocalization of $3d$-shell atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni), which revealed that the lightest $3d$ elements (Sc, Ti) delocalize their $4s$ and $3d$ electrons, while for the heavier $3d$ elements (Cr, Mn, Fe, Co, Ni), only $4s$ electrons are delocalized. Moreover, a number of researches about the adsorption of doped Au clusters were reported,[13–16] showing the difference of catalysis from the adsorption of pure gold clusters. These examples sufficiently illustrate that the doping metal atom of gold-based mixed cluster has a notable act to change the geometries, chemical

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activities and stabilities of the corresponding gold cluster. Hence, the transition metal-doped gold clusters are expected to design the desired structural, magnetic, and chemical properties for potential applications.[17-19]

The transition metal Cd has extensive applications in electronics, batteries and nuclear technologies and special alloys. An experiment[20] discovered that the Cd_3 and Cd_5 clusters can be constructed as metal−organic frameworks with small multidentate ligands. Another investigation[21] showed that the cadmium perchlorate hydrate is simple, novel and highly efficient catalyst, which synthesizes α-aminophosphonates with excellent yields under mild and solvent-free conditions. In addition, Frischmann et al.[22] found that the stable heptanuclear cadmium cluster complex can organize into tunable metallocavitand capsules with accessible metal sites on their interiors, and these capsule structures are alluring candidates for host–guest catalysis and molecular recognition. Furthermore, nano-sized cadmium compounds have many novel uses. In the experiment,[23] the CdSe nanoparticle is found to behave as a semiconductor material. The development[24] of cadmium-containing nanoparticles, known as quantum dots, show great promise for treatment and diagnosis of cancer and targeted drug delivery, owing to their size-tunable fluorescence and ease of functionalization for tissue targeting. Especially for Cd–Au system, 'the Shape Memory Effect' (SME) in gold cadmium (AuCd) alloy was discovered early in 1932, which is the first record of the shape memory transformation. Therefore, many chemists and physicists have drawn much attention to the properties of cadmium gold alloy. Particularly, a few studies demonstrated that nanometer-sized Au–Cd particles exhibit even better properties at small scale than their bulk counterparts. Asaka et al.[25] found that the β_2 phase in the Au–Cd nanosized alloys becomes stable and the martensitic transformation temperatures are lowered with size decreasing, which is much different from the corresponding bulks. Later, it was also observed that the martensitic transformation start temperature, Ms, of nanometer-sized AuCd particles was determined to be about 49 K and thus drastically lesser than that of the AuCd bulk alloys.[26] Although Au–Cd nanosystems have wide applications, the systematical and substantial studies on Cd-doped Au nanosystem are still relatively rare. It is well known that Au–Cd clusters of small size can establish a good bridge for the overall realization of a Cd-doped Au nanosystem.

On the other hand, cadmium and its congeners (Zn and Hg) are not always considered transition metals, in that they do not have partly filled d or f electron shells in the elemental or common oxidation states.[27]

However, gold atom has a completely filled d-shell and one valence s electron in the electronic ground state, and therefore Au clusters often are regarded as simple metal clusters similar to alkali metal clusters. Considering that cadmium, including its congeners (Zn and Hg), and gold atoms have distinctive valence electronic configurations compared to other transition metals, the impurity Cd atom including Hg and Zn inevitably influences the stability and electronic structure of bare gold clusters when doping Cd or its congener atom. Particularly, previous reportedly experimental and theoretical investigations of Au clusters doped with Hg and Zn have indicated that the electronic and geometric characteristics of Hg or Zn-doped gold clusters are extraordinary and different from another transition metal-doped gold system. The photoelectron spectra of Au_nZn were studied experimentally through anion photoelectron spectroscopy,[28] exhibiting even–odd alternation of electron affinities and characteristic spectral changes with cluster size. In the theoretical research[29] on $Au_nZn(n = 1–6)$, it was revealed that all the lowest-energy isomers of Au_nZn clusters and their cations are 2D structures very similar to those of pure Au cluster. Likewise, Au_nHg cluster was investigated using the relativistic effective core potential model,[30] also showing that equilibrium geometries prefer one- and two dimensional structures without nonplanar structures in the case of small cluster size. A study[18] discovered that the s–p orbital overlap of the HOMO of Au_nZn^+, which is responsible for the bonding character between Au and Zn in the HOMO, has a stabilizing effect on the HOMO, and the energy lowering of the HOMO results in a large HOMO–LUMO energy gap of the Au_nZn^+ clusters. In a study[31] on the Au_nHg_m system, it is found that all local minima and transition structures of Au_nHg_m clusters are planar. Meanwhile, this article also pointed out that Au_2Cd structure prefers a linear conformation with terminal gold atoms. Furthermore, in these investigations, we found that when cluster size is smaller, the energy minima states of the Au_nZn/Hg neutral or ionic clusters usually prefer two dimensional structures. Recently, a density functional comparison study[32] was presented on Au_{32} cluster doped with group IIB atoms, showing that the HOMO−LUMO gap of the Au_{32} cage doped with Zn, Cd or Hg atom all remain almost similar to that of the Au_{32} cage for high-symmetry clusters, and it decreases for the low-symmetry isomers. Here, considering that Cd, Hg and Zn all possess same valence electronic configuration s^2d^{10}, interesting questions are presented: Likewise, for cadmium from the group IIB, will the lowest-energy states of Au_nCd still retain planar structures? How will the electronic and chemical properties of pure gold cluster be changed obviously after

doping a cadmium atom and then will these properties of Cd-doped gold clusters be similar to those of Zn or Hg-doped gold systems?

In our study, we systematically investigate the influence of impurity Cd atom on the geometrical structures, relative stabilities, electronic properties, interaction between the dopant and host atoms and chemical hardness of Au$_n$Cd ($n = 1-12$) clusters, and the whole calculation is based on density functional theory with the generalized gradient approximation at BP level and all-electron scalar relativistic effects. In comparison with pure gold clusters, we hope to find the evolutionary patterns and characteristics with the growth of the cluster size. We expect our research to be constructive in understanding the influence of material structure on its properties and guide further theoretical and experimental studies

2. Computational Details

The geometrical structures and electronic properties of Au$_n$Cd ($n = 1-12$) clusters are calculated using the spin-polarized density functional theory (DFT) in the DMOL^3 program package.[33–35] The generalized gradient approximation (GGA) in the Becke exchange plus Perdew correlation (BP)[36,37] functional is chosen in the calculations. A double-numerical basis set including d-polarization functions (DNPs) are adopted for the description of the electronic wave functions. Due to heavy elements of gold and cadmium,[33,38–46] the all-electron scalar relativistic (AER) method is used in our work for greater accuracy of calculations. Meanwhile, the convergence criteria are set with 0.002 Ha/Å for the forces, 0.005 Å for the displacement, and10^{-5} Ha for the energy change in our calculation. To ensure the reliability of initial structures, first, we re-optimized the structures of pure gold clusters in previous studies[45,47–49] with the same methods and same parameters. And then, based on these optimized equilibrium geometries of pure gold clusters, we can construct numerous possible initial structures of Au$_n$Cd clusters by a Cd atom replacing one gold atom at every possible nonequivalent site or by adding Cd atom directly on each possible non-equivalent site in the Au$_{n+1}$ cluster. In the meantime, we also refer to the structures available of doped gold cluster in previous literatures.[9–11,29,49,50] These possible initial energy structures of Au$_n$Cd include one, two and three-dimensional geometries. Moreover, all initial structures are optimized by relaxing the atomic positions fully without any symmetry constraints. Additionally, the harmonic vibrational frequencies of all configurations are computed in order to confirm all the optimized structures that correspond to the local energy minima.

To examine the reliability of our scheme, we calculate the bond-length, dissociation energy and vibrational frequency of Au$_2$, Cd$_2$ and AuCd dimers for comparison with the corresponding experimental and theoretical data. In our calculations, the bond-length, dissociation energy and vibrational frequency are 2.489 Å, 2.296 eV and 181.5 cm^{-1} for Au$_2$ dimer and 3.59 Å, 0.0306 eV and 30.7 cm^{-1} for Cd$_2$ dimer, respectively. These calculated values are in good accordance with the corresponding experimental results[51–56] of 2.47 Å, 2.29 eV and 190.9 cm^{-1} for Au$_2$ and 4.07 Å, 0.0378 eV and 23.0 cm^{-1}for Cd$_2$, respectively. Additionally, for AuCd dimer, the dissociation energy of 1.02 eV, bond-length of 2.630 Å and frequency of 151 cm^{-1} in our work are consistent greatly with previous DFT calculation results[57] of 0.75 eV, 2.688 Å and 138 cm^{-1}.Thus, we can confirm that our calculations are precise and valid enough to investigate the properties of Cd-doped gold systems.

3. Results and Discussion

3.1 *Geometrical structure*

The lowest-energy structures of Au$_{n+1}$ and the typical and low-lying structures of Au$_n$Cd ($n = 1-12$) are shown with the symmetry and relative energy of these geometries in figure 1. Meanwhile, isomers are arranged according to the order of energies from low to high.

With respect to Au$_2$Cd clusters, the lowest-energy state 2a with D$_{\infty h}$ symmetry is a linear structure generated by a Cd atom doubly bonding with two gold atoms. The C$_{\infty v}$ isomer 2b is also a linear structure such that a Cd atom is added to one gold atom of Au$_2$ cluster. The isomer 2c is a triangular C$_{2v}$ structure produced by a Cd atom substituting an Au atom of Au$_3$ cluster.

As for Au$_3$Cd clusters, four low-lying isomers are optimized to find the energy minima. The lowest-energy state 3a and the metastable state 3b are rhombic structures with C$_{2v}$ symmetry, which are generated by a Cd atom replacing a gold atom at the triply and doubly coordinated sites in Au$_4$ cluster, respectively. The isomer 3c is regarded as hanging a Cd atom on a possible equivalent site of Au$_3$ cluster. The isomer 3d is obtained by a Cd atom triply bonding with three gold atoms.

For Au$_4$Cd clusters based on the trapezoid structure of the pure Au$_5$ cluster, the lowest-energy 4a, isomers 4b and 4c are obtained by substituting a Cd atom for one gold atom, respectively, at the triply, doubly and
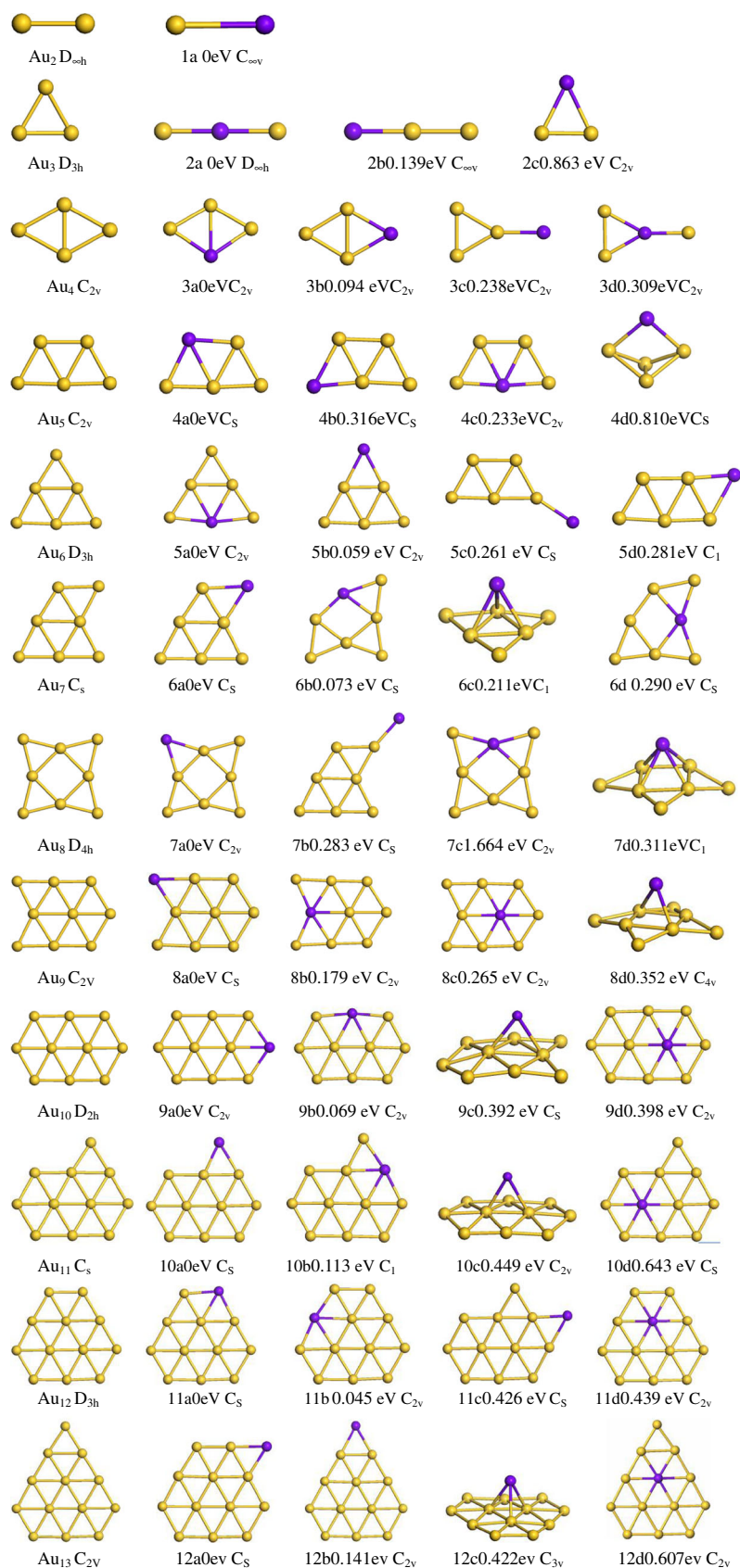
Figure 1. Optimized structures for Au_nCd ($n = 1-12$) clusters, and the ground-state structures of pure gold clusters are shown with symmetry, and relative energy The golden and purple balls represent Au and Cd atoms, respectively.

quadruply coordinated sites in Au$_5$ cluster. The isomer 4d is a 3D structure generated by placing a Cd atom above the plane of Au$_4$ cluster. Compared to their initial structures, the geometrical shapes of 4a, 4b and 4c are changed slightly, while the isomer 4d is changed relatively obviously.

In the case of Au$_5$Cd clusters, the lowest-energy isomer 5a is a planar C$_{2v}$ structure, which is a triangle that still resembles the Au$_6$ cluster. In the lower isomer 5b, the Cd atom is located at the doubly coordinated site in Au$_5$Cd, regarded as the metastable state. Structures of these two isomers are only minimally changed after optimization. The isomer 5c is obtained by hanging a Cd atom onto the possible non-equivalent site of Au$_5$ cluster. The isomer 5d which is produced by a Cd atom doubly bonding with Au$_5$ cluster, is 0.281 eV less stable than 5a.

For the Au$_6$Cd cluster, the lowest-energy isomer 6a has a planar Cs structure, which is similar to a capped triangular structure of Au$_7$. Initial structures of 6b and 6d are obtained by replacing a gold atom with a Cd atom at triply and quadruply coordinated sites, respectively. Additionally, the dopant Cd factures an Au–Au bond inside their initial structures after optimizing. The isomer 6c is a 3D structure generated by placing a Cd atom on the plane of Au$_6$.

About the Au$_7$Cd cluster, the lowest-energy C$_{2v}$ isomer 7a is a tera-edge-capped rhombus geometry with a Cd atom at the doubly coordinated site. The C$_S$ isomer 7b with one Au–Cd bond is 0.283 eV less stable than isomer 7a. The isomer 7c is produced by a Cd atom substituting an Au atom at the quadruply coordinated site in Au$_8$ cluster. The highest-energy structure 7d is a 3D structure, which is produced by placing a Cd atom above the planar structure of Au$_6$ cluster.

With respect to the Au$_8$Cd clusters, several typical low-lying isomers are optimized to find the energy minima. A conformation 8a with C$_S$ symmetry is at the lowest-energy structure. Isomers 8b and 8c are obtained by a Cd atom replacing one gold atom of Au$_9$ cluster, respectively, at the quintuply and sextuply coordinated sites. The 3D isomer 8d is generated by capping a Cd atom above the plane of Au$_8$ cluster. And the initial structure of 8d is bent and up-swelled after optimization.

With regard to the Au$_9$Cd cluster, the lowest-energy structure 9a, metastable configurations 9b and 9d can be obtained by substituting Cd for one gold atom at the triply, quadruply or sextuply coordinated site in Au$_{10}$ cluster, respectively. The isomer 9c is a 3D structure generated by capping a Cd atom above the plane of Au$_9$ cluster. Furthermore, the 3D initial structure of 9c is bent upwards after optimization, which is different from the 2D initial structures of 9a, 9b and 9d.

With regard to the Au$_{10}$Cd cluster, the lowest-energy state 10a has a planar C$_S$ geometry obtained by the impurity Cd atom replacing a gold atom at the doubly coordinated site in the Au$_{11}$ cluster. Isomer 10b is produced by a Cd atom substituting a gold atom with quadruple coordination number in the Au$_{11}$ cluster. Isomer 10c is a 3D structure obtained by capping a Cd atom above the planar structure of Au$_{10}$ cluster, and the impurity Cd atom draws Au$_{10}$ upwards. The energy isomer 10d is the planar structure obtained by a Cd atom replacing a gold atom at sextuply coordinated site in Au$_{11}$ cluster.

With respect to the Au$_{11}$Cd cluster, the lowest-energy structure 11a is produced by a Cd atom replacing an Au atom with the triply co-ordinated number in Au$_{11}$Cd. The isomer 11b is 0.045 eV less stable than 11a, which is obtained by a Cd atom substituting an Au atom at the *quadruply* coordinated site in Au$_{12}$. The isomer 11c is regarded as placing a Cd atom at a side of the Au$_{11}$ cluster with two Au–Cd bonds. The isomer 11d is obtained by a Cd atom replacing an Au atom at the sextuply coordinated site in the Au$_{12}$ cluster. Besides, the shapes of 11a, 11b and 11d still resemble a pentacapped hexagon structure of a pure Au$_{12}$ cluster.

For the Au$_{12}$Cd clusters the C$_S$ isomer 12a is the lowest-energy structure produced by a Cd atom doubly bonding with Au$_{12}$. The metastable state 12b is generated by a Cd atom substituting an Au atom at the doubly site in Au$_{13}$. The isomer 12c is a 3D C$_{3v}$ structure obtained by capping a Cd atom above the planar structure of Au$_{12}$ cluster, and this geometrical structure of 12d is bent to some extent. The isomer 12d with six Au–Cd bonds is generated by a Cd atom replacing a gold atom at the highest coordinated site in the Au$_{13}$ cluster.

According to the analysis on geometries of Au$_n$Cd, for lowest-energy geometries of Au$_n$Cd, the dopant Cd atom has a higher coordination number at $n = 2$–6 but a lower coordination number at $n = 7$–12. In the meantime, after optimizing, 3D structures are distorted obviously, while 2D structures are distorted slightly and still resemble initial structures. Moreover, all the lowest-energy structures of Au$_n$Cd clusters are 2D structures, signifying that scalar relativistic effects significantly influence the clusters composed of heavy elements.[33,38,42,45,46] Usually, the scalar relativistic effect is obvious and cannot be neglected in gold clusters or gold-based mixed metal clusters. The strong scalar relativistic effect caused by the high-speed motion of outer shell electrons and the spin–orbit coupling leads to the shrinking size of the *s* orbitals and therefore enhances the *s–d* hybridization and causes the frontier orbitals to disperse. Furthermore, the strengthened *s–d* hybridization lowers the corresponding energy

level and enhances the shielding effect of inner electrons. This favours planar bonding and thus drives the planarity of clusters. In addition, the lowest-energy structures in the previous literatures[31,45,58] are found to be planar geometries likewise, which is similar to the conclusion of our works.

3.2 *Stability trends*

The average binding energy of clusters is a measure of cluster stability, which is defined as

$$E_b \left(\mathrm{Au}_n \mathrm{Cd} \right) = \left[nE \left(\mathrm{Au} \right) + E \left(\mathrm{Cd} \right) \right.$$
$$\left. -E \left(\mathrm{Au}_n \mathrm{Cd} \right) \right] / \left(n + 1 \right)$$
$$E_b \left(\mathrm{Au}_{n+1} \right) = \left[(n+1)E \left(\mathrm{Au} \right) - E \left(\mathrm{Au}_{n+1} \right) \right] / \left(n+1 \right),$$

where $E(\mathrm{Au}_n\mathrm{Cd})$, $E(\mathrm{Au}_{n+1})$, $E(\mathrm{Au})$ and $E(\mathrm{Cd})$ represent the total energies of the lowest-energy structures for $\mathrm{Au}_n\mathrm{Cd}$, Au_{n+1}, Au and Cd, respectively.

As seen from figure 2, we can see that the tendency for a similar change of the average binding energy on both $\mathrm{Au}_n\mathrm{Cd}$ and Au_{n+1}. The average binding energy of pure gold cluster and gold cluster doped with Cd atom increases gradually with increase in cluster size, meaning the cluster stability is enhanced when the cluster size grows. Besides, the average binding energy of $\mathrm{Au}_n\mathrm{Cd}$ shows a monotonically increasing pattern, namely the stability of $\mathrm{Au}_n\mathrm{Cd}$ gradually increases and reaches maximum $\mathrm{Au}_{12}\mathrm{Cd}$. This reflects the fact that the larger the size of the cluster, the more stable is the cluster.

To further explore the stabilities of the $\mathrm{Au}_n\mathrm{Cd}$ clusters and the size-dependent properties, the fragmentation energy is calculated and plotted in figure 3. The
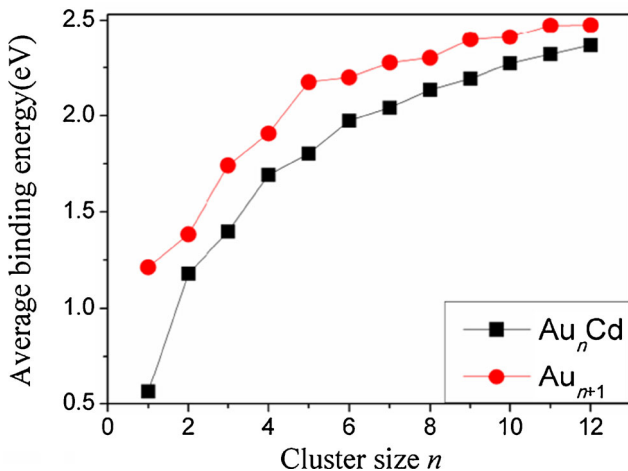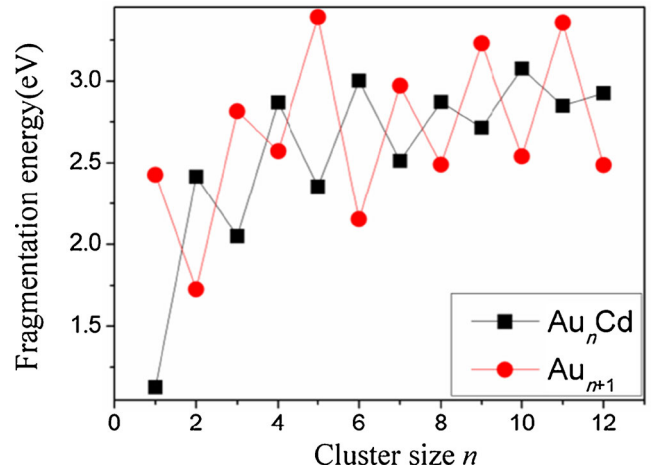

Figure 3. Size dependence of the fragmentation energies.

fragmentation energy can be defined by the following formulas:

$$E_f \left(\mathrm{Au}_{n+1} \right) = \left[E \left(\mathrm{Au}_n \right) + E \left(\mathrm{Au} \right) - E \left(\mathrm{Au}_{n+1} \right) \right]$$
$$E_f \left(\mathrm{Au}_n \mathrm{Cd} \right) = \left[E \left(\mathrm{Au}_{n-1} \mathrm{Cd} \right) + E \left(\mathrm{Au} \right) - E \left(\mathrm{Au}_n \mathrm{Cd} \right) \right].$$

From figure 3, we can find that the fragmentation energies of $\mathrm{Au}_n\mathrm{Cd}$ and Au_{n+1} clusters both show the obvious even–odd oscillation in the reverse order with increase in cluster size. The values of even-numbered $\mathrm{Au}_n\mathrm{Cd}$ are larger than those of odd-numbered $\mathrm{Au}_n\mathrm{Cd}$ and corresponding even-numbered Au_{n+1}, signifying that an impurity Cd atom can change the stable pattern of pure gold clusters, and namely even-numbered $\mathrm{Au}_n\mathrm{Cd}$ are more stable than odd-numbered $\mathrm{Au}_n\mathrm{Cd}$ and even-numbered Au_{n+1}. Second-order difference of cluster energy, as a function of cluster size, is a greatly sensitive parameter to reveal the relative stability of cluster. We define the relevant formulas as follows:

$$D_2 E(n) = E \left(\mathrm{Au}_{n+1} \right) + E \left(\mathrm{Au}_{n-1} \right) - 2E \left(\mathrm{Au}_n \right)$$
$$D_2 E(n) = E \left(\mathrm{Au}_{n+1} \mathrm{Cd} \right) + E \left(\mathrm{Au}_{n-1} \mathrm{Cd} \right) - 2E \left(\mathrm{Au}_n \mathrm{Cd} \right),$$

As can be seen in figure 4, we can also observe that $\mathrm{Au}_n\mathrm{Cd}$ has opposite even–odd oscillation, with Au_{n+1} on second-order difference of cluster energy with the increase in cluster size. This means that the presence of Cd changes the relative stability pattern of Au_{n+1}, namely the even-numbered $\mathrm{Au}_n\mathrm{Cd}$ are relatively more stable than the corresponding Au_{n+1} and neighbouring odd-numbered $\mathrm{Au}_n\mathrm{Cd}$.

According to the above discussion, we show that $\mathrm{Au}_{2,4,6,8,10,12}\mathrm{Cd}$ have pronouncedly relative stability compared to the neighbouring odd-numbered ones and corresponding even-numbered Au_{n+1}. This case is better explained by the electron paired effect. In the
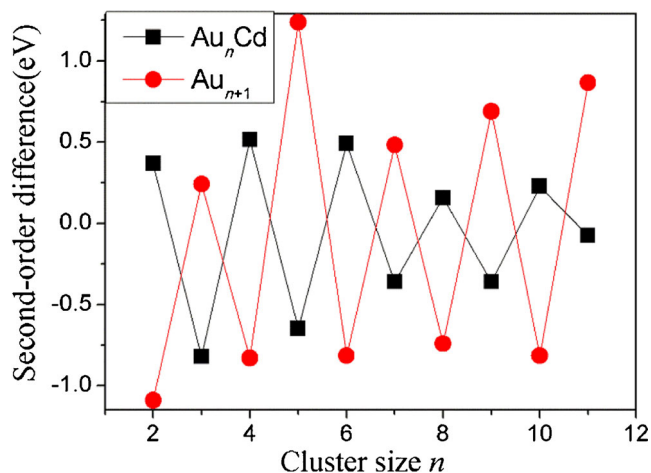

Figure 2. Size dependence of the atomic average binding energies.

Figure 4. Size dependence of the second-order difference of energies.

Figure 5. Size dependence of the HOMO–LUMO energy gaps.

meantime, by comparison between the electronic structures of Au$_n$Cd and Au$_{n+1}$ we can find that the even-numbered Au$_{n+1}$ systems have odd number of valence electrons and the odd-numbered Au$_{n+1}$ systems have even number of valence electrons; however the even-numbered Au$_n$Cd systems possess even number of valence electrons and the odd-numbered Au$_n$Cd systems possess odd number of valence electrons. This suggests that the occurrence of dopant Cd atom changes the electronic structures of host gold clusters. In the following section, we further analyze the influence of impurity Cd atom on the electronic properties of host gold clusters.

3.3 *Electronic properties*

The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is a useful quantity on electronic stability of clusters. The larger the HOMO–LUMO gap, the higher the energy required to excite the electrons from valence band to conduction band, which means stability of electronic structure is higher.

As shown in figure 5 we can observe that Au$_n$Cd and Au$_{n+1}$ have obvious even–odd oscillations for the HOMO–LUMO gap. The Au$_n$Cd clusters with even number of valence electrons have comparatively larger energy gap than the neighbouring Au$_n$Cd with odd number of valence electrons and corresponding Au$_{n+1}$ with even-number of valence electrons, meaning that the doped clusters with even number of valence electrons have higher electronic stability than neighbouring Au$_n$Cd with odd–number of valence electrons and corresponding Au$_{n+1}$ with even-number of valence electrons. This indicates that the presence of dopant
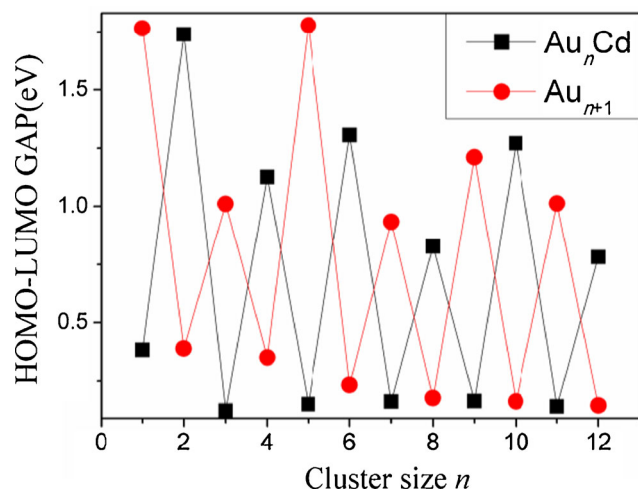
Cd atom obviously changes the electronic structure of Au$_{n+1}$. Moreover, this situation reflects that the system with even-number of valence electrons has higher stable electronic structure than the adjacent system with odd number of valence electrons.

To further reveal the influence of the electron properties caused by the impurity atom Cd, we implement the thorough Mulliken population analysis summarized in table 1 for pure Au$_{n+1}$ clusters and Au$_n$Cd clusters. The configurations of single Au and Cd atoms are $5d^{10}6s^1$, $4d^{10}5s^2$ of valence electrons and empty $5p$, $6p$ orbitals respectively. In terms of the Mulliken population analysis in table 1, the Cd atom in Au$_n$Cd cluster obviously has positive charge, signifying that the charges transfer from Cd atom to Au atoms, and that the Cd atom acts as an electronic donor, while most Au atoms act as electronic hosts. With regard to the impurity Cd atom, we figure out that the $4s$ states lose 0.412–0.870 electrons, while the $5p$ states receive 0.120–0.445 electrons for Au$_n$Cd clusters. Particularly, the contribution of the $4d$ states is 0.001–0.006 electrons as nearly zero, and thus it can be neglected. These indicate that there is strong $s–p$ hybridization in the Cd atom or between the Cd atom and Au atoms in Au$_n$Cd, which differs from the spd hybridization in the corresponding Au of Au$_{n+1}$. Besides, 9.997–10.005 electrons occupy the $4d$ orbital of Cd atoms in Au$_n$Cd, signifying that the $4d$ orbital of dopant Cd atom as well as the $5d$ orbital of Au atoms in Au$_n$Cd clusters are dominant core orbitals.

The HOMO and the LUMO are plotted in figure 6. We can clearly observe that for Au$_n$Cd with even number of valence electrons, HOMO as well as LUMO is a doubly degenerate state. The even-numbered Au$_n$Cd has an even number of s valence electrons and the paired s valence electrons with reverse spins doubly

Table 1. Calculated charges populations of 4*d*, 5*s*, 5*p* orbitals of Cd in Au$_n$Cd clusters and 5*d*, 6*s*,6*p* orbitals of corresponding Au in Au$_{n+1}$ clusters.

	Au$_n$Cd				Au$_{n+1}$			
n	4*d*	5*s*	5*p*	Cd	5*d*	6*s*	6*p*	Au
1	9.997	1.543	0.205	0.255	9.870	0.863	0.069	0.198
2	9.997	1.588	0.120	0.295	9.782	0.871	0.193	0.154
3	9.999	1.199	0.411	0.391	9.760	0.802	0.337	0.101
4	9.997	1.477	0.228	0.298	9.622	0.879	0.440	0.059
5	10.005	1.130	0.445	0.420	9.664	0.889	0.408	0.039
6	9.998	1.577	0.208	0.217	9.556	0.824	0.542	0.078
7	9.994	1.430	0.252	0.324	9.620	0.914	0.451	0.015
8	9.996	1.457	0.252	0.295	9.526	0.786	0.602	0.086
9	10.001	1.333	0.344	0.322	9.516	0.775	0.613	0.096
10	9.995	1.475	0.233	0.297	9.473	0.817	0.639	0.071
11	9.998	1.301	0.358	0.343	9.471	0.827	0.642	0.060
12	9.996	1.489	0.226	0.289	9.473	0.834	0.630	0.063

occupy the HOMO, while the odd-numbered cluster has an unpaired *s* valence electron and the HOMO is singly occupied. The electron in a doubly occupied HOMO feels a stronger effective core potential because the electron screening is weaker for electrons in the same orbital than for inner-shell electrons. Hence, the binding
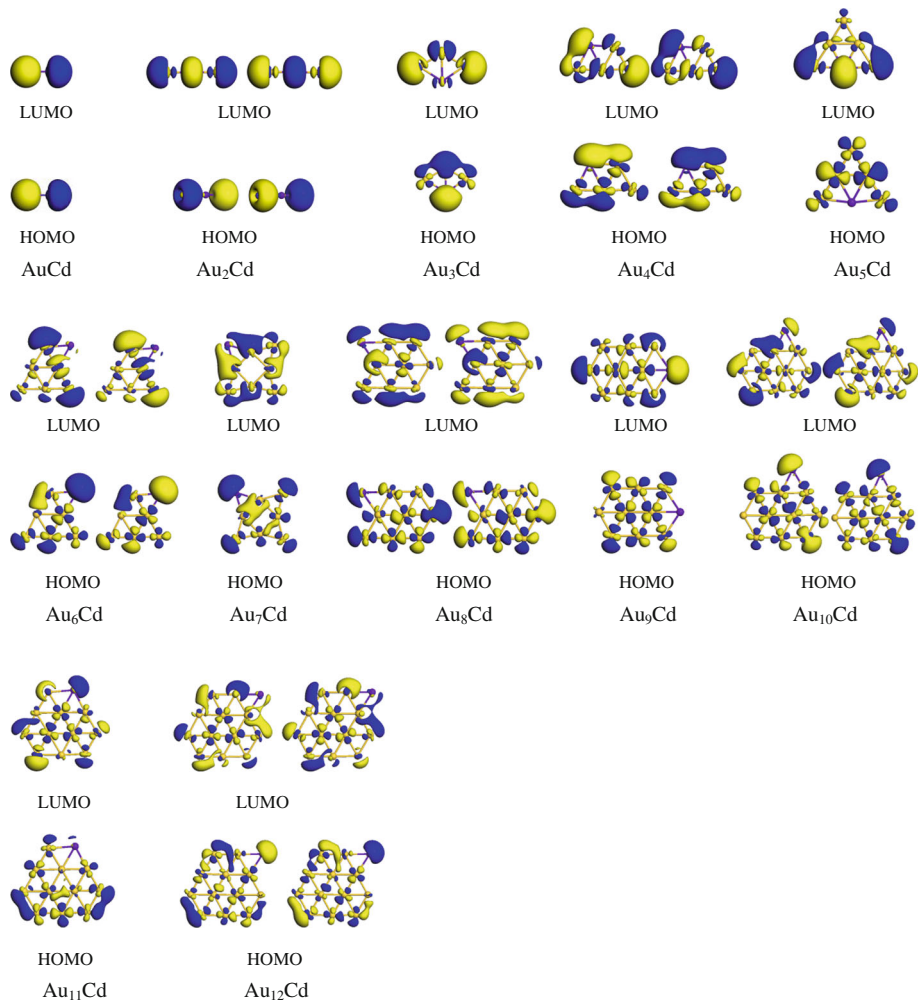

Figure 6. Molecular orbitals HOMO and LUMO for Au$_n$Cd.

energy of a valence electron in even-numbered Au$_n$Cd is larger than that of odd-numbered one. This further verifies that the stability of even-numbered Au$_n$Cd is higher than that of odd-numbered ones. Besides, due to the presence of dopant Cd atom, the distribution of electron cloud of Au$_n$Cd is no longer symmetric, uniform and well-mixed. Specifically, the delocalization of HOMO and LUMO is impaired obviously. In particular, for HOMOs of Au$_{2,5,9,11}$Cd systems, relatively little electron cloud appears around the impurity Cd atom. Additionally, it is noted that the overlap of electron cloud between the frontier orbitals of Cd and Au in Au$_n$Cd shows the pronounced *s–p* hybridization. Furthermore, the *s–p* overlap and the relativistic effects in Au$_n$Cd enhance the planarity of low-lying structures.

With the aim of having a clear view of the electron transferring between the dopant Cd and Au atoms, the electron deformation densities of several representative Au$_n$Cd and corresponding Au$_{n+1}$ for the lowest-energy structures as examples are plotted in figure 7 and the blue area represents electron accumulations. The electron deformation density in Au$_n$Cd clusters shows that just a few electrons distribute around the Cd atom and in the interval of Au–Cd bonds compared with electron distributions around adjacent Au atoms and in the interval of Au–Au bonds. This means more obviously ionic-like characteristics in the Au–Cd bond than that in the Au–Au bond. By contrast with pure Au$_{n+1}$ clusters, the electron accumulation between the Cd and Au atoms markedly decreases when the impurity Cd atom replaces an Au atom. This case indicates that a weaker Au–Cd interaction exists in Au$_n$Cd than the corresponding Au–Au interaction in Au$_{n+1}$.
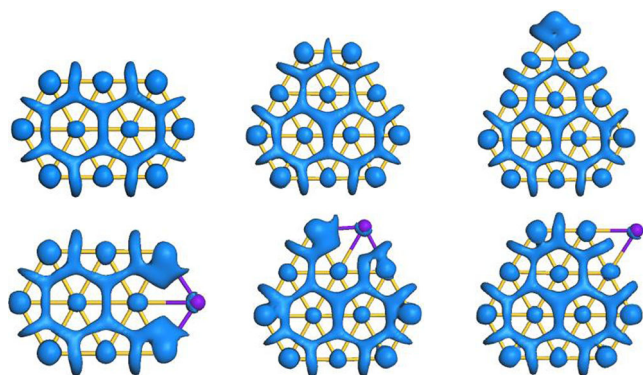
3.4 *Chemical reactivity*

Chemical hardness is regarded as a crucial parameter to assess reactivity of a system, where (η) may be approximated as

$$\eta = (VIP - VEA)/2,$$

where *VIP* and *VEA* are vertical ionization potential and the vertical electron affinity, respectively. As can be seen in figure 8, the chemical hardness of Au$_n$Cd with even number of valence electrons is higher than that of the neighbouring Au$_n$Cd with odd number of valence electrons and corresponding Au$_{n+1}$. Therefore, according to the principle of maximum hardness (PMH),[59] we can infer that Au$_n$Cd with even number of valence electrons have higher chemical stability than neighbouring Au$_n$Cd with odd number of valence electrons and corresponding Au$_{n+1}$. This demonstrates the impurity Cd atom can change the chemical stability model of pure gold cluster. In other words, the chemical reactivity of Au$_n$Cd with odd number of valence electrons is stronger than that of corresponding Au$_{n+1}$ and neighbouring Au$_n$Cd with even number of valence electrons. This phenomenon may be explained as an unpaired valence electron of Au$_n$Cd with odd number of valence electrons leading to these clusters being strongly reactive, so the chemical stability of odd-numbered Au$_n$Cd is greatly lower than that of even-numbered ones.

It is found that the odd–even variation of chemical hardness is greatly consistent with the odd–even variations of the HOMO–LUMO energy gap, fragmentation and second order difference energies. These phenomena reveal that since there is the valence paired effect in Au$_n$Cd system, Au$_{2,4,6,8,10,12}$Cd system with even number of valence electrons are markedly more
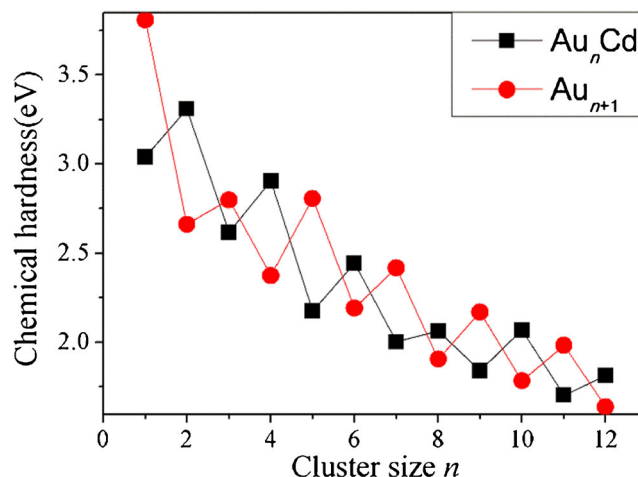

Figure 7. Comparison on electron deformation density of Au$_n$Cd clusters and corresponding Au$_{n+1}$ clusters for the lowest-energy structures with surface isovalue 0.023 e/Å̀3 for molecular orbital plotting.

Figure 8. Size dependence of chemical hardness.

stable than adjacent Au_nCd system with odd number of valence electrons and corresponding Au_{n+1} with odd number valence electrons geometrically, electronically and chemically.

4. Conclusions

We have systematically investigated the low-energy geometrical structures, growth-pattern behaviours, relative stabilities, chemical stabilities and electronic property of Au_nCd clusters by applying all-electron relativistic density functional theory with generalized gradient approximation.

1) In all geometrical structures, most low-lying energy structures are inclined to be 2D structures that have slight deformation and resemble the corresponding initial geometrical structures because of the strong scalar relativistic effects in Au_nCd clusters. Notably, for the lowest-energy structures the dopant Cd atom has higher coordination number at $n = 2$–6, while it has lower coordination number at $n = 7$–12 and is located at the edge of structures.

2) The fragmentation energies, second-order difference of energies and HOMO–LUMO energy gaps of Au_nCd and Au_{n+1} show markedly odd–even oscillations in the reverse order. Namely, the geometrical and electronic stabilities of Au_nCd with even number of valence electrons are higher than those of neighbouring Au_nCd and corresponding Au_{n+1} with odd number of valence electrons; besides, Au_nCd with odd number valence of electrons are chemically less stable and more reactive than corresponding Au_{n+1} clusters and neighbouring Au_nCd with even number of valence electrons. These imply that the presence of impurity Cd atom pronouncedly changes the stability trend of host gold clusters.

3) Mulliken population discovered that the Cd atom is the electronic donor and most Au atoms are the electronic hosts, and that there is the obvious charge transfer from the Cd atom to Au atoms for Au_nCd. Meanwhile, for the impurity Cd atom, the $4s$ orbitals lose 0.412–0.870 electrons, $4p$ orbitals receive 0.120–0.445 electrons, and the contribution of the $4d$ orbitals is 0.001–0.006 electrons as nearly zero. Hence it is found that the impurity obviously alters the electronic structure of host gold clusters. Especially, there are the strong s–p orbital interaction in the Cd atom or between the Cd atom and Au atoms in Au_nCd, which differs from the spd orbital interaction in the corresponding Au of

Au_{n+1} Besides, the less electron accumulation in the intervals between Cd and Au atoms indicates that Au–Cd bonds of Au_nCd clusters are weaker and have more obviously ionic-like characteristics than corresponding Au–Au bonds of Au_{n+1}.

Acknowledgements

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