Eur. Phys. J. D **43**, 15–18 (2007)
DOI: 10.1140/epjd/e2007-00059-y

**THE EUROPEAN
PHYSICAL JOURNAL D**

Global structure optimization study on Au_{2-20}

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Received 23 July 2006 / Received in final form 2 October 2006

Abstract. The geometries and electronic properties of the most stable small Au_n clusters with $n = 2$ to 20 are presented. An intensive search for low-energy minima of Au_n clusters was carried through using a density-functional tight-binding method combined with genetic algorithms for an unbiased global structure optimization. The structural and energetic properties of the small gold clusters are compared with those of planar Au_n clusters with $n = 5$ to 15.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.Bc Clusters

1 Introduction

Clusters formed by gold atoms are among the most intensively studied clusters, partly because they can be used in electronic devices [1], as nanomaterials [2], and as catalysts [3–6]. As a consequence, there exist many theoretical studies on the electronic and structural properties is Au_n clusters.

For instance, Häkkinen and Landman investigated neutral and anionic gold clusters Au_{2-10} using the density-functional theory with scalar-relativistic ab initio pseudopotentials and a generalized gradient approximation [7]. Wang et al. studied lowest-energy gold clusters with size from 2 to 20 [8], whereas Walker [9] performed density functional theory calculations on neutral and cationic gold clusters with up to nine atoms. Small gold clusters show catalytic activity, like Au_8 supported on MgO that can catalyze the oxidation reaction of CO to CO_2, and Au_{10} is used to catalyze CO oxidation on a TiO_2 support. It has also been suggested that the surface roughening plays an important role in the catalytic activity, since nonplanarity of gold clusters localizes the electron density and thus promote reactivity.

For an understanding of all the properties of small gold clusters it is mandatory to have a detailed information on the structural and electronic properties of these systems. Although much effort has been invested in this endeavour, there are still many open questions, of which one interesting one is at what size the gold cluster changes from 2D to 3D geometry [10].

Since the number of structural degrees of freedom of an Au_n cluster equals $3n - 6$, since the number of inequivalent (meta-)stable structures grows essentially exponentially with n, and since the computational demands for a single structure scales as n^k with $k \geq 3$, theoretical studies on Au_n clusters are in one or another way biased. Either many structures are studied with less accurate methods, or few, selected, structures are studied with more accurate methods.

As a typical example we mention the studies of Garzón et al. [11] and of Michaelian et al. [12] who used global optimization methods (based on genetic algorithms) combined with the simple Gupta potential for the description of interatomic interactions. The optimized structures were subsequently studied further using density functional calculations.

In the present work, we apply a parameterized density-functional tight-binding method combined with an unbiased global minimum search to determine the lowest energy structures of gold clusters with from 2 to 20 atoms. In contrast to previous unbiased structure optimizations, our total-energy method includes electronic degrees of freedom, making it, we believe, more accurate. Because of the recent interest in planar gold clusters [13–15], we also included such ones in our study, together with the icosahedral Au_{13} and tetragonal Au_{20} clusters.

2 Computational method

By using a parameterized tight-binding density-functional method combined with genetic algorithms we have determined the global total-energy-minimum structures for gold clusters containing up to 20 atoms. The planar gold clusters with $n = 5$–15 and the icosahedral Au_{13} and tetragonal Au_{20} clusters were relaxed locally.

The density-functional tight-binding method [16–18] is based on the density functional theory of Hohenberg and Kohn in the formulation of Kohn and Sham. Moreover,

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the Kohn-Sham orbitals ψ_i of the system of interest are expanded in terms of atom-centered basis functions $\{\phi_j\}$,

$$\psi_i(\mathbf{r}) = \sum_j c_{ij}\phi_j(\mathbf{r}). \tag{1}$$

This gives the secular equations

$$\sum_m c_{im}(h_{mn} - \epsilon_i S_{mn}) = 0, \tag{2}$$

where the matrix elements of Hamiltonian h_{mn} and the overlap matrix elements S_{mn} are defined as

$$\begin{aligned} h_{mn} &= \langle \phi_m | \hat{h} | \phi_n \rangle \\ S_{mn} &= \langle \phi_m | \phi_n \rangle \end{aligned} \tag{3}$$

and the Hamiltonian is defined as

$$\hat{h} = \hat{t} + V_{\text{eff}}(\mathbf{r}) \tag{4}$$

with $\hat{t}$ being the kinetic-energy operator and $V_{\text{eff}}(\mathbf{r})$ being the effective Kohn-Sham potential which is approximated as a simple superposition of the potentials of the neutral atoms

$$V_{\text{eff}}(\mathbf{r}) = \sum_j V_j^0(|\mathbf{r} - \mathbf{R}_j|). \tag{5}$$

In the present method, all three-center terms are ignored, but all two-center terms are calculated exactly.

From the Kohn-Sham eigenvalues $\{\epsilon_i\}$ of the system of interest and those of the isolated atoms, $\{\epsilon_{jm}\}$ (with m being an atom index and j an orbital index), we can arrive at an approximate total energy of the system of interest relative to that of the non-interacting atoms,

$$E_r \simeq \sum_i \epsilon_i - \sum_j \sum_m \epsilon_{jm} + \frac{1}{2} \sum_{j \neq j'} U_{jj'}(|\mathbf{R}_j - \mathbf{R}_{j'}|). \tag{6}$$

The last term is a set of short-ranged, repulsive pair potentials. These are obtained by requiring that the total energy of two-atomic systems (in our case, of Au_2) as a function of interatomic distance is accurately reproduced.

Finally, in the present study only the $5d$ and $6s$ electrons of the Au atom are explicitly included in the calculations, whereas the rest are treated within a frozen-core approximation.

Ultimately, we checked the accuracy of our approach by calculating the lattice constant of crystalline Au. The result is within 0.3% of the experimental value, giving us confidence that our calculations on the Au_n clusters are accurate although, of course, the existence of smaller inaccuracies cannot be excluded.

In optimizing the structures of gold clusters, we have used genetic algorithms. As we have shown in our studies on $(\mathrm{HAlO})_n$ clusters [19,20], this approach gives accurate results.

The genetic algorithms are based on the principles of natural evolution and are, therefore, also called evolutionary algorithms [21,22]. They provide an efficient tool for global geometry optimizations. Our version of the genetic algorithms is as follows. Suppose that we have optimized the structure of the cluster with $n-1$ atoms. From this structure we construct a first generation consisting of M independent clusters for the n-atom system by randomly adding one Au atom and letting each of these structures relax to its nearest total-energy minimum. Subsequently, a new set of clusters is constructed by cutting each of the original ones randomly into two parts that are interchanged (under the constraints that any atom should not be too close to any other atom or too far from all the other ones) and, afterwards, let relax. Out of the total set of $2M$ structures, the M ones of the lowest total energy are kept for the next generation. This procedure is repeated until the lowest total energy is unchanged for a large number of generations.

As we shall discuss below, in addition to the globally optimized structures we also considered other geometries. Among those were various planar ones that were obtained by locally relaxing the structures of Bonačić-Koutecký et al. [15] and of Häkkinen et al. [14] for $n \leq 14$. A planar structure for $n = 15$ was obtained by adding a single atom to the planar geometry for $n = 14$, making it maximally symmetric. Finally, also an icosahedral structure for $n = 13$ and a tetragonal structure for $n = 20$ were considered.

3 Results and discussion

In Figure 1 we show the structures that our global structure optimization has produced for Au_n with $3 \leq n \leq 20$. It is seen that up to $n = 6$ the clusters are planar, but above that the structures are truly three-dimensional ones. On the other hand, experimental and theoretical studies have found that planar structures are stable up to around 15 atoms [23,24]. Therefore, we considered these structures in addition to those of the unbiased structure optimization. For most planar clusters we considered more different structures, resulting in more different total energies, as seen in Figure 2. In one single case ($n = 10$) the planar geometry even resulted in a total energy that was slightly lower than that of the global optimization, indicating that despite the high reliability of the genetic algorithms, also they may at cases fail. As Figure 2 shows, the total energy per atom for the planar structures with up to 15 atoms is only slightly higher than that of the structures of Figure 1. In most cases the total-energy difference between the planar and the non-planar structures is smaller than the computational accuracy of *any* currently applied method on gold clusters.

For the icosahedral Au_{13} cluster, the total energy could be lowered upon a local symmetry-lowering relaxation, which is seen as the two triangles in Figure 2 (with the lower one corresponding to the lower-symmetry structure). For the tetragonal Au_{20} cluster the total energy was only marginally higher than that of the globally optimized structure.

It is interesting to compare the results of Figure 2 with those of Figure 3. In the latter figure we show the orbital energies for the different Au_n clusters. Here, the Fermi

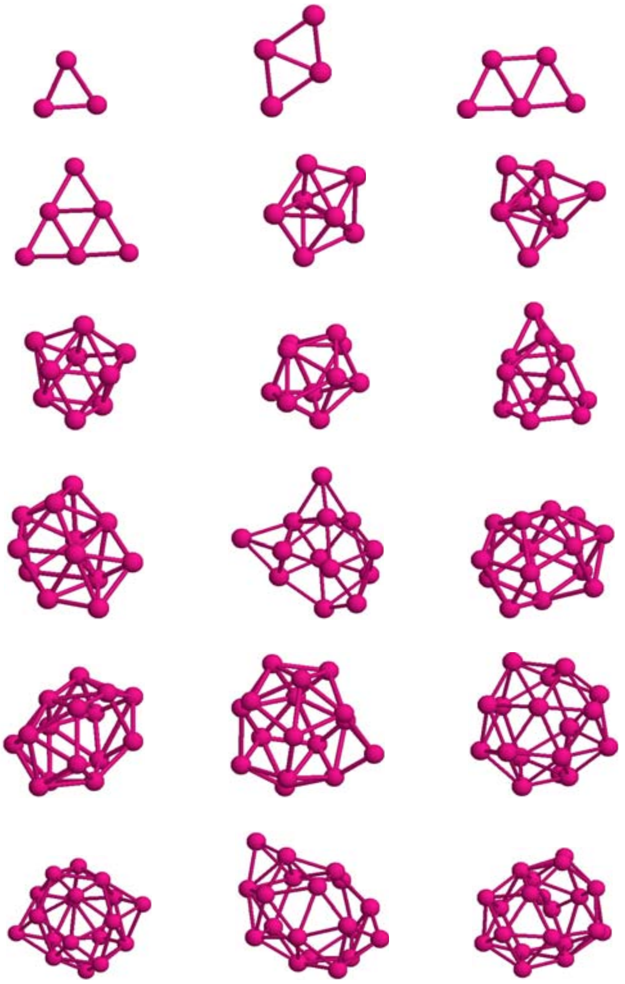

Fig. 1. The structures of the Au_n clusters from the global structure optimization. n goes from 3 in the upper left corner to 20 in the lower right corner.

energy possesses a locally maximum for $n = 3$, 9, and 20, which, with $n = 20$ partly being an exception, also are systems of low stability. Moreover, for the two former, the removal of a single electron would move the Fermi energy into a large energy gap, suggesting that Au_3^+ and Au_9^+ are particularly stable. Finally, Figure 3 shows how a deep-lying broad band of orbitals from the $5d$ functions is formed for the larger systems.

Figure 4 shows the radial distances for the different Au_n clusters. The radial distance of an atoms is its distance to the center of mass of the cluster. The figure shows that for n up to around 10 all atoms have a relatively large, but in many case quite scattered distance to the center, suggesting structures of very low symmetry. For $8 \leq n \leq 20$ all radial distances take quite large values suggesting that the structure of these clusters resembles a hollow cage. Actually, a recent study of Bulusu et al. [25] finds that hollow gold cages exist for Au_n^- with $n = 16$–18, both according to experimental and theoretical results. In Figure 1 we see that our study finds many Au_n clusters with $n = 7$–20 to have cage-like structures.

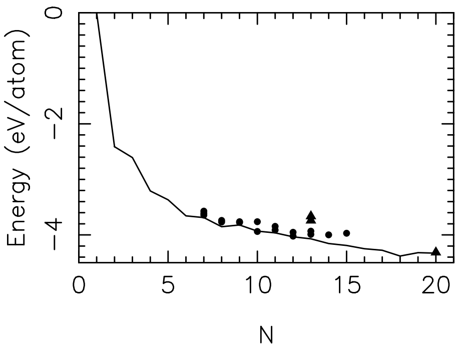

Fig. 2. The variation in the total energy per atom (relative to that of the isolated atom) for the optimized Au_n clusters (solid curve) together with those of planar structures (dark circles) and those of icosahedral Au_{13} and tetragonal Au_{20} clusters (dark triangles).

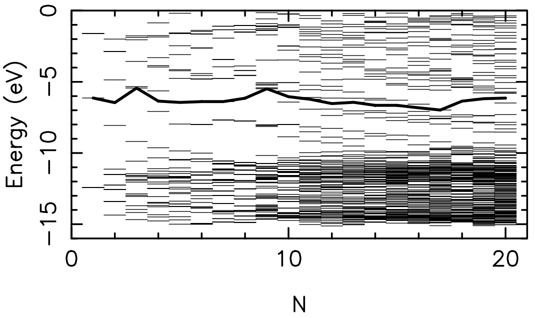

Fig. 3. The orbital energies for Au_n clusters as a function of n. Each line for a given n marks at least one orbital with that energy, and the thicker curve shows the Fermi energy.

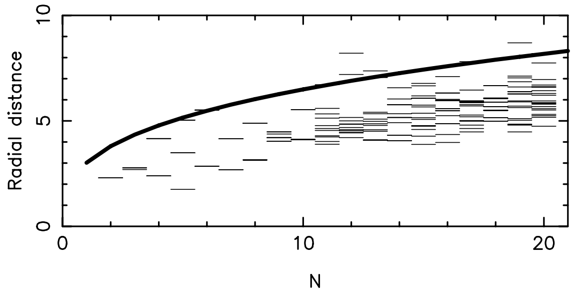

Fig. 4. The radial distances of the atoms for the Au_n clusters. For each value of n, a horizontal line indicates that at least one atom has that radial distance. The thicker curve marks the radius of a spherical jellium with the density as that of crystalline gold.

As may be seen from Figure 1, the structures we find in our global optimization are fairly irregular. This can also be extracted from the results of Table 1 that lists the symmetry groups of the structures. These are indeed all of low symmetry.

4 Conclusion

In this work we have presented results of our theoretical study on the electronic and structural properties of Au_n

Table 1. Symmetry of gold clusters from 3 to 20 atoms.

Size	Symmetry	Size	Symmetry	Size	Symmetry
3	D_2	9	D_{2v}/D_2	15	C_l
4	D_{2h}	10	D_2	16	C_s
5	C_{2v}	11	C_l	17	C_l
6	D_{3h}	12	C_l	18	C_2
7	D_{5h}	13	C_s	19	C_l
8	T_d	14	C_s	20	C_l

clusters. We have used an unbiased approach in optimizing the structure together with a parameterized density-functional method for calculating the total energy and the electronic properties of a given structure.

We found that for clusters with up to 6 atoms, the structure of the lowest total energy was planar. For larger clusters, truly three-dimensional objects are found but for clusters with up to 15 atoms, planar structures were found to lie very close in energy to those found in the unbiased search. We can not exclude that removing inaccuracies in our approach would change the relative ordering of those. Another interesting finding is that the high-symmetry structures for $n = 13$ and $n = 20$ (i.e., an icosahedron and a tetrahedron, respectively) are comparable in energy with those we optimized (in particularly for $n = 20$ this is the case), but that for $n = 13$, the icosahedron lowers its symmetry through local relaxation. Moreover, in many cases our structures possess a cage-like structure.

Indeed, the observation of low-symmetry structures was a general finding of our calculations. Thus, these clusters are far from spherical. Thus, neither the spherical jellium model nor model potentials that do not include electronic degrees of freedom do not at all provide an accurate description of the properties of the small Au_n clusters.

This work was supported by the DFG (German Research Foundation) through the SFB 277 at the University of Saarland.

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