

Stability of the Tetrahedral Motif for Small Gold Clusters in the Size Range 16 to 24 Atoms

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1. Introduction

The tetrahedral 20 atom gold cluster is surprisingly stable, and is believed to be the ground state structure as evidenced both by *ab initio* calculations [1-3] and experiment [3]. This structure is very ordered, has no internal atoms and is essentially a small section of fcc-bulk gold cut along four intersecting close-packed (111) planes. We have previously shown that it is considerably more stable than the lowest lying isomer, which is disordered, by more than 0.5 eV. This result, that the tetrahedral structure represents a deep minimum in the potential energy surface that is isolated from its isomers, gives rise to a well-defined melting point with a melting temperature comparable to bulk gold [4].

Relativistic effects are important to the stability of small gold clusters, the so-called aurophilic bond [5], and give rise to planar ground state structures up to 6 [2, 6] or 7 [7-9] atom neutral clusters and up to 14 atoms for anion clusters [10, 11]. Stability of the tetrahedral structure arises from an interplay between the tendency to form compact structures which maximise coordination of the gold atoms by inclusion of one or more internal atoms and this stability of flat structures.

Stability of the tetrahedral structure extends to other metal clusters. Johansson and Pyykko [12] have shown, by *ab initio* calculations, that this motif is stable in cadmium for the first five clusters containing 4, 10, 20, 35, and 56 atoms. By contrast, it appears that only the 20 atom cluster is stable for gold [1, 2].

Defective tetrahedral structures are also possible for sizes in the vicinity of 20 atoms, that is where one or more corner atoms are removed from the tetrahedron, or adatoms adsorbed onto its surfaces. Hence it might seem reasonable to search for energetically favourable ordered structures based upon the tetrahedral motif for clusters containing between 16 and 24 atoms. For anion clusters it has been shown recently that ordered

structures are indeed favourable in the size range of 16-19 atoms. [13]. Although in this case hollow-cage structures reminiscent of carbon fullerenes also compete for the energetically most favourable structure. Our previous calculations indicated that this was not the case for neutral clusters [2]. These calculations used parameters which reproduced the properties of bulk gold and gold dimers very well, but as well converged with respect to total cluster energy to obtain a definitive ordering of the various isomers.

In the present work we re-examine the stability of these defective tetrahedral structures using *ab initio* calculations performed at a high computational level and find that they are indeed energetically competitive compared with more disordered structures. Our calculations predict that 17-22 atom structures based upon the tetrahedral motif with missing corner atoms or adatoms are the lowest energy structures, at least among the structures we have tested. Beyond the fundamental interest in studying the stability of these types of systems, which stand between bulk materials and molecules, there are a number of potential implications to this work. Gold nanoclusters have received considerable attention in recent years motivated by their catalytic activity [14, 15], their increasing application as nanoscale building blocks [16-19] and therapeutic agents, and their unique optical properties [20].

2. Computational Methods

Calculations reported in this paper were conducted with the SIESTA software package [21, 22]. This program implements the SIESTA methodology for linear-scaling density functional theory (DFT) within periodic boundary conditions and is based on the linear combination of atomic orbitals approximation. The valence electrons are described by atom-centered basis sets, and the nucleus/core electrons are represented by norm-conserving pseudopotentials. The key feature of this methodology is that the orbitals are strictly localized in real-space, with a cut-off radius defined by a single energy shift parameter for all atoms that represents the energy increase in the orbitals due to confinement. Exploitation of this locality leads directly to linear-scaling without the requirement of neglecting integrals based on a threshold value.

The gold pseudo-potential was generated according to the scheme of Troullier and Martins [23] and included a scalar relativistic correction. The transferability of this

pseudo-potential has previously been tested by comparison with well-known experimental results and all-electron calculations [24]. The 6s and 5d valence electrons were represented by a double zeta plus single polarisation function basis set. Calculations were performed within the local spin density approximation (LSDA) as parameterised by Perdew and Zunger [25] for the exchange-correlation functional, and were spin-unrestricted throughout. No Fermi smearing was employed. Since the calculations are periodic the cluster has to be placed in a sufficiently large unit cell to avoid unwanted interaction between the periodic images. In our previous molecular calculations we found that a 20 Å cell gives negligible interaction [26], and we have here tested this condition and find that total energies are well converged. A real-space integration grid with an effective kinetic cut-off of 250 Ry was employed, this value represents the equivalent energy cut-off of a plane-wave which can be represented by this grid and yields numerically converged results. Only a single k-point is required in reciprocal space since the cluster is not periodic.

Minimum energy structures were obtained from conjugate-gradient optimisations with the forces converged to 0.04 eV/Å. Although this is not a particularly stringent criterion for force convergence, improving this value to 0.01 eV/Å changed the total energy by less than 0.01 eV for the 19 atom cluster. Initial disordered structures for the minimisations were taken from our previous paper where low energy candidates were identified from extensive empirical potential calculations and a number of other likely structures prior to a full DFT relaxation [2]. In all cases at least 12 initial disordered structures were optimised. The starting geometries for the defective tetrahedral structure optimisations were obtained by removing or adding atoms, as appropriate, to the optimised 20 atom tetrahedron. Overall, the computational conditions described above yield energies which are converged to better than about 0.2 eV with respect to numerical integration factors as opposed to the basis set expansion.

Binding energies have been calculated without including a correction for the basis set superposition error (BSSE). It would be expected that this effect would tend to overbind the clusters and lead to energies that are of the order of 10 % in error. However, we are not interested in calculating absolute binding energies, but rather comparing

relative binding energies. BSSE will contribute equally to all the calculated binding energies and this approach is therefore justified.

The critical parameter in these calculations is the extent to which the basis set is localised in real space. The confinement radius has a profound effect on the energy order of the optimised structures, a value which is too small can lead to the wrong energy ordering. Conversely, a very large cut-off, although desirable, increases the computational cost of the calculations considerably. In our previous work we used a value of 20 mRy to define this cut-off. This value corresponds to the increase in energy of the orbitals due to their confinement. These calculations were constrained, to some degree, by the computational resources available at the time. In order to identify a more appropriate trade-off between time and convergence we have performed optimisations of the 20 atom tetrahedron over a range of confinement energies. The results are shown in Figure 1 where the average pair distance and average binding energy are plotted as a function of confinement energy. Both quantities are very well converged at the largest cut-off radius corresponding to an energy confinement of 0.05 mRy. An acceptable level of convergence and reasonable computational time is achieved at a confinement energy of 1 mRy. This value was used through the calculations. We have also checked the energy order of two 19 atom isomers as a function of confinement energy. At 1 mRy the energy difference between the two clusters converges to about 0.1 eV of its value at 0.05 mRy. More importantly the energy ordering at 20 mRy is inverted for this pair of isomers.

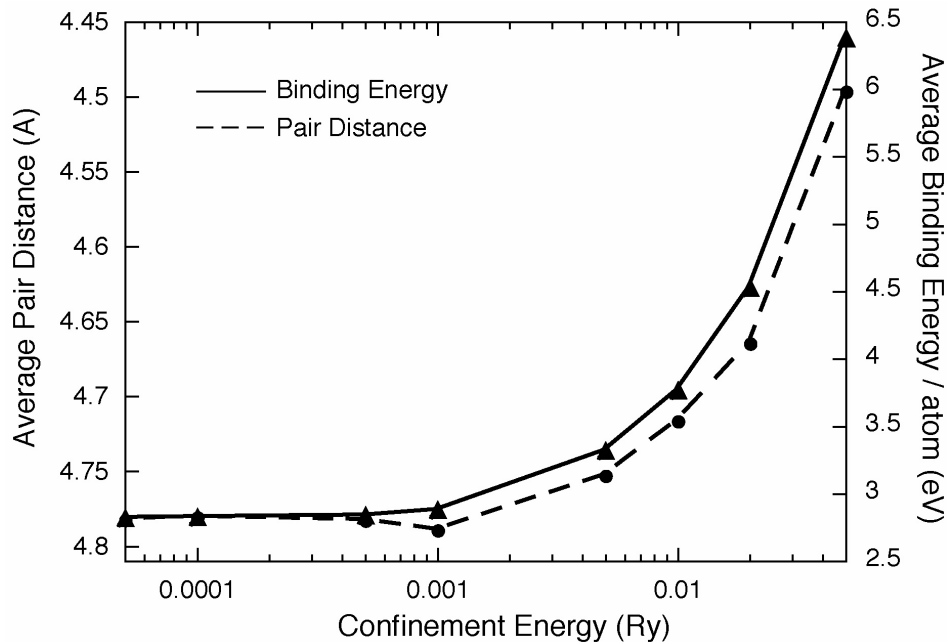


Figure 1. Average distance between pairs of atoms and average binding energy/atom for the tetrahedral 20 atom cluster optimised at different orbital confinement energies.

Overall, the computational conditions described above yield energies which are converged to better than about 0.15 eV with respect to numerical integration factors as opposed to the basis set expansion.

3. Results and Discussion

The results of the structure minimisations are shown in Figure 2, where the lowest energy disordered structure and optimised defective tetrahedral structure are shown for each cluster size. By disordered we mean structures which were optimised not starting from a tetrahedral motif, but rather from structures generated in empirical potential simulated anneals [2]. Clearly some of these structures are not totally disordered but form relatively ordered cage structures. We shall use the term disordered throughout as a convenient way to distinguish the two types of structures.

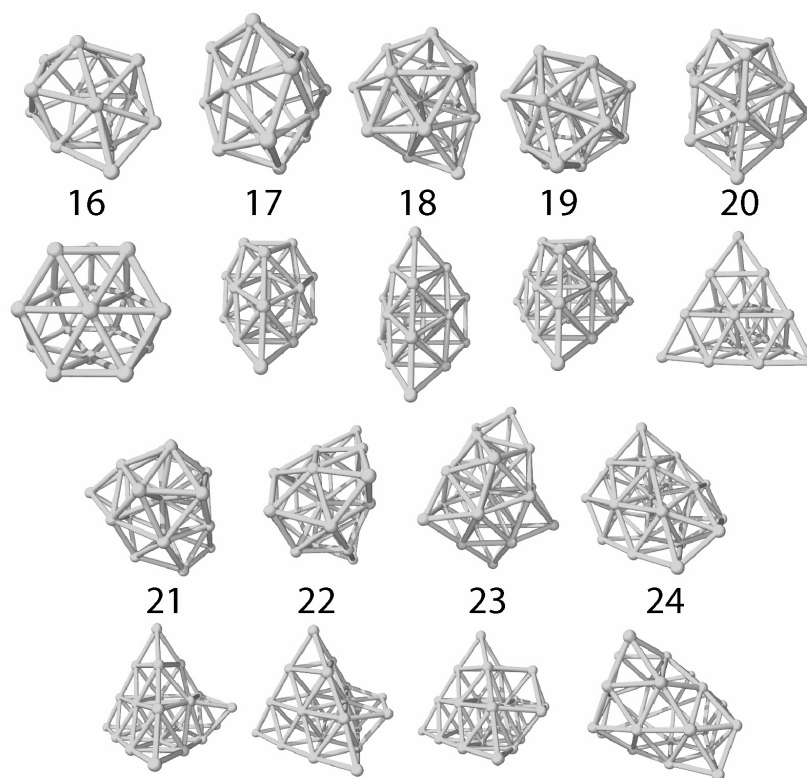


Figure 2. Optimised structures starting from tetrahedral motif structures (bottom) and disordered structures (top) for cluster containing 16 to 24 atoms

The 16 and 17 atom disordered structures are open cages, the remaining disordered structure contain one enclosed atom. For the 22 and 23 tetrahedral structures the minimum energy structure corresponds to the adatoms on a single surface of the tetrahedron. The 24 atom tetrahedral structure undergoes significant re-arrangement upon optimisation to a more disordered-like structure. The starting geometry in this case was with one adatom on each surface. For the 19, 20, 21 and 22 atom clusters the ordered structure is the lowest energy structure. For the 16,17,18,23 and 24 atom clusters the disordered structure is lowest, although the energy difference is small for the 17 and 18 atom clusters and below the likely energy convergence of the calculations. In all these cases there are a number of other disordered isomers lying between the minimum energy disordered structure and tetrahedral structure. The results of the calculations for the structures in Figure 1 are given in Table 1.

Table 1. Results of optimisations for structure shown in figure 1, difference in total energy between disordered and tetrahedral structure (δE_{Tot}), negative number indicates tetrahedral structure is lower, average pair distance (D) and percentage difference (δD), average binding energy/atom (E_B) and percentage difference (δE_B), and HOMO-LUMO (E_G) energy.

		δE_{Tot} (eV)	D (Å)	δD (%)	E_B (eV)	δE_B (%)	E_G (eV)
16	Disord	0.29	4.24	0.43	-2.72	0.67	0.5
	Tetra		4.23		-2.70		0.08
17	Disord	0.22	4.35	-0.62	-2.76	0.47	0.18
	Tetra		4.38		-2.75		0.13
18	Disord	0.08	4.30	-4.86	-2.80	0.16	1.14
	Tetra		4.52		-2.80		0.49
19	Disord	-0.3	4.38	-5.99	-2.82	-0.55	0.08
	Tetra		4.66		-2.83		0.1
20	Disord	-0.74	4.48	-6.40	-2.84	-1.28	0.81
	Tetra		4.79		-2.88		1.96
21	Disord	-0.15	4.60	-5.40	-2.85	-0.26	0.07
	Tetra		4.86		-2.85		0.11
22	Disord	-0.3	4.70	-3.83	-2.85	-0.48	0.47
	Tetra		4.88		-2.87		0.7
23	Disord	0.97	4.79	-2.31	-2.88	1.49	0.08
	Tetra		4.90		-2.83		0.08
24	Disord	0.65	4.88	-4.29	-2.90	0.94	0.58
	Tetra		5.10		-2.87		0.55

The energy difference between the lowest lying disordered structure and tetrahedral structure decreases from 16 to 20 atom, with the two energies being the same at 18 atoms, and then increases again beyond 20 atoms. The 23 atom cluster is an exception and has the largest energy difference between ordered and tetrahedral structures. However, the average binding energy for the 23 atom disordered structure is the same as the tetrahedral 20 atom structure. The same trend appears in the difference between the average binding energy/atom for the disordered and tetrahedral structures.

The average pair distance between all atoms increases down the table reflecting the fact that the cluster is increasing in overall size as more atoms are added. Interestingly, in all but the 16 atom cluster the disordered structure is more compact than the tetrahedral structure having a smaller average pair distance. The energy gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals alternates between relatively large and small values for even and odd clusters respectively as

expected because the orbital occupancy also alternates between a filled and half-filled HOMO. The 16 atom cluster is an exception in this case because the ground state electron configuration for the tetrahedral structure is a spin triplet.

The 20 atom tetrahedron stands out as particularly stable among the tetrahedral structures, separated by 0.74 eV from the next lowest isomer. It also has an extremely large band gap between the HOMO and LUMO of nearly 2 eV. This stability cannot necessarily be attributed to this band gap as the 19 and 21 atom tetrahedra are also relatively stable yet have small band gaps, with almost the same value for disordered and tetrahedral structures. Moreover, the 19, 20 and 21 atom clusters have the largest difference in pair distance between the tetrahedral and disordered structures.

The pair distributions for the structures in Figure 1 are shown in Figure 3(a) and (b), where the pair distances are plotted in ascending order against pair number. The 20 atom tetrahedron shows a shell-like structure in the pair distribution indicated by a number of sharp steps and plateaus. This ordering begins to diminish as the corner atoms are removed or adatoms added. For the 16, 17 atom clusters the pair distributions are similar for the disordered and tetrahedral structures. At 18 atoms the two distributions begin to differ in shape, particularly for the larger pair distances and remain so until 23 atoms where they are again similar. This trend is the same as observed in the relative stability of the tetrahedral versus disordered structures, suggesting this ordering favours the 18-22 atom tetrahedra over the disordered structures.

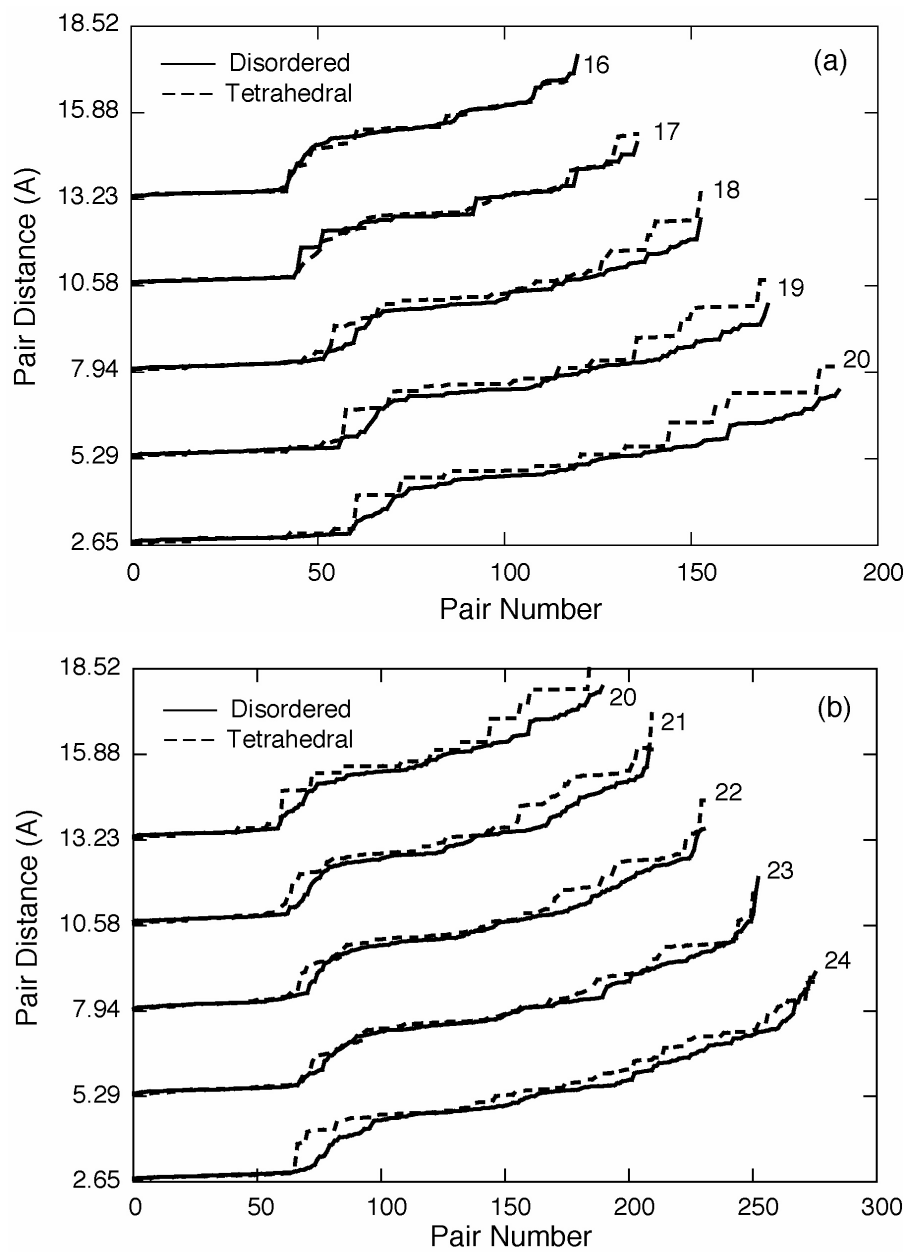


Figure 3. Pair Distances for the structures in Figure 1 plotted in ascending order. Pair number is an arbitrary index for each pair of atoms in the cluster. (a) 16 to 20 atom clusters and (b) 20 to 24 atom clusters. Pair distances have been offset by multiples of 2.65 A for clarity.

4. Conclusions

Minimum energy structures for gold clusters containing 16-24 atoms have been investigated using Density Functional Theory (DFT) calculations. A set of computational parameters have been identified which give well-converged structures and energies. A

range of starting geometries, taken from our previous work [2], and including new ordered structures have been optimised using the conjugate gradient method and a set of computational parameters that yield well-converged results.

The ground state of the 20 atom gold cluster is a surprisingly ordered tetrahedral structure with essentially the same geometry as atoms in bulk gold. This ordered structure is very stable with the next lowest isomer lying 0.74 eV above it. This tetrahedral motif extends to the minimum energy structure of other cluster sizes. Defective clusters can be created by sequentially removing corner atoms from the tetrahedron. This tends to destabilise the tetrahedron relative to more disordered isomers. Removing one corner atom to give the 19 atom cluster leaves the tetrahedron as the minimum energy structure, with the next lowest isomer still 0.3 eV higher in energy. Removal of another corner atom gives similar energies for the tetrahedron and disordered isomers. Further removal of corner atoms favours the more disordered structures over the tetrahedra as minima.

Adatoms can also be sequentially be adsorbed onto the faces of the 20 atom tetrahedron, with the effect of progressively destabilising the structure. In this case the tetrahedron persists as the minimum energy structure up to 22 atoms.

The tetrahedral structures are not compact structures relative to their more disordered counterparts, having a larger average pair distance (with the exception of the 16 atom cluster), neither do the tetrahedra have uniformly large band gaps. A result that suggests it is neither of these factors alone which favour the tetrahedra over the disordered structures as the minimum energy structure. The stable tetrahedra, however, do have a different pair distance distribution compared with the disordered structures. On the other hand the pair distributions are similar for clusters where the tetrahedron is not the minimum.

The 20 atom tetrahedron has been postulated as responsible for catalytic activity in small gold clusters. Stability of the 19 and 21 atom structures predicted here is interesting in this regard because these two structures, particularly the adatom structure, have uncoordinated gold atoms that could act as potential sites for catalysis.

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