

Systematic and Efficient Navigating Potential Energy Surface: A Case Study of Silver Doped Gold Clusters for Calibration

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Abstract. Locating global minimum of certain atomistic ensemble is known to be a highly challenging and resource consuming task. This work represents joint usage of the semi-empirical PM7 Hamiltonian, Broyden–Fletcher–Goldfarb–Shanno algorithm and basin hopping scheme to navigate a potential energy surface. The Au₂₀ nanocluster was used for calibration as its global minimum structure is well-known. Furthermore, Au₁₈Ag₂ and Au₁₅Ag₅ were simulated for illustration of the algorithm performance. The work shows encouraging results and, particularly, underlines proper accuracy of PM7 as applied to this type of heavy metal systems. The reported results motivate to use the benchmarked method for studying potential energy surfaces of manifold systems and locate their global-minimum atomistic configurations.

Key words: gold; silver; cluster; structure; potential surface; global minimum.

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Introduction

Reliable research in computational chemistry requires an appropriate sampling of potential energy surface (PES) for every system investigated. The chemical systems of more or less significant size possess certain number of local minima (stable conformations), which altogether determine their physical and chemical properties. Among numerous local minima, the deepest one is coined global constituting the most stable conformation with the most favorable formation energy. Knowing a global-minimum molecular conformation and low-energy local-minimum molecular conformations, their structures and formation energies, is essential for robust research practices. Prediction of a set of minima and their order for a given structure from solely theoretical principles is challenging and computationally expensive. In the meantime, such a prediction constitutes an excellent benchmark for model Hamiltonians and helps to assign structural formulas to experimental structures.

Geometry optimization (also known as energy minimization) algorithms find an arrangement of any collection of atoms in the three-dimensional space, which is characterized by negligible inter-atomic forces and a smaller total energy, as compared to a starting arrangement. The obtained atom arrangement corresponds to a stationary point on PES. The stationary point, in essence, depends on the starting configuration. Therefore, different local minima with different relative stabilities can be potentially located when an initial structure is varied. Global minimum cannot be proven without performing multiple local geometry

optimizations and comparing the energies of the corresponding atom arrangements. Thus, a global geometry optimization comprises a set of local geometry optimizations. In every case, it is up to the operator to prove that a number of the performed local optimizations is enough to claim location of a true global minimum. In the case of large molecules or nanostructures, this task is highly nontrivial.

The present work investigates a combination of the two mathematical and one computational chemistry method as a working set to locate a global minimum for a well-known structure. We will start from an arbitrary geometry of the Au₂₀ nanocluster, whose global-minimum conformation is known to be a pyramid with the T_d point group symmetry.¹ Having comprehensively navigated through PES and sampled a number of other local minima, we will come to the pyramid structure using a few global iterations. We will also apply the same combination of methods to derivative structures – Au₁₈Ag₂ and Au₁₅Ag₅ – and prove that they tend to maintain pyramidal arrangements, as must be expected.

Gold nanoclusters (GNCs) are actively pursued nowadays. This research field has been largely emerged during the last decade. GNCs found their niche within biomedical applications, including genomics, biosensorics, immunoassays, laser phototherapy of cancer cells and tumors, targeted delivery of drugs, optical bio-imaging etc.^{2,3} Since gold belongs to heavy elements (79 electrons), its theoretical investigation is quite challenging. An adequate basis set and normally pseudopotential must be found to represent electronic levels of a single gold atom

as well as its correct bonding parameters with other gold atoms in a cluster. The underlying calculations are particularly time consuming due to a number of valence electrons participating in bond formation. An ability to perform efficient and reliable description of GNCs would constitute an important contribution to the field.

The structures of Au₂₀ are being intensively reported: both naked and with different ligands.^{1,4-7} All works employ density functional theory (DFT), since higher levels of theory are prohibitively expensive for these sizes of systems. Some advances were reported on the global optimization of Au₂₀(SR)₁₆⁸ and naked Au₂₀⁹ using DFT.

Methods

The wave functions of the GNCs at every optimization step were represented by means of the PM7 semi-empirical Hamiltonian.¹⁰ PM7 uses the approximation of neglect of diatomic differential overlap, as applied to the Hartree-Fock (HF) method. In turn, all terms of the exact Hamiltonian in HF are expressed as a sum of one-electron operators. Unlike in HF, selected integrals in PM7 are parametrized in view of empirical data and may potentially provide more accurate results than HF. The convergence criterion of the wave function was set to 4.18×10^{-4} kJ mol⁻¹.

The local optimizations were done by means of the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.¹¹ This algorithm is essentially failure-proof

at the expense of a significant number of iterations (single-point calculations) before it converges. The geometry convergence criterion was set to $1.0 \text{ kJ mol}^{-1} \text{ \AA}^{-1}$, which systematically corresponds to less than 0.1 kJ mol^{-1} difference in total energy at two consequent BFGS steps.

The global optimization was propagated in the framework of the basin hopping (BH) algorithm.¹² Fifty one iterations were performed for every system and the resulting energies were compared to one another. The maximum displacement per gold atom was allowed to be 0.75 \AA whereas effective temperature was set to 2000 K. The effective temperature is used to accept or decline possible translations/perturbations within the Metropolis test. For an efficient search, the temperature must be comparable to the higher barrier separating local minima on PES. Since different conformations of GNCs involve different order of bonds between the gold atoms, the bond breakage is required to go from one stable conformation towards another. The effective temperature parameter must be significantly large for the above reason.

The in-home code for navigating PES makes use of the implemented optimization routines provided by SciPy and ASE with minor technical modifications.¹³ Implementation of PM7 in MOPAC2012 (openmopac.net), as provided by Dr. J.J.P. Stewart, was used. All structures and optimization pathways were visualized in VMD, version 1.9.1.¹⁴ Input structures were prepared in Gabedit.¹⁵

The primary motivation of this work is to assess performance and accuracy of PM7 to predict structures of gold nanoclusters in conjunction with known mathematical methods for a potential energy surface scan. PM7 is computationally much less expensive¹⁰ than any DFT model and its acceptable performance would be an encouraging sign.

Results

Three PESes – Au₂₀, Au₁₈Ag₂, Au₁₅Ag₅ – were navigated in the present work (Table 1). All systems contain large numbers of electrons; therefore, simulations of them are quite expensive. The core-potentials applied within PM7 allow to decrease computational costs significantly. A series of the single-point calculations is required for BFGS to converge to the requested small inter-atomic forces and negligible change in formation heat upon last iterations.

Table 1. Technical details of global minimum search: total number of electrons in each system; number of electrons simulated implicitly; total number of single-point computations (SPCs) performed; the largest number of SPC iterations per one geometry optimization

Cluster	Total Electrons	Implicit electrons	Total Number of SPCs	Largest number of SPCs per local optimization
Au ₂₀	1580	1360	35 350	4 611
Au ₁₈ Ag ₂	1516	1296	19 150	742
Au ₁₅ Ag ₅	1420	1200	32 267	3 025

Figure 1 exemplifies a local optimization flow in terms of formation energy, maximum force and energy change between the two consequent steps. GNCs require large perturbations/displacements to adequately sample their PESes.

Figures 2-4 summarize scans of PESes for the three investigated clusters derived from 51 global BH iterations. A few cases per system ended with the same most negative formation heat. By comparing them to a known structure of Au₂₀,^{1,7} it was found that the global minimum predicted by the PM7/BFGS/BH method is correct. This result is encouraging suggesting a new suitable method to scan PES of GNCs.

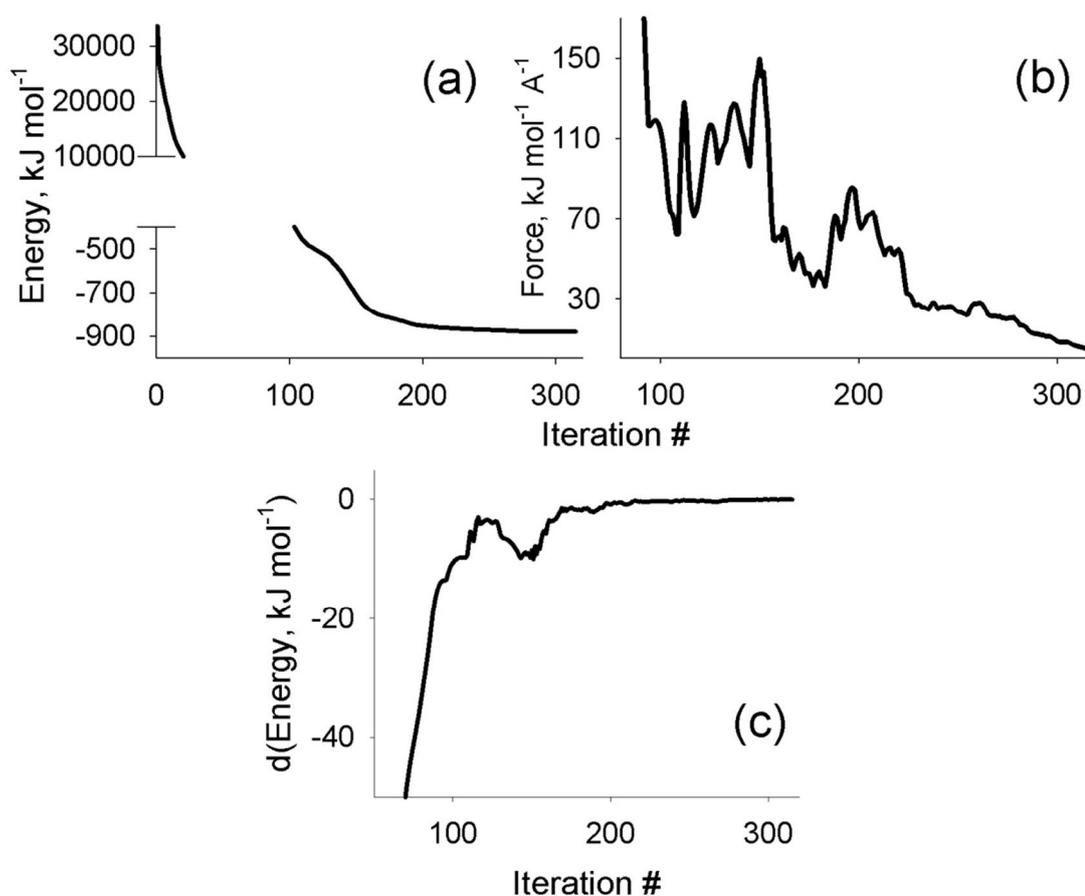


Figure 1. Geometry optimization of the silver doped gold nanoclusters. The minimized formation heat corresponds to local minimum structures.

A set of other minima, different for each structure, was located. The low-energy alternative GNC structures are likely possible in reality and depend on the synthetic approach and ligand coverage. Therefore, they are also important to know.

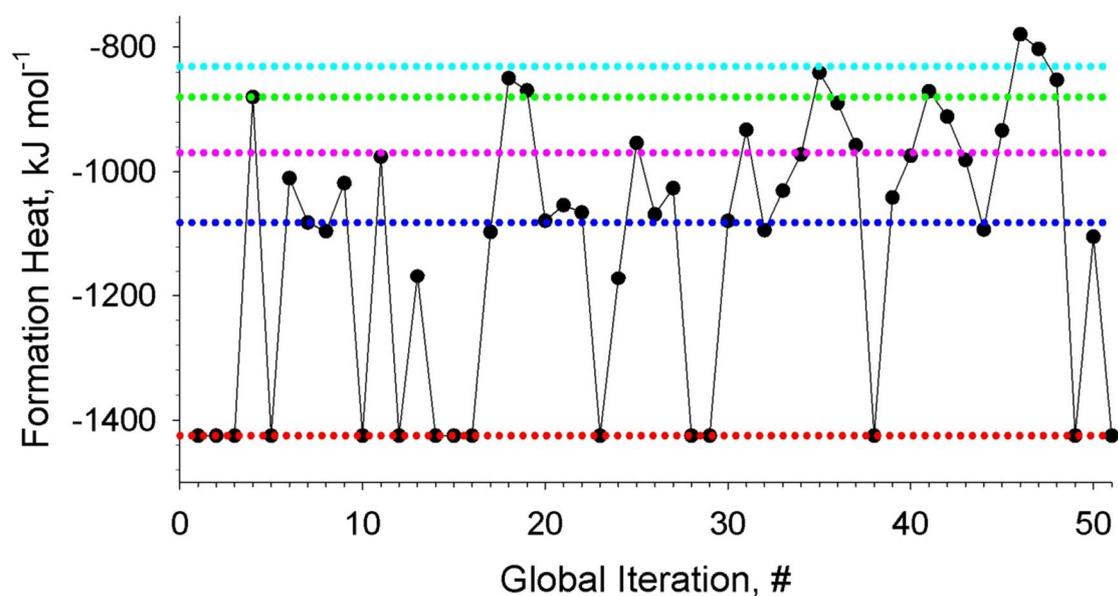


Figure 2. Formation energies of the revealed local-minimum structures of Au_{20} . The dotted color lines depict energies of the structures, which were obtained most frequently.

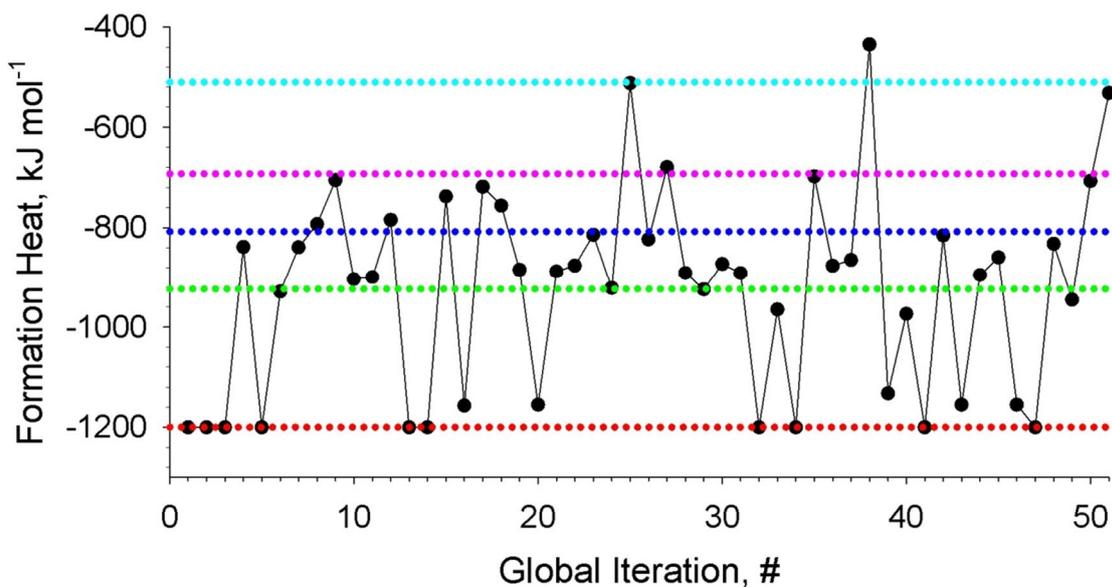


Figure 3. Formation energies of the revealed local-minimum structures of $\text{Au}_{18}\text{Ag}_2$. The dotted color lines depict energies of the structures, which were obtained most frequently.

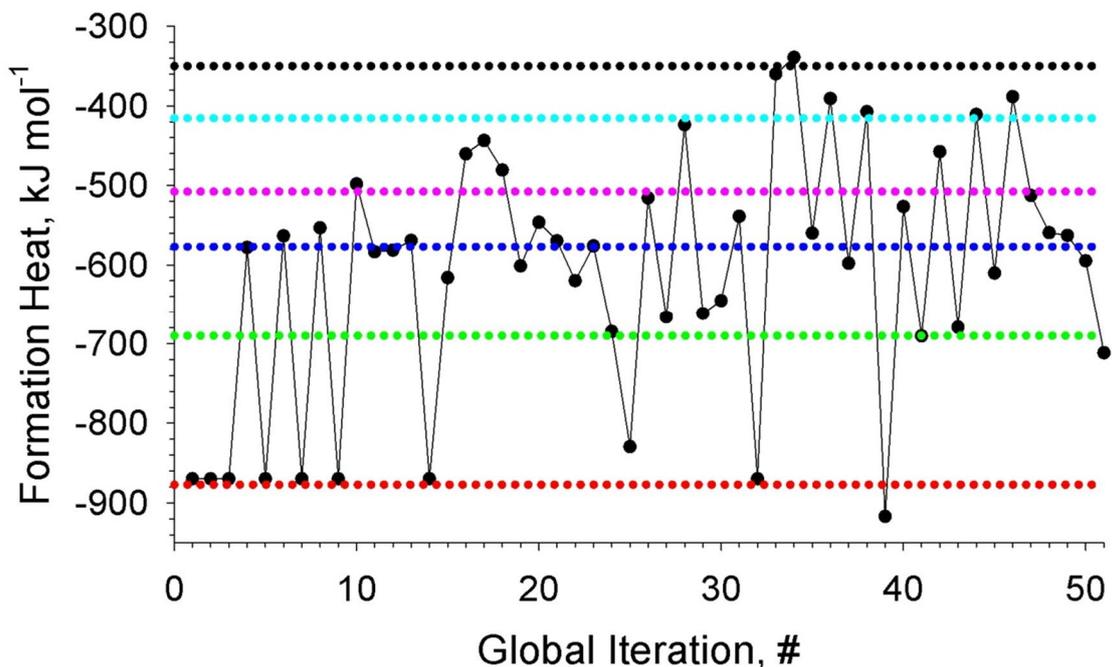


Figure 4. Formation energies of the revealed local-minimum structures of $\text{Au}_{15}\text{Ag}_5$. The dotted color lines depict energies of the structures, which were obtained most frequently.

Figures 5-7 visualize a number of most probable local-minimum GNCs along with the corresponding formation heats. Most structures are based on pyramid (T_d symmetry) with different degrees of perturbation (defects). In general, higher symmetry leads to better stability. The silver atom is isomorphic to the gold atom; thus, the silver-doped GNCs also maintain the pyramidal arrangement. Note that the formation heat of both silver-doped GNCs is smaller than that of Au_{20} . The expectation is that at certain molar fraction of the silver atoms, probably beyond 50%, T_d symmetry will vanish. Such computational experiments constitute a fundamental interest.

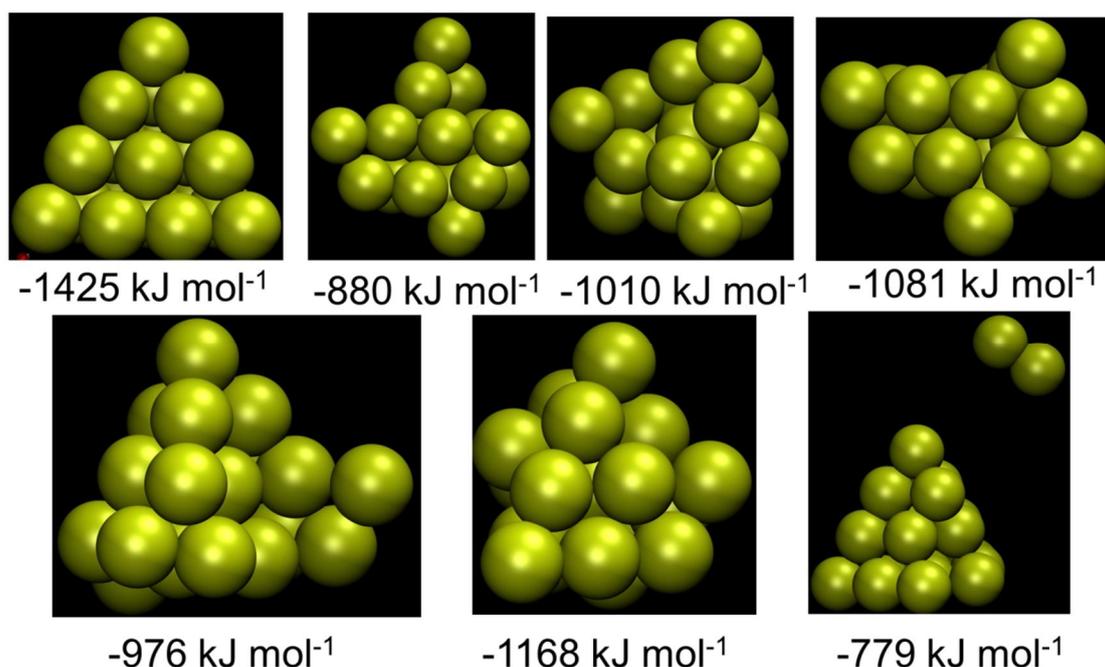


Figure 5. Representative stable structures of Au_{20} and corresponding formation energies.

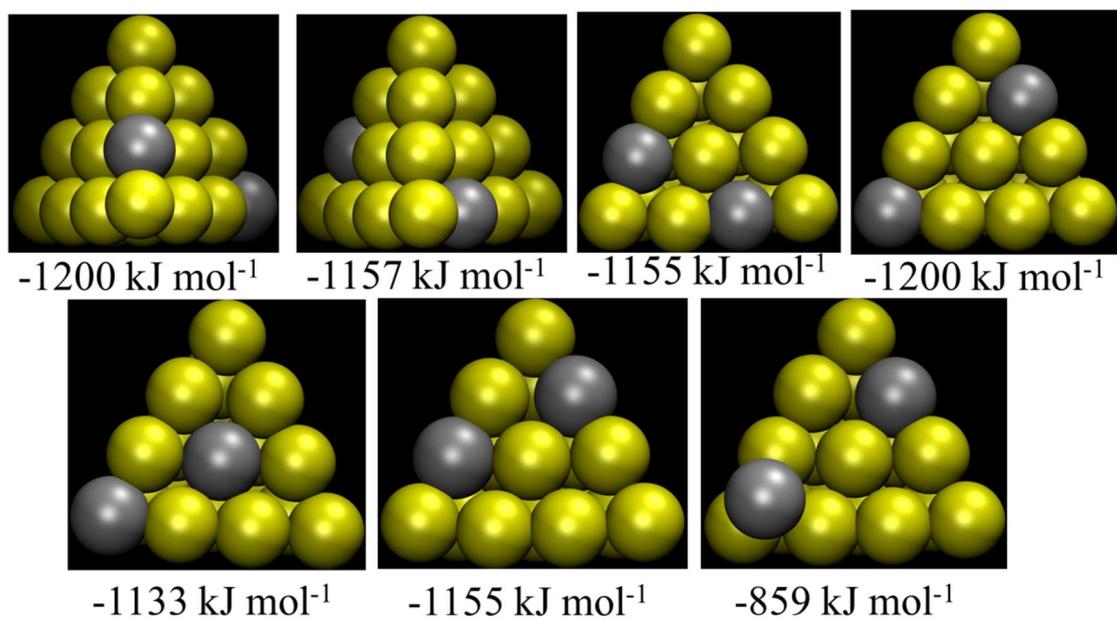
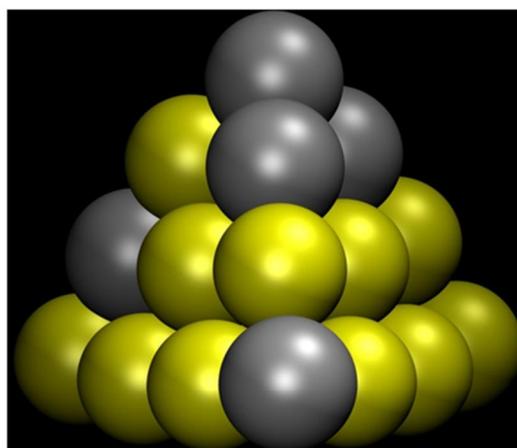
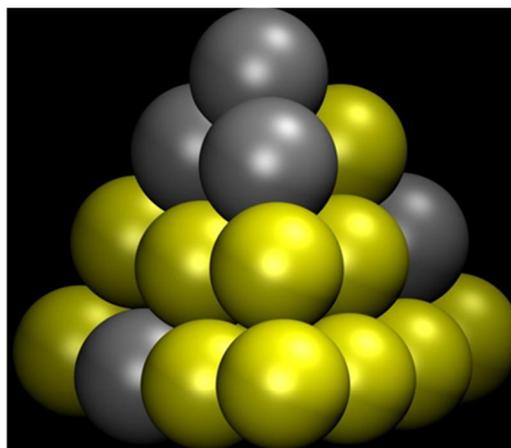


Figure 6. Representative stable structures of $\text{Au}_{18}\text{Ag}_2$ and corresponding formation energies.

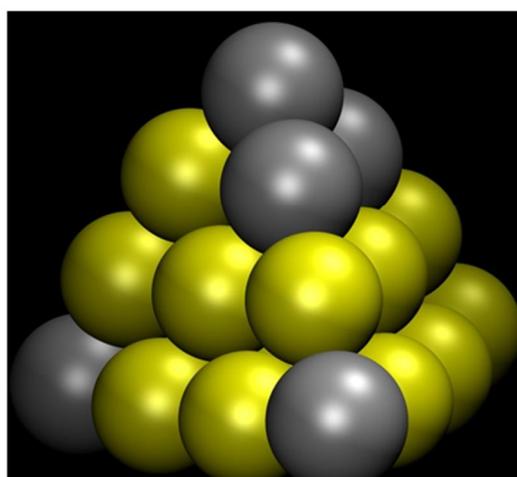
As follows from Figures 5-7, even a small perturbation of the pyramidal structure results in a few hundreds kJ mol^{-1} losses in heat of formation.



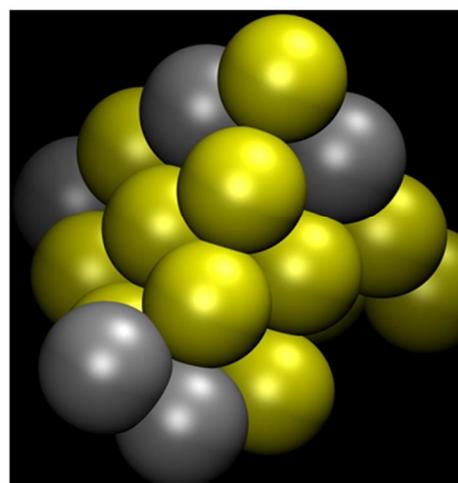
-870 kJ mol^{-1}



-829 kJ mol^{-1}



-917 kJ mol^{-1}



-679 kJ mol^{-1}

Figure 7. Representative stable structures of $\text{Au}_{15}\text{Ag}_5$ and corresponding formation energies.

Mutual location of the silver atoms within GNCs is an additional important question. Figure 8 shows structures and formation heats specifically for $\text{Au}_{18}\text{Ag}_2$ and $\text{Au}_{15}\text{Ag}_5$, in which the number of Ag-Ag chemical bonds is maximized. It appears that $\text{Au}_{18}\text{Ag}_2$ with the Ag-Ag bond is 14 kJ mol^{-1} more stable, as compared to $\text{Au}_{18}\text{Ag}_2$ without the Ag-Ag bond (Figure 6). The silver-silver bond is not absolutely favorable. For instance, five silver atoms on the same side of $\text{Au}_{15}\text{Ag}_5$

are less stable than different distributions of these bonds (Figure 7). Stability of GNCs suffers due to small differences between gold and silver, whereas the silver-silver bond itself is more energetically favorable than the gold-silver bond. Search for other interesting structure-thermodynamics correlations is left as an exercise for readers.

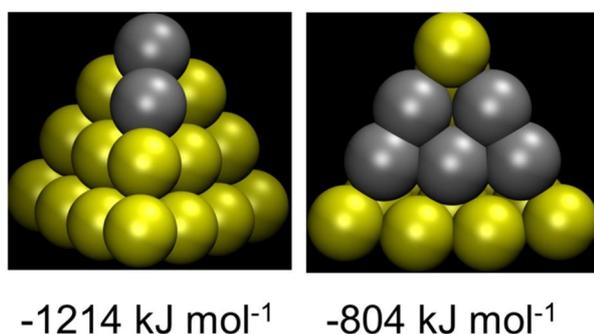


Figure 8. Local-minimum structures and formation energies of Au₁₈Ag₂ and Au₁₅Ag₅ with maximum number of chemical bonds between silver atoms.

The obtained geometries of GNCs deserve further consideration to shed light on their electronic properties. Since the accuracy of PM7 and other semi-empirical methods as applied to electronic properties is mediocre, ab initio or DFT theory methods are more advisable in this case. Pre-relaxation may be needed when continuing with the structures suggested by PM7/BFGS/BH.

Conclusions

This technical work, for the first time, proves a decent performance of the PM7/BFGS/BH methodology in navigating PES of the Au₂₀ GNC and silver-doped

GNCs. The Au₂₀, Au₁₈Ag₂, and Au₁₅Ag₅ GNCs were comprehensively investigated by the BH algorithm. The local optimization jobs were performed by means of the BFGS algorithm. The wave functions were represented by means of the PM7 semi-empirical Hamiltonian, as implemented in MOPAC2012.

Multiple local minima were found, which are generally consistent with previous knowledge and chemical expectations for the benchmarked structures. PM7 constitutes a promising alternative to DFT methods for finding stable conformations of the nanoclusters. If higher accuracy – particularly, in electronic properties – is desired, the obtained local-minimum geometries can be post-processed at higher levels of the ab initio theory. The computational time savings are associated with avoidance of total potential energy surface scans.

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