Two Novel Approaches Based on the Thompson Theory and Shape Analysis for Determination of Equilibrium Structures of Nanoclusters: Cu$_8$, Ag$_8$ and Ag$_{18}$ as study cases

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Abstract. Two new efficient methods for finding stable atomic clusters are introduced in this work. A purely algebraic and geometrical approach based on shape analysis provides a consistent set for optimization of structures which converge to local and global low-energy configurations. A second proposal based on the Thompson theory gives also candidate structures which became in equilibrium faster than the standard stochastic search models. The performance of the approaches is compared in three metal atomic clusters involving magic numbers. Both methods find the global and local low-energy structures reported in literature, but also obtain new structures. For Cu$_8$, Ag$_8$ and Ag$_{18}$ the shape analysis method provides more structures than the approach based on Thompson theory.

1. Introduction

Due to their remarkable (electrical, magnetic, optical, catalytic, thermal and mechanical) properties, atomic clusters or nanoclusters have attracted attention in the last decade [1, 2]. Geometrical structures of the nanocluster are of fundamental interest for determining their chemical and physical properties. Therefore, determination of the equilibrium structures in particular transition metal clusters is a challenge for both, theoreticians and experimentalists. From the theoretical framework, few studies have been focused in the search for lowest-energy structures [3-6] while most of the studies have assumed predefined structures [7], considering that to search of low energy cluster structures is usually a rather difficult task because the potential energy surface (PES) of a cluster containing N structural units has 3N degrees freedom. The number of local minima increases exponentially with N [8], this make that sampling on the PES of large clusters by computer simulation nearly impossible.

The standard chemical packages for computation of low-energy structures in nanoclusters are usually based on optimization routines involving random search. The stochastic search usually involves repeated unnecessary computation of energies associated with configurations very closed in shape. The time is also increasing by the inclusion of electronic information in all the stages of the analysis. A recent novel approach based on a mathematical problem, very far from the stochastic search of molecules, was combined with the use of the nuclear potential energy function restricted to a sphere. Then with a few original information of the structures, a feasible list of configurations can be proposed for a complete optimization program, the framework reported in Ref. [9] was successfully applied in Cu$_9$, Cu$_{11}$, Cu$_{38}$.
and Ni$_9$. Moreover, the low computational cost of the new method was remarkable. This is the second approach proposed in this work.

Now, from another side, conjectures about the use of intrinsic algebraic and geometrical information of the clusters, without any nuclear or electronic aspect can provide a priori pre-optimized structures which reduces the computation time. The theoretical group nature of a set of points is used in stochastic search of molecules to provide a priori motives, but only a few groups with small points has been used, see for example the magic number theory [10]. Then we can use this idea to explore the foundation of empirical equivalence classes of clusters.

This work proposes two uncorrelated theories for an effective and computationally cheap way to do an exhaustive sampling of the PES of metal nanoclusters. The first algorithm provides a number of empirical equivalent classes of configurations which are proven to be extremely different in shape. This algorithm exploits the algebraic and geometrical theoretical group nature of the lattices and set them in suitable neighborhood near to possible local and/or global minima energy. It avoids the repetition of energy analysis under randomness. The intensive exploration of the shape space leaves different structures which are rescaled and refined by standard chemical softwares. In contrast, a second strong filter based on the Thomson theory, requiring only nuclear information, also gives a number of structures which exceeds the proficiency and computation time of the classical standard packages. Both methods are briefly described in Section 2. Then in Section 3, the performance of the approaches are compared in Cu$_8$, Ag$_8$ and Ag$_{18}$, clusters of great relevance in material science.

2. Theoretical Framework

Generalities of the two referred methods are given next.

2.1. Shape analysis method: The first approach is a purely geometrical approach based on measures and comparisons in abstract quotient spaces induced by similarity transformations. The invariant group method provides certain empirical equivalent classes of structures, calibrated by a real parameter [11], which are the starting point of the standard optimization packages. Instead of the classical expensive random search in the Euclidian space, filtered by expert chemical software with minimum energy criteria, we consider the problem of finding, only from geometry, a number of possible neighborhoods for local minima energy; then the chemical expert algorithms work better and converge very fast to the equilibrium. All the experiments we have made with small and large nanoclusters show that a considerable proportion of the given equivalent classes are going into different equilibrium structures. The global minimum is usually reached too. Moreover, the geometrical approach can be calibrated by a real parameter (a shape distance), in such way that we can model the distance among the equivalent classes, and set a priori the number of possible different structures to be optimized by a chemical algorithm; this task is also characterized by a low computational cost. The shape distance is a real number between 0 and $\pi/2$, which measures the perfect match among the objects (zero) through the maxima discrepancy in shape (near to $\pi/2$). The algorithm also includes an exhaustive combinatorial search of trivial matching due relabel atoms, but it allows the isomers as different equivalent classes without filtering reflections. Finally, the resulting objects with different configurations are pre-optimized with Lennard Jones potential and then are further optimized with standard chemical packages.

2.2. Thomson Problem method: This second new approach performs a controlled stochastic search of the minima associated to the nuclear potential energy function
restricted to a sphere (similar to the Thomson problem), in order to guess configurations of the nuclear positions. Subsequently, the guessed configurations are further optimized driven by the total energy function using the conventional gradient descent method. This methodology is equivalent of using the Valence Shell Electron Pair Repulsion model in guessing initial configurations in the traditional molecular quantum chemistry. A detail discussion of the method can be found in [9]

3. Results and Discussions

The addressed two methods are not exclusive of metal nanoclusters, because they do not use a prior electronic information; only the location or geometrical properties are relevant for the shape analysis method, or the nuclear part, for the based Thomson theory approach. However, given the interest in the literature we applied them into the three special cases of magic numbers, Cu₈, Ag₈ and Ag₁₈.

For application of the shape analysis method, we just fixed a high tolerance of 1.4 for the dissimilarity in shape between two given configuration. Only if the tolerance is reached and no matching of exchanged labels is obtained, then we consider the configuration as a possible equivalent class. The comparison via the shape distance is also checked among the list of possible structures, in order to avoid repetitions. A list of hundreds of such candidates can be obtained in few minutes, then they are pre-optimized with Lennard Jones potential and then are further optimized with standard chemical packages.

Table 1. shows the number of different local minima: (1) in total, as generated by our shape and Thomson methods, (2) local minima determined at the B3LYP level (this work), (3) the number of minima reported in the literature. For 8 nanoclusters of eight atoms of copper and silver, the shape analysis obtained 19 initial configuration for each one, meanwhile the Thompson based method found 38. These configurations were optimized using the Becke-3-parameter-Lee-Yang-Parr or B3LYP functional with the LANL2DZ basis set (as implemented in the computational quantum chemistry software Gaussian09 [12]). For Ag₈ (Cu₈) the shape analysis method found 12 (7) equilibrium structures, and the Thomson approach obtained 4 (4) equilibrium configurations. In any case, the performance of the shape analysis method is superior to the reported in the literature [3,4,7,10].

Table 1. Number of different local minima: in total, as generated by our shape and Thomson methods, second and third columns respectively. Fourth column: local minima determined at the B3LYP level (this work). Fifth column: number of minima reported in the literature.

| System | Shape Analysis | Thomson Problem | B3LYP | Literature |
|--------|----------------|-----------------|-------|------------|
| Ag₈   | 19             | 38              | 12²|4² | 4[10] 6[7]  |
| Cu₈   | 19             | 38              | 7²|4² | 6[3,7] 4[4] |
| Ag₁₈  | 328            | N.A             | 97    | 8[10]      |

¹Shape analysis method; ²Thomson Problem method

The structural motifs are shown in Figure 1. Table 2 and Table 3 display the total energy E, nuclear energy Eₙu, sum of the Euclidean distances S, and population p of the different equilibrium structures [VE(X) = 0] of Ag₈ Cu₈, respectively, calculated at the B3LYP/LANL2DZ level of theory. The energetically lowest lying structures agree with the reported results [3,4,7,10]. However, in all the cases, we found no report on the planar structures M9 and M11. This also sets a new interesting branch of research, because we can specialize our shape theory method for 2D structures and the simplicity of the algorithm is notable because the reduction of the shape space. In order to apply our framework to
systems of large numbers, we have studied Ag\textsubscript{18} clusters using shape analysis methods. The case of Ag\textsubscript{18} is remarkable, because 97 stable structures were obtained with the shape analysis method instead of the 8 configurations reported in literature for this important magic number.

![Figure 1. Structural motif of M\textsubscript{8}](image)

**Table 2.** Total energy $E$, nuclear energy $E_{nu}$, sum of the Euclidean distances $S$, and population $p$ of the different equilibrium structures $[\nabla E(X) = 0]$ of Ag\textsubscript{8} calculated with B3LYP/LANL2DZ. All energies are in units of $E_h$ and distances are in units of $a_0$. Isomer populations $p$ estimated using the standard Boltzmann distribution at 298 K and 1 atm.

| Structure | $E_{B3LYP}$ (LANL2DZ) | $\Delta E$ | $E_{nu}$ | $S$  | $p$  |
|-----------|----------------------|-----------|---------|------|------|
| M1        | -1166.440720         | 0.0000    | 14113.832819 | 197.4832 | 97.01 |
| M2        | -1166.437223         | 2.1946    | 14324.802945 | 192.4670 | 2.67  |
| M3        | -1166.434912         | 3.6447    | 14064.865526 | 198.2888 | 0.23  |
| M4        | -1166.430143         | 6.6371    | 13786.675410 | 203.8103 | 0.00  |
| M5        | -1166.429449         | 7.0727    | 12304.595193 | 240.0201 | 0.00  |
| M6        | -1166.429069         | 7.3114    | 14022.292002 | 199.1054 | 0.00  |
| M7        | -1166.427588         | 8.2404    | 13277.399222 | 215.4927 | 0.00  |
| M8        | -1166.426700         | 8.7974    | 13036.814782 | 213.6283 | 0.00  |
| M9        | -1166.424164         | 10.3891   | 12635.025652 | 235.2405 | 0.00  |
| M10       | -1166.423226         | 10.9776   | 13564.770193 | 209.0867 | 0.00  |
| M11       | -1166.409304         | 19.7138   | 11662.164726 | 267.9091 | 0.00  |
| M12       | -1166.404338         | 22.8300   | 12195.103593 | 252.4903 | 0.00  |
Table 3. Total energy $E$, nuclear energy $E_{nu}$, sum of the Euclidean distances $S$, and population $p$ of the different equilibrium structures $[\nabla E(X) = 0]$ of Cu$_8$ calculated with B3LYP/LANL2DZ. All energies are in units of $E_h$ and distances are in units of $a_0$. Isomer populations $p$ estimated using the standard Boltzmann distribution at 298 K and 1 atm.

| Structure | $E_{B3LYP (LANL2DZ)}$ | $\Delta E$ | $E_{nu}$ | $S$ | $p$ |
|-----------|-----------------------|------------|----------|-----|-----|
| M1        | -1569.443518          | 0.0000     | 16166.508992 | 172.4475 | 92.82 |
| M2        | -1569.441034          | 1.5583     | 16437.800912 | 167.8697 | 7.11 |
| M3        | -1569.436249          | 4.5613     | 16147.664400 | 172.8981 | 0.05 |
| M12       | -1569.435362          | 5.1177     | 16234.450462 | 171.6225 | 0.00 |
| M4        | -1569.428914          | 9.1639     | 16229.565791 | 171.6790 | 0.00 |
| M9        | -1569.411879          | 19.8537    | 15838.575761 | 177.4860 | 0.00 |
| M11       | -1569.389402          | 33.9580    | 14499.800094 | 204.6005 | 0.00 |

4. Conclusions

In this work two new efficient methods, for pre-optimized nanocluster configurations, free of electronic information are provided. The method based on the Thompson theory only uses the nuclear energy of the atoms for suggesting a set of structures. The approach based on shape analysis only uses the algebraic and geometrical information and gives empirical group classifications which converges very fast to local and global low-energy structures, when the standard chemical packages are applied. An application of the methods are successfully provided in metal atomic clusters of magic numbers. The results involve new stable structures for the very elusive small group of 8 atoms of Cu and Ag. The findings for 18 metal nanoclusters over exceed the few known results of literature and verify the method for large groups. New further studies on metal planar nanoclusters are a feasible task with a simple modification of the provided 3D shape method.

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