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Assessment of Exchange-correlation Functionals for the Description and Prediction of electronic and optical properties (Circular Dichroism) in ultra-stable Silver (Ag44) clusters

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14. ABSTRACT
In this project, we studied the stability, electronic and optical properties of ultra-stable clusters, and nine thiolate ligands with aromatic and aliphatic groups, using density functional theory. We found differences in the energy gaps, atomic geometries, and charge distributions that depend on both, the metallic composition and ligands nature. By analyzing the charge density, we found a completely different behavior for aromatic and aliphatic ligands. For aromatic ligands, a charge balance between the metallic core and the sulfur atoms are observed, such that a kind of
charge compensation is found. The charge compensation is better when x=0 and x=12, in agreement with clusters that have been experimentally obtained. This charge balance between metals and sulfur atoms can be useful to explain the stability of these clusters and can be useful to propose the synthesis of clusters with aromatic ligands and different substituents, as the chiral ligands that we explore.

15. SUBJECT TERMS
Ag44, Exchange-Correlation Functionals, DFT, SIESTA, Circular Dichroism, Chirality, Optoelectonic Properties

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FINAL REPORT

Project title:
Assessment of exchange-correlation functionals for the description and prediction of electronic and optical properties (circular dichroism) in ultra-stable silver (Ag44) clusters.

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Estimated research progress–cost & schedule:
We finished the research project is in agreement with expenses. We have new physical insights about the stability of Ag44 clusters and bimetallic combinations, as well as Au25 and Ag25 clusters. We performed improvements to the code to calculate circular dichroism (CD). We published one paper and submitted for publication in Phys Chem Chem Phys. We are preparing another mauscript. We spent the total of the grant's funds.

Research accomplishments
In this project, we are interested in the study of electronic and optical properties of ultra-stable silver clusters, including electronic circular dichroism. We want to understand the original chiral properties of the cluster, being desirable to replace achiral ligands by chiral ligands to make the whole ultrastable silver nanocluster intrinsically chiral. However, many questions remain unanswered respect to the role of the ligands in the ultrastability. Thus, extracting the single-crystal X–ray structure from Ref. [1], we were able to make a systematic first-principle study to understand the structural and electronic properties of $Ag_{44}(p\text{-}MBA)_{30}^{4-}$ cluster.

In the first year, we reviewed the different criteria that have been used to explain the experimental stability of NC with a precise number of atoms that are protected with thiolate ligands. We discuss why these criteria are not enough to explain the stability. We conclude that other physical factors should be included when explaining the stability of these systems and could be important for the discovery of new noble metal NCs [1]. The experimental and theoretical study of NCs with a precise number of atoms represents a unique opportunity to understand their synthesis process and fundamental properties. In a recent article, we have

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discussed the available criteria to explain the stability of noble metal NCs with a precise number of atoms protected with thiolate ligands. These criteria are based on partial arguments of the atomic structure, electronic and energetic properties. Although these criteria have been useful to understand the stability of some NCs, they are not sufficient to explain all the experimental evidence. We analyze these criteria that have been used to explain the experimental stability of noble metal NCs with a precise number of atoms protected with thiolate ligands. Based on the experimental evidence, we discuss how these criteria are not enough to explain stability. We also propose to explore in detail the role of the ligand composition on the stabilization of these NC, which has not been fully considered. We believe that this will motivate other perspectives for the discovery of new noble metal NCs. Despite the significant advances in the synthesis and characterization, we conclude that the mechanisms that conduct the stability of NCs are still poorly understood. Several factors have not been studied yet, among them the role played by the different ligands in the electronic structure and their influence on the NC stability, the possible charge compensation of the ligands to the metallic core, and other elements that could unambiguously help to elucidate the formation and prediction of new NCs. We have presented these results in two different international meetings.

In this second year, we have been studied the stability and electronic properties of $[Ag_{44-x}Au_x(SR)_{30}]^{4-}$ clusters with x=0, 12, 20, and 32, and nine thiolate ligands with aromatic and aliphatic groups are investigated using density functional theory. We found differences in the energy gaps, atomic geometries, and charge distributions that depend on both, the metallic composition and ligands nature. By analyzing the charge density, we found a completely different behavior for aromatic and aliphatic ligands. For aromatic ligands, a charge balance between the metallic core and the sulfur atoms are observed, such that a kind of charge compensation is found. The charge compensation is better when x=0 and x=12, in agreement with clusters that have been experimentally obtained. These clusters show smaller atomic distortions than those with x=20 and x=32. On the other hand, aliphatic ligands do not show such charge compensation, also in agreement with the fact that these clusters with aliphatic ligands have not been reported. This charge balance between metals and sulfur atoms can be useful to explain the stability of these clusters and can be useful to propose the synthesis of clusters with aromatic ligands and different substituents, as the chiral ligands that we explore [2].

We have also studied the cluster $Ag_{25}SR_{18}^{1-}$, an interesting NP since this is the only one showing a golden analog, that is, $Au_{25}SR_{18}^{1-}$ possess the same structure than $Ag_{25}SR_{18}^{1-}$. It also has been experimentally obtained with several ligands and still shows great stability. In this sense, we studied several bimetallic clusters such as $Ag_{13}Au_{12}SR_{18}^{1-}$, $Au_{13}Ag_{12}SR_{18}^{1-}$, $AuAg_{12}Au_{12}SR_{18}^{1-}$, $AgAu_{12}Ag_{12}SR_{18}^{1-}$. In the case of $Ag_{44}SR_{30}^{4-}$ clusters, a charge compensation only for specific ligands was obtained. Also, there is a HOMO-LUMO gap dependence on

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the atoms composing the staple motifs. The largest stability is found for bimetallic clusters where the staple unit is formed by Au atoms [3].

In summary, we have obtained quite relevant results about the role of ligands and the metallic part of clusters, combined with electronic charge distributions of each building part. Beside large HOMO-LUMO gaps, the fulfillment of the superatom rule, staple motifs and stability in the core; we have found that the electronic charge distribution might contribute to these ultrastability in silver clusters. As part of these results, we are writing two papers related to our results covering stability and optical properties.

References

[1] C. Morera-Boado, F. Hidalgo, C. Noguez. EPL (Europhysics Letters). 2017, *119*, 56002.

[2] C. Morera-Boado, F. Hidalgo, C. Noguez. *Stability and Electronic Charge Compensation of* $[Ag_{44-x}Au_x(SR)_{30}]^{4-}$ *Clusters*, submitted to PCCP, 22 feb 2019.

[3] C. Morera-Boado, R. Zarmiento, F. Hidalgo, C. Noguez. In preparation