Spin-orbit coupling effects in gold clusters: The case of Au\textsubscript{13}

Mauricio A. Flores\textsuperscript{1} and Eduardo Menéndez-Proupin\textsuperscript{2}

\textsuperscript{1,2}Departamento de Física, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, 780-0003 Nuñoa, Santiago, Chile.

\textsuperscript{1}Departamento de Matemáticas, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile.

E-mail: mauricio.flores@ug.uchile.cl

Abstract. Non relativistic description of the chemical bonding for heavy atom systems is unrealistic. However, only few relativistic DFT calculations have been reported for gold clusters. In this work, we investigate the effect of the spin-orbit coupling in the structure, relative stability and HOMO-LUMO gap of the lowest-lying isomers of neutral Au\textsubscript{13} clusters. Our results show that spin-orbit coupling increases the energy gap between 2D and 3D isomers and a relativistic bond contraction appears. Moreover, the relative energy of some isomers change when the spin-orbit coupling is included.

1. Introduction

One of the largest challenges in the study of metal clusters is the determination of their ground-state structures. Neutral gold clusters up to 10 atoms adopt planar configurations, but the precise size for which they change from 2D to 3D structures still remains as an open issue mainly due to the scarcity of experimental study. It has been pointed out that the preferred planarity of small gold clusters is correlated with strong hybridization of the atomic 5\textit{d} and 6\textit{s} orbitals due to relativistic effects [1].

Relativistic effects can strongly influence the chemical and physical properties of heavy elements. For the sixth row elements (around W to Bi) relativistic effects are comparable to the usual shell-structure effects [2]. Non relativistic description of the chemical bonding for heavy atom systems is unrealistic. In a many-electron atom relativistic effects tend to contract and stabilize the \textit{s} and \textit{p} shells, and expand and destabilize the \textit{d} and \textit{f} shells [2]. In the case of gold the 6\textit{s} orbital is strongly contracted (by about 17%), whereas the 5\textit{d} orbitals slightly expand [3]. Spin-orbit (SO) interactions split the \textit{d}-band into \textit{d}_3/2 and \textit{d}_5/2 subbands, increasing the overlap of \textit{s} and \textit{d} bands leading to appreciable \textit{s-d} hybridization in the bonding molecular orbitals [4, 5].

A maximum of relativistic effects has been identified at gold [2, 6]. Inertness and many of its unusual properties such that yellow color, nobility, and trivalency derive from relativistic effects [7]. Spin-orbit coupling has a significant effect on the cohesive energy and the relative stability of the isomers of gold clusters [8]. Its electronegativity is a result of the relativistic contraction of the valence 6\textit{s} and 6\textit{p} orbitals. Using first-principles calculations, Takeuchi et al. [9] have shown that, due to the strong relativistic effects, it is energetically favorable for the top layer...
of the (100) surface of Au to transform from the ideal square lattice of a fcc metal to a slightly distorted and contracted hexagonal-close-packed arrangement.

In the present work, we report the results of first principles density functional theory calculations of Au$_{13}$ clusters with and without spin-orbit coupling. We investigate the stability, HOMO-LUMO gap, interatomic distances, and the role of the semicore orbitals when are considered as valence electrons.

2. Methodology

First-principles total energy calculations were performed using the generalized gradient approximation density functional of Perdew, Burke, and Ernzerhof (PBE) [10] as implemented in the plane-wave based Quantum-ESPRESSO package [11]. Electron-ion interactions were described using PAW pseudopotentials [12] from the PS Library 0.3.1 [13].

In order to elucidate the role of semicore states, two pseudopotentials are considered, namely PP1 and PP2. The first one contains 11 valence electrons ($5d^{10}6s^1$) and the second 19 valence electrons ($5s^25p^65d^{10}6s^1$). We used a plane wave energy cutoff of 40 Ry and 60 Ry, respectively to represent Kohn-Sham wavefunctions, and 500 Ry to represent the charge density. To have negligible interactions between periodic images of clusters, DFT calculations have been performed using a large cubic supercell with an edge of 24 Å. The Brillouin zone was sampled with the Γ point only. Structural optimizations of the lowest-energy isomers were carried out using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm until the Hellman-Feynman forces are less than 0.001 Ry/bohr.

3. Results and discussion

An exhaustive search of the potential energy surface was performed at DFT level using a novel global optimization algorithm [14]. Equilibrium geometries for the six lowest lying structures of neutral Au$_{13}$ clusters are presented in the Figure 1.

![Figure 1](image_url)

**Figure 1.** Structures the six lowest lying isomers of Au$_{13}$ after geometry optimization.

Relative energies are depicted in Figure 2 (Left). All methods considered in this work agree
that the lowest structure of the Au$_{13}$ is the planar isomer S$_1$ different from that predicted by previous DFT [15] and revTPSS [16] calculations. When spin-orbit coupling is taken into account the energy gap between planar and lowest-lying 3D isomers is increased. This effect is stronger when the semi core states are treated as valence electrons (PP2 + SO). We note that spin-orbit effects change the relative stability between isomers S$_5$ and S$_6$ predicted from the DFT calculations without spin-orbit coupling.

Figure 2. (Left) Relative energies compared to isomer S$_1$ obtained at DFT level with and without including the spin-orbit coupling. (Right) The HOMO-LUMO energy gaps of the lowest lying isomers of Au$_{13}$ obtained with and without including the spin-orbit coupling.

Figure 3. Average interatomic distance obtained for all Au$_{13}$ isomers after geometry optimization with and without including the spin-orbit coupling.

Figure 2 (Right) shows the effect of the spin-orbit coupling on the HOMO-LUMO energy gap. It is reported that a large energy gap between the highest occupied molecular orbital (HOMO)
and the lowest unoccupied molecular orbital (LUMO) implies high stability and small energy gap implies low stability. The energy gap of all 3D isomers decreases when SO is included while the HOMO-LUMO gap of planar clusters remains unchanged. Surprisingly, the most stable isomers with and without spin-orbit are S₄ and S₅. The HOMO-LUMO gap is unaffected when the semi core states are considered as valence electrons.

Figure 3 shows the average interatomic distance obtained for all isomers after geometry optimization. The first observation is that a relativistic bond contraction appears. It is dependent of the cluster shape and is stronger for planar isomers. The second observation is that the effects of SO coupling on the average atomic distances are monotonic, contrary to previous results reported for Pt clusters [17, 18] where relativistic effects are also very strong. We note that bond contractions are increased when the semi core states are considered as valence electrons.

4. Conclusions

We performed a exhaustive search of the potential energy surface of gold at DFT level reporting the six lowest-energy isomers of Au₁₃. Our relativistic DFT calculations show that spin-orbit coupling change the relative stability between some isomers predicted from DFT calculations without spin-orbit coupling. The energy gap of all 3D isomers decreases when SO is included while the HOMO-LUMO gap of planar clusters remains unchanged. A relativistic bond contraction dependent of the cluster shape appears. The inclusion of semi core 5s and 5p states in the valence shell increases the the relative energy stability of planar isomers and the relativistic bond contractions.

References

[1] H Häkkinen, M Moseler, and U Landman 2002 Phys. Rev. Lett 89 033401
[2] P Pyykkö 1988 Chem. Rev. 88 563
[3] Schwerdtfeger P et al. 1989 Journal of chemical physics 91 1762
[4] F Ramos, R Arratia-Perez, and G Malli 1987 Physical Review B 35 3790
[5] Qteish A et al. 1987 Physical Review B 72 155317
[6] N Kaltsoyannis 1997 J. Chem. Soc., Dalton Trans. 1
[7] P Pyykkö 2012 Annual review of physical chemistry 63 45
[8] Y Shi, Z Li, and K Fan 2010 J. Phys. Chem. A 114 10297
[9] N Takeuchi, C Chan, and K Ho 1991 Phys. Rev. B 43 14363
[10] J P Perdew, K Burke, and M Ernzerhof 1996 Phys. Rev. Lett. 77 3865
[11] P Giaommo S Baron N B et al. 2009 J. Phys.: Condens. Matter 21 395502
[12] P Bölchi 1994 Phys. Rev. B 50 17953
[13] A Dal Corso 2014 Comp. Material Science 95 337
[14] M Flores (in preparation) “Ground-state structures of 13-atom transition-metal clusters: Y - Cd”
[15] B Assadollahzadeh and P Schwerdtfeger 2009 J. Chem. Phys. 131 064306
[16] M Johansson, I Warnke, A Le, and F Furche 2014 J. Phys. Chem. C 118 29370
[17] M Huda, M Niranjan, B Sahu, and L Kleinman 1991 Phys. Rev. A 73 053201
[18] A Sebetci 2009 Phys. Chem. Chem. Phys 11 921