188 Spin-orbit coupling effects on the band structure and the 2D to 3D structural transition of gold clusters

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In the last years there has been great interest in the use of small gold clusters and nanoparticles for their potential applications in nanotechnologies and their good catalytic performance. Studies of their physical and chemical properties have become an active research area.

Many bare gold clusters have already been obtained in previous density functional theory (DFT) studies [1-3]. 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.

In this work, we present a new strategy for global optimization based on perturbation operators combined with first principles density functional theory (DFT) calculations using the plane-wave based Quantum ESPRESSO package [4].

We performed a systematic search for the low-lying minimum 2D and 3D structures of neutral gold clusters Au_n ($n = 2 - 20$). We have found that the 2D $\rightarrow$ 3D transition occurs at size 13, and that for Au_n (n = 14, 15) we cannot distinguish between the most stable 3D and 2D structures within the accuracy of DFT calculations (Fig. 1).

In order to determine the size evolution and the stability of gold clusters we determined the energy gap between the highest occupied and the lowest unoccupied orbitals (HOMO-LUMO), and the binding energy per atom including the spin-orbit coupling effects. Our results show that spin–orbit coupling does not alter the relative stability of gold clusters but increases their binding energy.

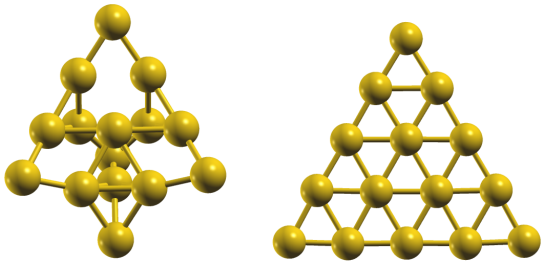

Fig 1. *3D and 2D most stable structures for the Au_{15} cluster.*

We also investigate the band structure of gold using the primitive unit cell (FCC lattice). We show a comparison between the band plot of a DFT-PBE calculation which only includes scalar-relativistic terms in the Kohn-Sham Hamiltonian with that one of a fully relativistic calculation, which also includes the spin-orbit coupling term. We have found that most of the relativistic effects come from the scalar-relativistic terms.

References

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