From Au or Ag clusters to nanoparticles: an ab initio and atomistic study

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For two decades intriguing physical/chemical properties have been reported for noble metal nanoparticles coated by ligand molecules [1]. In order to better understand the metal/ligand interactions which govern in part the morphology of these objects, numerical simulations are widely used. These are mainly based on two theoretical models: on one hand ab initio calculations (Density Functional Theory, DFT) and on the other hand atomistic simulations. If DFT allows an accurate description of the systems (electronic level) its use is unfortunately limited either to very small clusters or to periodic surfaces due to computational cost. Atomistic models allow a simulation of a whole coated nanoparticle [2] (from 5 nm to 9 nm) at the expense of electronic structure information. Furthermore classical force fields are unable to describe bond formation/breaking and so structural deformation/reorganization, the “staple” motif [3], as well as atomic diffusion on the surface of nanoparticles. However Reactive Force Fields (ReaxFF) have been developed to reproduce bond breaking [4] which could be an effective tool to compare Gold or Silver nanoparticle/ligand interaction.

In this presentation we will first introduce limits of Gold-Gold and Gold-thiolate ReaxFF results compared to ab initio data. Consequently both Gold-Gold and Gold-ligand ReaxFF need to be improved and Silver-Silver Silver-ligand ReaxFF have to be developed. We chose a set of Gold or Silver model systems as pyramidal clusters or both (111) and (100) surfaces in interaction with ligand molecules in order to determine preferential sites of reaction and structural deformations (DFT calculations). In a same time a topological analysis using the Quantum Theory of Atoms In Molecules (QTAIM) and Electron Localization Function (ELF) methods allows us to characterize the metal-metal and metal-ligand chemical bond nature and differences of reactivity between Gold and Silver nanoparticles through the behavior of electronic densities. We will present these ab initio results following by their topological analysis for atomic sulfur, alkane thiolate and alkane thiol as ligands.

References

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