Understanding Nanoparticle Properties using Theoretical Methods
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Theoretical investigations of monolayer-protected noble metal nanoparticles play an important role in determining the origins of the unique chemical and physical properties of these systems that lead to applications in photonics, sensing, catalysis, etc. Density functional theory (DFT) and time-dependent DFT (TDDFT) have been employed to calculate chemical reactivity and physical properties for a number of gold and silver nanoparticles of experimental interest.

Small thiolate-stabilized nanoparticles are of interest for their catalytic, fluorescent, and sensing properties. TDDFT calculations have recently been employed to elucidate the excitation spectrum of Au$_{25}$(SR)$_{18}^-$ and related nanoparticles. The ground-state geometric and electronic structure of the Au$_{25}$(SH)$_{18}^-$ nanoparticle (shown below) have been well-characterized. The inner core of this nanoparticle is approximately icosahedral, and it is surrounded by six SR-Au-SR-Au-SR motifs. The highest occupied molecular orbitals (HOMOs) in this system are approximately triply degenerate superatom P orbitals, with an approximately doubly degenerate set of lowest unoccupied molecular orbitals (LUMOs) with superatom D symmetry.

TDDFT calculations have recently been employed to elucidate the excitation spectrum of Au$_{25}$(SR)$_{18}^-$ and related nanoparticles. Silver atoms have recently been introduced experimentally into the Au$_{25}$(SR)$_{18}^-$ nanoparticle, and this work investigates the effect of silver doping by studying Au$_{25-n}$Ag$_n$(SH)$_{18}^-$ ($n = 1, 2, 4, 6, 8, 10, 12$) systems. Silver doping lowers the energy of ligand-based orbitals and facilitates the transitions between the superatom orbitals. Silver-doped systems show broader excitation spectra due to a breaking of the symmetry of the superatom orbitals.

In this work, photoexcitation in Au$_{25}$(SR)$_{18}^-$ and related nanoparticles will be discussed using TDDFT methods. We find significant changes in the geometric and electronic structure of this system upon photoexcitation.

Small silver clusters encapsulated by DNA have been of interest for biotagging applications since they display fluorescence. However, the structure of these systems is not well-established. Using TDDFT calculations, the absorption and circular dichroism (CD) spectra of helical silver nanowires is computed and compared with experimental absorption and CD spectra. Absorption peaks that are forbidden in perfectly linear wires are found to yield small absorption peaks that have very large rotatory strengths. The agreement between theory and experiment suggests that the silver-DNA clusters have a helical arrangement.

All are welcome. Coffee and Snacks will be served.