TDDFT Studies of Nanoparticle Optical Properties

Christine M. Aikens,
Kansas State University, Manhattan, KS 66506, USA

Theoretical investigations of 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 chemical and biological sensing, catalysis, etc. Time-dependent density functional theory (TDDFT) has been employed to calculate the absorption spectrum for a number of gold and silver nanoparticles of experimental interest.

The first system we will discuss is pentagonal silver nanorods, which have applications in cancer therapy. The wavelength of their absorption maxima extrapolates linearly with their length-to-diameter ratio. The nanorod orbitals and length dependence agree with a simple particle-in-a-box model. The origins of the transverse and longitudinal peaks are discussed. Similar behavior is also observed for other elongated systems such as nanowires and larger diameter nanorods.

Silver-DNA systems have been of interest for many years because these small systems are fluorescent and can be used as biotags. However, the structures of these systems are not yet known. In this work, we show that slightly bent, twisted nanowires could explain the optical absorption and circular dichroism (CD) spectra of these interesting experimental systems.

Small thiolate-stabilized nanoparticles are also 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. This particle can be interpreted as a "superatom", in which a core of essentially free electrons is surrounded by gold-thiolate oligomeric ligands. The ligand field arising from the surrounding gold-thiolate oligomers is responsible for the splitting of the intraband transition. In addition, we will examine the “magic” $Au_{38}(SR)_{24}$ nanocluster. Using a combination of electronic structure calculations, XRD, and optical and CD spectra, this nanocluster is shown to be chiral with D_3 symmetry. $Au_{38}(SR)_{24}$ is found to have an elongated structure; the electronic structure of this elongated “nanorod” is similar to that previously determined for silver nanorods. As for $Au_{25}(SR)_{18}$, delocalized superatom-like orbitals are responsible for its properties.