

Theoretical Models for the Study of Magnetic Properties in Metallic Nanoparticles

NIST researchers are building a theoretical infrastructure for the modeling and understanding of experimentally observed ferromagnetic and other collective phenomena (such as plasmon excitations and binding energy shifts) that have a dependence on the number of atoms in metallic nanoparticles. These phenomena therefore depend on the particle size distribution and its deviation from bulk lattice behavior. This work will lead to the development, implementation, and validation of reliable theoretical tools that will enable researchers to understand the underlying physics governing the magnetic behavior exhibited by metallic nanoparticles.

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Metallic nanoparticles have been receiving considerable attention by both experimental and theoretical researchers. A driving motivation in this research is the interest in industrial applications of the emerging nanotechnologies. Magnetic properties of nanoparticles, such as ferromagnetism in transition metals like iron and cobalt and as recently reported in gold, have been of interest as materials for data storage applications. Other applications are in the health and medicine sectors where gold nanoparticles have seen usage as cancer cell killing agents, medical imaging contrast (MRI), hyperthermia treatment, drug delivery systems, and signal enhancement (Raman, Plasmon) factors.

Some of the interesting features of gold nanoparticles are shared by nanoparticles composed of different types of materials. As the nanoparticle size is made smaller, the accompanying large surface-to-volume ratio and lattice contraction induce interesting quantum effects such as electron localization, binding energy shifts, novel surface reactivity, surface ferromagnetic effects, and surface collective charge excitations as seen in plasmon absorption spectra. These effects have been experimentally reported as functions of the number of gold atoms in the nanoparticle. Despite significant progress in this area, the design and fabrication of these particles with desired physico-chemical properties remains more of an art than a science, involving tedious and expensive trial-and-error approaches. In addition, important metrology issues related to the characterization of size, shape and composition have not been resolved. A proper theoretical modeling of the fundamental physics and chemistry behind these effects will undoubtedly aid in the rational design and characterization of metallic nanoparticles with novel properties. Despite being diamagnetic in the bulk lattice (large scale), gold's emergent ferromagnetism observed at the nanoscale

is interesting from a theoretical and technological point of view; a study of this type of emergent behavior will also shed light on the other and related novel quantum effects of lattice contraction and plasmon excitations as well as binding energy shifts at the intermediate nanoparticle sizes we are investigating. With reasonably accurate models, scientists will be able to predict beyond what has already been experimentally reported, testing the possibility of combined effects such as magnetization and plasmon oscillations coexisting at some desired particle scale.

The NIST team is working on an integrated approach that will lead to the development of a novel and reliable theoretical model based on *ab initio* molecular orbital calculations and a many-body quantum mechanical approach to explain all the quantum effects previously discussed.

Ab Initio Molecular Orbital Calculations of Magnetism in Bare Gold Nanoclusters.

A particularly interesting question is how a ferromagnetic moment arises in the gold nanoparticle given its diamagnetic behavior in the bulk. Specifically, how does the symmetry of directed spins occur, at what size scales, and what are the accompanying electron charge effects. In order to answer these questions, we have applied spin-dependent density functional theory (DFT) in the scalar relativistic pseudo-potential formalism to study the energetic tendency for the gold clusters to spin polarize. The computed electronic structures of various gold nanoclusters reveal that permanent size-dependent spin-polarization appears without geometry relaxation for bare clusters even though bulk gold is diamagnetic. The polarized ground states for clusters are favorable due to the hybridization of the *s* and *d* orbitals, indicating that gold clusters are intrinsically magnetic due to the hybridization of the atomic orbitals. The magnetism is localized to a monolayer on the outside of these clusters with the interior atoms remaining mostly diamagnetic. The results indicate that bare octahedral clusters are expected to be magnetic for cluster sizes of approximately 38 atoms and larger. As these clusters grow in size, the diamagnetic core dominates as soon as the surface-to-volume ratio becomes small and the core diamagnetism prevails. Thus, magnetism in gold clusters is a primarily a size-dependent effect. The results provided by the DFT calculations in this work are consis-

tent with the experimental evidence that suggests that gold magnetism is strongest when weakly interacting capping agents are used. Strongly interacting capping agents would likely quench this magnetic behavior. That the magnetism of gold nano-particles can be tunable in certain size regimes strongly supports their use in many applications.

Mean Field Model for the Study of Size Dependence Of Ferromagnetism In Gold Nanoparticles.

The DFT calculations discussed above provided the basis for a theoretical model to describe the size dependence of magnetism in gold nanoparticles. In this part of the project, a simple spin-spin Ising interaction model for the surface ferromagnetism was combined with the bulk gold diamagnetic response due to the effective surface interaction field to model the size dependence of the magnetization of the Au nanoparticle. This surface magnetic field is the Weiss field and acts as an effective applied field as seen by the core electrons. Using the Maximum Entropy formalism, we obtained the average temperature dependent magnetization within a mean-field model. It was found that the model reproduces the experimentally observed peak in magnetization reported in the literature for the case of gold nanoparticles. The results of this project indicate that the size dependence observed in the case of gold nanoparticles is a general effect and that the model should be applicable in all core-shell nanoparticles of diamagnetic metals.

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Impact: The interest in nanotechnology and theoretical modeling and simulation tools has been increasing steadily. This interest is shared by governmental and academic research institutions as well as industrial sectors that are interested in new technical innovations. Nanotechnology promises to revolutionize our infrastructure in the mid to longterm. A detailed examination of paradigmatic nanoscale systems that exhibit novel quantum effects such as gold nanoparticles can produce theoretical modeling tools and insight that will be of value to any research effort into nanoscale materials characteristics.

This work is creating the necessary infrastructure that could help researchers in industry develop more robust and cost-effective theoretical models for prediction and control of currently existing industrial nanoscale applications, as well as those proposed for the future as envisioned by scale plans in computing and electronics.

Future Plans: In the near future, this work will be extended to develop similar robust theoretical tools that will enable scientists obtain a fundamental understanding of the physics governing the size dependency of non-linear optics as well as electron transport properties in metallic nanoparticles. The development of these tools is critical for the rational design of novel devices (such as biomarkers, memory devices, sensors, etc.) at the nanoscale that can take advantage of these three physical properties simultaneously.