

Chemically Induced Magnetism in Gold Nanoparticles.

The investigation of novel effects that have been observed to emerge at the nanoscale has been receiving considerable interest of late. As an example of this, the recent experimental observation of ferromagnetic moment formation at the nanoscale in thiolate-capped Au nanoparticles has been an interesting departure from the bulk behavior of gold, which exhibits a diamagnetic property. The magnetization has also been reported to exhibit an interesting diameter size dependence, increasing with particle diameter at the smaller nanoparticle sizes, peaking at approximately 3 nm for Au-thiol nanoparticles, and subsequently decreasing with increasing nanoparticle size. This is consistent with the observation that as the nanoparticle size increases, the Au atomic configuration approaches that of the bulk gold lattice. There have been several ideas put forth as to the cause of the observed ferromagnetic moment in Au nanoparticles. These range from the Fermi hole charge imbalance at the surface, to Hund's rule electron filling at the smaller scales. Despite these efforts, the causes for the ferromagnetic moment formation in thiolate-capped Au nanoparticles remain elusive. In this work, we present a simple model to describe the induction of magnetic behavior on gold clusters upon chemisorption of one organic molecule with different chemical linkers. In particular, we address the problem of stability of the lowest-lying singlet and show that for some linkers there exists a spin symmetry-breaking that lowers the energy and leads to preferential spin density localization on the gold atoms neighboring the chemisorption site. The model is basically an adaptation of Stoner model for itinerant electron ferromagnetism to finite clusters and it may have important implications for our understanding of surface magnetism in larger nanosystems and its relevance to electronic transport in electrode-molecule interfaces.

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The appearance of ferromagnetism in thiol-capped gold nanoparticles (NPs) has been recently reported¹. This surprising finding reveals that under some conditions chemisorption seems to be able to induce permanent magnetism in small nanoparticles of a bulk-diamagnetic metal, such as gold, through an electronic mechanism, apparently involving the interaction of the sp-orbitals of adsorbates such as thiolates with the 5d-orbitals of gold, which leads to the emergence of 5d-

localized holes as a result of significant charge transfer from the gold atoms to the sulfur atom in the adsorbate. The existence of these holes in gold NPs capped with thiolates has been demonstrated by Au L₃-edge extended x-ray absorption near-edge structure (XANES) measurements performed by Zhang and Sham on alkanethiolate-capped gold NPs of 1.6 nm, 2.4 nm and 4.0 nm. The magnetism observed in the thiol-capped NPs was found to be accompanied with a strong suppression of the plasmon absorption, an indication of the existence of strong interactions between the thiolate (adsorbate) and the gold atoms lying on the surface of the gold nanoparticle, which suppress the itinerancy of gold's 5d electrons. Zhang and Sham report that in the case of gold NPs capped with thiolates, the suppression of plasmon absorption seems to be highly dependent on the size of the NP. Thus, for 4.0 nm NPs they observe a very distinctive plasmon absorption curve that disappears in the case of nanoparticles of 2.4 nm and 1.6 nm. Using nitrogen as a linker does not seem to have a noticeable effect neither in inducing magnetism nor for the disruption of the plasmon absorption¹. These results are in stark contrast to X-ray magnetic circular dichroism (XMCD) measurements performed by Yamamoto and collaborators³, which indicate a significant ferromagnetic spin polarization of gold NPs with a diameter of 1.9 nm capped with a weakly interacting polymer such as polyallyl amine hydrochloride. Reports of quenching or enhancement of local magnetic moments due to chemisorption in magnetic metals have long been known, and the reason for this behavior seems to be well understood⁴. The opposite phenomenon is much more complicated because the onset of magnetism is a complex manifestation of electronic correlation, and a delicate balance between the size effect of the nanoparticle and the strength of its interactions with the adsorbate. Historically, two schools of thought have attributed magnetism to either the appearance of localized magnetic moments in real space or to the itinerant character of conduction electrons. The modern tendency is to unify these two seemingly contradictory points of view in a single correlated model of the electronic structure.

In this work, we report on a quantum-chemical exploration of a symmetry-breaking electronic mechanism induced by single-molecule chemisorption that could provide a possible route for the onset of magnetism. The idea is simple and dates back to the application of the Finite Perturbation Theory (FPT) used to calculate NMR spin-spin coupling constants of molecules. The FPT main equations can be easily formulated within the realm of Density Functional Theory (DFT). Thus, at each self-

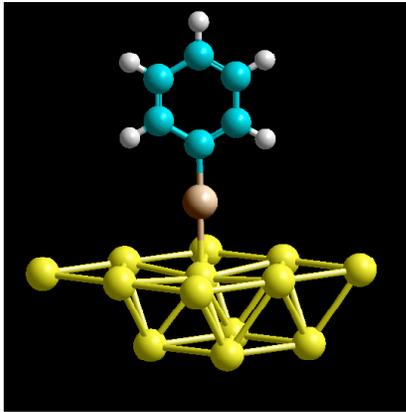
consistent cycle, a perturbation λ to the spin states of a particular atom is added to the Kohn-Sham Hamiltonian operator $h_{\mu\nu}^{\alpha,\beta}$:

$$h_{\mu\nu}^{\alpha,\beta} \rightarrow h_{\mu\nu}^{\alpha,\beta} \pm \lambda A_{\mu\nu}^N \quad (1)$$

where $A_{\mu\nu}^N$ are matrix elements (in the atomic basis set $\{\phi_\mu\}$) of the Dirac delta function $\delta(\vec{R}_N)$:

$$A_{\mu\nu}^N = \langle \phi_\mu | \delta(\vec{R}_N) | \phi_\nu \rangle = \phi_\mu(\vec{R}_N) \phi_\nu(\vec{R}_N) \quad (2)$$

and \vec{R}_N is the vector with the coordinates of atom N . In Eq. (1) above, the \pm sign in the form of the perturbation amounts to a local breaking of the zero spin condition (+ for α electrons and – for β electrons). The system we consider here is a small cluster of 13 gold atoms and one chemisorbed molecule (see Fig. 1). Even though this system is much simpler than the actual nanoparticles studied in the experiments, it provides with a reasonable prototype for understanding the basic electronic mechanism that might be responsible for the magnetism observed in these systems. We have probed the stability of the singlet state against a local breaking of the spin symmetry. Such a methodology is analogous to introducing an artificial external field, an approach that is used in problems where the effect of the perturbation is very small to be studied by conventional techniques.



= Au



= O, S, Se, N, P, As

Figure 1: Geometry of the $C_6H_5-L-Au_{13}$ system considered in this study, where the linker $L = O, S, Se, N, P, As$.

Adopting the mean field approach and making use of the Heisenberg Hamiltonian treatment, we have been able to show that for the overall singlet state, the relative energy

of the system with respect to the closed shell state is given by the following expression:

$$\Delta E(n_A) = \Omega + J \cdot \chi \cdot n_A + J \cdot n_A^2 \quad (3)$$

where n_A is the spin density localized at the Au atom where the perturbation has been applied, χ and Ω are terms that describe the interaction between the spin densities of the other Au atoms in the system, and J is the well known spin coupling constant. For a nonmagnetic state, the minimum energy is obtained for $n_A = 0$, whereas for a symmetry-broken magnetic state the minimum energy is obtained for $n_A > 0$, with a coupling constant $J > 0$, $\Omega \approx 0$ and $\chi < 0$. After applying this methodology, we find that, in agreement with the experimental results, for a sulfur linker, energetic stabilization is accompanied with the developing of spin localization preferentially in the gold atoms closest to the chemisorption site. Finally, using the value of the spin densities corresponding to the minimum of the plot displayed in Figure 2, we obtain a magnetic moment of $0.0025 \mu_B$ per S-Au bond for $C_6H_5-S-Au_{13}$, in very good agreement with the value of $0.0036 \mu_B$ obtained by Crespo et al. in their measurements of magnetization on thiolate capped-Au nanoparticles. For a nitrogen linker, no spin symmetry-breaking leading to lower energy states is found.

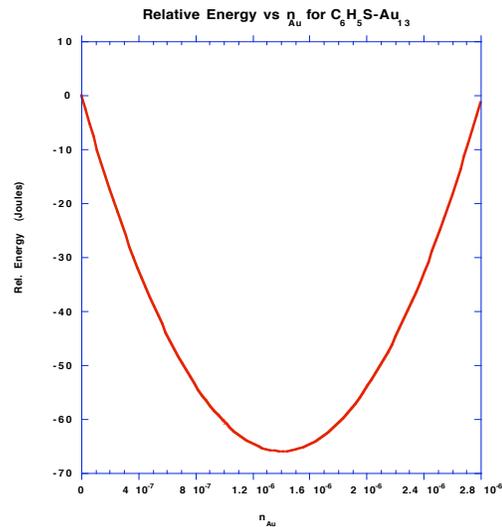


Figure 2: Relative energy (computed at the PBE/LanL2DZ level of theory) of the $C_6H_5-S-Au_{13}$ system as a function of the spin density n_{Au} on the the gold atom bonded to the sulfur linker.

We are currently applying this methodology to determine the dependence of the induced magnetic moment with the size of the cluster.